CONFIGURATION INTERACTION STUDIES OF

SMALL MOLECULES

by

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1972
To Jennifer
ERRATA
The appropriate passage should read as follows:

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CHAPTER 4A. Natural Spin-Orbital Analysis 23
APPENDIX IV .... FOR THE D_{∞h} SYMMETRY GROUP 165

page 3 line 18 .... of ambiguity. In ....
page 5 line 13 .... is S_z (when both ....
page 6 line 19 .... (HFR) self consistent ....
page 8 line 4 .... as a "primitive function" ....
page 24 \( \gamma(\vec{r}_1:\vec{r}_1) = 2 \sum f_{ij} \sum f_{lm} \varphi_i^*(\vec{r}_1) \varphi_j(\vec{r}_1) s_{jm} \) , (4.2)
page 24 line 7 \( \gamma(l|l) = \sum f_{ij} s_{jm} f_{jm} \)
page 24 line 8 .... \( f_{lm} = f_{ml} \). In ....
page 27 line 11 .... matrix, \( X^{-1} = X^+ \) thus ....
page 27 \( X^{-1} W^{-1} F \Delta F^+(W^{-1})+(X^{-1})^+ \) . (4.13)
page 60 line 26 .... , their wave function ....
page 66 line 19 .... consistent with the ....
page 72 line 25 .... origins at the nuclei ....
page 82 \( \Lambda = \sum m_i \) . (7.16)
page 83 line 5 .... even number of ungerade ....
page 95 line 18 .... for which \( C_{L1} \) is non-zero ....
page 96 line 13 .... two centres various ....
page 97 line 22 .... integrals follows immediately ....
page 104 line 8 .... step in evaluating ....
page 106 line 7 .... Kotani et alia (43) ....
page 106 line 11 .... which are listed ....
page 112 line 13 .... (Horner's method) ....
page 113 line 17 .... for all \( j \neq k \) ....
page 116 line 15 .... (40,41,66) ....
page 116 line 24 .... the configurations are ....
page 122 line 23 .... "primitive functions" ....
page 133 +Reference 56
page 134 \( a_5 \) 3.9409x10^5 -8.1705x10^5 -4.5959x10^4
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REFERENCES
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ABSTRACT

The method of Configuration Interaction (CI) has been used in a number of studies of small atomic and molecular systems.

In Part I, CI wave functions for a series of pseudomolecular ions \( \text{ZH}_2^{2Z-1} \) are reformulated in terms of natural orbitals. Changes in the electron density as a function of the nuclear charge \( Z \) and bond angle \( Z \) are investigated by means of an electron population analysis based on the natural orbitals. Contour diagrams of the electron density in the plane of the molecule are obtained. The total energy for each system is analysed in terms of the kinetic energy, nuclear attraction energy, and the electron and nuclear repulsion energies.

In Part II, the CI method is examined in detail. Techniques for obtaining CI wave functions of atoms and molecules are discussed in detail. Computer programs based on these techniques are described, and listed in the Appendices. The Valence Configuration Interaction (VCI) method is also examined as a means of reducing the size of the secular equation, and results of VCI calculations are given for various states of atomic and diatomic oxygen and sulphur. Spectroscopic constants for the \( X^3 \Sigma_g^- \) and \( b^1 \Sigma_g^+ \) states of \( O_2 \) and for the \( X^3 \Sigma_g^- \), \( a^1 \Delta_g \) and \( b^1 \Sigma_g^+ \) states of \( S_2 \) are given. The methods by which these results can be obtained are also discussed. Finally the results of the VCI calculations are compared with some recent SCF calculations on \( O_2 \) and \( S_2 \).
CHAPTER 1

METHODS OF SOLVING THE STATIONARY STATE

SCHRODINGER EQUATION

The mathematical basis of molecular quantum mechanics is the stationary state Schrödinger equation: in the Born-Oppenheimer approximation the separation of the electronic and nuclear motions leads to two equations, one describing the electronic, and the other describing the nuclear behaviour. For a system of n-electrons moving in the potential field of a fixed framework of nuclei the stationary state Schrödinger equation may be written as

\[ \mathbf{H}\psi(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_n) = E_E\psi(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_n) \]  \hspace{1cm} (1.1)

