FURTHER STUDIES IN CONFIGURATION

INTERACTION METHODS

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Abstract

The combined configuration interaction (CI)-perturbation approximations of Gershgorn and Shavitt and the orbitally ordered CI method of Cooper and Pounder (on its own or including a modification implied by Roos, Taylor and Siegbahn) are applied to the calculation of the electron spin resonance hyperfine coupling constants of two small doublet state radicals BeH and NH₂.

On the one hand, it is found that, despite the absence of variational upper bounds to the resultant energies effectively nullifying the selection of the optimum expansion from several alternatives on the basis of the criterion of least eigenvalue, generally acceptable calculated values for the BeH hyperfine coupling constants can be obtained using no more orbitals to construct the active space of the wave function than that number normally employed in a minimal basis set calculation. On the other hand, it is shown that, although the method to correctly order the orbitals is much more complicated for open-shell systems, indeed, the concept of an orbital order may be lost, over 80% of the correlation energy can be recovered besides closely reproducing the isotropic hyperfine coupling constants of, e.g., the NH₂ full single and double replacement CI calculation using only one-tenth of the configurations.

Of the four distinguishable methods to generate modified virtual orbitals (MVO's) considered, in addition, the modified Hartree-Fock operator is shown to be the best (i.e., in terms of optimum convergence properties of the corresponding MVO's for least computational effort). The optimum values of the variable associated parameter are found to lie close to $Y = -15$ for both singlet and doublet state molecules which is significant if the method is to have wide generality.
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TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>SECTION</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
</tbody>
</table>

**SECTION ONE: The calculation of electron spin resonance hyperfine coupling constants**

1.1 Theory 3

1.2 The restricted Hartree-Fock plus combined configuration interaction-perturbation method 7

1.3 The generation of modified virtual orbitals 59

   (i) Natural expansions 60
   (ii) Modified Hartree-Fock operator 62
   (iii) Projection 64
   (iv) State minimisation 68

1.4 Vibronic contributions 82

**SECTION TWO: A comparison of convergence improvements in two small doublet state radicals BeH and NH₂** 85

2.1 The BeH radical 85

2.2 The NH₂ radical 105

2.3 Conclusions 128

**APPENDIX:** FORTRAN 77 program to illustrate a matrix inversion technique based on Gram-Schmidt orthogonalisation 130

**REFERENCES** 135
INTRODUCTION
It is almost trivial to observe of quantum chemistry that the slow convergence of the configuration interaction (CI) expansion represents a major obstacle for the computation of accurate electronic wave functions. The additional motivation for the use of extended basis sets, provided by the requirement for accuracy and advances in computer soft and hard ware techniques, emphasises this observation.

The response of various workers is to propose methods to partition the calculation. To be useful partitioning should allow us, for a given level of approximation, to discern within the space spanned by the basis orbitals a relatively small orbital space $S$ with a more significant contribution in the wave function than that of its complement $S'$. Schemes to make effective use of the two spaces can then be found. Truncation of the full [i.e., all configuration state functions (CSF's) which can be constructed from the orbital set] CI expansion by partial inclusion of $S'$ is one scheme that immediately presents itself. The estimation from first-order perturbation theory (PT) of the set of components of the CI vector which have a first-order dependence on $S'$ another.

The principal disadvantage of choosing restricted Hartree-Fock (RHF) canonical basis orbitals for use in extended basis set CI calculations of this kind is the ill-defined and often far from optimum vacant valence part of orbital space. On the other hand, in a general CI expansion, the RHF determinant is often the dominant term and is, therefore, frequently chosen as the reference state.
configuration in the widely accepted full-class (i.e., all CSF's of a particular class that can be constructed from an orbital set) single and double replacement CI, [(S + D)CI].

The contrasting suitability of the occupied and virtual subspace for limited (S + D)CI calculations may be improved by noting that results of full-class CI are invariant to separate unitary transformation of the occupied and virtual space provided that the two spaces are orthogonal. One can, therefore, determine orbital sets at liberty using any element of the unitary group U(n) of transformations of the RHF orbitals provided that no orbital mixing occurs between the two spaces, e.g., a projection tensor is used to obtain the vacant valence space in CI calculations using an RHF reference state. In a similar vein, the inclusion of additional Coulomb and exchange operators in the RHF Hamiltonian is used to generate modified virtual orbitals (MVO's) for orbitally ordered CI calculations together with a general process to order them.

The aforementioned methods and CI schemes have been applied to the calculation of electron spin resonance (ESR) hyperfine coupling constants of doublet state radicals in this work. Results obtained from full (S + D)CI (i.e., using all of the basis-set orbitals) provide the benchmark by which these less complete theoretical treatments is judged.

NOTE

It should be noted that the work communicated here has been also largely reported in two published papers which are cited as an addendum to this thesis.
SECTION ONE: The calculation of electron spin resonance hyperfine coupling constants
1.1 Theory

The hyperfine terms of the molecular Hamiltonian, \( \hat{\mathbf{H}} \), involving electron-nucleus coupling are principally of interest in the interpretation of ESR experiments and can be expressed through the Hellmann-Feynman [1,2] theorem as

\[
\hat{\mathbf{H}}_0 + \hat{\mathbf{H}}_D + \hat{\mathbf{H}}_F = \sum_I \hat{\mu}_I \cdot (\delta \hat{\mathbf{H}} / \delta \hat{\mu}_I |_{\lambda=0}) \quad (1.1.1)
\]

where

\[
\hat{\mathbf{H}}_0 = 2 \beta_e \sum \sum r_{II}^{-3} (\hat{\mathbf{L}}_{II} \cdot \hat{\mu}_I) \quad (1.1.2)
\]

\[
\hat{\mathbf{H}}_D = g_e \beta_e \sum \sum r_{II}^{-5} [3(\hat{\mathbf{s}}_I \cdot r_{II})(r_{II} \cdot \hat{\mu}_I) - r_{II}^2 (\hat{\mathbf{s}}_I \cdot \hat{\mu}_I)] \quad (1.1.3)
\]

\[
\hat{\mathbf{H}}_F = \left( \frac{8\pi}{3} \right) g_e \beta_e \sum \sum \delta(r_{II})(\hat{\mathbf{s}}_I \cdot \hat{\mu}_I) \quad (1.1.4)
\]

\( \hat{\mu}_I \) is the magnetic moment operator for nucleus \( I \), \( \lambda \) is the complete collection of non-electronic operators appearing in \( \hat{\mathbf{H}} [3] \), \( \beta_e \) is the Bohr magneton, \( \hat{\mathbf{L}}_{II} \) is the orbital angular momentum operator for electron \( i \) about nucleus \( I \), \( g_e \) is the electronic g value, \( \hat{\mathbf{s}}_I \) is the spin angular momentum operator for electron \( i \) and \( \delta(r_{II}) \) is the three-dimensional Dirac delta function for electron \( i \) at nucleus \( I \), which has the property that

\[
\int \delta(r_{II}) f(r_i) d^3r_i = f(R_I) \quad (1.1.5)
\]

where \( f(r_i) \) is an arbitrary function of the coordinates of electron \( i \) and

\[
r_{II} = r_i - R_I. \quad (1.1.6)
\]

\( \hat{\mathbf{H}}_0 \), representing the nuclear magnetic moment acting on the moving electrons, merely causes a shift of all the
hyperfine levels but not a splitting; for this reason it is usually neglected in this context although it is not negligible in magnitude.

\( \hat{H}_D \), the dipolar or anisotropic term, representing the quantum mechanical equivalent of dipolar coupling, i.e., the interaction between the nuclear moments and the electron spins, may equally be expressed as

\[
\hat{H}_D = g_e \beta_e \sum \sum \mathbf{T}_i^{(B)}(\mathbf{s}_i, \mathbf{\mu}_i) \tag{1.1.7}
\]

where \( \mathbf{T}_i^{(B)} \) is a non-divergent tensor of the second rank. The components of \( \mathbf{T}_i^{(B)} \) are given by the set of equations

\[
[\mathbf{T}_i^{(B)}]_{\alpha\beta} = r_{i\alpha}^{-3} \left[ 3(1_{i\alpha})(1_{i\beta}) - \delta_{\alpha\beta} \right] \tag{1.1.8}
\]

where \((1_{i\alpha})\) are the direction cosines of \( r_{i\alpha} \), \( \delta_{\alpha\beta} \) is the Kronecker delta symbol and \( \alpha, \beta = 1, 2, \text{ or } 3 \). The means of \( \mathbf{T}_i^{(B)} \) taken over the unit sphere

\[
\sum_{\alpha} (1_{i\alpha}) (1_{i\alpha}) = 1 \tag{1.1.9}
\]

and of dipolar coupling equate to zero for gases and liquids.

\( \hat{H}_F \), the Fermi contact or isotropic term [4,5], arising from the interaction between the nuclear moments and the electron spins in contact with the nuclei, vanishes unless the electron has finite probability of being at the nucleus, i.e., for electrons with s-orbital character.

Introducing the magnetic hyperfine tensor, \( \mathbf{T}_i^{(A)} \), by the relation

\[
\mathbf{T}_i^{(A)} = \mathbf{T}_i^{(B)} + (8\pi/3)\mathbf{s}(r_{i\alpha})U \tag{1.1.10}
\]
where $U$ is the unit tensor, equation (1.1.1) becomes
\[ \hat{H}_D + \hat{H}_F = g_e \beta_e \sum \sum T_{i}^{(A)} (\hat{s}_i, \hat{\mu}_i) \quad (1.1.11) \]

where $T_{i}^{(B)}$ represents the anisotropic contribution to the magnetic hyperfine tensor and $(8\pi/3)\delta(r_{ii})$ represents the purely isotropic contribution. $T_{i}^{(A)}$ is, manifestly, a rank two symmetric tensor and can, therefore, always be expressed in the canonical form
\[ T_{i}^{(A)} = \sum_{\alpha} [\lambda_{i}^{(A)}]_{\alpha} P_{i}^{(A)} \quad (1.1.12) \]

where the $P_{i}^{(A)}$ are projection tensors associated with the eigenvectors $[l_{i}^{(A)}]_{\alpha}$ of $T_{i}^{(A)}$ belonging to the eigenvalues $[\lambda_{i}^{(A)}]_{\alpha}$.

The isotropic hyperfine coupling constant, $a_{i}$, for nucleus $I$, may be defined from equation (1.1.4) as
\[ a_{i} = (8\pi/3) g_e \beta_e \gamma_I \hbar D_3 (R_I). \quad (1.1.13) \]

The anisotropic hyperfine coupling constants, $(C_{i})_{\alpha\beta}$, for nucleus $I$, may be similarly defined from either equation (1.1.3) or the full operator expressed in equation (1.1.11) as
\[ (C_{i})_{\alpha\beta} = g_e \beta_e \gamma_I \hbar \int [T_{i}^{(C)}]_{\alpha\beta} D_3 (r_1) d^3 r_1 \quad (1.1.14) \]

where $\gamma_I$ is the gyromagnetic ratio of the nucleus $I$. The canonical forms of the symmetric, second rank, anisotropic hyperfine coupling tensors, $C_{i}$, specifying three anisotropic values $[\lambda_{i}^{(C)}]_{\alpha} = (C_{i})_{\alpha}$ and associated directions $[l_{i}^{(C)}]_{\alpha}$. $(8\pi/3)\delta(r_{ii})$ here is apparently relevant only in fixing a shift of all three anisotropic values $[\lambda_{i}^{(A)}]_{\alpha} = [\lambda_{i}^{(B)}]_{\alpha} + a_{i}$ and has no effect on the
associated directions \( l_{I}^{(B)} \). In the same way that the isotropic contribution to the hyperfine coupling constants gives an indication of \( s \)-orbital character, the anisotropic contribution to the hyperfine coupling constants gives an indication of \( p \)- or \( d \)-orbital character.

\( D_{S}(r_{1}) \) in equation (1.1.14) is the normalised spin density \([6]\) defined by

\[
D_{S}(r_{1}) = 2 \int_{s' = s_{1}}^{s_{1}} \hat{s}_{z}(1) \varphi_{1}(x_{1}; x_{1}') \, ds_{1} \quad (1.1.15)
\]

where \( x_{1} \) is a common designation for the space and spin coordinates \((r_{1}, s_{1})\) of an electron, the prime indicates that the \( z \)-component of the spin angular momentum operator, \( \hat{s}_{z}(1) \), has no effect on \( x_{1}' \) in \( \varphi_{1}(x_{1}; x_{1}') \) and \( s_{1}' = s_{1} \) indicates that \( s_{1}' \) is put equal to \( s_{1} \) after \( \hat{s}_{z}(1) \) has operated on \( \varphi_{1}(x_{1}; x_{1}') \) but before completion of the integration. \( \varphi_{1}(x_{1}; x_{1}') \) is the spin-dependent first-order reduced density matrix corresponding to the \( N \)-electron wave function, \( \varphi \)

\[
\varphi_{1}(x_{1}; x_{1}') = N \int \varphi(x_{1}, x_{2}, \ldots, x_{N}) \phi^{*}(x_{1}', x_{2}, \ldots, x_{N}) \, dx_{2} \ldots dx_{N} \quad (1.1.16)
\]

with \( S = M_{S} = 1/2 \) and therefore, \( D_{S}(R_{1}) \), the spin density at nucleus \( I \), in equation (1.1.13) is given by

\[
D_{S}(R_{1}) = \int_{r_{1}' = r_{1}}^{r_{1}} \delta(r_{11}) \, D_{S}(r_{1}; r_{1}') \, d^{3}r_{1}. \quad (1.1.17)
\]

Both definitions for the isotropic [equation (1.1.13)] and anisotropic [equation (1.1.14)] hyperfine coupling constants assume a total wave function in which the only nuclear variables are the nuclear spins. The modifications
necessary to include nuclear vibrations within the harmonic and essentially Born-Oppenheimer [7] approximations are discussed in Section 1.4.

1.2 The restricted Hartree-Fock plus combined configuration interaction-perturbation method

The N-electron RHF wave function, $\Phi_{RHF}$, of a closed-shell system [8,9] or of a half-closed shell system [10,11] is a single normalised Slater determinant or detor, i.e., an antisymmetrised product (AP) of $N$ one-electron functions, here the occupied molecular spin orbitals (MSO's), $\psi(r)\eta(s)$

$$\Phi_{RHF,x_1',x_2',...,x_N} = \hat{A} \prod_{a=1}^{n_1} \psi_a(r_{2a-1})\alpha(s_{2a-1})\psi_a(r_{2a})\beta(s_{2a})$$

$$\times \prod_{b=1}^{n_2} \psi_{n_1+b}(r_{2n_1+b})\alpha(s_{2n_1+b})$$

where $\hat{A}$ is the antisymmetriser,

$$\hat{A} = (N!)^{-1/2} \sum_{i=1}^{N!} (-1)^{\hat{p}_i} \hat{p}_i$$

$\hat{p}_i$ is an operator that generates the $i$th permutation of the electron coordinates and $\hat{p}_i$ is the number of pair interchanges required to obtain this permutation, $a$ labels the $n_1$ doubly occupied molecular orbitals (MO's), $\psi_a$, $b$ labels the $n_2$ singly occupied MO's, $\psi_b$, $\eta$ is the spin function $\alpha$ or $\beta$. $\psi_k'$ within the linear combination of atomic orbitals (LCAO) approximation, being expressed as

$$\psi_k'(r_1) = \sum_{l=1}^{m} \chi_l(r_1)c_{lk}$$
where \( \psi_1 \) refers to one of the, \( m \) in total, atomic orbitals (AO's) and \( C_{lk} \) is a set of MO coefficients. The doubly occupied set of MO's, \( k = 1, 2, \ldots, n_1 \) in equation (1.2.3), is referred to as the closed shell, the singly occupied set, \( k = n_1 + 1, n_1 + 2, \ldots, n_1 + n_2 \), the open shell and the unoccupied set, \( k = n_1 + n_2 + 1, n_1 + n_2 + 2, \ldots, m \), the empty shell. The doublet state (\( n_2 = 1 \)) alone is considered in this work.

Equation (1.2.3) can be written in matrix notation

\[
\psi^* = \chi^* C
\]  

(1.2.4)

where \( \chi^* \) and \( C \) are matrices of dimensions \( 1 \times m \) and \( m \times m \) respectively, \( \chi^* \) being the transpose of \( \chi \). The MO's form a real orthonormal set, i.e.,

\[
(\int \psi_k^* \psi_1 \, d^3r)^* = \int \psi_k^* \psi_1 \, d^3r = \delta_{kl}.
\]  

(1.2.5)

The AO's, in general, form a non-orthonormal set and it is, therefore, necessary to define the components of the metric tensor, \( S \), by the equations

\[
S_{kl} = \int \chi_k^* \chi_1 \, d^3r
\]  

(1.2.6)

where \( S \) is symmetric and of rank two (in \( m \) dimensions). Hence, equations (1.2.5) can be written as

\[
C^* S C = l_m
\]  

(1.2.7)

where \( l_m \) is the \( m \times m \) unit matrix.

The RHF energy, \( E(\psi_{\text{RHF}}) \), in terms of, in an orthonormal basis (\( \chi' \) say), the projection tensors associated with the numbers \( n_k \), with the matrices,

\[
R_k = T_k T_k^{**}
\]  

(1.2.8)
is given by
\[ E(\Phi_{RHF}) = \sum_k v_k \text{Tr} \frac{\Gamma_k}{2} \left[ h + \frac{1}{2} \gamma_k \right] \]  \hspace{1cm} (1.2.9)
where \( v_k \) is the occupation number of shell \( k \), \( \Gamma_k \) is a \( m \times n_k \) submatrix of the matrix \( C \) corresponding to the closed-shell \((v_1 = 2)\) and open-shell \((v_2 = 1)\) MO's respectively,
\[ G_1 = G(v_1 R_1) + G(v_2 R_2), \quad G(R) = J(R) - (1/2)K(R) \]  \hspace{1cm} (1.2.10)
\[ G_2 = G(v_1 R_1) + G'(v_2 R_2), \quad G'(R) = J(R) - K(R) \]  \hspace{1cm} (1.2.11)
\[ J(R)_{ij} = \sum_{k l} R_{1k}(ij|kl) \]  \hspace{1cm} (1.2.12)
\[ K(R)_{ij} = \sum_{k l} R_{1k}(il|kj) \]  \hspace{1cm} (1.2.13)
\[ h_{ij} = (i|\hat{h}|j) = (x_i|\hat{h}|x_j) = \int x_i^*(r_1) \hat{h} x_j(r_1) \, d^3r_1 \]  \hspace{1cm} (1.2.14)
\( \hat{h}(i) \) is a sum of the electronic kinetic energy and nuclear-electronic attraction
\[ \hat{h}(i) = \hat{t}(i) + \hat{v}_{en}(i) = -(1/2)\text{div grad}(i) - \sum_I Z_I r_{1i}^{-1} \]  \hspace{1cm} (1.2.15)
div grad is the Laplacian operator defined in terms of the general orthogonal coordinate system \((\lambda, \mu, \nu)\) as
\[ \text{div grad} = (h_\lambda h_\mu h_\nu)^{-1} \left\{ \delta/\delta \lambda (h_\lambda^{-1} h_\mu h_\nu \delta/\delta \lambda) + \delta/\delta \mu (h_\lambda h_\mu^{-1} h_\nu \delta/\delta \mu) \right. \]
\[ + \left. \delta/\delta \nu (h_\lambda h_\mu h_\nu^{-1} \delta/\delta \nu) \right\}, \]
\[ h_\lambda = |\delta r/\delta \lambda|, \quad h_\mu = |\delta r/\delta \mu|, \quad h_\nu = |\delta r/\delta \nu| \]  \hspace{1cm} (1.2.16)
\[ (ij|kl) = (x_i x_j | x_k x_l) \]
\[ = \int x_i^*(r_1) x_j(r_1) r_{12}^{i-1} x_k^*(r_2) x_l(r_2) \, d^3r_1 \, d^3r_2. \]  \hspace{1cm} (1.2.17)
\( R_1 \) and \( R_2 \) are obtained by requiring that \( E \) is a minimum
for variations

\[ R_k \rightarrow R_k + \delta R_k \quad (1.2.18) \]

subject to the MO's forming an orthonormal set, i.e., on multiplying equation (1.2.7) from the left by \( C \) and from the right with \( C^{+\ast} \), in terms of \( R_k \), to

\[ R_k S R_k = R_k, R_k S R_1 = 0 \quad (k \neq 1) \quad (all \ k, 1), \quad (1.2.19) \]

so that the variations (1.2.18) consistent with equations (1.2.19) also satisfy

\[ (R_k + \delta R_k) S (R_k + \delta R_k) = (R_k + \delta R_k), \]

\[ (R_k + \delta R_k) S (R_1 + \delta R_1) = 0 \quad (k \neq 1) \quad (all \ k, 1) \quad (1.2.20) \]

or to first order of small quantities

\[ R_k \delta R_k + \delta R_k S R_k = \delta R_k, R_k \delta R_1 + \delta R_k S R_1 = 0 \quad (k \neq 1) \quad (all \ k, 1) \quad (1.2.21) \]

if, on the other hand, equation (1.2.7) is multiplied from the left by \( C^{+\ast} \) and from the right by \( C^{-1} \) another equation results

\[ S = (CC^{+\ast})^{-1}, CC^{+\ast} = R_z + \sum_{k(\neq z)} R_k, R_z = T_z T_z^{+\ast} \quad (1.2.22) \]

introducing \( T_z (z = 3) \) for the \( m \times n_3 \) submatrix of the matrix \( C \) corresponding to the \( n_3 (= m - n_1 - n_2) \) empty-shell MO's. Evidently, only variations \( \delta R_k \) \((k \neq z)\) need be considered explicitly.

The matrices \( S^\alpha R_k S^{1-\alpha} \) possess properties analogous to those of \( R_k \) in an orthonormal basis, each is idempotent from equations (1.2.19)

\[ (S^\alpha R_k S^{1-\alpha})^2 = S^\alpha R_k S^{1-\alpha} = S^\alpha R_k S^{1-\alpha} S^\alpha R_k S^{1-\alpha} = S^\alpha R_k S^{1-\alpha}, \]

\[ (1.2.23) \]
the traces are equal to the number of MO's collected into $T_k$

$$\text{Tr } S_k^{a} S^{-1-a} = \text{Tr } S_k^{a} S_k^{+} S^{-1-a} = \text{Tr } S_k^{+} S^{-1-a} S_k^{a} = \text{Tr } S_k^{+} S_k^{a} = \text{Tr } 1_n = n_k \text{ (all } k)$$  

(1.2.24)

and on replacement of each side of equation (1.2.22) by its inverse the result of multiplication from the left by $S^a$ and from the right by $S^{-1-a}$ is the resolution of the identity, although it should be noted that since, in general, $S_k^{a} S^{-1-a} \neq S^{-1-a} S_k^{a}$ and

$$\left(S_k^{a} S^{-1-a}\right)^{+} = \left(S^{-1-a}\right)^{+} S_k^{+} \left(S^{a}\right)^{+} = S^{-1-a} S_k^{a} \quad (1.2.25)$$

the matrices are not necessarily Hermitian. Thus, a matrix, $M$, which is a representative of some operator in the basis $X$ can be resolved into its components, $S_k^{a} S^{-1-a} M S^{-1-a} R_k^{a} S^{a}$, on multiplication from the left by $S^{a} C^{+} S^{-1-a}$ and from the right by $S^{-1-a} C^{+} S^{a}$

$$M = S^{a} C^{+} S^{-1-a} M S^{-1-a} C^{+} S^{a} = \sum_{k,l} S_k^{a} S^{-1-a} M S^{-1-a} R_l^{a} S^{a}. \quad (1.2.26)$$

This resolution is unique and $M$ vanishes if and only if each of its components vanishes so that equality of two matrices implies equality of all corresponding components.

The implication on equating the components ($a = 0$) of each side of equations (1.2.21) is that the most general first-order variations $\delta R_k$ compatible with the first set of equations (1.2.19) are given by

$$\delta R_k = \sum_{l(xk)} \left(R_k S_{kl} S R_l + R_l S Y_{lk} S R_k\right) \quad (1.2.27)$$

where $X_{kl}$ and $Y_{kl}$ are arbitrary $m \times m$ matrices and with both sets of equations (1.2.19) by equation (1.2.27) introducing
the relations
\[ R_{k}S_{kl}S_{l} = -R_{k}S_{kl}S_{l} \] (1.2.28)

which in turn implies
\[ Y_{kl} = -X_{kl}' \] (1.2.29)

whilst the requirement that \( R \) remains Hermitian symmetric implies
\[ Y_{lk} = X_{lk}^{+*} \] (1.2.30)

The energy change, \( \delta E \), associated with the variations (1.2.18) is obtained easily to first order on noting the following properties of \( G \) (and similarly for \( G' \))
\[ G(A + B) = G(A) + G(B), \quad G(aA) = aG(A), \quad \text{Tr} AG(B) = \text{Tr} BG(A), \] (1.2.31)

for arbitrary \( A \) and \( B \), as
\[ \delta E = \sum_{k(xz)} v_{k} \text{Tr} \delta R_{k} h_{k}^{x}, \quad h_{k} = (h + G_{k}). \] (1.2.32)

The condition for stationary \( E \), with all constraints incorporated, follows on putting equation (1.2.30) into equation (1.2.27) and substituting into equation (1.2.32)
\[ \delta E = \sum_{k(xz)} \sum_{l(zk)} v_{k}[\text{Tr} X_{kl}S_{l}h_{k}R_{k}S + \text{Tr} X_{kl}^{+*}S_{l}h_{k}R_{k}S] = 0. \] (1.2.33)

The terms in brackets are complex conjugate so that each trace must vanish separately, for arbitrary \( X_{kl} \). Taking \( l = z \) and observing that \( \text{Tr} XA = 0 \) (\( X \) arbitrary) implies \( A = 0 \)
[12] this implies
\[ SR_{x}h_{k}R_{k}S = SR_{x}h_{k}R_{k}S = 0 \quad (\text{all } k(x z)) \] (1.2.34)

and on taking the remaining terms in pairs and noting from equations (1.2.29) and (1.2.30) that \( X_{kl} = -X_{lk}^{+*} \)

[-12-]
SR_k(v_k h_k - v_1 h_1)R_1 S = 0 \ (k \neq 1) \ (all \ k(z), l(z)). \hspace{1cm} (1.2.35)

It is not immediately apparent how to achieve the connection between equations (1.2.34) and (1.3.35), which together with equations (1.2.19) completely determine the solution and the actual method of obtaining this solution in the open-shell case but if all the previous equations are revised for the closed-shell case (n_2 = 0) then the closed-shell stationary value condition can be alternatively expressed as

\[ \text{FR}_k S - \text{SR}_k F = 0 \ (all \ k) \hspace{1cm} (1.2.36) \]

where matrix F is a representative the Hartree-Fock (HF) Hamiltonian. Thus, in the present case, a single matrix is sought such that equations (1.2.36) are entirely equivalent to equations (1.2.34) and (1.2.35) whereupon the conditions that each of the components (a_i = 1) of equations (1.2.36) must vanish reveals that the required open-shell analogue of F is

\[ F = \sum a_k \text{SR}_k z h_k R_k z S + \sum b_{k l} \text{SR}_k l (v_k h_k - v_1 h_1) R_{k l} S \]

\[ k(z) l(z) < 1(z) \hspace{1cm} (1.2.37) \]

where a_k, b_{k l} are arbitrary (non-zero) constants and

\[ R_{k l} = R_k + R_{1} \hspace{1cm} (1.2.38) \]

Hence, it remains only to show that equations (1.2.36) are in turn satisfied when the matrices R_k are constructed from the corresponding submatrices T_k of eigenvectors of the pseudo-eigenvalue problem

\[ FC = SC \hspace{1cm} (1.2.39) \]

where \( \epsilon \) is a diagonal matrix of the eigenvalues \( \epsilon_i \) of F and
to this end re-introduce the factorisation of $R_k$ according to equations (1.2.8) and (1.2.22), for when $C$ is determined by the eigenvalue procedure equations (1.2.19) are satisfied automatically, equations (1.2.36) become

$$FT_k^*T_k^*S - ST_k^*T_k^*F = 0 \quad (1.2.40)$$

or, on multiplication of equation (1.2.40) from the right by $T_k$ and noting that the MO's form an orthonormal set,

$$FT_k = ST_k\lambda_k, \quad \lambda_k = T_k^*FT_k. \quad (1.2.41)$$

$T_k$ is now subjected to a unitary transformation by means of a matrix $U_k$ to give the new matrix $T'_k$

$$T'_k = T_kU_k, \quad T_k = T'_kU_k^{\dagger}, \quad U_k^{\dagger}U_k = 1_{n_k} \quad (1.2.42)$$

and noting that $R_k$ and hence, $F$ is invariant under a unitary transformation

$$R'_k = T_kT'^{\dagger}_k = T_k^{\dagger}U_k^{\dagger}U_kT_k^{\dagger} = T'_kT'^{\dagger}_k = R'_k, \quad F' = F' \quad (1.2.43)$$

equation (1.2.41) becomes, after multiplication by $U_k^{\dagger}$ from the right,

$$F'T'_k = ST_k^\lambda_k', \quad \lambda'_k = U_k^{\dagger}\lambda_kU_k. \quad (1.2.44)$$

The matrix $\lambda'_k$ is Hermitian and hence, there exists a unitary matrix, $U_k$, such that $\lambda'_k$ is a diagonal matrix, so it is sufficient to assume $\lambda'_k$ diagonal and on dropping the primes in equation (1.2.44) the matrices $T'_k$ must then be identical to the corresponding submatrices of eigenvectors in equation (1.2.39). The matrices $T'_k$ that satisfy the eigenvalue equation, in contrast to the more general equation (1.2.41), are referred to as the canonical orbitals.