In (1.1) \( \mathbf{H} \) is the Hamiltonian operator, \( E_E \) is an eigenvalue of \( \mathbf{H} \), interpreted physically as the energy of the stationary state, and \( \psi \) is an eigenfunction of \( \mathbf{H} \) corresponding to the eigenvalue \( E_E \). The eigenfunction, or wave function, is a function of the space and spin co-ordinates of all of the electrons. The space-spin co-ordinates of electron \( \mu \) are denoted by \( \vec{x}_\mu \). The Hamiltonian operator has the form

\[ \mathbf{H} = \sum_\mu \hbar_\mu + \sum_{\mu < \nu} e_{\mu\nu} \]  \hspace{1cm} (1.2)

where \( \hbar_\mu \) is the one-electron Hamiltonian operator for electron \( \mu \):

\[ \hbar_\mu = -1/2v_\mu^2 + V_\mu \]  \hspace{1cm} (1.3a)

This operator, consisting of a sum of the kinetic and potential energy operators for electron \( \mu \), has dimensions and is written in terms of primary or atomic units described in Appendix I. The second summation
in (1.2) is the electrostatic repulsion of all pairs of the electrons 
\( \mu, \nu \),

\[ g_{\mu\nu} = \frac{1}{r_{\mu\nu}} \quad (1.3b) \]

and \( r_{\mu\nu} \) is the distance between electron \( \mu \) and electron \( \nu \).

An operator representing the electrostatic repulsion between the nuclei is sometimes included in (1.2). When this operator is omitted \( E_E \) is the electronic energy and when it is present \( E_E \) represents the total energy for the state. \( E_E \) is given by

\[ E_E = \frac{\langle \psi | h | \psi \rangle}{\langle \psi | \psi \rangle} \quad (1.4) \]

The operators \( h, n_\mu \) and \( g_{\mu\nu} \) are Hermitian.

Although it is not possible to obtain an exact solution of the stationary state Schrödinger equation for systems of more than one-electron and two nuclei, it is possible to obtain approximate solutions which yield good energies when compared with experimental values, and which may be used to calculate molecular properties. This thesis deals with one of the methods of solving (1.1); the method of Configuration Interaction (CI). In the first part, the CI wave functions for a series of three-centre two-electron pseudomolecular ions are analysed in terms of natural spin orbitals. An electron population analysis is developed in terms of the natural spin orbitals and variations of the results of this analysis are coupled with an analysis of the various components of the total energy, in an attempt to explain the unusual behaviour of these systems. In the second part the CI method is discussed in detail and it is applied to homonuclear diatomic molecules. Computer programs, developed for the purpose of obtaining CI wave functions, spectroscopic constants and various properties, are described, and results obtained
for the molecules $O_2$ and $S_2$ are presented. Wherever possible these results are given in the form of facsimiles of the computer output in order to remove the possibility of errors arising during transcription.

In this introductory chapter some of the current non-empirical methods for obtaining solutions of (1.1) are briefly reviewed. The most popular approach is that of molecular orbitals; the basis of which is the determination of approximate electronic wave functions for a molecule by assigning each electron to a one-electron wave function, which in general extends over the whole molecule and has symmetry properties corresponding to the nuclear framework of the molecule. One-electron wave functions which do not depend on the spin co-ordinate $s_\mu$ of electron $\mu$ will be denoted by $\varphi_1(\overline{r}_\mu)$, where $\overline{r}_\mu$ represents the spatial co-ordinates and 1 identifies the one-electron wave function or orbital. One-electron wave functions which are dependent on the spin co-ordinates are denoted by $\psi_1(\overline{r}_\mu)$, these are called spin-orbitals. The symbols $\varphi_1(\mu)$ and $\psi_1(\mu)$ may also be used for indicating orbitals and spin-orbitals where there is no possibility of ambiguity. The spin-orbitals may be written as a product of an orbital and a spin function $\Theta_1(s_\mu)$. There are only two linearly independent spin functions which are designated $\sigma$ and $\beta$.

Each orbital can be used to construct two spin-orbitals

$$
\psi_{21-1} = \varphi_1^\sigma,
\psi_{21} = \varphi_1^\beta.
$$

Thus spin-orbitals with odd valued identifiers are associated with an $\sigma$ spin, and those with even valued identifiers with a $\beta$ spin. It is well known (2) that if the set of orbitals $\{\varphi_1\}$ is subject to a unitary transformation, then the resulting set $\{\varphi_1'\}$ represents
the same physical situation. It is often convenient to choose the set 
\[ \{ \varphi_i \} \]
to be an orthonormal one,
\[ \int \varphi_i^*(\mu) \varphi_j(\mu) \, d\tau = \delta_{ij} , \quad (1.6a) \]
hence
\[ \int \psi_i^*(\mu) \psi_j(\mu) \, dx = \delta_{ij} , \quad (1.6b) \]
where \( d\tau \) is the one-electron volume element without spin, \( dx \) is the one-electron volume element with spin, and \( \delta_{ij} \) is the Kronecker delta. The \( n \)-electron wave function \( \psi \) is then written as a linear combination of antisymmetrized products of spin-orbitals. The Pauli principle states that a spin-orbital may be occupied by only one electron, hence each orbital may be occupied by two electrons and the antisymmetrized product, usually written in the form of a determinant \( D_{\lambda} \), satisfies this principle. Thus

\[
D_{\lambda} = (n!)^{-1/2} \left| \begin{array}{c}
\psi_{k1}(1) \psi_{k2}(1) \ldots \psi_{kn}(1) \\
\psi_{k1}(2) \psi_{k2}(2) \ldots \psi_{kn}(2) \\
\vdots \\
\psi_{k1}(n) \psi_{k2}(n) \ldots \psi_{kn}(n)
\end{array} \right| ,
\]

and

\[ \psi = \sum_K D_{\lambda} b_{KI} \quad . \quad (1.7) \]

The coefficients \( b_{KI} \) in (1.7) are determined by a variation method which minimizes \( E_{\rho} \). The subscript \( I \) is included in (1.7) because it is possible to construct more than one solution to (1.1) from a given set of determinants.

A reasonable approximation to a molecular orbital is a linear combination of atomic orbitals (LCAO) which are associated with the atoms.
constituting the molecule:

\[
\varphi_i = \sum_k \omega_k c_{ki},
\]

(1.8)

where \( \omega_k \) is a normalized atomic orbital. Hall (3) gives a list of the possible forms of \( \omega_k \). The coefficients \( c_{ki} \) are chosen so that the \( \varphi_i \) are at least normalized. Further restrictions may demand that (1.6a) is satisfied and that \( E_E \) is a minimum.

Before discussing methods of determining the coefficients \( b_{\vec{k}i} \) in (1.7) and \( c_{ki} \) in (1.8), it is necessary to examine the roles of electron spin and molecular symmetry. When spin-orbit effects are ignored the approximate or trial wave function must be an eigenfunction of the total spin operator \( S^2 \), and the operator \( S_z \) associated with the \( z \)-component of the total electron spin. The eigenvalue of \( S^2 \) is \( S(S + 1) \) and that of \( S_z \) is \( S_z \) (when both are in primary units):

\[
S^2 \psi = S(S + 1) \psi
\]

\[
S_z \psi = S_z \psi
\]

A single determinant is an eigenfunction of \( S_z \) with an eigenvalue of

\[
S_z = 2^{-1}(n_s - n_\beta),
\]

(4) where \( n_s \) is the number of spin-orbitals of \( \sigma \) spin and \( n_\beta \) the number with \( \beta \) spin.

\[
S_z \Omega_K = 2^{-1}(n_s - n_\beta) D_K.
\]

(1.9)

A single determinant is rarely an eigenfunction of \( S^2 \), but this is achieved when \( S = S_z \). However, it is possible to construct linear combinations of determinants which are eigenfunctions of \( S^2 \). Each determinant in such a linear combination corresponds to the same
eigenvalue of $S_z$. Thus, if

$$\psi_L = \sum_K D_K^{+} \chi_L$$  \hspace{1cm} (1.10)

and

$$S^2 \psi_L = S(S + 1) \psi_L,$$

then it is possible to write the trial wave function as a linear combination of the functions $\psi_L$:

$$\psi = \sum_L \psi_L a_{LL}.$$  \hspace{1cm} (1.11)

In (1.11), as in (1.7), there are several sets of the coefficients $\{a_{LL}\}$ which will give an acceptable $\psi$.