The foregoing discussion can be repeated perfectly well
with particular reference to an orthonormal basis and the modifications necessary to admit basis non-orthonormality verified easily on relating the $X'$ basis symmetrically to the $X$ basis used so far by Löwdin's [13-15] prescription
\[ x',\dagger = x\dagger x, \quad x = S^{-1/2} \]  
when this is done equation (1.2.4) introduces the following relations
\[ \varphi\dagger = x\dagger c = x',\dagger c' = x\dagger xc', \quad c = xc', \quad c' = x^{-1}c \]  
\[ R_k^i = T_k^i T_i^* = x^{-1}T_k (x^{-1}T_k)^* = x^{-1}T_k T_i^* x^{-1}\dagger = x^{-1}R_k x^{-1} \]
\[ h_{ij}^i = (x_i^j | \hat{h} | x_j^i) = \left( \sum_k x_k x_{ki} | \hat{h} | \sum_l x_l x_{lj} \right) = \sum_k \sum_l x_{ki}^* (x_k | \hat{h} | x_l) x_{lj} \]
\[ = \sum_{k l} \sum x_{ik} h_{kl} x_{lj}, \quad h' = xhx, \quad h' \in \{ M^i_i \} \]
so that the elements of the matrix $M^i_i \in \{ M^i_i | M^i_i = XM_i X \}$ may be regarded as matrix elements of a one-electron operator in the basis $X'$
\[ (i'j'|k'l') = (x_i^j x_k^l | x_i^j) \]
\[ = (\sum_a x_a x_{ai} \sum_b x_b x_{bj} | \sum_c x_c x_{ck} \sum_d x_d x_{dl}) \]
\[ = \sum_{m m m m} \sum x_{ai}^* x_{bj} x_{ck} x_{dl} (x_a^b | x_c^d) \]
\[ = \sum_{m m m m} \sum x_{ia} x_{bj} x_{kc} x_{dl} (ab | cd) \]
\[ J'(R')_{ij} = \sum_{k l} R_{lk}^i (i'j'|k'l') \]
\[
\sum_{k} \sum_{l} (X^{-1}RX^{-1})_{lk} \sum_{a} \sum_{b} \sum_{c} \sum_{d} x_{ia} x_{b} x_{kc} x_{dl} (ab|cd)
\]

\[
\sum_{a} \sum_{b} x_{ia} \sum_{c} \sum_{d} \sum_{k} \sum_{l} (X^{-1}RX^{-1})_{lk} x_{kc} (ab|cd) x_{bj}
\]

\[
\sum_{a} \sum_{b} x_{ia} J(R)_{ab} x_{bj}, \quad J'(R') = XJ(R) X, \quad J'(R') \in \{M_i^i\}
\]

\[
(i'l'|k'j') = (X_i^i X_i^i | X_k^k X_j^j)
\]

\[
\text{it then follows that } \{G'(R'), G''(R'), G_k^i, h^i_k \subseteq \{M_i^i\}, \text{ thus,}
\]

-16-
\[
F' = \sum_{k(z)} a_k R_{kz} h^i_k R_{ki} + \sum_{k(z) < l(z)} b_{kl} R_{kl} (v_k h^i_k - v_l h^i_l) R_{ki}
\]
\[
= \sum_{k(z)} a_k x^{-1}_{kz} x^{-1}_{kX} x^{-1}_{kX} x^{-1}_{kz} x^{-1}
\]
\[
+ \sum_{k(z) < l(z)} b_{kl} x^{-1}_{kl} x^{-1} (v_k x_{kX} - v_l x_{lX}) x^{-1}_{kl} x^{-1} x_{kl}
\]
\[
= XFX, F' \in \{ M_i \}. \quad (1.2.53)
\]

Now, with all quantities defined in the \( \chi' \) basis, equation (1.2.39) is replaced by a standard eigenvalue problem
\[
F' C' = C' \epsilon', \quad (1.2.54)
\]
which in turn, after multiplication by \( C'^{\dagger} \), from the left, becomes
\[
\epsilon' = C'^{\dagger} F' C' = (X^{-1} C)^{\dagger} C'^{\dagger} X F X^{-1} = C'^{\dagger} C X^{-1} X F X^{-1} C
\]
\[
= \epsilon', \quad (1.2.55)
\]
i.e., \( \epsilon' \) is invariant to Löwdin's transformation (or indeed to any non-singular linear transformation of the AO's) and on dropping the prime from this matrix, equation (1.2.54) gives
\[
F' C' = C' \epsilon, \quad X F X^{-1} C = X^{-1} C \epsilon, \quad X F C = X^{-1} C \epsilon, \quad F C = X^{-2} C \epsilon
\]
\[
(1.2.56)
\]
which is just another statement of equation (1.2.39), as required.

Equation (1.2.39) may be conveniently solved through a standard eigenvalue problem on defining new matrices
\[
F' = D^{-1/2} L'^{\dagger} F L D^{-1/2} \quad (1.2.57)
\]
\[
C' = D^{1/2} L^{-1} C, \quad C = L D^{-1/2} C' \quad (1.2.58)
\]
where the components of \( S \) and the components of the diagonal tensor, \( D \), are connected by the transformation law
and \( L \) is an orthogonal matrix. \( L \) can always be constructed and \( D^{-1/2} \) is easily found, each diagonal element of \( D^{-1/2} \) being the square root of the reciprocal of the corresponding element of \( D \). Hence, from equations (1.2.39) and (1.2.59),

\[
F LD^{-1/2} D^{1/2} L^{-1} C = SLD^{-1/2} D^{1/2} L^{-1} C, \quad D^{-1/2} L^{\dagger} F LD^{-1/2} D^{1/2} L^{-1} C = D^{-1/2} L^{\dagger} H DL^{\dagger} LD^{-1/2} D^{1/2} L^{-1} C = D^{1/2} L^{-1} C, \quad F'C' = C'e
\]

(1.2.60)

an exact same result as that obtained on replacing \( S^{-1/2} \) by \( LD^{-1/2} \) in equation (1.2.45). The certain arbitrariness in \( F \) is reflected by changes in the spectrum of eigenvalues for different choices of the constants \( a_k, b_{kl} \), although the eigenvectors and hence, \( E(\Phi_{RHF}) \), \( R_1 \) and \( R_2 \) remain invariant. The eigenvalues are, thus, of a non-physical nature and there is no direct analogue of, for instance, Koopmans' [16] theorem, which states that ionisation potentials are the negatives of the canonical orbital energies.

\( D_S(r_1) \) can be now expanded in the AO basis as

\[
D_S(r_1) = \sum \sum (R_2)_1 n \chi_1(r_1) \chi_n^{*}(r_1).
\]

(1.2.61)

Hence it can be also noted here that if \( \Gamma_{ij} = \int \chi_i(r) \chi_j(r) d^3r \) then

\[
\int \Gamma(r_{ii}) D_S(r_1) d^3r_1 = Tr \Gamma R_2
\]

(1.2.62)

for the anisotropic data.

Evidently, consideration of the RHF method alone is not sufficient, as \( D_S(r_1) \) contains only \( R_2 \), in an orthonormal basis, the matrix of the projection tensor associated with
the open shell, it can predict only the contribution to the hyperfine coupling constants referred to as direct coupling due to the coupling the unpaired electron with the nuclei and cannot predict negative spin densities in \( \pi \)-electron radicals in agreement with experiment.

The RHF wave function supplemented by the inclusion of CI (RHF + CI) is, therefore, considered for the purposes of this work. The RHF + CI method arises from the assumption that any \( N \)-electron wave function, \( \phi \), derivable from \( n \geq N \) elements of a complete set of one-electron functions, \( \psi(x) \), by analogy with equation (1.2.3), can be written as

\[
\phi(x_1, x_2, \ldots, x_N) = \sum_{a} \psi_a(x_1) c_a(x_2, \ldots, x_N)
\]

\[
= \sum_{a} \sum_{b} \sum_{u} \sum_{v} c_{ab} \psi_a(x_1) \psi_b(x_2) \cdots \psi_u(x_N).
\]  

(1.2.63)

subject to

\[
\hat{P}_i \phi = (-1)^i \phi,
\]  

(1.2.64)

i.e., to \( c_{ab} \ldots u = c_{a\beta} \ldots v \) if \( a, \beta, \ldots, v \) is an even permutation of \( a, b, \ldots, u \), \(-c_{a\beta} \ldots v \) if \( a, \beta, \ldots, v \) is an odd permutation of \( a, b, \ldots, u \) and 0 if any pair of \( a, b, \ldots, u \) are the same, or

\[
\phi(x_1, x_2, \ldots, x_N)
\]

\[
= \sum_{a<b} \sum_{u<v} c_{ab} \psi_a(x_1) \psi_b(x_2) \cdots \psi_u(x_N).
\]  

(1.2.65)

Thus, \( \phi \), can be expanded as a linear combination of unique AP's formed from the elements of a matrix \( \psi \) analogous to \( \chi \) in equation (1.2.4). In an \( N \)-electron RHF + CI expansion
the \( n = 2m \) elements of \( \psi \) can be expressed by the direct product of matrices \( \psi \) and \( \eta \)

\[
\psi = \psi \times \eta
\]  

(1.2.66)

where \( \psi_k \) is an eigenfunction of the HF Hamiltonian and

\[
\eta^\dagger = (\alpha \beta).
\]  

(1.2.67)

Using the notation \( \{ |\psi_{ab}^{pq} \ldots \rangle \} \) to denote the set of AP's formed by replacing in \( \Phi_{\text{RHF}} \) any number of occupied MSO's \( \psi_a, \psi_b, \ldots \), by the same number of unoccupied MSO's \( \psi_p, \psi_q, \ldots \), the RHF + CI wave function, \( \Phi_{\text{CI}} \), can be, therefore, written as

\[
\Phi_{\text{CI}}(x_1', x_2', \ldots, x_N') = c_0^\dagger \Phi_{\text{RHF}} + \sum_p c_p^d |\psi_p^d\rangle + \sum_{a<b} c_{ab}^{pq} |\psi_{ab}^{pq}\rangle + \sum_{a<b<c} c_{abc}^{pqr} |\psi_{abc}^{pqr}\rangle + \sum_{a<b<c<d} c_{abcd}^{pqrst} |\psi_{abcd}^{pqrst}\rangle + \ldots
\]  

(1.2.68)

\[\text{the, } N_{C_t}^n - N_{C_t}^n \text{, upon summation over all } t^nc_n \text{, in numbers, individual terms in equation (1.2.68) being referred to as single, double, in general } t \text{-tuple, replacements. The vector of expansion coefficients, } c, \text{ is chosen to minimise the value of the energy functional}
\]

\[
E(\Phi_{\text{CI}}) = \langle \Phi_{\text{CI}} | \hat{H} | \Phi_{\text{CI}} \rangle / \langle \Phi_{\text{CI}} | \Phi_{\text{CI}} \rangle = \text{Tr } H \varphi, \quad \varphi = cc^\dagger / c^\dagger c
\]  

(1.2.69)

where \( H_{ij} \) is a matrix element of the Hamiltonian operator

\[
\hat{H} = \sum_i \hat{h}(i) + \sum_{j>i} \hat{g}(i,j)
\]  

(1.2.70)

\( \hat{h}(i) \) being the one-electron operator defined in equation (1.2.15) and
\[ g(i, j) = r_{ij}^{-1} \quad (1.2.71) \]

is the two-electron Coulomb repulsion term. Hence,

\[
H_{ij} = \int \frac{\hat{\rho}(1)}{x_i = x_1} \varrho_1(ij|x_1; x_1^i) \, dx_1
\]

\[ + \frac{1}{2} \int \frac{\hat{\rho}(1, 2)}{x_1^i = x_1} \varrho_2(ij|x_1, x_2; x_1^i, x_2^i) \, dx_1 \, dx_2 \quad (1.2.72) \]

where \( \varrho_1(ij|x_1; x_1^i) \) and \( \varrho_2(ij|x_1, x_2; x_1^i, x_2^i) \) are the one- and two-electron transition density matrices corresponding to the elements \( \psi_i \) and \( \psi_j \) of matrix \( \psi \),

\[
\varrho_1(ij|x_1; x_1^i) = N \int \psi_i(x_1, x_2, \ldots, x_N) \psi_j^*(x_1^i, x_2, \ldots, x_N) \, dx_2 \ldots dx_N \quad (1.2.73)
\]

\[
\varrho_2(ij|x_1, x_2; x_1^i, x_2^i) = N(N - 1) \int [\psi_i(x_1, x_2, \ldots, x_N) \psi_j^*(x_1^i, x_2^i, \ldots, x_N)] \, dx_3 \ldots dx_N, \quad (1.2.74)
\]

for which Slater's rules \([17,18]\) then give the following non-vanishing expansions in the MSO's

\[
\varrho_1(ij|x_1; x_1^i) = \sum_k \psi_k(x_1) \psi_k^*(x_1^i) \quad (1.2.75)
\]

\[
\varrho_2(ij|x_1, x_2; x_1^i, x_2^i) = \sum_{k,l} [\psi_k(x_1) \psi_l(x_2) \psi_k^*(x_1^i) \psi_l^*(x_2^i) - \psi_k(x_2) \psi_l(x_1) \psi_k^*(x_1^i) \psi_l^*(x_2^i)] \quad (1.2.76)
\]

if \( \psi_i \) is identical to \( \psi_j \),

\[
\varrho_1(ij|x_1; x_1^i) = (-1)^q \psi_r(x_1) \psi_u^*(x_1^i) \quad (1.2.77)
\]

\[
\varrho_2(ij|x_1, x_2; x_1^i, x_2^i) = (-1)^q \sum_k [\psi_r(x_1) \psi_k(x_2) \psi_u^*(x_1^i) \psi_k^*(x_2^i)]
\]
- \psi_r(x_2)\psi_k(x_1)\psi_u(x_1^r)\psi_k(x_1^r) + \psi_k(x_1)\psi_r(x_2)\psi_k(x_1^r)\psi_u(x_2) \\
- \psi_k(x_2)\psi_r(x_1)\psi_k(x_1^r)\psi_u(x_1^r)] \tag{1.2.78}

if \psi_i differs from \psi_j by only one replacement \psi_r \neq \psi_u,

\varrho_2(ij|x_1, x_2; x_i^r, x_i^s) = (-1)^q [\psi_r(x_1)\psi_s(x_2)\psi_k(x_1)\psi_u(x_2) \\
- \psi_r(x_2)\psi_s(x_1)\psi_k(x_1)\psi_u(x_2) + \psi_s(x_1)\psi_r(x_2)\psi_k(x_1)\psi_u(x_2)] \tag{1.2.79}

if \psi_i differs from \psi_j by two replacements \psi_r \neq \psi_u, \psi_s \neq \psi_v,

where the summations in the above equations are over the intersection of the two sets of MSO's in \psi_i and \psi_j and q is the number of pair interchanges required to put equal MSO's into equal positions in the two determinants. Now if,

$$d_i = |c_i|D^{-1/2}, D = c^+c, |H_{ij}| \leq M \tag{1.2.80}$$

for \(i, j = 1, 2, \ldots, N_D = mC_{N/2} + S^mC_{N/2} - S\) then

$$|E(\Phi_{CI})| \leq M(\sum_j d_j)^2 \tag{1.2.81}$$

but \(0 \leq d_i \leq 1\), so that

$$-N_D^2M \leq E(\Phi_{CI}) \leq N_D^2M \tag{1.2.82}$$

and \(E(\Phi_{CI})\) is a bounded, manifestly continuous, function of the components of \(c\) (assumed real). Hence, \(E(\Phi_{CI})\) has a lower bound which will be attained when

$$\frac{\delta E}{\delta c_i} = 0, \tag{1.2.83}$$

i.e., when

$$\sum_{ij} H_{ij} c_j = E(\Phi_{CI})c_i \tag{1.2.84}$$
or in matrix notation

\[ Hc = Ec. \]  

Thus, the problem of evaluating the ground state RHF + CI wave function and energy may be formulated in terms of computing the lowest eigenvalue, \( E \) and the corresponding eigenvector, \( c \), of matrix \( H \) in equation (1.2.85). The iterative method of Nesbet [19] performs this task. One component of \( c \), \( c_k \), is fixed at unity, whilst the other components, \( c_i \), are incremented for values of the index \( i \neq k \) in increasing sequence according to the equations

\[
\sigma_i = \sum_j H_{ij} c_j - E c_i
\]

\[
\Delta c_i = \sigma_i / (E - H_{ii})
\]

\[
\Delta D = (2c_i + \Delta c_i) \Delta c_i
\]

\[
\Delta E = \sigma_i \Delta c_i / (D + \Delta D)
\]

unless some value \( |\Delta c_i| \) exceeds a variable criterion, when the iteration is repeated from the initial value of \( i \). The computation terminates after a complete iteration if the largest increment \( |\Delta c|_{\text{max}} \) is less than a fixed criterion. An initial approximation to an eigenvector is required. This can be the unit basis vector corresponding to the initial value of \( E = H_{11} \) in equation (1.2.69).

The RHF + CI expansion may be related to the Brillouin-Wigner (BW) and the Rayleigh-Schrödinger (RS) perturbation series as follows. The matrices \( H \) and \( c \) in equation (1.2.85), if written in "super-matrix" notation [20], assume the abbreviated forms

\[
[H_{st;uv}] = [M_{su}], [c_{st;11}] = [d_{sl}]
\]
where
\[ [M_{st}]_{tv} = H_{st;uv} \quad [d_{sl}]_{tl} = c_{st;ll}. \] (1.2.91)

Hence,
\[ Md = Ed \] (1.2.92)

where, in the partitioning technique of Löwdin [21], \( M \) and \( d \) are conformable matrices of dimensions 2 x 2 and 2 x 1 respectively. Equation (1.2.92) is then equivalent to two matrix equations
\[ M_{11}d_{11} + M_{12}d_{21} = Ed_{11} \] (1.2.93)
\[ M_{21}d_{11} + M_{22}d_{21} = Ed_{21}. \] (1.2.94)

From equation (1.2.94) then
\[ d_{21} = (E_{122} - M_{22})^{-1}M_{21}d_{11} \] (1.2.95)

and by substitution of equation (1.2.95) into equation (1.2.93)
\[ \bar{Md}_{11} = Ed_{11} \] (1.2.96)

where
\[ \bar{M} = M_{11} + M_{12}(E_{122} - M_{22})^{-1}M_{21} \] (1.2.97)

provided that, for an eigenvalue \( E \) having a degeneracy of finite order \( g \),
\[ M_{11} = [H_{lt;lv}], \quad t,v = 1, 2, \ldots, k \] (1.2.98)

where \( k = g \) since the inverse matrix in equations (1.2.95) and (1.2.97) will then exist. For the inverse of \( (A - B) \) where \( A \) and \( B \) are arbitrary non-singular square matrices, one always has the identity
\[ (A - B)^{-1} = A^{-1} + (A - B)^{-1}BA^{-1} \] (1.2.99)

leading by iteration to a set of identities in the form of a geometric series plus a remainder term.
\[(A - B)^{-1} = (A - B)^{-1}(BA^{-1})^{m'} + A^{-1}\sum_{n'=0}^{m'-1}(BA^{-1})^{n'} \quad (1.2.100)\]
as is easily proven for \(m' = 1, 2, \ldots\) by summation to \(m'\) terms, \(S_{m'}\),
\[
S_{m'} = (A - B)^{-1}[1 - (BA^{-1})^{m'}] + (A - B)^{-1}(BA^{-1})^{m'}
\]
\[(A - B)^{-1}. \quad (1.2.101)\]
The infinite series minus the remainder term holds whenever
\[
||A^{-1}B|| < 1 \text{ where } ||A^{-1}B||, \text{ the modulus of the matrix } A^{-1}B,
\]
is defined as
\[
||A^{-1}B|| = \sum_{r,s} |(A^{-1}B)_{rs}|^2. \quad (1.2.102)
\]
Further, the convergence of this series is slow unless
\[
||A^{-1}B|| \ll 1 [22]. \text{ Taking } k = 1, \text { for a non-degenerate } \text{ E}
\]
value and intermediate normalisation of an approximation to
the required \(\phi_{CI'}, \phi_{PT}\)
\[
<\phi_{RHF}|\phi_{PT}> = |c_{ll;ll}|^2 = 1 \quad (1.2.103)
\]
then equation (1.2.96) defines a function
\[
f(E) = E \quad (1.2.104)
\]
with the property that
\[
f^{(n')}(E) = (-1)^{n'} n'! M_{12}(E_{122} - M_{22})^{-(n' + 1)} M_{21} \quad (1.2.105)
\]
n' = 1, 2, \ldots which gives the BW series
\[
E = H_{11} + \sum_{p \neq 1} H_{1p}^c c_{p1} \quad (1.2.106)
\]
\[
c_{p1} = H_{p1}^c (E - H_{pp})^{-1} + \sum_{q \neq 1} H_{pq}^c H_{q1}^c [(E - H_{pp})(E - H_{qq})]^{-1}
\]
\[
+ \sum_{q, r \neq 1} H_{pq}^c H_{qr}^c H_{rl}^c [(E - H_{pp})(E - H_{qq})(E - H_{rr})]^{-1}
\]
-25-
on division of $M_{22}$ in equation (1.2.96) into its diagonal, $M'_{22}$, and non-diagonal, $M_{22}''$, parts and expansion of the inverse matrix in powers of,

$$A = E_{122} - M_{22}, \quad B = M_{22}''.$$  \hfill (1.2.108)

The right-hand side of equation (1.2.104) contains the unknown energy of the system and it is, therefore, necessary to solve iteratively. It, e.g., follows easily from equation (1.2.105) using the mean value theorem that the direct iteration of equation (1.2.104) determines a series of numbers $E(0)$, $E(1)$, $E(2)$, ... with the property that any two consecutive numbers $E + e_1$, $E + e_2$ bracket a true eigenvalue, $E$, viz.

$$E + e_2 = f(E + e_1) = f(E) + e_1f'(E + e_1),$$  \hfill (1.2.109)

i.e.,

$$e_2 = -e_1|d_{21}(E + je_1)|^2$$  \hfill (1.2.110)

where $0 < j < 1$, which proves the bracketing theorem since $e_1$ and $e_2$ have different signs. The series $E(0)$, $E(1)$, ..., which will be convergent if $|f(1)| < 1$ and divergent if $|f(1)| > 1$, is determined by Burton [23] in the calculation of nuclear spin-spin coupling constants and found to run into convergency problems. Further, on inspection of equation (1.2.93), a given term, $E(i)$, in the series $E(0)$, $E(1)$, ..., is discovered to be the energy value associated with $d_{21}(E(i))$ in the transition formula

$$E(i) = \langle \Phi_{RHF} | \hat{H} | \Phi_{PT} \rangle / \langle \Phi_{RHF} | \Phi_{PT} \rangle$$  \hfill (1.2.111)

rather than just the expectation value associated with
d_{21}(E^{(i)}). Both of these difficulties are removed [24] by going over to the Newton-Raphson tangential construction, which implies that if $\xi$ is an approximate solution of the equation

$$y(E) = 0$$

(1.2.112)

a better approximation is rendered by the formula

$$E = E - y(E)/y'(E), \quad (1.2.113)$$

i.e., by

$$E^{(1)} = E^{(0)} + \frac{(E^{(1)} - E^{(0)})}{(1 + |d_{21}(E^{(0)})|^2)}. \quad (1.2.114)$$

The convergence properties of the series expansion of the inverse matrix will obviously determine the validity of calculating the components of $d_{21}(E)$ from equation (1.2.107) but even when the conditions for the convergence of this series are not fulfilled equations (1.2.104) and (1.2.114) are still valid provided that the inverse matrix is obtained by other methods, e.g., the biorthogonalisation technique of Prosser and Hagstrom [25] appears to be the fastest known method of obtaining the inverse of a non-singular matrix. The method based on Gram-Schmidt [26] orthogonalisation described here requires an upper triangular matrix, $T$, of dimension $n' \times n'$ to be found such that for an arbitrary non-singular square matrix, $V$,

$$VT = 0, \quad O^\top O = 1,$$

(1.2.115)

hence, using the rule that the inverse (or transpose) of a product of matrices is obtained by multiplying the inverses (or transposes) of the individual factors in reverse order,

$$V^{-1} = T(VT)^{-1} = TO^\top = TT^\top V^\top$$

(1.2.116)

where the elements of the orthogonal matrix $O$ satisfy the
recurrence formula,

\[ o_{pr} = a_{rr}^{-1/2} (v_{pr} + \sum_{q=1}^{r-1} o_{pq} a_{qr}) \]  

(1.2.117)

and the coefficients \( a_{qr} \) are determined by the condition of orthonormality of the matrix 0 according to the equations

\[ a_{rr} = \sum_{s=1}^{n'} v_{rs}^+ v_{sr} - \sum_{q=1}^{r-1} a_{qr}^2 \]  

(1.2.118)

\[ a_{qr} = -\sum_{s=1}^{n'} o_{qs}^+ v_{sr} \quad (q < r). \]  

(1.2.119)

Thus, by comparison of equations (1.2.115) and (1.2.117), the procedure to construct matrix T can be formulated as

\[ T = \prod_{r=1}^{n'} T_r \]  

(1.2.120)

where

\[ T_{pq}^{(r)} = \delta_{pq} (q \neq r), \quad T_{pq}^{(r)} = a_{pq}^{-1/2} (p < q, q = r), \]

\[ T_{pq}^{(r)} = a_{qq}^{-1/2} (p = q = r) \]  

(1.2.121)

and \( T_{pq}^{(r)} \) is an element of the matrix \( T_r \). The form of 0 and T give rise to an interesting property of this procedure in regard of the determinant of V since from equation (1.2.116)

\[ |v^{-1}| = |v|^{-1} = |to^+| = |t|. |0^+| = |t|. |0| = t |t|, \]  

(1.2.122)

hence,

\[ |\det v| = |t|^{-1} = \prod_{r=1}^{n'} t_{rr}^{-1} = \prod_{r=1}^{n'} a_{rr}^{1/2}. \]  

(1.2.123)

This property suggests that a natural criterion exists for determining whether or not V actually possesses an inverse.
and indeed this is the case, for if any \( r \)th column of \( V \) depends linearly on the lower 1, 2, ..., \( r - 1 \) columns of \( V \) one has \( a_{rr} = 0 \).

The Gram-Schmidt orthogonalisation is considerably more computationally expensive in terms of arithmetic operations than biorthogonalisation but avoids the possibility of having to reorder the rows and the columns of \( V \) which, if performed by a numerically sound method, necessitates time-consuming searches and matrix reorganisations, also it requires only one transformation matrix to found whereas, for the general inverse, biorthogonalisation requires two.