If the nuclei of the molecule are assumed to be fixed, i.e. the molecule is rigid, it is possible to assign the molecule to a specific symmetry group, and the wave function must be a basis for an irreducible representation of the symmetry group to which the molecule belongs. This requirement is most easily satisfied if the molecular orbitals (1.8) are themselves bases for the irreducible representations of the molecular symmetry group. Thus, the $\psi_L$ in (1.10) are also required to be eigenfunctions of the operators of the molecular symmetry group.

The simplest non-empirical form of trial wave function is a single determinant. This leads to the Hartree-Fock-Roothaan (HFR) self consistent field method (2,5) and the Unrestricted Hartree-Fock (UHF) method. The former assumes that the determinant is constructed from a set of doubly occupied molecular orbitals (2,5) and the energy is minimized with respect to the coefficients determining the molecular orbitals of (1.8). It is
a condition of the method that the resulting orbitals are orthonormal. The HFR method suffers from several disadvantages. Two important ones are that it is not always possible to represent a molecular spin state by a single determinant, and the method makes no allowance for correlation between electrons with different spins; the wave function does not vanish as the antisymmetry requirement implies when electrons of different spin have the same spatial co-ordinates (6). The UHF method is an attempt to overcome the shortcomings of the HFR method, whilst maintaining some of its simplicity (7). In the UHF theory the spatial orbitals associated with the \( \alpha \) spins are different from those associated with \( \beta \) spins. A determinant of such orbitals is no longer an eigenfunction of \( \mathbf{S}^2 \), and it is necessary to operate on the determinant with a projection operator (7, 8) to obtain the required spin eigenfunction. The energy is then minimized with respect to the orbitals. The basis of both methods and their derivatives (6) is an iterative or self consistent field (SCF) procedure (2,5), in which a trial set of orbitals is used to obtain a better set; the process is terminated when the energies obtained using two successive sets of orbitals differs by an acceptably small amount. The problem with the SCF method is that the convergence of the iterative process cannot be guaranteed. Occasionally the HFR method predicts, as in the case of the fluorine molecule \( \text{F}_2 \) (9), that the molecule is unstable relative to dissociation, contrary to experiment. Despite these drawbacks many of the most successful calculations of molecular structure have been based on the single determinant approach (10).

The logical progression from the single determinant trial wave function is to use a linear combination of determinants grouped together as in (1.10). This is the basis of the CI method. Unfortunately, there is a great deal of ambiguity attached to the word 'configuration'; its usage is reviewed by McWeeny and Sutcliffe (11). If the wave function is written as a sum of determinants (1.7), then each term is defined by
specifying a 'configuration of occupied spin-orbitals', which is then
antisymmetrized to form a determinant. Alternatively if (1.11) is used,
each term is defined by specifying a 'configuration of occupied (spatial)
orbitals'; often referred to as a 'primate function'. This is then
multiplied by a total spin eigenfunction \( \left( \right) \) and the whole may then be
antisymmetrized. The unknown coefficients in the expansion of the trial
wave function are determined by the requirement that the energy should
be a minimum. The number of terms in the summation of (1.11) is much
reduced by the fact that functions (1.10), belonging to different
irreducible representations, are orthogonal; as are those corresponding
to different eigenfunctions of \( S^2 \) and \( S_z \). Thus, for a given
symmetry it is only necessary to include terms in the expansion which
belong to the same irreducible representation and correspond to the same
eigenvalues of \( S^2 \) and \( S_z \). It must be emphasized that in the CI
method it is the expansion coefficients \( b_{ki} \) of (1.7) or \( a_{LI} \) of
(1.11) and not the \( c_{ki} \) of (1.8) that are varied to minimize the energy.
The CI method is straightforward. Differentiation of the expression which
results from substituting (1.11) in (1.4) with respect to the \( a_{LI} \) leads
to a set of simultaneous linear equations which are equal to zero if \( E_E \)
is a minimum. These equations are conveniently written in matrix form as

\[
(H - E_S)A = 0
\]  

(1.12)

The elements of the real symmetric matrices \( H \) and \( S \) are

\[
H_{IJ} = \langle \psi_I | \hat{H} | \psi_J \rangle
\]  