The various forms of the RS series can be obtained by iteration on development of the right-hand side of the equation

\[
\hat{E} = M_{12}(E_{122} - M_{22})^{-1}M_{21}
\]  
(1.2.124)

in a power series in

\[
A = [M_{11}]_{11} l_{22} - M_{22}, \quad B = -\hat{E}_{122}
\]  
(1.2.125)

and various choices of \( A \) and \( B \) prior to the expansion of the inverse matrices in a given order of iteration. The first iterate

\[
E = f(H_{11})
\]  
(1.2.126)

contains the RS exact first- and second-order contributions to the wave function plus parts of all the higher order contributions [27] and if

\[
A = [M_{11}]_{11} l_{22} - M_{22}, \quad B = M_{22}^{-1}
\]  
(1.2.127)

corresponds to starting Rayleigh-Schrödinger perturbation theory (RSPT) using the Epstein-Nesbet [28,29] Hamiltonian

\[
\hat{H} = \hat{H}_0 + \hat{H}_1 = \sum_i |\psi_i\rangle <\psi_i| \hat{H} |\psi_i\rangle <\psi_i| + \sum_{i \neq j} |\psi_i\rangle <\psi_i| \hat{H} |\psi_j\rangle <\psi_j|.
\]  
(1.2.128)
The second iterate
\[ E = f(H_{11}) + \sum_{n' = 1} (n')^{-1}E(H_{11}^{n'})f(n')(H_{11}) \] (1.2.129)
contains the exact third-order contribution adding
\[- \sum_{q \neq 1} H_{p1}^q H_{1q}^q (H_{11} - H_{pp})^{-2}(H_{11} - H_{qq})^{-1} \] (1.2.130)
to the final term in equation (1.2.107) if \( E = H_{11} \). If,
\[ A = [\Lambda]_{11}^{1,2} \Lambda_{22}, \quad B = M_{12}^{1,2} \Lambda_{22} - [\Lambda]_{11}^{1,2} \Lambda_{22} \] (1.2.131)
where \( \Lambda, \Lambda_{11}, \Lambda_{22} \) and \( \Lambda', \Lambda_{11}', \Lambda_{22}' \) are the diagonal matrices
\[ [\Lambda_{su}]_{tv} + [\Lambda_{su}']_{tv} = H_{st:uv} \delta_{st:uv} \] (1.2.132)
the exact same arguments apply and corresponds to starting RSPT using the conventional form
\[ \hat{H} = \hat{H}_0 + \hat{V} \] (1.2.133)
where \( \hat{H}_0 \) is, e.g., the HF Hamiltonian [30]. Thus,
\[ \hat{H}_0 |\psi_i> = E_i^{(0)} |\psi_i>, \quad E_i^{(0)} = \sum_j \epsilon_j \] (1.2.134)
where \( \epsilon_j \) is the diagonal element of \( \epsilon \) in equation (1.2.60) corresponding to MSO \( \psi_j \) in \( \psi_i \). The first iterate becomes
\[ E = E_1^{(0)} + V_{11} + \sum_{p \neq 1} V_{lp} c_{pl} \] (1.2.135)
\[ c_{pl} = V_{pl}(E_1^{(0)} - E_p^{(0)})^{-1} \]
\[ + [ \sum_{q \neq 1} V_{pq} V_{1q} ((E_1^{(0)} - E_p^{(0)})(E_1^{(0)} - E_q^{(0)}))^{-1} \]
\[ - V_{11} V_{pl}(E_1^{(0)} - E_p^{(0)})^{-2}] \]
\[ + [ \sum_{q,r \neq 1} V_{pq} V_{qr} V_{rl} ((E_1^{(0)} - E_p^{(0)})(E_1^{(0)} - E_q^{(0)})(E_1^{(0)} - E_r^{(0)}))^{-1} \]
\[ - V_{11} V_{pl}(E_1^{(0)} - E_p^{(0)})^{-2}] \]
\[-30-\]
\[ + v_{11} v_{11} (E_1^{(0)} - E_p^{(0)})^{-3} \]
\[ - v_{11} \sum_{q \neq 1} v_{pq} v_{q1} (E_1^{(0)} - E_p^{(0)})^{-1} (E_1^{(0)} - E_q^{(0)})^{-2} \]
\[ - v_{11} \sum_{q \neq 1} v_{pq} v_{q1} (E_1^{(0)} - E_p^{(0)})^{-2} (E_1^{(0)} - E_q^{(0)})^{-1} \]
\[ + \ldots \quad (1.2.136) \]

The second iterate again contains the exact third-order contribution adding

\[ - \sum_{q \neq 1} v_{pq} v_{q1} (E_1^{(0)} - E_p^{(0)})^{-2} (E_1^{(0)} - E_q^{(0)})^{-1} \quad (1.2.137) \]

to the final collection of terms in equation (1.2.136).

Evidently, \( E(\Phi_{CT}) \), when carried through to an infinite order of iteration and assuming the expansion converges, will be identical to \( E(\Phi_{CI}) \) if the same basis set is used. Gershgorn and Shavitt [31] have, in addition, considered approximations to \( \Phi_{CI} \) denoted by \( A_0 \) and \( B_k \), correct to first order in Brillouin-Wigner perturbation theory (BWPT).

The \( A_0 \) approximation is obtained by neglecting the matrix \( M_{12} \) in equation (1.2.108) whereupon the right-hand side of equation (1.2.107) reduces exactly to the first term. Here matrix \( H \) represents the Hamiltonian operator in the CSF basis \( \{ | \Omega \rangle \} \), i.e., in \( \lambda \)th eigenfunctions of the \( \hat{S}_z \) and \( \hat{S}_2 \) operators with \( S = N/2, N/2 - 1, \ldots, 1/2 \) or 0, \( M_S = S, S - 1, \ldots, -S \) and which transform like the \( \xi \)th basis vector of irreducible representation \( D_\xi \) of the symmetry group \( G \) of the radical, as determinants constructed from \( \mu \alpha \)–MSO's, \( v \beta \)–MSO's and hence, \( | \Omega \rangle = | \mu - \nu \rangle \) odd \( \eta \)–MSO's, although eigenfunctions of \( \hat{S}_z \) belonging to \( M_S = 0/2 \), are neither usually eigenfunctions of \( \hat{S}_2 \) nor always symmetry
adapted for a non-Abelian G. \( |\Xi(\gamma)\rangle \) - \( |\psi_i\rangle \) is a set of linear combinations of determinants constructed from \( \mu = (N + o)/2 \) and \( \nu = (N - o)/2 \) MSO's corresponding to the same set of HF eigenvalues. Only those determinants which have but \( |o| \) unpaired spins can be common to \( |\Xi(\gamma)\rangle \) and \( |\psi_i\rangle \).

The subset of \( |\Xi(\gamma)\rangle \) in the \( \Phi_0 \) wave function, \( \Phi_0 \), is called the first-order interacting space and according to equations (1.2.75) - (1.2.79), will consist of, at most, all unique determinants in the set \( \{|\psi_{\alpha}^p\rangle, |\psi_{ab}^{pq}\rangle, |\psi_{abc}^{pqr}\rangle | M_S = 1/2 \} \). It should be noted that \( |\psi_{abc}^{pqr}\rangle \leq |\psi_{abc}^{pqr}\rangle \) is required to complete the set for \( \Phi_{CI} \) to be an eigenfunction of \( \hat{s}^2 \).

The \( B_k \) approximation is obtained for a non-degenerate \( E \) value if \( k > 1 \) in equation (1.2.98) reducing to the \( \Phi_0 \) approximation if \( k = 1 \). The corresponding expression for \( E \) in equation (1.2.96) is the expectation value of \( \bar{M} \)

\[
E = \sum_{i=1}^{k} \left[ M_{11} + M_{12}(E_{122} - M_{22})^{-1}M_{21} \right] d_{11}/|d_{11}|^2 \tag{1.2.138}
\]

which gives the BW series in terms of \( \Phi_{\text{proj}} \), the normalised projection of \( \Phi_{CI} \) onto the part of configuration space spanned by the first \( k \) elements of \( |\Xi(\gamma)\rangle \), on expansion of the inverse matrix in powers of the matrices \( A \) and \( B \) in equation (1.2.108). The \( B_k \) wave function, \( \Phi_{B_k} \) and energy is expressed in terms of an approximation to \( \Phi_{\text{proj}}' \) \( \Phi'_{\text{proj}} \) obtained by neglecting the matrix \( M_{22}^{11} \) in equation (1.2.108) whereupon this series reduces exactly to

\[
E = \sum_{p \leq \text{r}, k} \left[ \sum_{p \leq q} H_{pq}^c p^* c_q + \sum_{p \leq r} H_{pr}^c p^* c_r \right] \tag{1.2.139}
\]

where
\[ c_r = \sum_q H_{r q} (E - H_{rr})^{-1} c_q. \] (1.2.140)

Thus, as \( n(\{|E^{(a)}_{i \lambda}\}^S = M_{S} = 1/2\} = N_C = (2S + 1)(m + 1)^{-1} x m + 1 c_{N/2 - S} m + 1 c_{m - N/2 - S} [32,33], \) a maximum total of \((2N_C - k)(1 + k)/2\) Hamiltonian matrix elements will be required to evaluate \( \Phi_{B_k} \) compared with one of \( N_C(N_C + 1)/2 \) for \( \Phi_{CI} \). This total may be reduced by a further \((N_C - k) x (k - 1)\) if the \((k - 1) x (N_C - k)\) and \((N_C - k) x (k - 1)\) submatrices of \( M_{12} \) and \( M_{21} \) obtained by ignoring the first row of \( M_{12} \) and the first column of \( M_{21} \) in equation (1.2.138) are considered to be null matrices whereupon the right-hand side of equation (1.2.107) reduces exactly to the first term if \( p > k \) and indices \( q, r, \ldots \) therein take the values \( q, r, \ldots = 2, \ldots, k \) if \( p \leq k \), hence, \( k \) components of the corresponding vector \( c \) are computed as a near variational solution within the \( k \) dimensional part of \( \{|E^{(a)}_{i \lambda}\} \) and \( N_C - k \) components connected with the \( N_C - k \) dimensional part complementary to the \( k \) part are determined to first order in BWPT.

This next approximation, retaining the notation of Gershgorin and Shavitt [31], although not considered by them, will be denoted by \( A_k \).

The \( k \) value of particular relevance for the \( A_k \) or \( B_k \) approximations occurs when the \( k \) part is appreciably more important for the expansion of \( \Phi_{A_k} \) or \( \Phi_{B_k} \) than is the complementary part. The \( k \) value corresponding to the first-order interacting space and truncation of the total basis after quadruple and required quintuple replacements is an
obvious example which can be applied in the $B_k$ approximation but in the $A_k$ approximation, as $N_C - k$ refers to a subspace of the first-order interacting space, methods to partition the virtual orbital space into active and inactive regions become necessary and these are discussed in Section 1.3.

Unfortunately, a series for $E$ obtained to second order in the non-diagonal elements of $H$ no longer necessarily gives an upper bound to the true ground state energy, $E_0$, of the system whereas Eckart's theorem [34] shows that the projection of $H$ onto the subspace spanned by the $k$ CSF's leads to an $E$ value which is never lower than $E_0$. One method by which the unboundedness of $E$ can be remedied thus replaces $\phi_{CI}$ in equation (1.2.69) with $\phi_{A_0}$, $\phi_{A_k}$ or $\phi_{B_k}$ and obtains an $E'$ which is exact to third order [35] when in effect another requires a systematic expansion of $\phi_{CI}$ as has been proposed by Cooper and Pounder [36]. Once again, it is unfortunate that in order to obtain an $E'$ one needs a maximum total of Hamiltonian matrix elements identical with that required to evaluate $E(\phi_{CI})$ which is almost in direct ideological conflict with the foregoing assumption that a certain number of these matrix elements can be neglected. On a computational level this restricts $N_C$ to values below that at which $H$ becomes intractable. Naturally, this does not imply that only those radicals which are already within the range of an accurate treatment can be considered as choosing the optimum wave function from several alternatives on the basis of the criterion of lowest energy can be an insensitive one with respect to the hyperfine coupling constants. Nevertheless, once the Cooper and Pounder [36]
preselection scheme is agreed, a systematic expansion of $\Phi_{CI}$ also offers the largest reduction in the maximum total of Hamiltonian matrix elements required to evaluate $\Phi_{CI}$ of $(N_C - k)(N_C + k + 1)/2$ and therefore, has been chosen as the one for examination in more detail here.

In order to introduce a symbolic representation of a systematic expansion of $\Phi_{CI}$ it should be noted that, for an Abelian $G$, a CSF can be expressed in the form

$$\Xi^{(a)}_{i\lambda}(x_1, x_2, \ldots, x_N) = \Delta \{ \Omega^{(a)}_i(x_1, x_2, \ldots, x_N) \times \Theta_\lambda(s_1, s_2, \ldots, s_N) \} \ (1.2.141)$$

where, in the methodology of Cooper and Pounder [36], $\Omega^{(a)}_i$ is a product of $N$ MO's $\psi^{(j)}_j$ built from a set $\{ \psi^{(j)}_j \}$ which at least contains those occupied in $\Phi_{RHF}$ together with those in the orthogonal complement of remaining solutions of equation (1.2.41) most appropriate to a systematic expansion of $\Phi_{CI}$

$$\Omega^{(a)}_i(x_1, x_2, \ldots, x_N) = \psi^{(a)}_{i_1}(x_1)\psi^{(\mu)}_{i_2}(x_2) \ldots \psi^{(v)}_{i_N}(x_N) \ (1.2.142)$$

and $\Theta_\lambda$ is generally a linear combination of products of $N$ spin functions $\alpha$ and $\beta$ in the set of $n_S$ linearly independent spin eigenfunctions $\{ \Theta_{\lambda} | S M_S, \lambda = 1, 2, \ldots, n_S \}$ that can be constructed for the desired spin eigenvalues. It is, hence, of no loss in generality to express $\{ |\Xi^{(a)}_{i\lambda} > \}$ as $\{ |\Xi^{pq \ldots} > \}$ as this presumes use of the relationship between the number of closed-shell and open-shell MO's $\psi_i, \psi_j, \ldots$, that have been replaced by the same number of open-shell and virtual MO's $\psi_p, \psi_q, \ldots$, on changing $\Phi_{RHF}$ into $\Xi^{(a)}_{i\lambda}$. If this
number is \( t \), \( \varepsilon^{(a)}_{\lambda} \) is a \( t \)-tuple replacement but in our case it may be necessary to add to the corresponding index list additional open-shell members, counting two same members as one member, in keeping with the foregoing observation that \( t \)-tuple replacement individual terms within the replacement of MO's formalism may include MSO replacements of higher orders than \( t \). On reference to the individual MO's using indices \( a, b \) for the closed-shell MO's, \( r, s \) for the open-shell MO's and \( u, v \) for MO's of neither set, equation (1.2.68) can be then written as

\[
\phi_{CI}(x_1, x_2, \ldots, x_N) = c^t \varepsilon = c_0 |\Phi_{RHF} \rangle + \sum \sum c_a^{r} |\varepsilon^{r}_{a} \rangle \\
+ \sum \sum c_a^{u} |\varepsilon^{u}_{a} \rangle + \sum \sum c_r^{u} |\varepsilon^{u}_{r} \rangle + \sum \sum \sum c_{ab}^{rs} |\varepsilon^{rs}_{ab} \rangle \\
+ \sum \sum \sum c_{ab}^{ur} |\varepsilon^{ur}_{ab} \rangle + \sum \sum \sum c_{sa}^{ur} |\varepsilon^{ur}_{sa} \rangle + \sum \sum \sum c_{ab}^{uv} |\varepsilon^{uv}_{ab} \rangle \\
+ \sum \sum \sum c_{ab}^{uu} |\varepsilon^{uu}_{ab} \rangle + \sum \sum \sum c_{ra}^{uv} |\varepsilon^{uv}_{ra} \rangle + \sum \sum \sum c_{rs}^{uv} |\varepsilon^{uv}_{rs} \rangle \\
+ \sum \sum \sum \sum c_{rab}^{uv} |\varepsilon^{uv}_{rab} \rangle + \sum \sum \sum \sum c_{rab}^{ur} |\varepsilon^{ur}_{rab} \rangle \\
+ \sum \sum \sum \sum \sum c_{rsab}^{uv} |\varepsilon^{uv}_{rsab} \rangle + \ldots. \tag{1.2.143}
\]

It is evident that the full expansion of \( \phi_{CI} \) according to equation (1.2.143) will be normally impractical for all but the smallest of systems or when using rather poor basis sets as, for \( m \gg N, N_C \) increases very roughly in proportion to \( m^N [31] \) and that this number has to be first reduced by a certain preselection scheme [37]. One scheme to reduce this number ideally is to go over to the full-class expansion of
OCI according to a chosen t-tuple replacement limit that will be normally practical for small systems with good basis sets noting, for $m \gg N$, the $m^t$ dependence on $m$ of the number of t-tuple replacements [31]. One of the most widely used schemes of this type has been the choice $t = 2$, i.e., the full-class expansion of $\phi_{CI}$ on preselection of all singles and double replacements, as suggested by the fact that, for a RHF reference state configuration, the Löwdin [38] definition of the correlation energy, $E_{\text{corr}}$, can be written in terms of none other than these replacements.

$$E_{\text{corr}} = \xi_0 - E_0$$ (1.2.144)

where $E_0$ corresponds to $\xi_0$ at the HF limit [39,40] reflects the fact that the HF Hamiltonian contains the average, rather than instantaneous, interelectronic potential and thus neglects the electron correlation effects which prevents electrons of opposite spin from being close to each other in space. Roos [41] first demonstrated the particular suitability of this choice for a closed-shell reference configuration within the very efficient direct CI method which has been generalised to a wide class of systems [42]. Nevertheless, the problem of scale remains a formidable one since for the case $n_2 = 0$ alone the number of double replacements increases as $n_1^2 n_3^2/2$.

One alternative scheme, therefore, has been to take advantage of the subdivision of the RHF MO's for preselection by occupancy-limit, e.g., an effective reduction in $n_1$ or $n_3$ can be made by constraining one or more closed-shell MO's to remain doubly occupied in all CSF's [43] or truncating the virtual MO's at an arbitrary point [44]. On application to
the $n_1$ MO's this scheme has led to known discrepancies [45], the most serious for radicals being the removal of electron correlation effects near heavy nuclei [46] which, in turn, will affect the hyperfine coupling constants. Both this and its counterpart on the $n_3$ MO's can ignore certain single and direct double replacements that have proven to be important in obtaining reliable expectation values [47]. On the other hand, more elaborate schemes involve a generalisation of preselection by orbital set occupancy assignments, e.g., using the following perturbation approach to estimate the extent to which a number of the $n_3$ MO's interact with $\phi_{RHF}$ but at the same time taking fully into account these classes of important replacements.

On noting how an equivalent formulation of the linear variation method allows equation (1.2.85) to be rewritten as

$$\hat{H}|\phi_{CI}^\prime > = \xi_0 |\phi_{CI}^\prime > \quad (1.2.145)$$

or, by subtracting $E_0|\phi_{CI}^\prime >$ from both sides of this equation, enables $E_{corr}$ in equation (1.2.144) to be redefined as

$$(\hat{H} - E_0)|\phi_{CI}^\prime > = (\xi_0 - E_0)|\phi_{CI}^\prime > = E_{corr}|\phi_{CI}^\prime > \quad (1.2.146)$$

and multiplying this equation from the left by $<\phi_{RHF}|$, once more taking intermediate normalisation of $\phi_{CI}^\prime$, it follows that [48]

$$<\phi_{RHF}|\hat{H} - E_0|\phi_{CI}^\prime > = E_{corr}<\phi_{RHF}|\phi_{CI}^\prime > = E_{corr}$$

$$= \sum \sum c_{ar}^r \phi_{RHF} |\hat{H}| \Xi_{ar}^r > + \sum \sum c_{au}^u \phi_{RHF} |\hat{H}| \Xi_{au}^u > + \sum \sum c_{ru}^u \phi_{RHF} |\hat{H}| \Xi_{ru}^u >$$

$$+ \sum \sum \sum c_{abrs}^{rs} \phi_{RHF} |\hat{H}| \Xi_{abrs}^{rs} > + \sum \sum \sum c_{abru}^{ur} \phi_{RHF} |\hat{H}| \Xi_{abru}^{ur} >$$

$$+ \sum \sum \sum c_{ursa}^{ur} \phi_{RHF} |\hat{H}| \Xi_{ursa}^{ur} > + \sum \sum \sum c_{abuv}^{uv} \phi_{RHF} |\hat{H}| \Xi_{abuv}^{uv} >$$

-38-
On its own, this shows that $E_{corr}$ can be expressed in terms of, at most, all the single and double replacements, an observation which has stimulated the development of perturbation approaches to estimate the coefficients $c^r_a$, $c^u_a$, $c^r_u$, $c^{ur}_a$, $c^{ra}_u$, $c^{ur}_r$, $c^{rs}_a$, $c^{rs}_r$, $c^{cab}_a$, $c^{cab}_b$, $c^{cab}_ab$, $c^{cab}_rs$, $c^{crs}_r$ since these depend on the presence of triple and higher order replacements. Nevertheless, a common practice has been to concentrate on the single and double replacements as a route to reducing the size of the CI expansion. Once the decision has been made to adopt this practice it means that first-order perturbation approaches, e.g., Gershgorn and Shavitt's [31] approximations, can provide estimates for all the required coefficients. On the other hand, it is rather more simple and perhaps, quite adequate in this work to use

\[
\frac{\phi_{\text{RHF}} | \hat{H} | \Xi^r_a}{E_0 - E^r_a}, \quad \frac{\phi_{\text{RHF}} | \hat{H} | \Xi^u_a}{E_0 - E^u_a}, \quad \frac{\phi_{\text{RHF}} | \hat{H} | \Xi^r_r}{E_0 - E^r_r}, \quad \frac{\phi_{\text{RHF}} | \hat{H} | \Xi^{ur}_a}{E_0 - E^{ur}_a},
\]

\[
\frac{\phi_{\text{RHF}} | \hat{H} | \Xi^{ur}_r}{E_0 - E^{ur}_r}, \quad \frac{\phi_{\text{RHF}} | \hat{H} | \Xi^{rs}_a}{E_0 - E^{rs}_a}, \quad \frac{\phi_{\text{RHF}} | \hat{H} | \Xi^{rs}_b}{E_0 - E^{rs}_b}
\]  

(1.2.148)

and

\[
\frac{\phi_{\text{RHF}} | \hat{H} | \Xi^{ur}_a}{E_0 - E^{ur}_a}, \quad \frac{\phi_{\text{RHF}} | \hat{H} | \Xi^{rs}_a}{E_0 - E^{rs}_a}, \quad \frac{\phi_{\text{RHF}} | \hat{H} | \Xi^{rs}_b}{E_0 - E^{rs}_b}
\]  

(1.2.148)
\[
c_{ur} = \frac{\phi_{RHF}[\hat{\mathcal{H}}]_{ur}}{E_0 - E_{ur}}, \quad c_{uv} = \frac{\phi_{RHF}[\hat{\mathcal{H}}]_{uv}}{E_0 - E_{uv}}
\]
\[
c_{ra} = \frac{\phi_{RHF}[\hat{\mathcal{H}}]_{ra}}{E_0 - E_{uv}}, \quad c_{rs} = \frac{\phi_{RHF}[\hat{\mathcal{H}}]_{rs}}{E_0 - E_{rs}}
\]
\[
c_{uv} = \frac{\phi_{RHF}[\hat{\mathcal{H}}]_{uv}}{E_0 - E_{uv}}, \quad c_{uvrs} = \frac{\phi_{RHF}[\hat{\mathcal{H}}]_{uvrs}}{E_0 - E_{uvrs}}
\]
\[
(1.2.149)
\]

where
\[
E_r = \xi_{ra}^{a} \xi_{r}^{a}, \quad E_u = \xi_{ua}^{u} \xi_{u}^{a}, \quad E_u = \xi_{ur}^{u} \xi_{u}^{r},
\]
\[
E_{ur} = \xi_{ur}^{u} \xi_{r}^{r}, \quad (1.2.150)
\]

and
\[
E_{us} = \xi_{us}^{a} \xi_{s}^{a}, \quad E_{rs} = \xi_{rs}^{s} \xi_{s}^{s}, \quad E_{ur} = \xi_{ur}^{u} \xi_{ur}^{r},
\]
\[
E_{uv} = \xi_{uv}^{u} \xi_{uv}^{r}, \quad E_{ra} = \xi_{ra}^{r} \xi_{ra}^{a}, \quad E_{rs} = \xi_{rs}^{r} \xi_{rs}^{s},
\]
\[
E_{uvr} = \xi_{uvr}^{r} \xi_{uvr}^{a}, \quad E_{uvrs} = \xi_{uvrs}^{s} \xi_{uvrs}^{s}, \quad (1.2.151)
\]

so that there is a direct comparison with the formulae used by Cooper and Pounder [49]. \(E_{corr}\) is, therefore, given by
\[
E_{corr} = \sum_{a} \sum_{u} \frac{\phi_{RHF}[\hat{\mathcal{H}}]_{ur}^{2}}{E_0 - E_{ur}} + \sum_{r} \sum_{u} \frac{\phi_{RHF}[\hat{\mathcal{H}}]_{ur}^{2}}{E_0 - E_{ur}}
\]
\[
+ \sum_{a} \sum_{b} \sum_{u} \frac{\phi_{RHF}[\hat{\mathcal{H}}]_{ur}^{2}}{E_0 - E_{ur}} + \sum_{a} \sum_{s} \sum_{u} \frac{\phi_{RHF}[\hat{\mathcal{H}}]_{ur}^{2}}{E_0 - E_{ur}}
\]
\[
+ \sum_{a} \sum_{b} \sum_{u} \frac{\phi_{RHF}[\hat{\mathcal{H}}]_{ur}^{2}}{E_0 - E_{ur}} + \sum_{a} \sum_{r} \sum_{u} \frac{\phi_{RHF}[\hat{\mathcal{H}}]_{ur}^{2}}{E_0 - E_{ur}}
\]
\[
+ \sum_{a} \sum_{b} \sum_{u} \frac{\phi_{RHF}[\hat{\mathcal{H}}]_{ur}^{2}}{E_0 - E_{ur}} + \sum_{a} \sum_{b} \sum_{u} \frac{\phi_{RHF}[\hat{\mathcal{H}}]_{ur}^{2}}{E_0 - E_{ur}}
\]
\[
-40-
\]
\[
\begin{align*}
&+ \sum \sum \sum \sum \frac{\left| \langle \psi_{RHF} | \hat{H} | \Xi^u v \rangle \right|^2}{E_0 - E_{uv}} + \sum \sum \sum \sum \frac{\left| \langle \psi_{RHF} | \hat{H} | \Xi^r s \rangle \right|^2}{E_0 - E_{rs}} \\
&+ \sum \sum \sum \sum \frac{\left| \langle \psi_{RHF} | \hat{H} | \Xi^{ur} \rangle \right|^2}{E_0 - E_{ur}} + \sum \sum \sum \sum \frac{\left| \langle \psi_{RHF} | \hat{H} | \Xi^{rs} \rangle \right|^2}{E_0 - E_{rs}} \\
&+ \sum \sum \frac{\left| \langle \psi_{RHF} | \hat{H} | \Xi^a \rangle \right|^2}{E_0 - E_a} + \sum \sum \frac{\left| \langle \psi_{RHF} | \hat{H} | \Xi^b \rangle \right|^2}{E_0 - E_b} \\
&= -\sum E^*(u) - \sum E^*(u, v) + \text{constant}, \quad (1.2.152)
\end{align*}
\]

where

\[
-E^*(u) = \sum \frac{\left| \langle \psi_{RHF} | \hat{H} | \Xi^u \rangle \right|^2}{E_0 - E_u} + \sum \frac{\left| \langle \psi_{RHF} | \hat{H} | \Xi^r \rangle \right|^2}{E_0 - E_r}
\]

\[
+ \sum \sum \sum \frac{\left| \langle \psi_{RHF} | \hat{H} | \Xi^{ur} \rangle \right|^2}{E_0 - E_{ur}} + \sum \sum \frac{\left| \langle \psi_{RHF} | \hat{H} | \Xi^{rs} \rangle \right|^2}{E_0 - E_{rs}}
\]

\[
+ \sum \sum \frac{\left| \langle \psi_{RHF} | \hat{H} | \Xi^a \rangle \right|^2}{E_0 - E_a} + \sum \sum \frac{\left| \langle \psi_{RHF} | \hat{H} | \Xi^b \rangle \right|^2}{E_0 - E_b}
\]

\[
(1.2.153)
\]

and

\[
-E^*(u, v) = \sum \sum \frac{\left| \langle \psi_{RHF} | \hat{H} | \Xi^{uv} \rangle \right|^2}{E_0 - E_{uv}} + \sum \sum \frac{\left| \langle \psi_{RHF} | \hat{H} | \Xi^{ur} \rangle \right|^2}{E_0 - E_{ur}}
\]

\[
+ \frac{\left| \langle \psi_{RHF} | \hat{H} | \Xi^{uv} \rangle \right|^2}{E_0 - E_{uv}} + \sum \sum \frac{\left| \langle \psi_{RHF} | \hat{H} | \Xi^{rs} \rangle \right|^2}{E_0 - E_{rs}}
\]

\[
+ \sum \sum \sum \frac{\left| \langle \psi_{RHF} | \hat{H} | \Xi^{uv} \rangle \right|^2}{E_0 - E_{uv}} + \sum \sum \sum \sum \frac{\left| \langle \psi_{RHF} | \hat{H} | \Xi^{rs} \rangle \right|^2}{E_0 - E_{rs}}
\]

\[
(1.2.154)
\]
Under certain circumstances, for the classes identified by such preselection schemes, particularly when using large basis sets, it may turn out that many replacements are of negligible importance and for instance, on extension to larger systems, it may also turn out that the number of replacements remains much too large for practical use in the final CI expansion and thus this number has to be often second reduced by an individual replacement selection scheme.

Of course, it is difficult to be certain of the overall effect of individual replacement selection carried out in terms of a threshold criterion based on PT [50] without the refinement of an extrapolation technique to account for the large number of replacements which are excluded [51] or done on the basis of the CI coefficients [36] as these two criteria can lead to significantly different selected lists [52].

In contrast, it is convenient to label the different types of CI expansions as \( (S + D)C\bar{m}(\bar{n}) \) where \( \bar{m} \) is the number of virtual MO's used in constructing all the single and double replacements and \( \bar{n}(> \bar{m}) \) is the number of virtual MO's used to construct the remaining single replacements of the types \( |\Xi^u_a \rangle, |\Xi^u_r \rangle, |\Xi^ur_{ra} \rangle \) and the remaining direct double replacements \( |\Xi^{uu}_{aa} \rangle \).

If \( \bar{m} = \bar{n} = n_3 \) this corresponds to the full \( (S + D)CI \). If \( \bar{m} = \bar{n} \) otherwise it is a truncated \( (S + D)CI \) which only refers to \( \bar{m} \) of the virtual MO's. If \( \bar{m} < \bar{n} \) the CI expansions are analogous to those proposed by Cooper and Pounder [49]. In this terminology, these CI expansions can be further
illustrated symbolically as follows

\[ \phi_{CM}(x_1, x_2, \ldots, x_N) = c_0 \phi_{RHF} + \sum_{a} \sum_{r} c_a^r |z^r_a> + \sum_{a < b} \sum_{r < s} c_{ab}^{rs} |z_{ab}^{rs}> + \sum_{a} \sum_{b < r < u} c_{ab}^{ur} |z_{ab}^{ur}> + \sum_{a} \sum_{u > m} c_a^u |z^u_a> + \sum_{a} \sum_{r < s} c_{ur}^{sa} |z_{ur}^{sa}> + \sum_{a < b < r < u} c_{ab}^{uv} |z_{ab}^{uv}> + \sum_{a} \sum_{r < u > m} c_r^u |z^u_r> + \sum_{a < b < r < s} c_{ur}^{ra} |z_{ur}^{ra}> + \sum_{a < b < r < s} c_{ra}^{uv} |z_{ra}^{uv}> + \sum_{a < b < r < u} c_{ab}^{uu} |z_{ab}^{uu}> + \sum_{a} \sum_{b < r < u} c_{rab}^{ur} |z_{rab}^{ur}> + \sum_{a} \sum_{u > m} c_a^a |z^a_a> + \sum_{a < b < r < s < u < v} c_{uv}^{rsab} |z_{uv}^{rsab}>. \] (1.2.155)

\[ (S + D)\overline{CM}(\bar{m}) \]

\[ (S + D)\overline{CM}(\bar{n}) \]

On the other hand, this \((S + D)\overline{CM}(\bar{n})\) approach has one common disadvantage, i.e., it no longer avoids the necessity of a preselection on symmetry grounds [36] (e.g., \(C_{\infty v}\) and \(D_{\infty h}\) symmetries corresponding to the restricted class of linear radicals that possess an additional dynamical variable \(\Lambda(= |M_L|)\) [53] and schemes based on \(S\) specification only are, therefore, precarious to use unless the summations
over spin-state indices range over all permitted values).

Often, more than one alternative practices have been followed, for similar ends, in two distinct categories, i.e., schemes which are designed to accommodate the simplifications arising in particular or wider classes of G's [54] but in the above-mentioned G's this distinction disappears. Once again, a great amount of detail being, perhaps, unnecessary here, in essence, CSF's are constructed from Boys and Reeves' [55,56] bonded functions (BF's) by application of step-down (\(\bar{S}^-\)) and (\(\mathcal{C}_{\nu\nu}\)) symmetrising) Wigner (\(\mathcal{W}\)) operators, it then turns out that the schemes so designed are applicable to any G which has no higher than two-dimensional \(D_\alpha\)'s [57]. Overall, this two-stage process can be equivalently expressed by the matrix equation

\[
\Xi_t = \Xi_u = \Psi_t = \Psi = \Psi^t = \Psi^t = \Psi^t \mathcal{U} = \Psi^t \mathcal{U}
\]

where the elements \(\Xi_i\) collected in the \(\Xi\) matrix are spin states, i.e., eigenfunctions of the \(\hat{S}_2\) and \(\hat{S}_z\) but not necessarily of \(\hat{L}_z\) operators and the \(\mathcal{U}, \mathcal{U}'\) and hence, \(\mathcal{U}\) matrices are all unitary. Obviously, the comparison between equations (1.2.45) and (1.2.156), by analogy with equations (1.2.4) and (1.2.68), admits the additional relations

\[
\Phi = c^\dagger \Psi = c^\dagger \Xi = c^\dagger \mathcal{U} \Psi, \quad c = \mathcal{U} c', \quad c' = \mathcal{U}^{-1} c
\]

\[
\varphi' = c' \mathcal{U} \mathcal{U}^{-1} c' = \mathcal{U}^{-1} c (\mathcal{U}^{-1} c)^{\dagger} / (\mathcal{U}^{-1} c)^{\dagger} \mathcal{U}^{-1} c
\]

\[
= \mathcal{U}^{-1} c \mathcal{U} \mathcal{U}^{-1} c / c^{\dagger} \mathcal{U} \mathcal{U}^{-1} c = \mathcal{U}^{-1} c \mathcal{U} \mathcal{U}^{-1} c
\]

\[
H_{pq} = \langle \Xi_p | \hat{H} | \Xi_q \rangle = \sum \sum \mathcal{U}_r \mathcal{U}_s \langle \hat{H} | \psi \rangle \langle \psi | \mathcal{U}_s \mathcal{U}_r \psi \rangle = \sum \sum \mathcal{U}^* \mathcal{U}_{r'} \mathcal{U}_{s'} \langle \hat{H} | \psi \rangle \langle \psi | \mathcal{U}_{s'} \mathcal{U}_{r'} \psi \rangle
\]

\[
= \sum \mathcal{U}_{r'} \mathcal{U}_{s'} \mathcal{H}_{r's'} \mathcal{U}_{s'} \mathcal{U}_{r'}, \quad \mathcal{H}' = \mathcal{U}^{-1} \mathcal{H} \mathcal{U}, \quad \mathcal{H}' \in \{ \mathcal{M}_1 \}
\]

-44-
whereas the elements of the matrix $M_i^j \in \{M_i^j | M_i^j = U^{-1}M_i U \}$ now correspond to matrix elements of an $N$-electron operator in the basis $\bar{\varepsilon}$

$$H'c' = E'c'$$  (1.2.160)

$$E'(\phi_{CI}) = \langle \phi_{CI} | \hat{\mathcal{A}} | \phi_{CI} \rangle / \langle \phi_{CI} | \phi_{CI} \rangle = \text{Tr } H'\varphi' = \text{Tr } U^{-1}HU^{-1}\varphi U$$

$$= \text{Tr } UU^{-1}\varphi = \text{Tr } H\varphi = E(\phi_{CI})$$  (1.2.161)

$$H'c' = Ec', \quad U^{-1}HU^{-1}c = EU^{-1}c = U^{-1}Ec, \quad Hc = Ec.$$  (1.2.162)

The Gershgorn and Shavitt [31] type Hamiltonians

$$H' = |\phi_{RHF}><\phi_{RHF}| \hat{A} |\phi_{RHF}><\phi_{RHF}| + \sum_{i>1} [ |\bar{\varepsilon}_i><\bar{\varepsilon}_i| \hat{A} |\phi_{RHF}><\phi_{RHF}|$$

$$+ |\phi_{RHF}><\phi_{RHF}| \hat{A} |\bar{\varepsilon}_i><\bar{\varepsilon}_i| + |\bar{\varepsilon}_i><\bar{\varepsilon}_i| \hat{A} |\bar{\varepsilon}_i><\bar{\varepsilon}_i|]$$  (1.2.163)

$$H''' = \sum_{k} \sum_{i,j} |\bar{\varepsilon}_i><\bar{\varepsilon}_i| \hat{A} |\bar{\varepsilon}_j><\bar{\varepsilon}_j| + \sum_{i>k} [ |\bar{\varepsilon}_i><\bar{\varepsilon}_i| \hat{A} |\phi_{RHF}><\phi_{RHF}|$$

$$+ |\phi_{RHF}><\phi_{RHF}| \hat{A} |\bar{\varepsilon}_i><\bar{\varepsilon}_i| + |\bar{\varepsilon}_i><\bar{\varepsilon}_i| \hat{A} |\bar{\varepsilon}_i><\bar{\varepsilon}_i|]$$  (1.2.164)

$$H''' = \sum_{k} \sum_{i,j} |\bar{\varepsilon}_i><\bar{\varepsilon}_i| \hat{A} |\bar{\varepsilon}_j><\bar{\varepsilon}_j| + \sum_{i>k} [ |\bar{\varepsilon}_i><\bar{\varepsilon}_i| \hat{A} |\bar{\varepsilon}_j><\bar{\varepsilon}_j|$$

$$+ |\bar{\varepsilon}_j><\bar{\varepsilon}_j| \hat{A} |\bar{\varepsilon}_i><\bar{\varepsilon}_i| + \sum_{i>k} |\bar{\varepsilon}_i><\bar{\varepsilon}_i| \hat{A} |\bar{\varepsilon}_i><\bar{\varepsilon}_i|]$$  (1.2.165)

can thus be set up in the determinantal basis but if, as suggested here, this is done the construction of $M_{22}$ will be troublesome as it must contain some off-diagonal terms to ensure correct symmetry of the final wave function. The selection of terms is trivial for spin symmetry these being just the interactions between determinants with identical orbital configurations but for spacial symmetry in the above mentioned $G$'s it is considerably more demanding needing the
interactions between, e.g., doubly replaced configurations by π orbitals which differ only by both partners in the representation (see Figure 1.1 and Table 1.1 respectively).

The CSF's constructed from BF's are not necessarily the best ones to use since the expression for $E_{\text{corr}}$ is not yet in its most compact form. The dimension of the $(S + D)\text{CI}$ space in the CSF basis for an Abelian G is given in Figure 1.1 by

$$N_C^i = \sum_i M_i N_i$$  \hspace{1cm} (1.2.166)

and for detors $N_D^i$ with $M_i$ replaced by $M_i$. This total being the dependent variable of a sixth-degree polynomial of $n_1$, $n_2$ and $n_3$ a discussion of methods to reduce $N_C^i$ appears to be inevitable. One method is to determine the generalised Brillouin's theorem of the half-closed shell system.

The HF occupied orbitals are varied an infinitesimal amount $\psi_i = \psi_i + \delta \psi_i$ then the first-order change in the RHF wave function becomes

$$\delta \psi = \sum_i |\psi_1 \psi_2 \ldots \delta \psi_i \ldots \psi_N|.$$  \hspace{1cm} (1.2.167)

It is possible to expand the variations $\delta \psi_i$ in terms of the RHF MO's $\psi_j$ from which the MSO's $\psi_j$ are built, i.e., to write

$$\delta \psi_i = \sum_j X_{ij} \psi_j$$  \hspace{1cm} (1.2.168)

subject to

$$<\psi_i + \delta \psi_i | \psi_j + \delta \psi_j> = <\psi_i | \psi_j> + <\psi_i | \delta \psi_j> + <\delta \psi_i | \psi_j>$$

$$+ <\delta \psi_i | \delta \psi_j> = <\psi_i | \delta \psi_j> + <\delta \psi_i | \psi_j> = <\psi_i \sum_k X_{jk} \phi_k>$$
FIGURE 1.1 ELECTRONIC CONFIGURATIONS WHICH ARE USED TO FORM THE FOLLOWING MINIMAL HARTREE-FOCK INTERACTING SPACE STATES:
(a) refers to no more than one virtual orbital

\[ \phi_{RHF} = \psi_{oo}^0; \quad \xi_{ur}^{oo} = (1/\sqrt{6})[2\psi_{ur}^{oo} - \psi_{oa}^{oo} - \psi_{ao}^{oo}]; \quad \xi_{aa} = \psi_{aa}^{oo}; \]

\[ \xi_{ur}^{oo} = (1/\sqrt{6})[2\psi_{ur}^{oo} - \psi_{oa}^{oo} - \psi_{ao}^{oo}]; \]

\[ \xi_{ab}^{oo} = (1/\sqrt{2})[\psi_{ab}^{oo} - \psi_{ba}^{oo}]; \quad \xi_{ra} = (1/\sqrt{2})[\psi^{uu}_{ra} + \psi^{uu}_{aa}]; \]

\[ \xi_{ab}^{oo} = (1/\sqrt{2})[\psi_{ab}^{oo} - \psi_{ba}^{oo}]; \]

\( u = \sigma \) symmetry \( u' \) partner of \( u \)

\[ \xi_{uu}^{ra} = (1/\sqrt{2})[\xi_{uu}^{ra} + \xi_{uu}^{aa}]; \quad \xi_{aa}^{ra} = (1/\sqrt{2})[\xi_{aa}^{ra} + \xi_{ua}^{ra}]; \]

\[ \xi_{ab}^{aa} = (1/\sqrt{2})[\xi_{ab}^{aa} + \xi_{ab}^{ba}]; \]

\( u = \tau \) symmetry, \( v = \sigma \) symmetry

\[ \xi_{uv}^{ra} = (1/\sqrt{6})[2\psi_{uv}^{ra} - \psi_{uv}^{ra} - \psi_{uv}^{ra}]; \quad \psi_{ra}^{uv} = (1/\sqrt{2})[\psi_{ra}^{uv} - \psi_{ra}^{uv}]; \]

\[ \xi_{aa}^{uv} = (1/\sqrt{2})[\psi_{aa}^{uv} - \psi_{aa}^{uv}]; \]

\[ \xi_{ab}^{uv} = (1/(2\sqrt{3})[2\psi_{ab}^{uv} + 2\psi_{ab}^{vu} - \psi_{ab}^{vu} - \psi_{ab}^{vu} - \psi_{ab}^{vu}]; \]

\[ \xi_{ab}^{uv} = (1/2)[\psi_{ab}^{uv} + \psi_{ab}^{vu} - \psi_{ab}^{vu} - \psi_{ab}^{vu}]; \]

\( u = \pi \) symmetry, \( v = \pi \) symmetry (same row) \( v' \) partner of \( v \)

\[ \xi_{uv}^{ra} = (1/\sqrt{2})[\xi_{uv}^{ra} + \xi_{uv}^{ra}]; \quad \psi_{ra}^{uv} = (1/\sqrt{2})[\xi_{ra}^{uv} + \xi_{ra}^{uv}]; \]

\[ \xi_{aa}^{uv} = (1/\sqrt{2})[\xi_{aa}^{uv} + \xi_{aa}^{uv}]; \]

\[ \xi_{ab}^{uv} = (1/\sqrt{2})[\xi_{ab}^{uv} + \xi_{ab}^{uv}]; \quad \xi_{ba}^{uv} = (1/\sqrt{2})[\xi_{ba}^{uv} + \xi_{ba}^{uv}]. \]

Other states which either do not interact with the ground state and thus violate the concept of an interacting space or possess a multiplicity \( 2S + 1 \) different from two have not been described, the extension to these latter states being indicated by dotted lines.
TABLE 1.1 REQUIRED MATRIX ELEMENTS BETWEEN DETORS AND CSF's BUILT FROM REAL ORBITALS IN TERMS OF HARTREE-FOCK $\lambda$-VALUES

\[
\langle \psi^o_0 | \hat{\psi}^{ur}_{ra} \rangle = (ar|ru); \quad \langle \psi^{ur}_{ra} | \hat{\psi}^{ur}_{ra} - E_0 | \psi^{ur}_{ra} \rangle = (1/2)(\lambda_u - \lambda_a) + (3/4)(K_{ar} + K_{ru}) - J_{au}
\]

\[
\langle \psi^o_0 | \hat{\psi}^{ou}_{oa} \rangle = -(1/2)(ar|ru); \quad \langle \psi^{ou}_{oa} | \hat{\psi}^{ou}_{oa} - E_0 | \psi^{ou}_{oa} \rangle = (1/2)(\lambda_u - \lambda_a) - (1/4)(K_{ar} - 3K_{ru}) - (J_{au} - K_{au})
\]

\[
\langle \psi^o_0 | \hat{\psi}^{uo}_{ao} \rangle = -(1/2)(ar|ru); \quad \langle \psi^{uo}_{ao} | \hat{\psi}^{uo}_{ao} - E_0 | \psi^{uo}_{ao} \rangle = (1/2)(\lambda_u - \lambda_a) + (1/4)(3K_{ar} - K_{ru}) - (J_{au} - K_{au})
\]

\[
\langle \psi^o_0 | \hat{\psi}^{ur}_{aa} \rangle = -(ar|ar); \quad \langle \psi^{ur}_{aa} | \hat{\psi}^{ur}_{aa} - E_0 | \psi^{ur}_{aa} \rangle = (1/2)(\lambda_u + \lambda_r) - \lambda_a + K_{aa} - (2J_{ar} - (3/2)K_{ar}) - (2J_{au} - K_{au}) + (1/2)K_{rr} + (1/2)(2J_{ru} - (1/2)K_{ru})
\]

\[
\langle \psi^o_0 | \hat{\psi}^{our}_{oab} \rangle = (au|br) - (ar|bu); \quad \langle \psi^{our}_{oab} | \hat{\psi}^{our}_{oab} - E_0 | \psi^{our}_{oab} \rangle = (1/2)(\lambda_r + \lambda_u - \lambda_a - \lambda_b) + (1/2)[K_{rr} + (2J_{ru} - (1/2)K_{ru}) - (2J_{ar} - (3/2)K_{ar}) - (2J_{br} - (3/2)K_{br})] + (J_{ab} - K_{ab}) - (J_{au} - K_{au}) - (J_{bu} - K_{bu})
\]

\[
\langle \psi^o_0 | \hat{\psi}^{ur}_{ab} \rangle = -(au|br); \quad \langle \psi^{ur}_{ab} | \hat{\psi}^{ur}_{ab} - E_0 | \psi^{ur}_{ab} \rangle = (1/2)(\lambda_r + \lambda_u - \lambda_a - \lambda_b) - (J_{au} - K_{au}) + (1/2)[K_{rr} + (2J_{ru} - (1/2)K_{ru}) - (2J_{ar} - (3/2)K_{ar}) - (2J_{br} - (3/2)K_{br})] + J_{ab} - J_{bu}
\]

\[
\langle \psi^o_0 | \hat{\psi}^{ur}_{ba} \rangle = (ar|bu); \quad \langle \psi^{ur}_{ba} | \hat{\psi}^{ur}_{ba} - E_0 | \psi^{ur}_{ba} \rangle = (1/2)(\lambda_r + \lambda_u - \lambda_a - \lambda_b) - (J_{bu} - K_{bu}) + (1/2)[K_{rr} + (2J_{ru} - (1/2)K_{ru}) - (2J_{ar} - (3/2)K_{ar}) - (2J_{br} - (3/2)K_{br})] + J_{ab} - J_{au}
\]
\[
\langle \psi_{oo} | \hat{H} | \psi_{ra} \rangle = -(au|ru) + \langle \psi_{ra} | \hat{H} - E_0 | \psi_{ra} \rangle = \lambda_u - (1/2)(\lambda_a + \lambda_r) + (1/2)(2J_{ar} - (1/2)K_{ar}) + (1/2)K_{rr} - (2J_{au} - K_{au}) - (2J_{ru} - (3/2)K_{ru}) + K_{uu}
\]

\[
\langle \psi_{oo} | \hat{H} | \psi_{ua} \rangle = (au|au); \quad \langle \psi_{ua} | \hat{H} - E_0 | \psi_{ua} \rangle = \lambda_u - \lambda_a + K_{aa} + (1/2)(K_{ar} + K_{ru}) - 2(2J_{au} - K_{au}) + K_{uu}
\]

\[
\langle \psi_{oo} | \hat{H} | \psi_{ab} \rangle = (au|bu); \quad \langle \psi_{ab} | \hat{H} - E_0 | \psi_{ab} \rangle = \lambda_u - (1/2)(\lambda_a + \lambda_b) + (3/4)K_{ar} - (1/4)K_{br} + (1/2)K_{ru} + J_{ab} - (2J_{au} - K_{au}) - (2J_{bu} - K_{bu}) + K_{uu}
\]

\[
\langle \psi_{oo} | \hat{H} | \psi_{uo} \rangle = (av|ru) - (au|rv); \quad \langle \psi_{uo} | \hat{H} - E_0 | \psi_{uo} \rangle = (1/2)(\lambda_u + \lambda_v - \lambda_a + \lambda_r) + (1/2)[K_{rr} + (2J_{ar} - (1/2)K_{ar}) - (2J_{ru} - (3/2)K_{ru}) - (2J_{rv} - (3/2)K_{rv})] + (J_{uv} - K_{uv}) - (J_{av} - K_{av}) - (J_{au} - K_{au})
\]

\[
\langle \psi_{oo} | \hat{H} | \psi_{uv} \rangle = -(av|ru); \quad \langle \psi_{uv} | \hat{H} - E_0 | \psi_{uv} \rangle = (1/2)(\lambda_u + \lambda_v - \lambda_a - \lambda_r) - (J_{av} - K_{av}) + (1/2)[K_{rr} + (2J_{ar} - (1/2)K_{ar}) - (2J_{ru} - (3/2)K_{ru}) - (2J_{rv} - (3/2)K_{rv})] + J_{uv} - J_{au}
\]

\[
\langle \psi_{oo} | \hat{H} | \psi_{uv} \rangle = (av|rv); \quad \langle \psi_{uv} | \hat{H} - E_0 | \psi_{uv} \rangle = (1/2)(\lambda_u + \lambda_v - \lambda_a - \lambda_r) - (J_{au} - K_{au}) + (1/2)[K_{rr} + (2J_{ar} - (1/2)K_{ar}) - (2J_{ru} - (3/2)K_{ru}) - (2J_{rv} - (3/2)K_{rv})] + J_{uv} - J_{av}
\]

-50-
\[
\begin{align*}
\langle \psi_0 | \hat{H} | \psi_{uv} \rangle &= (au | av) ; \quad \langle \psi_{uv} | \hat{H} - E_0 | \psi_{uv} \rangle = (1/2)(\lambda_u + \lambda_v) - \\
&\lambda_a + (1/2)K_{ar} - (1/4)K_{ru} + (3/4)K_{rv} + K_{aa} - (2J_{au} - K_{au}) - \\
&(2J_{av} - K_{av}) + J_{uv}
\end{align*}
\]
\[\lambda_a - \lambda_b - \frac{1}{4}K_{ar} + \frac{3}{4}K_{br} - \frac{1}{4}K_{ru} + \frac{3}{4}K_{rv} + J_{ab} - J_{au} - (J_{bu} - K_{bu}) - (J_{av} - K_{av}) - J_{bv} + J_{uv}\]

\[\psi_{oo}^{|\hat{a}}|\psi_{uv}^{\dagger} = -(av|bu) ; \psi_{ab}^{\dagger}|\hat{a} - E_0|\psi_{ab}^{\dagger} = \frac{1}{2}(\lambda_u + \lambda_v - \lambda_a - \lambda_b) + \frac{3}{4}K_{ar} - \frac{1}{4}K_{br} + \frac{3}{4}K_{ru} - \frac{1}{4}K_{rv} + J_{ab} - J_{au} - (J_{bu} - K_{bu}) - (J_{av} - K_{av}) - J_{bv} + J_{uv}\]

\[\psi_{oo}^{|\hat{a}}|\xi_{ur}^{\dagger} = \sqrt{3/2}(ar|ru) ; \xi_{ab}^{\dagger}|\hat{a} - E_0|\xi_{ab}^{\dagger} = \frac{1}{2}(\lambda_u - \lambda_a) + \frac{5}{4}(K_{ar} + K_{ru}) - J_{au}\]

\[\psi_{oo}^{|\hat{a}}|\xi_{ur}^{\dagger} = \sqrt{3/2}(au|br) - (ar|bu) ; \xi_{ba}^{\dagger}|\hat{a} - E_0|\xi_{ba}^{\dagger} = \frac{1}{2}(\lambda_u + \lambda_v - \lambda_a - \lambda_b) + \frac{1}{2}[K_{rr} + (2J_{ru} - (1/2)K_{ru}) - (2J_{ar} - (3/2)K_{ar}) - (2J_{br} - (3/2)K_{br})] + (J_{ab} - K_{ab}) - (J_{au} - (3/2)K_{au}) - (J_{bu} - (3/2)K_{bu})\]

\[\psi_{oo}^{|\hat{a}}|\xi_{uu}^{\dagger} = \sqrt{2}(au|bu) ; \xi_{ab}^{\dagger}|\hat{a} - E_0|\xi_{ab}^{\dagger} = \lambda_u - (1/2)(\lambda_a + \lambda_b) + (J_{ab} + K_{ab}) + (1/4)(K_{ar} + K_{br}) + (1/2)K_{ru} - (2J_{au} - K_{au}) - (2J_{bu} - K_{bu}) + K_{uu}\]

\[\psi_{oo}^{|\hat{a}}|\xi_{rr}^{\dagger} = -\sqrt{2}(au|ru) ; \xi_{ba}^{\dagger}|\hat{a} - E_0|\xi_{ba}^{\dagger} = \xi_{bb}^{\dagger}|\hat{a} - E_0|\xi_{bb}^{\dagger} + K_{uu}\]

\[\psi_{oo}^{|\hat{a}}|\xi_{uu}^{\dagger} = \sqrt{2}(au|au) ; \xi_{aa}^{\dagger}|\hat{a} - E_0|\xi_{aa}^{\dagger} = \]
\[ \langle \hat{H} \rangle - E_0 \langle \hat{\Xi}_{aa} \rangle + K_{uu} \]

\[ \langle \Xi_{ab} \rangle = 2(au|bu) \]

\[ \langle \Xi_{ab} \rangle = \langle \hat{H} \rangle - E_0 \langle \Xi_{ab} \rangle + K_{uu} \]

\[ \langle \Xi_{uv} \rangle = \sqrt{3/2}((av|ru) - (au|rv)) \]

\[ \langle \Xi_{ra} \rangle = (1/2)(\lambda_u + \lambda_v - \lambda_a - \lambda_r) + (1/2)[K_{rr} + (2J_{ar} - (1/2)K_{ar}) - (2J_{ru} - (3/2)K_{ru}) - (2J_{rv} - (3/2)K_{rv})] - (J_{au} - (3/2)K_{au}) - (J_{av} - (3/2)K_{av}) + (J_{uv} + K_{uv}) \]

\[ \langle \Xi_{uv} \rangle = \sqrt{2}(au|av) \]

\[ \langle \Xi_{va} \rangle = (1/2)(\lambda_u + \lambda_v - \lambda_a - \lambda_r) + (1/2)(K_{rr} + (2J_{ar} - (1/2)K_{ar}) - (2J_{ru} - (3/2)K_{ru}) - (2J_{rv} - (3/2)K_{rv})] - (J_{au} - (1/2)K_{au}) - (J_{av} - (1/2)K_{av}) + (J_{uv} + K_{uv}) \]

\[ \langle \Xi_{uv} \rangle = \sqrt{3}((av|bu) - (au|bv)) \]

\[ \langle \Xi_{ba} \rangle = (1/2)(\lambda_u + \lambda_v - \lambda_a - \lambda_b) + (1/4)(K_{ar} + K_{br} + K_{ru} + K_{rv}) + (J_{ab} - K_{ab}) - (J_{au} - (3/2)K_{au}) - (J_{bu} - (3/2)K_{bu}) - (J_{av} - (3/2)K_{av}) - (J_{bv} - (3/2)K_{bv}) + (J_{uv} - K_{uv}) \]

\[ \langle \Xi_{uv} \rangle = (au|bv) + (av|bu) \]

\[ \langle \Xi_{ba} \rangle = (1/2)(\lambda_u + \lambda_v - \lambda_a - \lambda_b) + (1/4)(K_{ar} + K_{br} + K_{ru} + K_{rv}) + (J_{ab} + K_{ab}) - (J_{au} - (1/2)K_{au}) - (J_{bu} - (1/2)K_{bu}) - (J_{av} - (1/2)K_{av}) - (J_{bv} - (1/2)K_{bv}) + (J_{uv} - K_{uv}) \]
\(<\psi_{oo}^{uv} | \hat{\mathbf{z}} | \psi_{ra}^{uv} > = \sqrt{3} [(av|ru) - (au|rv)]; \ \langle \mathbf{z}_{ra}^{uv} | \hat{\mathbf{z}} - E_0 | \mathbf{z}_{ra}^{uv} > = \\
\langle \mathbf{z}_{ra}^{uv} | \hat{\mathbf{z}} - E_0 | \mathbf{z}_{ra}^{uv} > + (uv'|vv') - (uv'|vu')
\)

\(<\psi_{oo}^{uv} | \hat{\mathbf{z}} | \psi_{ra}^{uv} > = -(av|ru) + (au|rv)]; \ \langle \mathbf{z}_{ra}^{uv} | \hat{\mathbf{z}} - E_0 | \mathbf{z}_{ra}^{uv} > = \\
\langle \mathbf{z}_{ra}^{uv} | \hat{\mathbf{z}} - E_0 | \mathbf{z}_{ra}^{uv} > + (uv'|vv') + (uv'|vu')
\)

\(<\psi_{oo}^{uv} | \hat{\mathbf{z}} | \psi_{aa}^{uv} > = 2(au|av); \ \langle \mathbf{z}_{aa}^{uv} | \hat{\mathbf{z}} - E_0 | \mathbf{z}_{aa}^{uv} > = \\
\langle \mathbf{z}_{aa}^{uv} | \hat{\mathbf{z}} - E_0 | \mathbf{z}_{aa}^{uv} > + (uv'|vv') + (uv'|vu')
\)

\(<\psi_{oo}^{uv} | \hat{\mathbf{z}} | \psi_{ab}^{uv} > = \sqrt{6} [(av|bu) - (au|bv)]; \ \langle \mathbf{z}_{ab}^{uv} | \hat{\mathbf{z}} - E_0 | \mathbf{z}_{ab}^{uv} > = \\
\langle \mathbf{z}_{ab}^{uv} | \hat{\mathbf{z}} - E_0 | \mathbf{z}_{ab}^{uv} > + (uv'|vv') - (uv'|vu')
\)

\(<\psi_{oo}^{uv} | \hat{\mathbf{z}} | \psi_{ba}^{uv} > = \sqrt{2} [(au|bv) + (av|bu)]; \ \langle \mathbf{z}_{ba}^{uv} | \hat{\mathbf{z}} - E_0 | \mathbf{z}_{ba}^{uv} > = \\
\langle \mathbf{z}_{ba}^{uv} | \hat{\mathbf{z}} - E_0 | \mathbf{z}_{ba}^{uv} > + (uv'|vv') + (uv'|vu')
\)

where in the HF Hamiltonian \( a_1 = a_2 = b_{12} = 1 \)

\( \lambda_a = 2h_{aa} + 2\sum_b (2J_{ab} - K_{ab}) + (2J_{ar} - (1/2)K_{ar}) \)

\( \lambda_r = 2h_{rr} + 2\sum_b (2J_{rb} - K_{rb}) + K_{rr} \)

\( \lambda_u = 2h_{uu} + 2\sum_b (2J_{ub} - K_{ub}) + (2J_{ur} - (3/2)K_{ur}) \)

\( h_{pq} = \int \psi^*(r_1) \hat{\mathbf{n}} \psi(q(r_1)) d^3r_1 \)

\( J_{pq} = \int \psi^*(r_1) \psi_p(r_1) \frac{1}{r_{12}} \psi_q(r_2) \psi(r_2) d^3r_1 d^3r_2 \)

\( K_{pq} = \int \psi^*(r_1) \psi_p(r_1) \frac{1}{r_{12}} \psi_q(r_2) \psi(r_2) d^3r_1 d^3r_2 \)

\( (pq|rs) = \int \psi^*(r_1) \psi_q(r_1) \frac{1}{r_{12}} \psi(r_2) \psi(s(r_2) d^3r_1 d^3r_2 \)

-54-
preserving to first order orthonormality of orbitals. Thus, the $X_{ij}$ are elements of a skew- or anti-Hermitian matrix.