(1.13a)

and

\[
S_{IJ} = \langle \psi_I | \psi_J \rangle
\]  

(1.13b)
A is a column vector with elements $a_{II}$. The matrix equation, called the secular equation, represents a pseudo-eigenvalue problem, which may be solved by well known methods \((13)\). The solution of \((1.12)\) produces several values of $E$, each an eigenvalue, or characteristic root, of $H$ and its associated eigenvector $A$. Each value of $E$, and its corresponding eigenvector, represents a different energy level of a particular symmetry and spin state. The actual number of levels is equal to the number of eigenvalues of $H$, hence it is equal to the number of terms in \((1.11)\).

While the CI method does attempt to include an allowance for electron correlation \((14)\), it has disadvantages concerning the size of the expansion \((1.11)\), and the slow rate of convergence, since many terms are required to produce a good energy. The matrix elements $H_{IJ}$ and $S_{IJ}$ may be obtained by calculating $\langle D_k | IJ | D_L \rangle$ and $\langle D_k | D_L \rangle$ first, and then transforming into $H_{IJ}$ and $S_{IJ}$ by use of \((1.10)\). The calculation of $H_{IJ}$ and $S_{IJ}$ is simplified if the determinants are constructed from an orthonormal set of molecular orbitals, when the matrix $S$ becomes the identity matrix:

$$S_{IJ} = \delta_{IJ}.$$  

In this case it is also possible to obtain the $H_{IJ}$ 's directly from integrals over the basis set of molecular orbitals using the formalism of Kotani et alia \((12)\).

The extension of the SCF and CI methods leads to a combination called the multi-configuration SCF (MC-SCF) method \((15)\). While this approach has produced some interesting results, \((10, 16, 17, 18)\) the problem of the non-convergence of the SCF process still lacks a satisfactory solution.
PART I
Many of the studies of electron bonds in molecules and molecular ions have concentrated on the "normal" two-electron bond, the prototype of which is the $\text{H}_2$ molecule. The very detailed computational studies of Kolos\textsuperscript{(19)} are examples of the considerable attention that this molecule has received. The subsequent analysis of this type of calculation by Shull\textsuperscript{(20,21)} has resulted in a considerable increase in our understanding of the nature of the two-electron bond.

It is significant that, until recently\textsuperscript{(10)}, another type of chemical bond has received little or no attention from the theoreticians. This is the electron-deficient bond, the prototype of which is the hydrogen molecular ion ($\text{H}_3^+$), consisting of three protons which are bound together by two electrons. A very detailed study of this system by Christoffersen\textsuperscript{(22)} provided information about its structure and about the electron distribution within the bonds. More complex examples of electron-deficient bonds are to be found in the boron hydrides, in certain aluminium and beryllium hydrides, and in the trihalogens BF$_3$, BCl$_3$, and BBF$_3$.

One of the smaller boron hydrides is diborane: ($\text{B}_2\text{H}_6$). For many years the structure of diborane was thought to be the same as that of ethane ($\text{C}_2\text{H}_6$) shown in Fig. 1. The C-H bonds of this molecule have
the normal two-electron character and there is a three-fold axis of symmetry along a line joining the two carbon atoms. Careful analysis of the rotation-vibration spectrum of $\text{B}_2\text{H}_6$ by Price\(^{(23)}\) showed that it has a two-fold axis of symmetry about a line joining the two boron atoms (the structure is shown in Fig. 2). The terminal BH$_2$ groups are coplanar and the central hydrogen atoms lie symmetrically above and below this plane. These hydrogen atoms form "bridge structures" with the two BH$_2$ groups, and the bridge structures are characterized by their electron deficiency, since in the case of diborane only four electrons constitute the four B-H bonds\(^{(24)}\).