The Pauli principle which states that no two electrons can occupy the same MSO else the determinant vanishes and $X_{ii} = 0$ means in the notation of Figure 1.1 that

$$
\delta \psi = \sum_{a=1}^{n_1} \sum_{r=n_1+1}^{n_2} x_{ar} \psi_{oa}^{or} + \sum_{r=n_1+1}^{n_1+n_2} \sum_{u=n_1+n_2+1}^{m} x_{ru} \psi_{uo}^{uo} \\
+ \sum_{a=1}^{n_1} \sum_{u=n_1+n_2+1}^{m} x_{au} (\psi_{ao}^{uo} - \psi_{oa}^{ou}).
$$

(1.2.170)

The associated change in energy is given by the expression

$$
\langle \psi + \delta \psi | \hat{H} | \psi + \delta \psi \rangle = \langle \psi | \hat{H} | \psi \rangle + \langle \psi | \hat{H} | \delta \psi \rangle + \langle \delta \psi | \hat{H} | \psi \rangle \\
+ \langle \delta \psi | \hat{H} | \delta \psi \rangle = E + \delta E
$$

(1.2.171)

and for stationary $E$ to first order it is required that

$$
\delta E = \langle \psi | \hat{H} | \delta \psi \rangle + \langle \delta \psi | \hat{H} | \psi \rangle = 0.
$$

(1.2.172)

The variations $|\delta \psi \rangle$ and $<\delta \psi |$ being conjugate to one another are clearly not independent but they may be treated as such for if equation (1.2.172) is satisfied by any $|\delta \psi \rangle$ it must also be satisfied by $i|\delta \psi \rangle$ thus obtaining a second equation

$$
\delta E = i\langle \psi | \hat{H} | \delta \psi \rangle - i\langle \delta \psi | \hat{H} | \psi \rangle = 0
$$

(1.2.173)

and on taking linear combinations of equations (1.2.172) and (1.2.173) two equivalent equations result

$$
\langle \psi | \hat{H} | \delta \psi \rangle = 0, \quad \langle \delta \psi | \hat{H} | \psi \rangle = 0
$$

(1.2.174)

these are equivalent to the single equation (1.2.172) if it is agreed to consider the variations $|\delta \psi \rangle$ and $<\delta \psi |$ as arbitrary and independent. Thus, it follows that
\[ \delta E = \sum_{a=1}^{n_1} \sum_{r=n_1+1}^{n_1+n_2} x_{ar} \langle \psi_{oo}^0 | \hat{H} | \psi_{oa}^{or} \rangle + \]
\[ \sum_{r=n_1+1}^{n_1+n_2+m} \sum_{u=n_1+n_2+1}^{m} x_{ru} \langle \psi_{oo}^0 | \hat{H} | \psi_{uo}^{uo} \rangle + \]
\[ \sum_{a=1}^{n_1} \sum_{u=n_1+n_2+1}^{m} x_{au} \langle \psi_{oo}^0 | \hat{H} | \psi_{ao}^{uo} - \psi_{oa}^{au} \rangle \]  

(1.2.175)

then the matrix elements in (1.2.175) must all vanish and this implies that the RHF wave function cannot interact with any of the singly replaced configurations in equation (1.2.170). In the notation of Table 1.1 this leads to the equations

\[ \langle \psi_{oo}^0 | \hat{H} | \psi_{oa}^{or} \rangle = h_{ar} + \sum_{b} [2(ar|bb) - (ab|br)] + \sum_{s} (ar|ss) = 0 \]  

(1.2.176)

\[ \langle \psi_{oo}^0 | \hat{H} | \psi_{uo}^{uo} \rangle = h_{ru} + \sum_{b} [2(ru|bb) - (rb|bu)] + \sum_{s} [(ru|ss) - (rs|su)] = 0 \]  

(1.2.177)

\[ \langle \psi_{oo}^0 | \hat{H} | \psi_{ao}^{uo} - \psi_{oa}^{ou} \rangle = h_{au} + \sum_{b} [2(au|bb) - (ab|bu)] + (1/2)\sum_{s} [2(au|ss) - (as|su)] = 0 \]  

(1.2.178)

or on defining the operator

\[ F_{pq} = h_{pq} + \sum_{b} [2(pq|bb) - (pb|bq)] + (1/2)\sum_{s} [2(pq|ss) - (ps|sq)] \]  

(1.2.179)
to the more compact form

\[ F_{au} = 0 \]  \hspace{1cm} (1.2.180)

\[ F_{ru} - \frac{1}{2} \sum_s (rs|su) = 0 \]  \hspace{1cm} (1.2.181)

\[ F_{ar} + \frac{1}{2} \sum_s (as|sr) = 0 \]  \hspace{1cm} (1.2.182)

these constraints being just the equations (1.2.34) and (1.2.35) in the molecular basis. Operator \( \hat{F} \) leads to the approximate RHF orbitals obtained by Longuet-Higgins and Pople [58]. One additional doublet configuration can thus be eliminated from the expression for \( E_{\text{corr}} \) if the correct spin coupling is used.

A second method is to introduce Bunge's [59] concept of the minimal HF interacting space and to construct CSF's either by inspection from the symmetrised BF's, which has been done here and the results listed in Figure 1.1, or more systematically according to McLean and Liu's [60] pivotal-reduction algorithm.

Other methods have to be based on ideas concerning the importance of different classes of CSF's such as Cooper and Pounder's [46] inner-shell orbital approximation.

It is possible to develop several variants of equation (1.2.155) which are similar in appearance to the complete active space self-consistent field (CASSCF) wave function of Roos, Taylor and Siegbahn [61] and to accordingly extend the notation \((S + D)C\overline{m}(\overline{n})\) to, e.g., \((\text{Full} + S + D)C\overline{m}(\overline{n})\) where \(\overline{m}\) and \(\overline{n}\) have their usual meanings but \(\overline{I}\) of the orbitals have been used to construct all permissible replacements. The notation \((\text{Full valence} + S + D)C\overline{m}(\overline{n})\)
will be used to describe the same calculation but where only single and double replacements have been allowed from the inner-shell occupied orbital of the radical. If the CI label is replaced with PT in any of the notations used to describe an orbitally ordered CI calculation the Gershgorn and Shavitt [31] type approximations are defined where $\bar{m}$ and $\bar{n}(> \bar{m})$ are the number of virtual MO's used in constructing all single and double replacements in the $k$ and $N_C - k$ spaces of the CSF basis respectively. However, in these approximations, $\bar{1}$ of the orbitals, which would normally be used to form all remaining replacements in the $k$ space of the basis, have been distinguished but not enforced in this work.

The spin-dependent first-order reduced density matrix according to equations (1.1.16), (1.2.68) and (1.2.73) is

$$
\rho^S_1(x_1; x_1^i) = \sum_{ij} c_i c_j^* \rho_1(ij|x_1; x_1^i) = \sum_{ij} \rho_{lij} \psi_i(x_1) \psi_j^*(x_1^i)
$$

(1.2.183)

the last equality coming from equations (1.2.75) and (1.2.77). Thus, from equation (1.1.15) the normalised spin density becomes

$$
D_S(\mathbf{r}_1) = \sum_{ij} \rho_{lij} \psi_i(\mathbf{r}_1) \psi_j^*(\mathbf{r}_1)
$$

$$
= \sum_{ij} \sum_{k} \chi_k(\mathbf{r}_1) c_{ki} \sum_{l} \chi_l^*(\mathbf{r}_1) c_{lj}^*
$$

$$
= \sum_{ij} \sum_{k} \sum_{l} c_{ki} \rho_{lij} c_{lj}^* \chi_k(\mathbf{r}_1) \chi_l^*(\mathbf{r}_1)
$$

$$
= \sum_{k} (c_{ki} c_{lj}^*)_{kl} \psi_k(\mathbf{r}_1) \psi_l(\mathbf{r}_1).
$$

(1.2.184)
Using this expression containing the improved density matrix representing $D_S$ in equations (1.1.13) and (1.1.14) it is possible to predict the contribution to the hyperfine coupling constants due to the effects of the unpaired electron on the other electrons known as indirect coupling.

In general and for the considerations of Section 1.4 it is the total energy that is required. The internuclear repulsion term

$$v = \sum_{i>j} Z_i Z_j R_{ij}^{-1}$$

(1.2.185)

is treated classically and added on after the electronic energy calculation.

1.3 The generation of modified virtual orbitals

Using an equivalent notation to that already identified in Section 1.2 the occupied RHF orbitals, $|a\rangle$, are defined by the equation

$$\hat{h}^F |a\rangle = \epsilon_a |a\rangle$$  

(1.3.1)

where $\hat{h}^F$, in this work, is the effective open-shell Hamiltonian as defined in equation (1.2.37) (using $a_1 = a_2 = b_{12} = 1$ in that terminology) but normally it would be the corresponding operator for closed-shell molecules where appropriate [49].

Canonical virtual orbitals (CVO's), $|u\rangle$, are given as the remaining solutions of equation (1.3.1)

$$\hat{h}^F |u\rangle = \epsilon_u |u\rangle.$$  

(1.3.2)

The deficiencies of CVO's have been known for a long time [62-64]. The cancellation of equal Coulomb and exchange
self-energy terms in $\hat{h}^F$ means that the occupied orbitals are determined under an $N-1$ electron potential, $v^{N-1}$, but CVO's experience an $N$-electron potential, $v^N$. CVO's are thus more appropriate to the negative ion than the neutral molecule itself [65,66].

In order to overcome these deficiencies, MVO's are defined as

$$|u'\rangle = \sum_u c_{uu'}|u\rangle$$  \hspace{1cm} (1.3.3)

where $c_{uu'}$ are elements of a unitary matrix obtained from the eigenvalue equation

$$\hat{H}|u'\rangle = \varepsilon_{u'}|u'\rangle$$  \hspace{1cm} (1.3.4)

where $\hat{H}$ is an operator which must be chosen. The following four distinguishable methods can be chosen to construct $\hat{H}$.

(i) **Natural expansions**

In matrix notation, the spin-dependent first-order reduced density matrix from equation (1.2.183) can be expressed as

$$\varrho_1(x_1; x_1') = \psi_1^*\psi_1 = \psi^\dagger U U^\dagger \psi_1 U U^\dagger \psi^* = (U^\dagger \psi)^\dagger U^\dagger \varrho_1 U(U^\dagger \psi)^*.$$  \hspace{1cm} (1.3.5)

$\varrho_1$ is a Hermitian matrix so that it is possible to find a unitary matrix $U$ which brings this matrix to diagonal form and thus to rewrite equation (1.3.5) as

$$\varrho_1(x_1; x_1') = \sum_i \sum_j \psi_i^*(x_1)n_i \delta_{ij}\psi_j^*(x_1') = \sum_i n_i \psi_i^*(x_1)\psi_i^*(x_1')$$  \hspace{1cm} (1.3.6)

where the components of the transformed basis $\psi'$ are the
natural spin orbitals (NSO's) of the system first introduced by Löwdin [67] and the $n_i$ are their occupation numbers with values ranging between zero and one. It is easy to show that the sum of the $n_i$ equals $N$ by putting $x_i^1 = x_i^1$ and integrating. In the single term approximation the RHF MSO's are the NSO's with $n_i$ either zero or one depending on whether or not the corresponding orbital is in the RHF wave function.

It can be be seen that the use of NSO's considerably simplifies the expressions for the calculation of hyperfine coupling constants but these orbitals are important for another reason since it can be proven that NSO's with the highest $n_i$ possess optimum convergence properties in a CI calculation [68]. On the other hand, it is more convenient to diagonalise $P_1$ the spinless counterpart of $\mathbf{P}_1$ obtained by integrating over spin to give natural orbitals (NO's) with $n_i$ ranging in value between zero and two these orbitals exhibiting near-optimum convergence characteristics.

Here $\hat{H}$ is identified with the frozen natural orbitals (FNO's) of Barr and Davidson [69]. Only the virtual orbital block of $P_1$ is diagonalised. Thus, the occupied orbitals are frozen whereas the virtual orbitals are allowed to mix freely amongst themselves. Shavitt, Rosenberg and Palalikit [44] found little difference between FNO's and conventional NO's in a study of various orbital sets. Unfortunately, the work required to compute FNO's directly can be unacceptably large and other methods have been sought to obtain these or similar orbitals more cheaply as discussed from now on.
(ii) Modified Hartree-Fock operator

Here $\hat{H}$ is the operator

$$\hat{H} = \hat{h}_F + \gamma \hat{\delta},$$  \hspace{1cm} (1.3.7)

where $\gamma$ is a parameter to be determined and $\hat{\delta}$ is a one-electron mixing operator, which following Cooper and Pounder [49] is chosen to be the HF exchange operator (restricted to summation over the occupied valence orbitals), $\hat{\delta}_{\text{val}}$.

Unfortunately, the empirical operator represented in equation (1.3.7) is known [49] to give MVO's which are not necessarily correctly ordered by the eigenvalues of the operator in an orbitally ordered CI expansion $(S + D)\text{CI}(n)$. Here an orbital ordering method is presented which refers exclusively to such MVO's but of course could be applied to any set.

It has been proposed [49] that, although only applied to a closed-shell molecule,

$$-E^*(u) = \sum_a \frac{|\langle \Phi_{\text{RHF}} | \hat{H} | \tilde{\xi}_{aa} \rangle|^2}{E_0 - E_{uu}^{uu}}$$ \hspace{1cm} (1.3.8)

can be used to order any set of virtual orbitals, $\{ |u\rangle \}$.

For doublet state radicals the problem may be complicated since some singly excited configurations interact with the ground state RHF wave function which is not possible with closed-shell systems because of Brillouin's theorem. It is therefore possible that these terms must be included in $E^*(u)$ in the ordering process because of their traditional importance in spin density calculations. Since the object is to reduce the size of the $(S + D)\text{CI}(n)$ expansion by neglecting some of the virtual
orbitals, i.e., using only \( \overline{m} \) of the \( \overline{n} \) (\( \overline{m} < \overline{n} \)) virtual orbitals, it is necessary to select those \( \overline{m} \) orbitals such that

\[
E_{\text{corr}}(\overline{m}) = - \sum_u E^*(u) - \sum_{u<v} E^*(u, v) \tag{1.3.9}
\]

is a minimum, where \( u \) and \( v \) sum over only the \( \overline{m} \) selected orbitals. The construction of the \( E^* \) matrix is not a trivial matter although it is considerably facilitated by use of Table 1.1. Even so, finding the minimum of equation (1.3.9) will be computationally demanding since it is possible to select \( \overline{m} \) orbitals from the \( \overline{n} \) available in \( \binom{\overline{n}}{\overline{m}} \) ways and there seems to be no established algorithm to make this selection. On the other hand, neither step is a major element in the total work to be carried out in a \( (S + D)\text{CI}(\overline{n}) \) calculation. The number of diagonal elements in the matrix is only the number of virtual orbitals. It is clear that if the \( E^*(u, v) \) terms can be ignored \( E_{\text{corr}}(\overline{m}) \) is a minimum if the \( \overline{m} \) highest values of \( E^*(u) \) are used. This means that the orbital \( |u> \) can be ordered according to the decreasing values of \( E^*(u) \).

Because equation (1.3.8) may be insufficient to approximate equation (1.2.153) for open-shell molecules all terms in equation (1.2.153) are studied here. The basic assumption is that the \( \overline{m} \) highest values of \( E^*(u) \) also give the minimum for equation (1.2.152).

To be more explicit let us extract those terms in the full CI expansion which make reference to just one virtual orbital \( |u> \):

\[
|\Phi(u)> = \sum_a (\text{cur}|ur> + c_{ra}|ra> + c_{aa}|aa> + c_{uu}|uu> + c_{ra}|ra>)
\]
where \( r \) denotes the orbital containing the unpaired electron in the ground state wave function and e.g., \(|\zeta_{ab}\rangle\) represents a state function as defined in Figure 1.1. It follows that 

\[-E^*(u) = \langle \Phi_{RHF} | \hat{H} | \Phi(u) \rangle\]

using the coefficients determined by equations (1.2.148) and (1.2.149). Should this not be the case then a much more difficult problem needs to be solved since the concept of an order may disappear. Using the expression [equation (1.3.9)] an order can only be determined if the set obtained for \( m = m' \) contains the set \( m = m' - 1 \). The additional orbital is placed at position \( m' \) in the list [the first \( (m' = 1) \) being \(|u\rangle\), corresponding to the largest \( E^*(u) \)].

(iii) Projection

It is traditional for workers to divide the orbitals in a molecule into groups. The occupied orbitals can normally, without transformation, be subdivided unequivocally into inner-shell and valence occupied orbitals by inspection of the eigenvalues \( \epsilon_a \). A unitary transformation of the doubly occupied orbitals may improve localisation of the inner-shell orbitals onto particular atomic centres but this is not done since it is not critical to the calculations described here. It has long been the custom to associate valence virtual or antibonding orbitals with those valence occupied orbitals which are distinctly bonding in character. In RHF theory this set is adequately represented by what is commonly known as a minimal basis set of orbitals. Minimal
basis set calculations have serious deficiencies which can be overcome if the basis set is extended by dividing up each function of the minimal basis set into at least two or double-zeta basis functions. The extra virtual orbitals produced by this procedure will be called extended virtual orbitals. Similarly the extra virtual orbitals resulting from the addition of polarisation functions to the basis can be called polarisation virtual orbitals. Since the properties of (S + D)CI(n(n) wave functions are invariant to unitary transformation of the virtual orbitals, the division of the virtual orbitals is as arbitrary as any division of the doubly occupied orbitals but nevertheless such classifications are useful. It is possible that the benefits of incorporating polarisation orbitals in the ground state RHF wave function is not reflected in the virtual orbitals, particularly in a CI calculation. To test this possibility it is proposed to project the virtual orbital space from a calculation involving polarisation functions onto the orbital space of calculations which do not use polarisation functions.

If |u> are the virtual orbitals of the calculation, including polarisation functions and |v> are the occupied and virtual orbitals for the smaller basis-set calculation, it is required to find the orbitals

\[ |u'\rangle = \sum_u c_{u',u} |u\rangle \]  \hspace{1cm} (1.3.11)

such that

\[ \sum_v (\langle u' | v \rangle)^2 c_{u'}^2 = \sum_v \frac{\langle u' | v \rangle^2}{\langle u' | u' \rangle} \]  \hspace{1cm} (1.3.12)
is maximised. On substituting equation (1.3.11) into (1.3.12) it is found that

\[ \epsilon_{u'} = \frac{u/v = \sum \sum c_{u'u} c_{u'u_w} <u|v><v|w>}{\sum \sum c_{u'u} c_{u'u_w} <u|w>}\]  \hspace{1cm} (1.3.13)

so that

\[ \frac{d\epsilon_{u'}}{d\epsilon_{u_m}} = \frac{v du/d\epsilon_{u_m} - udv/d\epsilon_{u_m}}{v^2} = \frac{du/d\epsilon_{u_m} - (u/v) dv/d\epsilon_{u_m}}{v} = \frac{du/d\epsilon_{u_m} - \epsilon_{u'} dv/d\epsilon_{u_m}}{v}. \]  \hspace{1cm} (1.3.14)

Now

\[ \frac{du/d\epsilon_{u_m}}{v} = 2\sum \sum c_{u'u} <u|v><v|m> \]  \hspace{1cm} (1.3.15)

and

\[ \frac{dv/d\epsilon_{u_m}}{v} = 2\sum c_{u'u} <u|m> \]  \hspace{1cm} (1.3.16)

therefore

\[ 2\sum c_{u'u} \left[ \sum <u|v><v|m> - \epsilon_{u'}\delta_{um} \right] \frac{d\epsilon_{u'}}{d\epsilon_{u_m}} = \frac{u}{v} \frac{\sum \sum c_{u'u} c_{u'u_w} <u|w>}{\sum \sum c_{u'u} c_{u'u_w} <u|w>} = 0. \]  \hspace{1cm} (1.3.17)

On dividing equation (1.3.17) through by \(2/\sum \sum c_{u'u} c_{u'u_w} <u|w>\) then

\[ \sum c_{u'u} \left[ \sum <u|v><v|m> - \epsilon_{u'}\delta_{um} \right] = 0. \]  \hspace{1cm} (1.3.18)

This is a well known eigenvalue expression from which it is easy to identify \(\hat{N}\) in equation (1.3.4). \(\epsilon_{u'}\) is a measure of the extent that \(|u'>\) overlaps with the space defined by the orbitals, \(|v>\), of the smaller basis set. For simplicity, it
is assumed that both sets of orbitals, $|u\rangle$, and $|v\rangle$, are definable in terms of the set of orbitals, $|w\rangle$, i.e.,

$$|u\rangle = \sum_w c_{uw} |w\rangle \quad (1.3.19)$$

$$|v\rangle = \sum_w c_{vw} |w\rangle. \quad (1.3.20)$$

In general, there will be no exact relationship of this kind between the two bases, $|u\rangle$ and $|v\rangle$, so that the required transformation between these sets has to be found in other ways. If $c_i$ is the contraction coefficient of the primitive Gaussian type orbital (GTO) for the smaller basis set of orbitals and $d_i$ is the similar coefficient for the larger basis set there will generally be an over-determined system of linear equations, i.e.,

$$c_1 = d_1 x, \ c_2 = d_2 x \ldots c_n = d_n x. \quad (1.3.21)$$

The best solution of these equations will be obtained on minimising the sum of the squares of the residuals, $\sum_i r_i^2$, where

$$d_1 x - c_1 = r_1, \ d_2 x - c_2 = r_2 \ldots d_n x - c_n = r_n; \quad (1.3.22)$$

i.e., to find $x$ when

$$\frac{d(\sum_i r_i^2)}{dx} = 0 \quad (1.3.23)$$

therefore

$$2(d_1 x - c_1)d_1 + 2(d_2 x - c_2)d_2 + \ldots + 2(d_n x - c_n)d_n = 0 \quad (1.3.24)$$

or

$$(d_1 + d_2 + \ldots + d_n)x^2 - c_1 d_1 - c_2 d_2 - \ldots - c_n d_n = 0 \quad (1.3.25)$$
so that

\[ x = \frac{(c_1d_1 + c_2d_2 + \ldots + c_nd_n)(d_2^2 + d_2^2 + \ldots + d_n^2)}{(\sum_i c_i d_i)^2} \]  \hspace{1cm} (1.3.26)

(iv) State minimisation

One method to obtain MVO's, following the ideas of Huzinaga and Arnau \[70\], is to optimise the energies of the excited states themselves with the constraint that only the virtual orbitals can be mixed amongst themselves by a unitary transformation. The least complicated method is to minimise the trace of the Hamiltonian corresponding to orbital \(|u>|\), i.e., the sum of the eigenvalues. Orbitals such as these resemble those of excited states and lead to compact CI expansions. Of course, it is necessary to show that the energies of such states are not invariant to a unitary transformation of the virtual orbitals. Here the emphasis is on direct double replacements but similar proofs could be found for all the terms to be studied in this work.

The (S)CI and (S + D)CI wave functions are invariant to unitary transformation of the virtual orbitals. Only, here, concentrating on the double replacement configurations of the CI wave function which can be expressed as

\[ \sum \sum \sum \sum c_{ab}^{uv} \psi_{ab}^{uv} \]  \hspace{1cm} (1.3.27)

It is readily apparent that certain groups of these terms are also invariant to the same transformation, e.g.,

\[ \sum \sum c_{aa}^{uv} \psi_{aa}^{uv} \]  \hspace{1cm} (1.3.28)
where $|a\rangle$ is any doubly occupied orbital. The discussion will centre about such terms since they are relatively simple to study and conceivably reflect the behaviour of the neglected terms. If $U$ is a unitary matrix such that

$$\psi' = U\psi,$$  \hfill (1.3.29)

where $\{\psi\}$ and $\{\psi'\}$ are sets of virtual orbitals, it follows that

$$\psi'_{aa} = U\psi_{aa} U^\dagger$$  \hfill (1.3.30)

where $(\psi_{aa})_{uv} = |\psi_{aa}^{uv}\rangle$. Invariance to unitary transformation implies

$$\sum U_{au} C_{uv} U_{va} = \sum C_{aa}$$  \hfill (1.3.31)

from which

$$C = U^\dagger C' U$$  \hfill (1.3.32)

where $(C)_{uv} = C_{aa}^{uv}$ and

$$\text{Tr} \ C'^\ast C = \text{Tr} \ (U^\dagger C' U)^\ast \ U^\dagger C' U = \text{Tr} \ U^\dagger C'^\ast U^\dagger U^\dagger C' U$$

$$= \text{Tr} \ U^\dagger C'^\ast C' U = \text{Tr} \ U U^\dagger C'^\ast C' = \text{Tr} \ C'^\ast C'.$$  \hfill (1.3.33)

On writing

$$\sum U_{au} C_{uv} U_{va} = \sum C_{aa}^{uu} |\psi_{aa}^{uu}\rangle + \sum C_{aa}^{uv} |\psi_{aa}^{uv}\rangle$$  \hfill (1.3.34)

it is noted that $C_{aa}^{uu} |\psi_{aa}^{uu}\rangle$ is not invariant to unitary transformation since if $(T)_{uu} = C_{aa}^{uu}$ is a diagonal matrix

$$\sum U_{au} C_{uv} U_{va} = \text{Tr} \ T_{aa} \psi_{aa} = \text{Tr} \ T U^\dagger \psi_{aa} U^\ast.$$

$U^\ast T U^\dagger$ is not necessarily a diagonal matrix so that direct doubles do not form a set that is invariant to unitary transformation. It is meaningful, therefore, to minimise
the energy of the expression \( \sum_{u'v'} c^{u'u'}_{aa} |\psi^{u'u'}_{aa} \rangle \) allowing only unitary transformation of the virtual orbitals. This means that the energy of the term \( \sum_{u'v'} \sum_{aa} c^{u'v'}_{aa} |\psi^{u'v'}_{aa} \rangle \) will be maximised, i.e., the contribution to \( E_{\text{corr}} \) will be minimised.

In order to obtain the required energy expressions, it is convenient here to introduce a modification of Slater's rules \([17,18]\) used to compile Table 1.1 in which the energy of one state, \(|L>\), is given in terms of another state, \(|K>\). The first case to be considered is where \(|K> = |...mn...>\) and \(|L> = |...pn...>\). Using these rules where \( \hat{\Delta} = \hat{h} + \hat{g} \) it is found that

\[
<K|\hat{\Delta}|K> = \sum \frac{1}{2} \left( (mm|nn) - (mn|nm) \right) \tag{1.3.37}
\]

where the notation is the same as Table 1.1 except that the integrations are over the MSO's. It follows that

\[
<L|\hat{\Delta}|L> = (1/2) \sum \sum \left( (nn|oo) - (no|on) \right)
+ \sum \left( (nn|pp) - (np|pn) \right) + \sum \left( (pp|oo) - (po|op) \right)
+ \left( (pp|pp) - (pp|pp) \right). \tag{1.3.39}
\]
Now
\[
\sum_{n \neq m} \sum_{m} \{(nn|oo) - (no|on)\} = \sum_{n \neq m} \sum_{m} \{(nn|oo) - (no|on)\}
\]
\[
- \sum_{n \neq m} \{(nn|mm) - (nm|mn)\} = \sum_{n \neq m} \{(nn|oo) - (no|on)\}
\]
\[
- \sum_{n \neq m} \{(mm|oo) - (mo|om)\} = \sum_{n \neq m} \{(nn|mm) - (nm|mn)\} \quad (1.3.40)
\]
so that
\[
\langle L|G|L\rangle = \frac{1}{2} \left[ \sum_{n \neq m} \{(nn|oo) - (no|on)\} - 2\sum_{n \neq m} \{(nn|mm) - (nm|mn)\} + 2\sum_{n \neq m} \{(nn|pp) - (np|pn)\} - 2\{(mm|pp) - (mp|pm)\} \right]
\]
\[
= \langle K|G|K\rangle - \sum_{n \neq m} \{(nn|mm) - (nm|mn)\} + \sum_{n \neq m} \{(nn|pp) - (np|pn)\} - \{(mm|pp) - (mp|pm)\} \quad (1.3.41)
\]
therefore
\[
\langle L|\hat{A}|L\rangle = \langle K|\hat{A}|K\rangle - \sum_{n \neq m} \{(nn|mm) - (nm|mn)\} - (p|\hat{h}|p) + \sum_{n \neq m} \{(nn|pp) - (np|pn)\} - \{(mm|pp) - (mp|pm)\} \quad (1.3.42)
\]
The second case for consideration is where \( |K\rangle = |...mn...\rangle \) and \( |L\rangle = |...pq...\rangle \). It follows similarly that
\[
\langle L|\hat{A}|L\rangle = \sum_{o \neq m} \sum_{m} \{(o|\hat{h}|o) + (p|\hat{h}|p) + (q|\hat{h}|q) \}
\]
\[
= \sum_{o} \{(o|\hat{h}|o) - (m|\hat{h}|m) - (n|\hat{h}|n) + (p|\hat{h}|p) + (q|\hat{h}|q) \}
\]
-71-
\[ <L|\hat{O}|L> = \left(\frac{1}{2}\right) \left[ \sum_{k=1}^{m} \sum_{l=1}^{n} (\hat{K}_k|\hat{L}_l) - (\hat{L}_1|\hat{K}_k) \right] \]

\[ + \sum_{k=1}^{m} \sum_{l=1}^{n} (\hat{K}_k|\hat{P}_k) - (\hat{P}_k|\hat{K}_k) + \sum_{k=1}^{m} \sum_{l=1}^{n} (\hat{Q}_k|\hat{Q}_k) - (\hat{Q}_k|\hat{Q}_k) \]

\[ + \sum_{l=1}^{n} \sum_{m=1}^{l} (\hat{P}_l|\hat{P}_l) - (\hat{P}_l|\hat{P}_l) + \sum_{l=1}^{n} \sum_{m=1}^{l} (\hat{Q}_l|\hat{Q}_l) - (\hat{Q}_l|\hat{Q}_l) \]

\[ + (\hat{P}_m|\hat{Q}_k) - (\hat{Q}_k|\hat{P}_m) + (\hat{Q}_m|\hat{P}_k) - (\hat{P}_k|\hat{Q}_m) \]

\[ + (\hat{P}_m|\hat{P}_p) - (\hat{P}_p|\hat{P}_m) + (\hat{Q}_m|\hat{Q}_q) - (\hat{Q}_q|\hat{Q}_m) \].

\[ (1.3.44) \]

Now

\[ \sum_{k=1}^{m} \sum_{l=1}^{n} (\hat{K}_k|\hat{L}_l) - (\hat{L}_1|\hat{K}_k) = \sum_{k=1}^{m} \sum_{m=1}^{l} (\hat{K}_k|\hat{P}_k) - (\hat{P}_k|\hat{K}_k) \]

\[ + \sum_{k=1}^{m} (\hat{K}_k|\hat{P}_m) - (\hat{P}_m|\hat{K}_k) + \sum_{k=1}^{m} (\hat{K}_k|\hat{Q}_k) - (\hat{Q}_k|\hat{K}_k) \]

\[ + \sum_{l=1}^{n} (\hat{P}_l|\hat{P}_l) - (\hat{P}_l|\hat{P}_l) + \sum_{l=1}^{n} (\hat{Q}_l|\hat{Q}_l) - (\hat{Q}_l|\hat{Q}_l) \]

\[ + (\hat{P}_m|\hat{Q}_k) - (\hat{Q}_k|\hat{P}_m) + (\hat{Q}_m|\hat{P}_k) - (\hat{P}_k|\hat{Q}_m) \]

\[ + (\hat{P}_m|\hat{P}_p) - (\hat{P}_p|\hat{P}_m) + (\hat{Q}_m|\hat{Q}_q) - (\hat{Q}_q|\hat{Q}_m) \].

\[ (1.3.44) \]
\[
+ \{(mm|mm) - (mm|mm)\} + \{(nn|mm) - (nm|mn)\}
- \sum_k \{(kk|nn) - (kn|nk)\} + \{(mm|nn) - (mn|nm)\}
+ \{(nn|nn) - (nn|nn)\}
\]

so that

\[<L|\hat{G}|L> = (1/2) \sum_k \sum_l \{(kk|ll) - (kl|lk)\}
- 2 \sum_k \{(kk|mm) - (km|mk)\} - 2 \sum_k \{(kk|nn) - (kn|nk)\}
+ 2 \{(mm|nn) - (mn|nm)\} + 2 \sum_k \{(kk|pp) - (kp|pk)\}
+ 2 \sum_k \{(kk|qq) - (kq|qk)\} - 2 \{(mm|pp) - (mp|pm)\}
- 2 \{(nn|pp) - (np|pn)\} - 2 \{(mm|qq) - (mq|qm)\}
- 2 \{(nn|qq) - (nq|qn)\} + 2 \{(pp|qq) - (pq|qp)\}
\]

\[= <K|\hat{G}|K> - \sum_k \{(kk|mm) - (km|mk)\} - \sum_k \{(kk|nn) - (kn|nk)\}
+ \{(mm|nn) - (mn|nm)\} + \sum_k \{(kk|pp) - (kp|pk)\}
+ \sum_k \{(kk|qq) - (kq|qk)\} - \{(mm|pp) - (mp|pm)\}
- \{(nn|pp) - (np|pn)\} - \{(mm|qq) - (mq|qm)\}
- \{(nn|qq) - (nq|qn)\} + \{(pp|qq) - (pq|qp)\}
\]

therefore

\[<L|\hat{H}|L> = <K|\hat{H}|K> - (m|\hat{h}|m) - \sum_k \{(kk|mm) - (km|mk)\}
- (n|\hat{h}|n) - \sum_k \{(kk|nn) - (kn|nk)\} + \{(mm|nn) - (mn|nm)\}
+ (p|\hat{h}|p) + \sum_k \{(kk|pp) - (kp|pk)\} + (q|\hat{h}|q)
\]
\[ + \sum \{(kk|qq) - (kq|qk)\} + \{(pp|qq) - (pq|qp)\} \]

\[- \{(mm|pp) - (mp|pm)\} - \{(nn|pp) - (np|pn)\} \]

\[- \{(mm|qq) - (mq|qm)\} - \{(nn|qq) - (nq|qn)\}. \quad (1.3.47) \]

The simplest procedure (a) is to minimise the energy of the state wave function \( |\psi_{u_0}^{u_0}\rangle \), obtained from the ground state wave function by exciting the unpaired electron, in orbital \(|r_0\rangle\), to a virtual orbital \(|u\rangle\). The expression for this energy is given by equation (1.3.42) after integration over spin as

\[
<\psi_{u_0}^{u_0}|\hat{H}|\psi_{u_0}^{u_0}> = E(r_0 \rightarrow u) = E_0 - h_{rr} - \sum_{a} (2J_{ar} - K_{ar}) + h_{uu} \]

\[+ \sum_{a} (2J_{au} - K_{au}) = E_c + E_u \quad (1.3.48) \]

where \(E_c\) is a constant and \(E_u\) a function of orbital \(|u\rangle\). It is a straightforward matter to show by direct substitution of equation (1.2.3) into (1.3.48) that, in the notation of equations (1.2.8) - (1.2.17), \(E_u\) is given by

\[E_u = Tr \{P_u(h + G(2R_1))\} \quad (1.3.49)\]

where

\[(P_u)_{ij} = C_{iu}C_{uj}^\dagger \quad (1.3.50)\]

From which it follows that

\[\delta E_u = Tr \{\delta P_u(h + G(2R_1))\} \quad (1.3.51)\]

since \(E_u\) can be rewritten as

\[E_u = \sum \sum (P_u)_{ij}(h + G(2R_1))_{ji} \]

\[= \sum \sum C_{iu}C_{uj}^\dagger(h + G(2R_1))_{ji} \]

-74-
\[ = \sum_i \sum_j c_{ij}^{+} (h + G(2R_1))_{ij} c_{iu} = c_u^{+} (h + G(2R_1)) c_u = \varepsilon_u, \]

(1.3.52)

where \( \varepsilon_u \) is an orbital energy, sufficient conditions for a stationary minimum of \( E_u \) are now obvious. Orbital energy \( \varepsilon_u \) will be stationary against variation of \( c_u \), subject to the normalising condition \( c_u^{+} S c_u = 1 \), provided that \( c_u \) is an eigenvector of \( h + G(2R_1) \) and the stationary value will be a minimum if \( \varepsilon_u \) is the lowest eigenvalue. Obviously, though, with the additional constraint that the MVO's are determined from the CVO's by a unitary transformation, the required operator cannot be \( h + G(2R_1) \) alone as it is necessary to project the operator onto the virtual orbital space in order to prevent mixing of the occupied and virtual orbitals and thus the required operator is

\[ H = S R_3 (h + G(2R_1)) R_3 S, \]

(1.3.53)

in addition, the required orthogonality of the MVO's is satisfied automatically when determined by an eigenvalue procedure. A direct comparison of equation (1.3.4) with (1.3.53) is possible if \( H \) is transformed into the molecular basis. The condition that \( \delta E_u = 0 \), subject to orthogonality constraints and the MVO's being a unitary transformation of the CVO's, may be therefore satisfied by solving the corresponding eigenvalue problem.

A similar, but rather more complicated, procedure (b) is to minimise the function \( |\psi_{ro}^{u_0} + I |\psi_{a_0}^{u_r} \rangle \), with respect to energy, which effectively is a linear combination of all states derived from the ground state by exciting a pair of electrons from any occupied orbital, \( |a\rangle \), one to a virtual
orbital, $|u\rangle$, and the other to pair with the unpaired electron in orbital $|r\rangle$. It can be regarded to sum over all occupied orbitals if $|\psi_{rr}^{ur}\rangle$ is interpreted as $|\psi_{ro}^{uo}\rangle$. It should be possible to weight the ($|\psi_{aa}^{ur}\rangle$) electronic states differently in the sum using PT but this is not attempted here. The expression for the energy $<\psi_{aa}^{ur}|\hat{H}|\psi_{aa}^{ur}>$ is given by equation (1.3.47) as

$$<\psi_{aa}^{ur}|\hat{H}|\psi_{aa}^{ur}> = E(aa \rightarrow ur) = E_0 + 2h_{aa} - 2\sum_{b} (2J_{ab} - K_{ab})$$

$$- 2(2J_{ar} - K_{ar}) + J_{aa} + h_{rr} + \sum_{b} (2J_{br} - K_{br}) + J_{rr} + h_{uu}$$

$$+ \sum_{b} (2J_{bu} - K_{bu}) + (2J_{ru} - K_{ru}) - (2J_{au} - K_{au}). \quad (1.3.54)$$

Hence

$$E(r \rightarrow u) + \sum_a E(aa \rightarrow ur) = (\mu - f + 1)E_0 + (\mu - f)J_{rr}$$

$$+ (\nu - f)[h_{rr} + \sum_{b} (2J_{br} - K_{br})] + \sum_{a=f}^{v} [-2h_{aa}$$

$$- 2\sum_{b} (2J_{ab} - K_{ab}) - 2(2J_{ar} - K_{ar}) + J_{aa}] + (\mu - f + 1)h_{uu}$$

$$+ (\mu - f)[(2J_{ru} - K_{ru}) - \sum_{b} (2J_{bu} - K_{bu})] + \sum_{a=1}^{f-1} (2J_{au} - K_{au})$$

$$= E_c + E_u$$

so that

$$E_u = Tr P_u ((\mu - f + 1)h + G(2((\mu - f)(R_1 + R_2) + Q_f))) \quad (1.3.55)$$

where

$$Q_f^{ij} = \sum_{a=1}^{f-1} C_{ia}C_{aj}^* \quad (1.3.57)$$
and
\[ \delta E_u = \text{Tr} \delta P_u ((\mu - f + 1)h + G(2(\mu - f)(R_1 + R_2) + Q_f)) \]

(1.3.58)

it follows similarly that the required operator is
\[ H = SR_3((\mu - f + 1)h + G(2((\mu - f)(R_1 + R_2) + Q_f)))R_3S. \]

(1.3.59)

Two other procedures (c) are to minimise the energies the functions \( \sqrt{(1/2)}| \psi_{oa}^u \rangle + | \psi_{ao}^u \rangle \) akin to the singlet and triplet states of a closed-shell molecule. The terms \((c, f)\) are used to denote these procedures with the summations beginning at orbital \( |f\rangle \), in order of increasing eigenvalue, e.g., \( f = 1 \) implies no restriction whereas \( f = 2 \) means that the contributions from the states obtained by exciting a single electron from the inner-shell occupied orbital of the radical are neglected. Once again, the expressions for the energies \( \langle \psi_{oa}^u | H | \psi_{oa}^u \rangle \) and \( \langle \psi_{ao}^u | H | \psi_{ao}^u \rangle \) are given by equation (1.3.42) as

\[ \langle \psi_{oa}^u | H | \psi_{oa}^u \rangle = E_0 - h_{aa} - \sum_b (2J_{ab} - K_{ab}) - J_{ar} + h_{uu} + \sum_b (2J_{bu} - K_{bu}) + J_{ru} - (J_{au} - K_{au}) \]

(1.3.60)

\[ \langle \psi_{ao}^u | H | \psi_{ao}^u \rangle = E_0 - h_{aa} - \sum_b (2J_{ab} - K_{ab}) - (J_{ar} - K_{ar}) + h_{uu} + \sum_b (2J_{bu} - K_{bu}) + (J_{ru} - K_{ru}) - (J_{au} - K_{au}) \]

(1.3.61)

and

\[ \langle \psi_{oa}^u | H | \psi_{ao}^u \rangle = -K_{au} \]

(1.3.62)

therefore
\[
(1/2) \langle \psi_{ou}^{\dagger} | \hat{H} | \psi_{ou} \rangle \pm 2 \langle \psi_{oa}^{\dagger} | \hat{H} | \psi_{ao} \rangle + \langle \psi_{ao}^{\dagger} | \hat{H} | \psi_{ao} \rangle = E^z(a \rightarrow u) \\
= E_0 - h_{aa} - \sum_b (2J_{ab} - K_{ab}) - (1/2)(2J_{ar} - K_{ar}) + h_{uu} \\
+ \sum_b (2J_{bu} - K_{bu}) + (1/2)(2J_{ru} - K_{ru}) - (J_{au} - K_{au}) \pm K_{au} \\
\]

(1.3.63)

where the \pm sign in the energy term is the reverse of the sign on \(E^z(a \rightarrow u)\). Hence

\[
\sum_{a} E^z(a \rightarrow u) = (\mu - f)E_0 + \sum_{a=f}^{v} [-h_{aa} - \sum_{b} (2J_{ab} - K_{ab}) \\
- (1/2)(2J_{ar} - K_{ar})] + (\mu - f)[h_{uu} + \sum_{b} (2J_{bu} - K_{bu}) \\
+ (1/2)(2J_{ru} - K_{ru})] - \sum_{a=f}^{v} (J_{au} - K_{au}) \pm \sum_{a=f}^{v} K_{au} = E_c + E^z_u \\
\]

(1.3.64)

so that

\[
E^z_u = \text{Tr} \, P_u((\mu - f)(h + G(2R_1 + R_2)) - G'(Q^i_f) \pm K(Q^i_f)) \\
\]

(1.3.65)

where

\[
(Q^i_f)_{ij} = \sum_{a=f}^{v} C^+_{ia} C_{aj} \\
\]

(1.3.66)

and

\[
\delta E^z_u = \text{Tr} \, \delta P_u((\mu - f)(h + G(2R_1 + R_2)) - G'(Q^i_f) \pm K(Q^i_f)) \\
\]

(1.3.67)

it follows again that the required operators are

\[
H = SR_3((\mu - f)(h + G(2R_1 + R_2)) - G'(Q^i_f) \pm K(Q^i_f))R_3S. \\
\]

(1.3.68)
Since direct double replacements are thought to be important in CI calculations the energy of the function \( |\psi_{uu}^{\alpha\alpha}\rangle\), procedure \((d,f)\) is also minimised. This is summed over the doubly occupied orbitals only. The expression for the energy \( \langle \psi_{\alpha\alpha}^{uu}|\hat{H}|\psi_{\alpha\alpha}^{uu}\rangle \) is given by equation (1.3.47) as

\[
\langle \psi_{\alpha\alpha}^{uu}|\hat{H}|\psi_{\alpha\alpha}^{uu}\rangle = E(\alpha\alpha \rightarrow uu) = E_0 - 2h_{\alpha\alpha} - 2\sum_{b} (2J_{\alpha\beta} - K_{\alpha\beta}) - (2J_{\alpha r} - K_{\alpha r}) + J_{\alpha\alpha} + 2h_{uu} + 2\sum_{b} (2J_{\beta u} - K_{\beta u}) + (2J_{ru} - K_{ru}) + J_{uu} - 2(2J_{\alpha u} - K_{\alpha u}) \tag{1.3.69}
\]

therefore

\[
\sum_{\alpha} E(\alpha\alpha \rightarrow uu) = (\mu - f)E_0 + \sum_{\alpha\neq f} \left[ -2h_{\alpha\alpha} - 2\sum_{b} (2J_{\alpha\beta} - K_{\alpha\beta}) - (2J_{\alpha r} - K_{\alpha r}) + J_{\alpha\alpha} \right] + (\mu - f)[2h_{uu} + (2J_{ru} - K_{ru}) + J_{uu}] + 2(\nu - f)\sum_{b} (2J_{\beta u} - K_{\beta u}) + 2 \sum_{a=1} (2J_{\alpha u} - K_{\alpha u}) = E_{c} + E_{u} \tag{1.3.70}
\]

so that

\[
E_{u} = 2Tr \, P_{u}((\mu - f)(h + G(R_{2} + P_{u})) + (\nu - f)G(2R_{1}) + G(2Q_{f})) \tag{1.3.71}
\]

and to first order of small quantities

\[
\delta E_{u} = 2Tr \, \delta P_{u}((\mu - f)(h + G(R_{2} + 2P_{u})) + (\nu - f)G(2R_{1})) + G(2Q_{f})) \tag{1.3.72}
\]

therefore the required operator of the first orbital \( |u\rangle \) is

\[
H = SR_{3}((\mu - f)(h + G(R_{2} + 2P_{u})) + (\nu - f)G(2R_{1}) + G(2Q_{f})) \times R_{3}S \tag{1.3.73}
\]
for subsequent orbitals \( R_3 \) is replaced with \( R_3 - \frac{1}{2} P_u \). \( \mathbb{H} \) contains \( P_u \) and it is therefore necessary to solve the corresponding eigenvalue equation iteratively.

Lastly, procedure (e, f) minimises the energy of the function \( \sqrt{(1/2)} \sum_{a \neq u} (|\psi_{aa}^{uv}|^2 - |\psi_{aa}^{vu}|^2) \), where the summation counts over all doubly occupied orbitals, \(|a>\), starting at \(|f>\). The energies \( <\psi_{aa}^{uv}\mid \hat{H} \mid \psi_{aa}^{uv}> \) and \( <\psi_{aa}^{vu}\mid \hat{H} \mid \psi_{aa}^{vu}> \) are given by equation (1.3.47) as

\[
<\psi_{aa}^{uv}\mid \hat{H} \mid \psi_{aa}^{uv}> = E_0 - 2h_{aa} - 2\sum_b (2J_{ab} - K_{ab}) - (2J_{ar} - K_{ar})
+ J_{aa} + h_{uu} + \sum_b (2J_{bu} - K_{bu}) + (J_{ru} - K_{ru}) + h_{vv}
+ \sum_b (2J_{bv} - K_{bv}) + J_{rv} + J_{uv} - (2J_{au} - K_{au}) - (2J_{av} - K_{av})
\]

(1.3.74)

\[
<\psi_{aa}^{vu}\mid \hat{H} \mid \psi_{aa}^{vu}> = E_0 - 2h_{aa} - 2\sum_b (2J_{ab} - K_{ab}) - (2J_{ar} - K_{ar})
+ J_{aa} + h_{uu} + \sum_b (2J_{bu} - K_{bu}) + J_{ru} + h_{vv} + \sum_b (2J_{bv} - K_{bv})
+ (J_{rv} - K_{rv}) + J_{uv} - (2J_{au} - K_{au}) - (2J_{av} - K_{av})
\]

(1.3.75)

and

\[
<\psi_{aa}^{uv}\mid \hat{H} \mid \psi_{aa}^{vu}> = -K_{uv}
\]

(1.3.76)

therefore

\[
(1/2)(<\psi_{aa}^{uv}\mid \hat{H} \mid \psi_{aa}^{uv}> - 2<\psi_{aa}^{uv}\mid \hat{H} \mid \psi_{aa}^{vu}> + <\psi_{aa}^{vu}\mid \hat{H} \mid \psi_{aa}^{vu}>)
= E(aa \rightarrow uv) = E_0 - 2h_{aa} - 2\sum_b (2J_{ab} - K_{ab}) - (2J_{ar} - K_{ar})
+ J_{aa} + h_{uu} + \sum_b (2J_{bu} - K_{bu}) + (1/2)(2J_{ru} - K_{ru}) + h_{vv}
\]
\[+ \sum_b (2J_{bv} - K_{bv}) + (1/2)(2J_{rv} - K_{rv}) + J_{uv} - (2J_{au} - K_{au}) - (2J_{av} - K_{av}) + K_{uv}. \] 

(1.3.77)

Hence

\[\sum_a \sum_v E(aa \rightarrow uv) = (\mu - f)(m - \mu - 1)E_0 + (m - \mu - 1) \sum_v v\sum_a f [h_{aa} - 2\sum_b (2J_{ab} - K_{ab}) - (2J_{ar} - K_{ar}) + J_{aa}] + (\mu - f)\sum_v [h_{vv} + \sum_b (2J_{bv} - K_{bv}) + (1/2)(2J_{rv} - K_{rv})]
- \sum_a \sum_v (2J_{av} - K_{av}) + (\mu - f)(m - \mu - 2)h_{uu} + (1/2)(2J_{ru} - K_{ru})] + (\mu - f)(m - \mu - 2)\sum_b (2J_{bu} - K_{bu}) + f-1
(m - \mu - 2) \sum_a (2J_{au} - K_{au}) + (\mu - f)\sum_v (J_{uv} + K_{uv}) - 2J_{uu} \]

= \(E_c + E_u\) 

(1.3.78)

so that

\[E_u = \text{Tr} P_u ((m - \mu - 2)((\mu - f)h + G((\mu - f)R_2 + 2(\nu - f)R_1 + 2Q_f)) + (\mu - f)(J(R_3) + K(R_3) - 2G(2P_u))) \] 

(1.3.79)

and to first order of small quantities

\[\delta E_u = \text{Tr} \delta P_u ((m - \mu - 2)((\mu - f)h + G((\mu - f)R_2 + 2(\nu - f)R_1 + 2Q_f)) + (\mu - f)(J(R_3) + K(R_3) - 4G(2P_u))) \] 

(1.3.80)

therefore the required operator of the first orbital \(\mid u \rangle\) is

\[H = SR_3 ((m - \mu - 2)((\mu - f)h + G((\mu - f)R_2 + 2(\nu - f)R_1 + 2Q_f)) + (\mu - f)(J(R_3) + K(R_3) - 4G(2P_u)))R_3S \] 

(1.3.81)
for subsequent orbitals $R_3$ is again replaced, outside the parentheses, with $R_3 - \sum u P_u$. In common with the previous case, this is also an iterative calculation.

1.4 Vibronic contributions

In some radicals a marked dependence of the hyperfine couplings on temperature has been noted. This effect is believed to arise from a vibrational contribution augmenting the hyperfine coupling constant of the rigid radical [71]. This vibrational effect is generally considered to be relatively small except in radicals where only an indirect coupling mechanism is operative in the rigid system but where direct coupling is introduced by a particular molecular vibration. Such radicals usually have the unpaired electron virtually localised in a p- or d-type orbital and so the effect on the anisotropic coupling constants will be small. Thus, only vibrational corrections to isotropic coupling constants will be considered.

The estimation of the vibrational contributions to hyperfine coupling constants involves no new principles in quantum chemical calculations. It involves the calculation of total energies and hyperfine coupling constants at non-equilibrium nuclear configurations. Beveridge and Miller [72] have considered the theoretical basis for estimating these contributions using the intermediate neglect of differential overlap (INDO) method.

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

$$\psi_{vib} = (\pi/\alpha)^{1/4} \exp(-\alpha x^2/2)$$  \hspace{1cm} (1.4.1)
where $x$ is the displacement from the equilibrium configuration along a normal coordinate and

$$a = 2\mu E^0_{\text{vib}}$$  \hspace{1cm} (1.4.2)

where $\mu$ is the reduced mass and $E^0_{\text{vib}}$ is the zero-point energy for the vibration

$$E^0_{\text{vib}} = (\nu + (1/2))(k/\mu)^{1/2} \nu = 0, 1, 2, \ldots$$  \hspace{1cm} (1.4.3)

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

$$E = E_0 + (1/2)kx^2$$  \hspace{1cm} (1.4.4)

$E_0$ and $E$ are the energies at zero and non-zero displacements respectively.

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

$$a(x) = \sum_{n=0}^\infty c_n x^n.$$  \hspace{1cm} (1.4.5)

If it is assumed that terms with $n > 2$ can be neglected and noting that for a harmonic oscillator terms with odd powers of $x$ disappear, then equation (1.4.5) reduces to

$$a(x) = c_0 + c_2x^2$$  \hspace{1cm} (1.4.6)

where $c_0$ is the coupling constant calculated at the equilibrium nuclear configuration.

Then $\langle a \rangle$, the vibrationally correct hyperfine coupling constant, is the mean value of the calculated hyperfine coupling constants over the amplitude of the normal coordinate sampled during the execution of the zero-point vibration, as is given by

$$\langle a \rangle = \langle \psi_{\text{vib}} | a | \psi_{\text{vib}} \rangle = c_0 + c_2/(2\alpha).$$  \hspace{1cm} (1.4.7)
The estimates obtained from equation (1.4.7) may not be satisfactory in situations where the simple harmonic approximation is unreasonable, for instance, with large displacements or small force constants.
SECTION TWO: A comparison of convergence improvements in two small doublet state radicals BeH and NH$_2$
2.1 The BeH radical

BeH was chosen as the first test radical \((R_{\text{BeH}} = 2.538 \, \text{a}_0)\) for the following reasons: (i) it is very small only a five electron system, (ii) it is an example of a \(\sigma\) radical, i.e., the unpaired electron occupies an orbital of \(\sigma\) symmetry, (iii) it has been studied before using a basis set of 15 orbitals \([73, 74]\), i.e., a (9s5p) primitive basis set on beryllium contracted to (5s1p) and a (6s) primitive basis for hydrogen contracted to (4s) to which was added on the same atom one p-type GTO (exponent 0.75) (see Table 2.1) and a large basis set of 39 orbitals \([75]\), i.e., a (13s4p) primitive basis set on beryllium and (8s2p) primitive set for hydrogen (see Table 2.2) which are used here and (iv) the \((S + D)\text{CIn}(n)\) or \(\text{SDCIn}(n)\) in the contracted form \(\text{SDCIm}(n)\) which will be used to describe an orbitally ordered CI calculation \([\text{SDCI36}(36)\) for the larger of the two basis sets in the notation introduced here\] was possible.

The basis set of 15 orbitals because of its relatively small size appears to be a useful one to gain information concerning the various methods that are available to order the orbitals in a CI calculation. On the other hand, it can be stated at the outset that none of the orders obtained has been adopted in the combined CI-perturbation approaches used exclusively with this basis set because of the difficulty in evaluating the results without a variational upper bound to the energies. Of course, variational upper bounds would have been available for this basis but were not calculated taking the view of their non-availability in general. It is for the same reason that the operators of Section 1.3 have
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The sum of terms for $|\Phi(u)>$ in equation (1.3.10) can be annotated as follows: $b = |\Xi_{\text{aa}}^{uu}>; c = b$ and $|\Xi_{\text{ra}}^{ur}>; d = c$ and $|\Xi_{\text{aa}}^{ur}>; e' = d$ and $|\Xi_{\text{ba}}^{ur}>; e = e'$ and $|\Xi_{\text{ab}}^{ur}>; f = e$ and $|\Xi_{\text{ab}}^{uu}>; g = f$ and $|\Xi_{\text{ra}}^{uu}>$. The corresponding values of $E^*(u)$ for the RHF orbitals, numbered as indicated in the natural order of increasing eigenvalue, have been plotted in Figure 2.1. It was noted, as previously [49], that some of the high energy virtual core orbitals principally orbital 15 appeared early in the list so that Figure 2.2 shows the same plot with the inner-shell occupied orbital neglected thus placing this orbital automatically at the end of the list with the remaining order largely unaffected but at the same time drastically reducing the number of terms that can be included in $E^*(u)$. The radical belongs to the $C_{\text{nv}}$ of $G$ and the orbitals can have only symmetries and representations $\sigma(A_1)$ or $\pi(E_1)$. It is important to note that whilst the majority of terms are unaffected by symmetry this prevents some terms from making a contribution to the orbital order, i.e., $|\Xi_{\text{ra}}^{ur}>$, $|\Xi_{\text{aa}}^{ur}>$, $|\Xi_{\text{ba}}^{ur}>$ and $|\Xi_{\text{ab}}^{ur}>$ only affect $\sigma$ orbitals. The orbital orders were found to be relatively stable on going from terms a to g with the exception of orbital 9. The relative position of this orbital cannot be obtained by direct calculation since the next orbitals in the list 10 and 11 are $\pi$ orbitals and these have to be taken together to ensure correct symmetry of the final wave function. This leaves the $E^*(u, v)$ method as only one with which to attempt to obtain the correct orbital order. It remained to determine in this method whether or not there would be a
FIGURE 2-1 VALUES OF $E^*(u)$ FOR THE B•H RADICAL.
FIGURE 2.2 VALUES OF $E^*(u)$ FOR THE B eH RADICAL

TERMS USED
difference in the orbital order if determinants or minimal HF interacting states were used to set up the $E^*(u, v)$ matrix. The results of this analysis are shown in Table 2.3. It was found that although the estimates of $E_{\text{corr}}$ were not invariant to the change of basis the orbitals selected were invariant. Both estimates of $E_{\text{corr}}$ shown in the upper half of Table 2.3 are good ones with the value for states being closer to the actual value obtained from a CI calculation as $-0.04898$. This suggests that the simpler functions can be used in the $E^*(u, v)$ ordering method and these will be used from now on. Here $E^*(u, v)$ seemed to suffer from the same difficulty with regard to the early positions of the high energy virtual core orbitals so that the same calculation was performed with the inner-shell occupied orbital neglected and shown in the lower half of Table 2.3. It was found that if the $E^*(u, v)$ method is annotated as order $h$ for $h(\overline{m} < 8)$ the upper half of Table 2.3, i.e., all terms included in $E^*(u, v)$, gives the order 8 15 13 9 12 6 7 and for $h(\overline{m} \geq 8)$ 4 5 8 9 10 11 13 15 12 6 7 14 but the lower half of Table 2.3 gives the order for $h(\overline{m} < 4)$ 8 9 6 and for $h(\overline{m} > 4)$ 4 5 8 10 11 9 6 12 7 14 13 15 showing that the concept of an order was partially lost and thus this analysis yields no more information concerning the relative positions of the orbitals in $E^*(u)$, rather, if $E^*(u, v)$ is accepted as the best method to order the orbitals, it tends to invalidate the method as a suitable one for doublet state radicals.

Because, as more terms were included in $E^*(u, v)$, the orbital order approximates to the natural one this was used.
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in all calculations although it appears not to be the best order as the wave function is progressively truncated. Here again, the contracted form SDPTm(n) will be used to describe a combined CI-perturbation calculation. Tables 2.4, 2.5 and 2.6 show the energies, isotropic hyperfine coupling constants and anisotropic hyperfine coupling constants perpendicular to the applied field for the A_k, A_k (including all single replacements in the k space of the basis) and B_k approximations respectively. The effect of including direct double replacements into the k space of the A_k approximation was not investigated. For comparison Tables 2.7 and 2.8 show the same results for SDCIm(n) and SDCIm(m) expansions respectively.

Tables 2.4, 2.5 and 2.6 show that the aBe and BBe values remained in close agreement with experiment as the dimension of the k space was progressively reduced but the aH value tends to deviate from experiment with values of m < 6 this being greater for approximations not including all single replacements in the k space of the basis. This serves to illustrate the traditional importance of these replacements in spin density calculations. In contrast, the aH results shown in Table 2.7 reproduce the experimental results almost throughout the range of m values indicating the benefits of including direct double replacements into the basis. The aBe and BBe results shown in Table 2.8 indicate that although the BBe values are generally in good agreement with experiment the aBe values begin to deviate from this value immediately the basis is truncated. Here again, the correspondence with the aH experimental value is
### TABLE 2.4 ENERGIES AND HYPERFINE COUPLING CONSTANTS USING THE \( a_k \) APPROXIMATION

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<td>-6.885</td>
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<tr>
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<tr>
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<td>-7.010</td>
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<tr>
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<td>-15.1951022</td>
<td>-7.043</td>
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<tr>
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<td>-7.062</td>
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<tr>
<td>SDPT0(12)</td>
<td></td>
<td>-15.1948547</td>
<td>-7.362</td>
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</tbody>
</table>

**experiment [76]**

-7.11 6.93 -0.158 0.122

### TABLE 2.5 ENERGIES AND HYPERFINE COUPLING CONSTANTS USING THE \( a_k \) APPROXIMATION (ALL SINGLE REPLACEMENTS IN \( k \) SPACE)

<table>
<thead>
<tr>
<th>description of calculation</th>
<th>number of detors</th>
<th>total energy/ hartree</th>
<th>hyperfine coupling constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td></td>
<td>( a_{Be}/mT )</td>
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<tr>
<td>SDPT11(12)</td>
<td>1 683</td>
<td>-15.1958726</td>
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</tr>
<tr>
<td>SDPT10(12)</td>
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<td>-15.1960126</td>
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<tr>
<td>SDPT9(12)</td>
<td></td>
<td>-15.1956576</td>
<td>-6.964</td>
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<tr>
<td>SDPT8(12)</td>
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<td>-15.1958739</td>
<td>-6.954</td>
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<td>-15.1971195</td>
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<td>-15.1960745</td>
<td>-6.626</td>
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<tr>
<td>SDPT0(12)</td>
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<td>-15.1951327</td>
<td>-7.034</td>
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### Table 2.6 Energies and Hyperfine Coupling Constants Using the $B_k$ Approximation

<table>
<thead>
<tr>
<th>Description of Calculation</th>
<th>Number of Detors</th>
<th>Total Energy/ Hartree</th>
<th>$a_{Be}/mT$</th>
<th>$a_{H}/mT$</th>
<th>$B_{Be}/mT$</th>
<th>$B_{H}/mT$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDPT11(12)</td>
<td>1 683</td>
<td>-15.1957568</td>
<td>-6.948</td>
<td>6.844</td>
<td>-0.1567</td>
<td>0.2032</td>
</tr>
<tr>
<td>SDPT10(12)</td>
<td>&quot;</td>
<td>-15.1957745</td>
<td>-6.949</td>
<td>6.827</td>
<td>-0.1567</td>
<td>0.2032</td>
</tr>
<tr>
<td>SDPT9(12)</td>
<td>&quot;</td>
<td>-15.1953234</td>
<td>-6.925</td>
<td>6.838</td>
<td>-0.1567</td>
<td>0.2031</td>
</tr>
<tr>
<td>SDPT8(12)</td>
<td>&quot;</td>
<td>-15.1951788</td>
<td>-6.924</td>
<td>6.835</td>
<td>-0.1566</td>
<td>0.2030</td>
</tr>
<tr>
<td>SDPT6(12)</td>
<td>&quot;</td>
<td>-15.1954371</td>
<td>-6.925</td>
<td>6.834</td>
<td>-0.1565</td>
<td>0.2031</td>
</tr>
<tr>
<td>SDPT5(12)</td>
<td>&quot;</td>
<td>-15.1956019</td>
<td>-6.931</td>
<td>6.612</td>
<td>-0.1565</td>
<td>0.2032</td>
</tr>
<tr>
<td>SDPT4(12)</td>
<td>&quot;</td>
<td>-15.1953738</td>
<td>-6.841</td>
<td>6.161</td>
<td>-0.1594</td>
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</tr>
<tr>
<td>SDPT3(12)</td>
<td>&quot;</td>
<td>-15.1952840</td>
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</tr>
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<td>SDPT2(12)</td>
<td>&quot;</td>
<td>-15.1951051</td>
<td>-6.912</td>
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<td>0.2088</td>
</tr>
<tr>
<td>SDPT0(12)</td>
<td>&quot;</td>
<td>-15.1951727</td>
<td>-6.885</td>
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<td>0.2167</td>
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</table>

### Table 2.7 Energies and Hyperfine Coupling Constants Using the $SCDIm(\pi)$ Expansion

<table>
<thead>
<tr>
<th>Description of Calculation</th>
<th>Number of Detors</th>
<th>Total Energy/ Hartree</th>
<th>$a_{Be}/mT$</th>
<th>$a_{H}/mT$</th>
<th>$B_{Be}/mT$</th>
<th>$B_{H}/mT$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDC11(12)</td>
<td>1 431</td>
<td>-15.1901409</td>
<td>-6.911</td>
<td>6.926</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SDC10(12)</td>
<td>1 291</td>
<td>-15.1896945</td>
<td>-6.899</td>
<td>6.835</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SDC9(12)</td>
<td>993</td>
<td>-15.1877941</td>
<td>-6.869</td>
<td>6.877</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SDC8(12)</td>
<td>807</td>
<td>-15.1857099</td>
<td>-6.855</td>
<td>6.996</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SDC6(12)</td>
<td>501</td>
<td>-15.1829073</td>
<td>-6.794</td>
<td>7.072</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SDC5(12)</td>
<td>381</td>
<td>-15.1785259</td>
<td>-6.793</td>
<td>6.826</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SDC4(12)</td>
<td>283</td>
<td>-15.1763380</td>
<td>-6.860</td>
<td>6.754</td>
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<td>-</td>
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<tr>
<td>SDC3(12)</td>
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<td>-15.1754816</td>
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<td>6.761</td>
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<tr>
<td>SDC2(12)</td>
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<td>6.722</td>
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<td>SDC0(12)</td>
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<td>5.332</td>
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TABLE 2.8 ENERGIES AND HYPERFINE COUPLING CONSTANTS USING THE SDCI(m) EXPANSION

<table>
<thead>
<tr>
<th>description of calculation</th>
<th>number of detors</th>
<th>total energy/ hartree</th>
<th>hyperfine coupling constants</th>
<th>$a_{Be}/mT$</th>
<th>$a_{H}/mT$</th>
<th>$B_{Be}/mT$</th>
<th>$B_{H}/mT$</th>
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</thead>
<tbody>
<tr>
<td>SDCI12(12)</td>
<td>1 683</td>
<td>-15.1959551</td>
<td>-6.941</td>
<td>6.841</td>
<td>-0.1567</td>
<td>0.2032</td>
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</tr>
<tr>
<td>SDCI11(11)</td>
<td>1 422</td>
<td>-15.1850360</td>
<td>-6.102</td>
<td>7.013</td>
<td>-0.1567</td>
<td>0.2019</td>
<td></td>
</tr>
<tr>
<td>SDCI10(10)</td>
<td>1 183</td>
<td>-15.1844227</td>
<td>-6.083</td>
<td>6.702</td>
<td>-0.1569</td>
<td>0.2018</td>
<td></td>
</tr>
<tr>
<td>SDCI9(9)</td>
<td>966</td>
<td>-15.1812044</td>
<td>-5.857</td>
<td>6.758</td>
<td>-0.1571</td>
<td>0.2011</td>
<td></td>
</tr>
<tr>
<td>SDCI8(8)</td>
<td>771</td>
<td>-15.1783403</td>
<td>-5.836</td>
<td>6.856</td>
<td>-0.1579</td>
<td>0.2020</td>
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</tr>
<tr>
<td>SDCI6(6)</td>
<td>447</td>
<td>-15.1710345</td>
<td>-5.680</td>
<td>7.262</td>
<td>-0.1603</td>
<td>0.2012</td>
<td></td>
</tr>
<tr>
<td>SDCI5(5)</td>
<td>318</td>
<td>-15.1640018</td>
<td>-5.685</td>
<td>5.948</td>
<td>-0.1586</td>
<td>0.1923</td>
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</tr>
<tr>
<td>SDCI4(4)</td>
<td>211</td>
<td>-15.1557083</td>
<td>-6.146</td>
<td>3.781</td>
<td>-0.1661</td>
<td>0.2548</td>
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<tr>
<td>SDCI3(3)</td>
<td>126</td>
<td>-15.1546487</td>
<td>-6.118</td>
<td>3.860</td>
<td>-0.1681</td>
<td>0.2581</td>
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<td>SDCI2(2)</td>
<td>63</td>
<td>-15.1532243</td>
<td>-6.028</td>
<td>3.539</td>
<td>-0.1663</td>
<td>0.2479</td>
<td></td>
</tr>
</tbody>
</table>

A good one up to about $m > 5$. As observed previously [74], a serious difficulty arises with the $B_H$ value all tabulated predictions giving values about twice that of experiment. It appears that, certainly in the case of the $a_{Be}$ values, there are benefits to be had by including at some level of approximation that part of the basis normally neglected in a CI calculation.

In the 39 orbital basis only the $k$ part was admitted to the wave function. This means that an upper bound to the energy is obtained automatically and actual calculations on the orbital order predicted by the various methods could be performed. The NO's from the SDCI36(36) calculation were obtained and the order suggested by their occupation numbers was used although, perhaps, in keeping with Section 1.3 and
for direct comparison with the operators therein, the FNO's should have been used. Because the view was taken that the NO's will not be available generally the operator of Section 1.3 (ii) was used to generate the MVO's. Other work on the following radical showed that, apart from P₁ of Section 1.3 (i), this operator was likely to give the best results and the other operators were not investigated. As the operator contains an empirical parameter it is necessary to find the value where the corresponding total energy of the wave function minimises. A plot of total energy as function of this parameter for unordered SDCI8(36) calculations given in Figure 2.3 shows that the value required is \( Y = -15 \) as was found to give the best MVO's for FCN [49]. This result is very significant because it is the first indication that the variable parameter \( Y \) could be the same for molecules of different multiplicity and therefore would considerably enhance the usefulness of the method. In order to ascertain the effectiveness of incorporating MVO's into the wave function it followed that two extreme values of \( Y \) should be compared, i.e., \( Y = 0 \), corresponding to the RHF case giving CVO's and \( Y = -15 \), in the orbital ordering methods. Figure 2.4 shows the results of this analysis for the \( E^*(u) \) method when CVO's were used. There were marked changes in the order as a function of the terms added. Figure 2.5 shows the same analysis with the inner-shell occupied orbital excluded from the calculation here displacing several of the higher energy virtual orbitals in the list but in this case slightly disturbing the remaining order. Figures 2.6 and 2.7 respectively show the same results for \( Y = -15 \). It is
FIGURE 2.3 TOTAL ENERGY AS A FUNCTION OF $\gamma$ FOR SDCI(36) CALCULATIONS ON THE BeH RADICAL.
FIGURE 2.4 VALUES OF $E^*(U) \gamma = 0$, FOR THE BH RADICAL.
FIGURE 2-5 VALUES OF $E^*(u)$, $\gamma = 0$, FOR THE B=H RADICAL.
FIGURE 2.6 VALUES OF $E^*(u)$, $\gamma = -15$, FOR THE BeH RADICAL.
FIGURE 2.7 VALUES OF $E^*(u)$, $\gamma = -15$, FOR THE $B\cdot H$ RADICAL.
seen from these results, in contrast to CVO's, that the terms added had no effect on the predicted order suggesting that equation (1.3.8) is sufficient for its original purpose but it remained to be determined whether or not this accurately reflected the order which would be obtained using the $E^*(u, v)$ ordering method. To test this possibility the two sets of orbitals were ordered using this method and the following orders were found for $\gamma = 0$ : $h(6 \leq \overline{m} < 9)$ 8 11 16 20 25 30 14 28 and for $h(\overline{m} = 11)$ 8 11 16 20 25 30 14 4 5 9 10 whilst for $\gamma = -15$ the order was $h(8 \leq \overline{m} < 12)$ 4 5 6 7 9 10 25 30 20 8 28. It was arbitrarily decided to use $\overline{m} \leq n/3$ in $SDCIm(n)$, so that the amount of work was reduced by an order of magnitude, then only $\overline{m} = 8$ and $\overline{m} = 11$ are sensible in this region because of the degeneracies of the orbitals of $\pi$ symmetry. With these values of $\overline{m}$ it was possible to use the natural orders of the MVO's as well as almost all of the orders predicted by the $E^*(u)$ method as shown in Table 2.9. On the other hand, because the calculable differences in the orders of the CVO's are merely permutations within these groups and as already stated the orders of the MVO's were invariant against the terms added, it was not possible to annotate the effect of using equation (1.3.10) (but see Section 2.2). It is seen from Table 2.9 that whilst NO's were by far the best orbitals to use in the $SDCIm(n)$ expansions there remained considerable energetic advantages in admitting MVO's to the wave function over CVO's. The CVO's ordered by the full $E^*(u)$ method without manual intervention in the orbital order for $\overline{m} = 8$ give higher energies than the natural order but the reverse is true for

-103-
TABLE 2.9 ENERGIES AND HYPERFINE COUPLING CONSTANTS FOR THE BeH 39 ORBITAL BASIS

<table>
<thead>
<tr>
<th>description of calculation</th>
<th>number of detors</th>
<th>total energy/hartree</th>
<th>( e ) corr</th>
<th>isotropic hyperfine coupling constants</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>( a_{Be} )/mT</td>
<td>( a_{H} )/mT</td>
</tr>
<tr>
<td>RHF</td>
<td>1</td>
<td>-15.1500</td>
<td>0.0</td>
<td>-6.286</td>
</tr>
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<td>SDCI36(36)</td>
<td>8 067</td>
<td>-15.2232</td>
<td>100.0</td>
<td>-6.850</td>
</tr>
<tr>
<td>SDCI8(36): NO's</td>
<td>567</td>
<td>-15.2159</td>
<td>90.0</td>
<td>-6.745</td>
</tr>
<tr>
<td>SDCI11(36): NO's</td>
<td>873</td>
<td>-15.2199</td>
<td>95.5</td>
<td>-6.744</td>
</tr>
<tr>
<td>SDCI8(36): ( \gamma = 0 )</td>
<td>567</td>
<td>-15.1897</td>
<td>54.2</td>
<td>-6.679</td>
</tr>
<tr>
<td>SDCI11(36): ( \gamma = 0 )</td>
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<td>-15.1940</td>
<td>60.1</td>
<td>-6.712</td>
</tr>
<tr>
<td>SDCI8(36): ( \gamma = 0 # )</td>
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<td>-6.957</td>
</tr>
<tr>
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<td>-6.437</td>
</tr>
<tr>
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<td>59.1</td>
<td>-6.717</td>
</tr>
<tr>
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<td>-15.1957</td>
<td>62.5</td>
<td>-6.734</td>
</tr>
<tr>
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<td>-15.1959</td>
<td>62.7</td>
<td>-6.932</td>
</tr>
<tr>
<td>SDCI11(36): ( \gamma = 0 * )</td>
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<td>-15.2024</td>
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<td>-6.701</td>
</tr>
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<td>SDCI8(36): ( \gamma = -15 )</td>
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</tr>
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<td>SDCI11(36): ( \gamma = -15 )</td>
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<td>-6.716</td>
</tr>
<tr>
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<td>-15.1970</td>
<td>64.2</td>
<td>-6.390</td>
</tr>
<tr>
<td>SDCI11(36): ( \gamma = -15 # )</td>
<td>873</td>
<td>-15.2056</td>
<td>75.9</td>
<td>-6.792</td>
</tr>
<tr>
<td>SDCI8(36): ( \gamma = -15 # )</td>
<td>645</td>
<td>-15.2012</td>
<td>70.0</td>
<td>-6.752</td>
</tr>
<tr>
<td>SDCI11(36): ( \gamma = -15 # )</td>
<td>873</td>
<td>-15.2017</td>
<td>70.6</td>
<td>-6.540</td>
</tr>
<tr>
<td>SDCI8(36): ( \gamma = -15 * )</td>
<td>567</td>
<td>-15.2041</td>
<td>73.9</td>
<td>-6.782</td>
</tr>
<tr>
<td>SDCI11(36): ( \gamma = -15 * )</td>
<td>927</td>
<td>-15.2107</td>
<td>82.9</td>
<td>-6.741</td>
</tr>
</tbody>
</table>

\# indicates ordering by the \( E^*(u) \) method as illustrated by Figures 2.4 - 2.7 in descending sequence.

* indicates ordering by the \( E^*(u, v) \) method. Otherwise the order is natural. \( a \) This is defined as

\[
\frac{E[SDCI^{-1}(\bar{n})] - E[RHF]}{E[SDCI36(36)] - E[RHF]} \times 100.
\]
this method with the inner-shell occupied orbital removed from the calculation. The \( \overline{m} = 11 \) results are both lower than the natural order and indicates that removing the inner-shell occupied orbital is a justifiable modification of the original method but the \( E^*(u, v) \) method gives the best results for both values of \( \overline{m} \). It can be seen that just by reordering the CVO's using \( E^*(u, v) \) in the order of an additional nine to twelve per cent of \( E_{\text{corr}} \) can be recovered and thus emphasises that even CVO's are not well ordered by the eigenvalues of the RHF operator. The results for \( i = -15 \) exhibit a different trend for the \( E^*(u) \) method the only result being better than the natural order and perhaps, unexpectedly, is the \( \overline{m} = 11 \) result for the full method. Here the method seems to break down completely and only \( E^*(u, v) \) seems to be capable of predicting the correct order reliably extracting for \( \overline{m} = 11 \) some eleven per cent more of \( E_{\text{corr}} \) than obtained using the natural order. In general, although the values calculated for the \( a_{\text{Be}} \) isotropic hyperfine coupling constants are in good agreement with experiment and do not assist the assignment, this energetic advantage is reflected in improved \( a_H \) values.

2.2 The \( \text{NH}_2 \) radical

\( \text{NH}_2 \) was chosen as the second test radical (\( R_{\text{NH}} = 2.0a_0 \); bond angle 105°) for similar reasons to the first using the (9s5p) primitive basis set for nitrogen contracted to [5s3p] and the (4s) primitive basis for hydrogen contracted to [3s] [77]. To this set was added one d-type GTO on nitrogen
(exponent 0.98 [78, 79]) and one p-type GTO on hydrogen (exponent 1.0 [80]) giving a total of 32 basis orbitals (see Table 2.10). Extended (E) or minimal (M) basis sets obtained by contracting the (9s5p) set to [3s2p] or [2s1p] and the (4s) to [2s] or [1s] [73, 81], giving a total of 13 or 7 orbitals respectively, were also used for comparison (see Table 2.11). The larger set is therefore the extended set (eight virtual orbitals) plus polarization functions (19 virtual orbitals) (E + P).

The radical belongs to the $C_{2v}$ G and the orbitals can be classified according to the symmetries or representations $\sigma(A_1)$, $\sigma'(A_2)$, $\pi(B_1)$ and $\pi'(B_2)$. With nine electrons a SDCI$\overline{\pi}$ calculation is feasible since, making use of the $\sigma$ and $\pi$ symmetry, only 18,697 determinants are constructed. This calculation is used as the reference calculation since the energy and isotropic hyperfine coupling constants are invariant to a unitary transformation of the virtual orbitals. Here again, because only the $k$ part of the basis was admitted to the wave function thereby gaining automatic upper bounds to the energy it was possible to investigate the effect of the operators of Section 1.3. Taking these operators in numerical sequence the NO's were computed from the SDCI$27(27)$ calculation although as in the case of the previous radical for direct comparisons to be made perhaps the FNO's should have been used. Because these orbitals will not be available in general the modified HF operator was set up for open-shell systems in an analogous manner to that of the closed shell but there remained the problem of ordering the orbitals produced for inclusion in the CI. It
<table>
<thead>
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<th>Atom</th>
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<th>exponent</th>
<th>contraction coefficient</th>
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<td>0.243846</td>
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<td>0.817193</td>
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<td>p</td>
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## Table 2.11 Contraction Matrices for the 32 into 13 Orbital and 7 Orbital Basis Sets Respectively Ordered as Shown

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</tr>
<tr>
<td>s</td>
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<tr>
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</tr>
<tr>
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</tr>
<tr>
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</tr>
<tr>
<td>p</td>
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</tr>
<tr>
<td>p</td>
<td>0.0000000 0.000000 0.0 0.0000000 1.0 0.0000000 0.0</td>
</tr>
<tr>
<td>d</td>
<td>0.0000000 0.000000 0.0 0.0000000 0.0 0.0000000 0.0</td>
</tr>
<tr>
<td>s</td>
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</tr>
<tr>
<td>s</td>
<td>0.0000000 0.000000 0.0 0.0000000 0.0 0.8172260 0.0</td>
</tr>
<tr>
<td>s</td>
<td>0.0000000 0.000000 0.0 0.0000000 0.0 0.0000000 1.0</td>
</tr>
<tr>
<td>p</td>
<td>0.0000000 0.000000 0.0 0.0000000 0.0 0.0000000 0.0</td>
</tr>
<tr>
<td>s</td>
<td>0.1906907 -0.0457436 0.0000000 0.0000000</td>
</tr>
<tr>
<td>s</td>
<td>0.4497094 -0.1198022 0.0000000 0.0000000</td>
</tr>
<tr>
<td>s</td>
<td>0.4461100 -0.1855600 0.0000000 0.0000000</td>
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<td>s</td>
<td>0.0012700 1.0584340 0.0000000 0.0000000</td>
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<tr>
<td>s</td>
<td>0.0008000 0.5374700 0.0000000 0.0000000</td>
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<tr>
<td>p</td>
<td>0.0000000 0.0000000 0.0000000 0.0000000</td>
</tr>
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</table>
has been suggested [49] that, at least for closed-shell molecules, that the MVO's of the modified HF operator can be ordered for SDCIM(n) expansions by using equation (1.3.8) rather than the natural order governed by their increasing eigenvalues \( \xi_n \), appearing in equation (1.3.4). To test the applicability of this suggestion to doublet state radicals it was again decided to use two extreme cases, \( Y = 0 \), corresponding to the RHF case giving CVO's and \( Y = -15 \), since this was found to give the best MVO's for FCN [49] and as Figure 2.8 shows there is reason to believe that this is also close to the optimum for the present radical. This result is again very significant because it is the second indication that it may not be necessary to vary the parameter \( Y \) for molecules of different multiplicity and therefore would have the attendant benefits as outlined previously. These are considered to be extreme cases since the SDCIB(27) calculations using the natural order are very different: -55.6750 hartrees for \( Y = 0 \) and -55.7123 hartrees for \( Y = -15 \) [noting that the \( E^*(u) \) orders can be seen in the usual sequence in Figures 2.9 - 2.12 and that the RHF energy is -55.5701 hartrees] (see Table 2.12).

Since the energy of a SDCIM(n) wave function depends not only on \( \bar{m} \) and \( \bar{n} \) but also on which \( \bar{m} \) orbitals are selected, Table 2.13 is presented to illustrate the effect that different ordering processes can have on the natural order [using the operator of Section 1.3 (ii)]. This order is denoted by the letter a which also attaches the symmetry species of each orbital. Order b results from using equation (1.3.8) as suggested by Cooper and Pounder [49].
FIGURE 2.8 TOTAL ENERGY AS A FUNCTION OF $\gamma$ FOR SDCI(127) CALCULATIONS ON THE $\text{NH}_2$ RADICAL*
FIGURE 2-9 VALUES OF E^*(u), γ = 0, FOR THE NH\(_2\) RADICAL. 

TERMS USED
TERMS USED

FIGURE 2-10 VALUES OF $E^*(u)$, $\gamma = 0$, FOR THE $\text{NH}_2$ RADICAL.
FIGURE 2.11 VALUES OF $E^*(u)$ FOR THE NH$_2$ RADICAL.
Figure 2.12 Values of $E^*(u)$, $\gamma = -15$ for the NH$_2$ radical.
### TABLE 2.12 TOTAL ENERGIES AND ISOTROPIC HYPERFINE COUPLING CONSTANTS FOR THE NH₂ RADICAL

<table>
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<tr>
<th>description of calculation</th>
<th>number of detors</th>
<th>total energy/ hartree</th>
<th>$E_a^{corr}$</th>
<th>isotropic hyperfine coupling</th>
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<td>$a_N/mT$</td>
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<td>SDCI27(27)</td>
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<td>0.637</td>
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<tr>
<td>SDCI8(8): NO's</td>
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<td>69.6</td>
<td>1.928</td>
</tr>
<tr>
<td>SDCI8(27): NO's</td>
<td>1 851</td>
<td>-55.7151</td>
<td>76.0</td>
<td>0.800</td>
</tr>
<tr>
<td>SDCI9(9): NO's</td>
<td>1 852</td>
<td>-55.7152</td>
<td>76.1</td>
<td>1.798</td>
</tr>
<tr>
<td>SDCI9(27): NO's</td>
<td>2 107</td>
<td>-55.7260</td>
<td>81.7</td>
<td>0.685</td>
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<tr>
<td>SDCI8(8): $\gamma = 0^b$</td>
<td>1 880</td>
<td>-55.6528</td>
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<td>2 129</td>
<td>-55.6750</td>
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<tr>
<td>SDCI9(9): $\gamma = 0$</td>
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</table>

experiment [82]  
[83]  

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<th>$a_N/mT$</th>
<th>$a_H/mT$</th>
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</table>

a This is defined as
\[
\frac{E[SDCI\text{m}(\text{n})] - E[RHF]}{E[SDCI27(27)] - E[RHF]} \times 100.
\]

b The best order for each $\gamma$ is used unless specified otherwise.

c Ordered by increasing eigenvalues of the operator given in Section 1.3 (ii) (natural).
<table>
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<th>Υ</th>
<th>order</th>
<th>valence and extended virtual orbitals</th>
<th>polarization virtual orbitals</th>
<th>energy/ Hartree</th>
<th>isotropic hyperfine coupling constants</th>
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<td>π ' π σ' σ σ σ σ' σ σ' σ σ σ σ</td>
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<td>b</td>
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<td>0.804</td>
</tr>
<tr>
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<td>6 7 8 11 9 13 12 14</td>
<td>10 18 19 22 17 21 24 25 15 26 27 16 28 30 29 23 31 32</td>
<td>-55.7073</td>
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<td>d</td>
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<td>10 17 16 18 19 22 20 26 21 24 25 15 27 23 28 30 29 31 32</td>
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<tr>
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<td>e'</td>
<td>σ σ σ σ σ σ σ σ σ σ σ σ</td>
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<td>e</td>
<td>σ σ σ σ σ σ σ σ σ σ σ σ</td>
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<td>f</td>
<td>σ σ σ σ σ σ σ σ σ σ σ σ</td>
<td>π' π σ' σ σ σ σ σ σ σ σ σ σ σ</td>
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<td>7 6 8 13 12 14 10 11</td>
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</tr>
<tr>
<td></td>
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<td>σ σ σ σ σ σ σ σ σ σ σ σ</td>
<td>π' π σ' σ σ σ σ σ σ σ σ σ σ σ</td>
<td>-55.7136</td>
<td>0.802</td>
</tr>
<tr>
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<td></td>
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<td>12 18 17 22 24 31 16 30 15 26 20 23 25 21 32 19 28 27 29</td>
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<td>0.802</td>
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<tr>
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<td>σ σ σ σ σ σ σ σ σ σ σ σ</td>
<td>π' π σ' σ σ σ σ σ σ σ σ σ σ σ</td>
<td>-55.7136</td>
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<td>12 18 17 22 24 31 16 30 15 26 20 23 25 21 32 19 28 27 29</td>
<td>-55.7136</td>
<td>0.802</td>
</tr>
</tbody>
</table>
It was observed, as previously [49], that some high energy virtual core orbitals unexpectedly appeared low down in the ordered list, e.g., orbitals 31 and 32 resulting from order b in Figure 2.11. It was found that the origin of the high position of these orbitals was an unexpectedly large interaction of $<\psi_{ii}|u>\psi_{ii}$, where $i$ refers to the inner-shell occupied MO (essentially the 1s orbital on nitrogen) and $|u>$ is orbital 31 or 32, with the ground state ($<\psi_{ii}|\hat{H}|\Phi_{RHF}>$).

If orbital $|i>$ is ignored in the evaluation of all terms in $E^*(u)$ [equations (1.3.8) or (1.3.10)], it was found that both orbitals 31 and 32 are placed automatically at the end of the list with the remaining order largely unaffected as can be seen in Figure 2.12. This procedure is to be contrasted with the manual intervention of placing these orbitals at the end of the list as previously suggested [49]. The fact that it is necessary to interfere with the order at all seems to invalidate the usefulness of $E^*(u)$ as an ordering procedure. Nevertheless, should it establish itself as a reliable method to order the orbitals, excluding easily identifiable inner-shell MO's from the summations [equations (1.3.8) and (1.3.10)] seems to be far better than trying to identify high energy virtual core orbitals which are themselves a function of the variable parameter $\gamma$. All ordering procedures which do not include the terms $E^*(u, v)$ neglect the inner-shell occupied MO's.

For both $\gamma = 0$ and $\gamma = -15$ the orders predicted by equation (1.3.8), order b in Table 2.13, the calculated CI energies are higher than the natural orders. This implies that equation (1.3.8) is unsuitable for doublet state
This led us to consider other possible terms in $|\phi(u)\rangle$ [equation (1.3.10)]. Although Brillouin's theorem states that single replacement configurations do not interact with the ground state configuration for closed-shell molecules, some do contribute for doublet state radicals and may be a possible cause of the discrepancy in the predicted order. Unfortunately, the symmetry of the virtual orbitals takes on a decisive role on whether the terms $|\Xi_{ur}\rangle_{ra}$ (Figure 1.1) contribute; orbital $|u\rangle$ must belong to the $\sigma$ or $\sigma'$ symmetry species. This arises because the doubly occupied orbitals belong to either of these symmetry species and the unpaired electron is in an orbital of $\pi$ symmetry. The inclusion of terms $|\Xi_{ur}\rangle_{ra}$ (order c in Table 2.13) improved the $\gamma = 0$ result but not the $\gamma = -15$ when compared with order b (direct double replacements only).

The only term in equation (1.3.10) which makes no contribution, because of the symmetry of this radical, is $|\Xi_{uu}\rangle_{ra}$. Symmetry plays no direct part with the term $|\Xi_{uu}\rangle_{ab}$ but for the remaining terms only the virtual orbitals of $\pi$ or $\pi'$ symmetry make any contribution to the sum that determines the orbital order. Figure 2.12 shows the cumulative effect of these terms for $\gamma = -15$. Although the choice of terms in equation (1.3.10) will influence the predicted order of the MVO's, there is no one selection of terms for both $\gamma = 0$ and $\gamma = -15$ which gives lower energies for the SDCI8(27) calculations than the corresponding natural orders. It must be concluded that not only is equation (1.3.8) inadequate to predict the best order for
doublet state radicals, so is all or any selection of terms in equation (1.2.153).

This effectively leaves the calculation of the contribution of each MVO to $E_{\text{corr}}$ [equation (1.3.9)] as the only way in which the MVO's can be ordered. The calculation of the $E^*$ matrix is not a trivial matter and even then the extraction of the best $\bar{m}$ MVO's is not obvious particularly if the $E^*(u, v)$ elements are large as they are for $\gamma = 0$. As already discussed, the concept of an order may be lost as illustrated in Table 2.13 (order h). For $\bar{m} = 8$ the MVO's selected for $\gamma = 0$ are the same as the first eight in the natural order but for $\gamma = -15$ the set is different to any other predicted and gives the lowest SDCI8(27) energy calculated. For $\bar{m} = 9$ the natural order for $\gamma = 0$ is not the best since order h (Table 2.13) gives a lower energy, as it should if the ordering process is correct (see Table 2.12). Reluctantly, it must be concluded that, at present, equation (1.3.9) is the only procedure that will predict the best $\bar{m}$ MVO's for a SDCI$\bar{m}(n)$ calculation.

It may be noted that the MVO's for $\gamma = -15$ are much more stable to the different methods of ordering. This can be traced, in part, to much smaller $E^*(u, v)$ elements. Indeed, apart from order c, the selection of the first nine orbitals is the same. It is probably coincidental but nine virtual orbitals is that number expected from an orbital basis set of double-zeta quality. There is a significant improvement in the energy if nine MVO's are included instead of eight for a very modest increase in the number of configurations. In addition, the MVO's for this value of $\gamma$,
ordered by the $E^*$ method, compare extraordinarily well with the NO's ordered by their occupation number (see Table 2.12).

The calculated hyperfine coupling constants for nitrogen $a_N$ can be divided into groups identified in the regions of 1 and 2 mT. The latter group are from SDCI$\overline{m}(\overline{m})$ calculations ($\overline{m} = 8$ or 9) and the former from SDCI$\overline{m}(27)$ calculations ($\overline{m} = 8$, 9 or 27), clearly showing the importance of including the polarisation MVO's. It also shows that it is sufficient, as suggested by Cooper and Pounder [49], to incorporate the polarisation MVO's in single and direct double replacements only. The $\overline{m} = 27$ result appears to require a vibronic correction but this would have been impractical using the method outlined in Section 1.4. Comparing all the results (Tables 2.12 and 2.13) it is apparent that, from the energy, it is far more important to obtain an optimum value for $\gamma$ than to reorder the MVO's. Perhaps this observation will put into perspective the importance of using the operator discussed in Section 1.3 (ii) to obtain the MVO's even though there may be difficulties in deciding the best order. If future work confirms that $\gamma = -15$ is universally applicable to predict MVO's that lead to compact CI expansions, efficient methods for determining the best order is not a difficult proposition. Perhaps the most important result which can be deduced from Table 2.12 is the possibility to obtain an extremely compact CI expansion which can be smaller in size by an order of magnitude and yet recover over 80 per cent of the SDCI$\overline{n}(\overline{n})$ $E_{\text{corr}}$ and closely reproduce the isotropic
The importance of ordering the MVO's has been forcibly stressed before [63]. Although the \( E^* \)-matrix method of ordering the MVO's has been discussed here, it is not easy to demonstrate its success over a wide variety of situations. In our search for the best method to use it was necessary to try and solve the problem in other ways. One way was to follow the orbitally ordered CI energy as a function of small changes in \( \gamma \) such that small changes in the MVO's could be monitored. In the case of \( \text{NH}_2 \) there are four symmetry species which can assist in the assignment: \( a_1, a_2, b_1 \) and \( b_2 \). Using the terminology \((4, 3, 1, 0)\) to denote that of the \((m =) 8\) selected MVO's, four are of \( a_1 \) symmetry, three are of \( a_2 \) symmetry, one is of \( b_1 \) symmetry and none have \( b_2 \) symmetry, it is possible to trace the development of this orbital set as a function of \( \gamma \) as shown in Figure 2.13. The first eleven CVO's, ordered by their eigenvalues, have symmetries \( a_1, a_2, a_2, b_1, a_1, a_1, a_2, a_1, b_2, a_1, b_1 \). Thus \((4, 3, 1, 0)\) refers to the first 8. This \((4, 3, 1, 0)\) set gives the lowest SDCIS(27) energy in accordance with the \( E^* \) method prediction for \( \gamma = 0 \). If the CVO of \( a_2 \) symmetry (seventh in the list) is replaced with the CVO of \( b_2 \) symmetry (ninth in the list), the set \((4, 2, 1, 1)\) is defined. Additionally this orbital of \( a_2 \) symmetry was replaced with the CVO of \( b_1 \) symmetry (eleventh in the list) to define the \((4, 2, 2, 0)\) set. This choice was influenced from other work which implied that the above order is incorrect and the fact that it would be difficult to identify groups with the same label; e.g., if \( a_1 \) were

-121-
FIGURE 243 TOTAL ENERGY AS A FUNCTION OF $\gamma$ FOR SCICIBZ71 CALCULATIONS ON THE NH$_2$ RADICAL. THE 8 VIRTUAL ORBITALS ARE IDENTIFIED BY THEIR SYMMETRIES $(a_1, a_2, b_1, b_2)$. SEE TEXT. $\circ$, $(4, 3, 1, 0)$; $\sigma$, $(4, 2, 1, 1)$; $\circ$, $(4, 2, 2, 0)$. 

-122-
replaced with another \( a_1 \) it might be difficult to identify the orbital list by inspection as a function of \( \gamma \). As it turned out the behaviour of these sets was quite complicated as shown in Figure 2.13. The \((4, 3, 1, 0)\) set gave the lowest orbitally ordered SDCI8(27) energy when \( \gamma = 0 \) but the \((4, 2, 1, 1)\) set was lowest at \( \gamma = -5 \) and the \((4, 2, 2, 0)\) set was lowest at \( \gamma = -15 \). This situation seemed to provide the right test for the \( E^* \) method. At the 3 values of \( \gamma \) indicated the \( E^* \) method predicted the correct order.

In view of the empirical nature of the operator of Section 1.3 (ii) and the fact that in other work [62] \( \hat{O} \) has been replaced by \( \hat{V}_{en} \), the attractive Coulomb potential between an electron and all the nuclei in the molecule, \( \hat{J}_0 \), the corresponding HF Coulomb operator and its valence-only version, \( \hat{J}^{\text{val}}_0 \), where all summations over the occupied orbitals are restricted to the valence orbitals only, the following operator was studied (see Figure 2.14):

\[
\hat{h}^F + (a/z) \hat{V}_{en} + \beta \hat{J}^{\text{val}}_0 + Y \hat{R}^{\text{val}}_0, \tag{2.2.1}
\]

where \( z \) is the total nuclear charge. Since a full analysis of all ranges of the variables \( a, \beta \) and \( \gamma \) would be very time consuming it was decided to fix \( \gamma \) at its optimum value, \(-15\), when both \( a \) and \( \beta \) are zero. If \( \beta \) was varied keeping \( a = 0 \) Figure 2.14 shows that \( \beta \) was optimised to zero or close to zero. Similarly the optimum value for \( a \) is zero if \( \beta \) is fixed at zero. Only a few data points were evaluated and fitted to collocation polynomials but this brief analysis clearly indicates that the best operator to use for the purpose of obtaining MVO's is probably \( \hat{h}^F - 15R^{\text{val}}_0 \). On the other hand, more data points would be needed to prove this.
FIGURE 244  TOTAL ENERGY AS A FUNCTION OF PARAMETERS $\alpha$ (---, WHEN $\beta = 0$) AND $\beta$ (----, WHEN $\alpha = 0$) (AS DEFINED IN THE OPERATOR $H^F + \alpha \beta \gamma \delta \epsilon + \beta_0^\text{val} - 15 \delta_0^\text{val}$) FOR SDCI8(27) CALCULATIONS ON THE NH$_2$ RADICAL. THE 8 VIRTUAL ORBITALS ARE IDENTIFIED BY THEIR SYMMETRIES ($a_1$, $a_2$, $b_1$, $b_2$): SEE TEXT.
observation conclusively.

The results for the projection and state-minimisation procedures are collected in Table 2.14. Both of these methods appear to select automatically the orbitals for the orbitally ordered CI method and were used as such. If this is not the case it would seem to invalidate the arguments used to construct the methods in the first place. The results suggest that both the minimal and extended basis set CI calculations can be significantly improved by the projection technique without any more work at the CI level [compare the SDCI2(2) and SDCI8(8) calculations for the CVO's and P(E + P) -> MVO's]. The use of these projected orbitals in the SDCI8(27) calculations show an additional improvement, as expected and the results, although not as good, are not significantly different from the calculation which uses orbitals from the energy minimisation of function (d, 1). The importance of direct double replacements is again emphasised in the result for (d, 2) giving the best energy. There is a surprising improvement with both functions (d) and (e) if the inner-shell 1s orbital on nitrogen is excluded, i.e., orbitals obtained from (d, 2) and (e, 2). This does correlate with the use of $\hat{R}_0^\text{val}$ in the empirical operator, which is better than using the proper HF exchange operator $\hat{R}_0$. Once again, the similarly contracted forms FSDCI[\(\overline{m}(\overline{n})\)] and FVSDCI[\(\overline{m}(\overline{n})\)] are used to describe (Full + S + D)CI[\(\overline{m}(\overline{n})\)] and (Full valence + S + D)CI[\(\overline{m}(\overline{n})\)] calculations here. For CVO's these wave functions exhibit negligible improvement over their SDCI\(\overline{m}(\overline{n})\) counterparts serving to illustrate, perhaps, the diffuse nature of the
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<th>total energy/hartree</th>
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\[ P(E + P)\rightarrow M \] (or \(-\rightarrow E\) or \(-\rightarrow E\rightarrow E\)) means that 2 (or 8) virtual orbitals used in, e.g., the SDCI2(27) \(\text{[or SDCI8(27)]}\) calculations were obtained by projecting the \((E + P)\) orbitals onto the minimal (or extended or both) basis set orbitals.

Valence virtual part of the basis. This is to be contrasted with projected orbitals which show a slight improvement for the additional configurations generated. Perhaps these results serve to justify only the briefest study undertaken here of CASSCF-type wave functions. On the other hand, non of these results compare favourably with those derived from the operator \(\hat{h}^F + \hat{Y}_{\text{val}}\), so the methods were not further developed. Projected orbitals have an added disadvantage in a slowly convergent Nesbet's routine. Of course, this can be described as only a preliminary analysis there still might be a combination of states, perhaps weighted by PT, that could rival the \(\hat{h}^F + \hat{Y}_{\text{val}}\) operator although it must be stated that, even so, poorly convergent eigenvalue equations with the added difficulty of double iteration procedures.
would be a disadvantage over a single diagonalisation method.

2.3 Conclusions

The Gershgorn and Shavitt [31] combined CI-perturbation approximations significantly reduce the size of the $M$ matrix compared with that of more accurate treatments and the results of SDPTm($\overline{n}$) calculations compare favourably with those of SDCIn($\overline{n}$) calculations for values of $\overline{m}$ not less than the value required for a minimal basis set calculation. On the other hand, these calculations remain nominally in the order $\overline{n}$ of the orbitals and coupled with the fact that variational upper bounds to the energies will be absent for most molecular basis sets of interest, lead us to their abandonment in favour of the Cooper and Pounder [49] approach.

The use of MVO's can shorten the $(S + D)CI$ expansion by an order of magnitude and yet recover, e.g., 75 per cent of the SDCIn($\overline{n}$) $E_{\text{corr}}$ compared with only 55 per cent with an equivalent CVO calculation. The operator $h^F + \gamma^\text{val}_0$ seems to have an optimum value close to $\gamma = -15$ for both singlet and doublet state molecules which is significant if the method is to have wide generality. A serious problem remains involving the correct ordering of the MVO's although from an energy point of view in the NH$_2$ radical, in contrast to BeH, the differences are small if the wrong orders are used. It seems that it is necessary to use every term in the expression for $E_{\text{corr}}$ (with coefficients calculated using PT) to correctly predict which MVO's should be selected for
the SDCI$^\infty(m)$ expansion. Although there is an energy improvement in going from an SDCI$^\infty(m)$ calculation to a SDCI$^\infty(27)$ calculation for $m = 8$ or 9 in the NH$_2$ radical, the major advantage is the improvement of the isotropic hyperfine coupling constants which now closely approximate the results for the SDCI$^\infty(n)$ calculation.

The method which projects the virtual orbitals of large basis-set calculations, those which use polarisation functions, onto either the double-zeta, minimal or both basis sets in order to try to divide the virtual orbitals into an active and inactive region does lead to better orbitally ordered CI energies than a straight separation of the CVO's based on their eigenvalues. On the other hand, the improvement is not substantial and better results are obtained from various operators which effectively perform a unitary transformation on the CVO's. The best operator so far is $h^F - 15k_0^{\text{val}}$, although it is important to reorder the MVO's using the E$^*$ method.

It appears that attempts to further divide the active orbital space, one into a small region in which a full or full valence CI can be performed, as implied by Roos, Taylor and Siegbahn [61], do not lead to significant improvements over the results of comparable SDCI$^\infty(n)$ calculations.
APPENDIX: FORTRAN 77 program to illustrate a matrix inversion technique based on Gram-Schmidt orthogonalisation
C********************************************************************
PROGRAM INVERS
C THE DECLARED ARRAY SIZES ARE SUFFICIENT FOR A 10 BY 10
C DIMENSIONAL PRELIMINARY MATRIX TO BE INVERTED, FOR
C N' BY N' DIMENSIONAL MATRICES THE MINIMUM ARRAY SIZES
C ARE V(N',N'), T(N'*(N'+1)/2), U(N',N'), W(N'), LM(N'+1)
C********************************************************************
INTEGER P, Pl, Q, R, S
REAL MDET
DIMENSION V(10,10), T(55), U(10,10), W(10), LM(11)
READ(*,35)NPRIME,((V(P,Q),Q=1,10),P=1,NPRIME)
DO 1 P=1,NPRIME
DO 1 Q=1,NPRIME
1 U(Q,P)=V(Q,P)
WRITE(*,37)
CALL MATOUT(V,10,NPRIME)
MDET=1.
LM(1)=0
C RECURRENCE PROCEDURE
DO 3 P=1,NPRIME
LM(P+1)=LM(P)+P
Pl=P-1
DO 5 Q=1,Pl
SUM=0.
DO 7 R=1,NPRIME
7 SUM=SUM+V(R,Q)*V(R,P)
5 T(Q+LM(P))=-SUM
DO 9 R=1,NPRIME
SUM=0.
-130-
DO 11 S=1, P1
11 SUM=SUM+V(R, S)*T(S+LM(P))
9 V(R, P)=SUM+V(R, P)
SUM=0.
DO 13 R=1, NPRIME
13 SUM=SUM+V(R, P)*V(R, P)
IF(SUM.LT.1.E-10) THEN
WRITE(*, 39)
STOP
END IF
SUM=SQRT(SUM)
MDET=MDET*SUM
SUM=1./SUM
DO 15 R=1, NPRIME
15 V(R, P)=SUM*V(R, P)
T(P+LM(P))=SUM
DO 17 R=1, P1
17 T(R+LM(P))=T(R+LM(P))*SUM
DO 3 R=1, P1 .
SUM=0.
DO 19 S=R, P1
19 SUM=SUM+T(R+LM(S))*T(S+LM(P))
3 T(R+LM(P))=SUM
WRITE(*,41)
CALL MATOUT(V, 10, NPRIME)
C TRANSFORMATION TO INVERSE MATRIX
DO 21 P=1, NPRIME
DO 23 Q=P+1, NPRIME
SUM=V(Q, P)
-131-
\[ v(Q, P) = v(P, Q) \]

23 \[ v(P, Q) = \text{SUM} \]

DO 21 Q=1,NPRIME

SUM = 0.

DO 25 R=Q,NPRIME

25 \[ \text{SUM} = \text{SUM} + T(Q+LM(R)) \cdot v(R, P) \]

21 \[ v(Q, P) = \text{SUM} \]

WRITE(*, 43)

CALL MATOUT(V, 10, NPRIME)

C GENERATION OF UNIT MATRIX

DO 27 P=1,NPRIME

DO 29 Q=1,NPRIME

SUM = 0.

DO 31 R=1,NPRIME

31 \[ \text{SUM} = \text{SUM} + U(Q, R) \cdot v(R, P) \]

29 \[ W(Q) = \text{SUM} \]

DO 27 Q=1,NPRIME

27 \[ v(Q, P) = W(Q) \]

WRITE(*, 45)

CALL MATOUT(V, 10, NPRIME)

DO 33 P=1,NPRIME

U(P, P) = T(P+LM(P))

DO 33 Q=P+1,NPRIME

U(P, Q) = T(P+LM(Q))

33 \[ U(Q, P) = 0. \]

WRITE(*, 47)

CALL MATOUT(U, 10, NPRIME)

WRITE(*, 49) MDET

STOP
C*******************************************w***************
SUBROUTINE MATOUT(A, M, N)
C PRINT MATRICES OF SIZE N BY N
C *****************************************y***************
INTEGER P, Q, R, S
DIMENSION A(M, N)
Q=0
1 P=Q+1
Q=Q+3
IF(N.LT.Q)Q=N
WRITE(*, 5)(S, S=P, Q)
DO 3 R=1, N
3 WRITE(*, 7)R, (A(R, S), S=P, Q)
IF(N-Q.GT.0)GOTO 1
RETURN
5 FORMAT(1H0,3(15X,I2,1X))
7 FORMAT(1H0,I2,4X,3(3X,G15.8))
END
**I/O EXAMPLE**

**PRELIMINARY MATRIX**

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.0000000</td>
<td>-2.0000000</td>
<td>-3.0000000</td>
</tr>
<tr>
<td>2</td>
<td>3.0000000</td>
<td>3.0000000</td>
<td>5.0000000</td>
</tr>
<tr>
<td>3</td>
<td>-4.0000000</td>
<td>1.0000000</td>
<td>6.0000000</td>
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**ORTHOGONAL MATRIX**

<table>
<thead>
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<th>1</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>0.70710678</td>
<td>-0.40824829</td>
<td>0.57735027</td>
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<tr>
<td>2</td>
<td>0.42426407</td>
<td>0.89814624</td>
<td>0.11547005</td>
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<tr>
<td>3</td>
<td>-0.56568542</td>
<td>0.16329932</td>
<td>0.80829038</td>
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**INVERSE MATRIX**

<table>
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</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.13541667</td>
<td>0.93750000E-01</td>
<td>-0.10416667E-01</td>
</tr>
<tr>
<td>2</td>
<td>-0.39583333</td>
<td>0.18750000</td>
<td>-0.35416667</td>
</tr>
<tr>
<td>3</td>
<td>0.15625000</td>
<td>0.31250000E-01</td>
<td>0.21875000</td>
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**UNIT MATRIX**

<table>
<thead>
<tr>
<th></th>
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<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>-0.11350494E-08</td>
<td>0.</td>
</tr>
<tr>
<td>2</td>
<td>0.</td>
<td>1.0000000</td>
<td>-0.46566129E-09</td>
</tr>
<tr>
<td>3</td>
<td>0.46566129E-09</td>
<td>-0.75669959E-09</td>
<td>1.0000000</td>
</tr>
</tbody>
</table>

**TRIANGULAR MATRIX**

<table>
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</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.14142136</td>
<td>0.27216553E-01</td>
<td>0.80588475E-01</td>
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<td>2</td>
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<tr>
<td>3</td>
<td>0.</td>
<td>0.</td>
<td>0.27063294</td>
</tr>
</tbody>
</table>

**MODULUS OF DETERMINANT**

96.0000000


[34] C. Eckart, Phys. Rev. 36, 878 (1930).
ADDENDUM