Theoretical calculations of the structure and properties of molecules are relatively complex and the difficulties involved increase rapidly as the number of electrons and nuclei increase. It seems reasonable that a study of electron-deficient bonds should begin with a study of a relatively small molecular system. H$_3^+$ is the obvious molecular system to begin with, but is not sufficiently typical to provide much information about the electron-deficient bonds of diborane. However, its structure is an equilateral triangle\(^{(21)}\) of side 1.66 bohr\(^{(22)}\); a geometry very

\begin{center}
\includegraphics[width=0.5\textwidth]{fig2}
\end{center}

FIG. 2. DIBORANE B$_2$H$_6$
similar to that of one of the BHB bridge structures in diborane. This apparent similarity led to the proposal, by Banyard and Shull\(^{(25)}\), of the ZHZ\(^{2Z-1}\) pseudomolecular ion as a model for the study of a bridge bond as found in B\(_2\)H\(_6\). The model (shown in Fig. 3.) consisted of an isosceles triangle BAC with a proton at A, and two nuclei B and C which had equal but variable nuclear charges Z; two electrons were associated with this nuclear framework. The bond length \(R_{AB} (= R_{AC})\) was fixed at the equilibrium bond length of H\(_3^+\) so that when \(Z = 1.0\) the ZHZ\(^{2Z-1}\) system became H\(_3^+\) and comparisons with other calculations on this molecular ion were then possible. The variable nuclear charge provided some allowance for the nuclear shielding caused by the presence of other electrons which were otherwise unaccounted for in the calculation.

The variation of the molecular energy of the ZHZ\(^{2Z-1}\) ions, as a function of the variable nuclear charges and bond angle (\(\theta\) in Fig. 3.), was studied for \(Z\) in the range \(0.8 \leq Z \leq 2.2\) and \(\theta\) in the range \(30^\circ \leq \theta \leq 180^\circ\); in addition, for \(Z = 1.8\) the variation of energy, as a function of bond angle and bond length (\(R_{AB}\) in Fig. 3.), was computed. The angle BHB in the bridge structure of diborane is about \(80^\circ\) and it
might reasonably be expected that as the nuclear charge $Z$ is increased in the $ZH_2Z^{-1}$ model, the optimum bond angle, that is the angle corresponding to the minimum molecular energy, would increase from the 60° of $H_3^+$. However the computed results exhibit an initial decrease in the optimum bond angle. At $Z = 1.8$ a double minimum is observed and for $Z > 1.8$ the optimum bond angle is 180° and the system is linear. These results invited further investigation as it was felt that although the unusual behaviour of the $ZH_2Z^{-1}$ systems prevented them from being regarded as a representative fragment of $B_2H_6$, a study of the quantum mechanical behaviour of such systems might nevertheless shed some light on the nature of electron-deficient bonds.

In order to understand and interpret the results for $ZH_2Z^{-1}$ it is necessary to examine them in detail and, where possible, to give a firm mathematical basis to tentative suggestions concerning the nature of the electron distribution in the ions. This is true for the suggested existence of two components of the electron density. The natural spin orbital (NSO) analysis of Löwdin provides an excellent means of examining these results, particularly as Shull has shown that the results of such an analysis are not greatly affected by the method of calculation of the original wave function nor by the size of the basis set (this second point is illustrated in Chapter 4). By using an electron population analysis similar to that of Mulliken, but based on the natural spin orbital analysis, it has been possible to define the "shared" and "local" density components used in the tentative explanation of the behaviour of the $ZH_2Z^{-1}$ ions. A detailed analysis of the various components of the molecular energy of the ions is also included in this thesis and possible relations between variations in these components and the results of the population analysis are discussed. Thus an attempt has been made to examine nearly all of the aspects of the
behaviour of the $\text{ZH}_2^{22-1}$ pseudomolecular ions and to provide a detailed account of the electron distribution in these ions. Finally, comparisons between the results presented here are made with those of other authors.
CHAPTER 3
WAVE FUNCTIONS AND ENERGIES

The wave functions and energies of the $\text{ZH}Z^\text{Z-1}$ pseudomolecular ions examined here were obtained by the configuration interaction (CI) method. The object of the CI method is to provide an approximation to the solution of the Schrödinger equation for the three-centre two-electron system under consideration. Ignoring relativistic effects, and working within the Born-Oppenheimer approximation (1) yields the Hamiltonian (in atomic units)

$$\mathbf{H} = -\frac{1}{2} \sum_{t=1}^{2} \nabla_t^2 - \sum_{t=1}^{2} \left( \frac{1}{r_{At}} + \frac{Z}{r_{Bt}} + \frac{Z}{r_{Ct}} \right) + \frac{1}{r_{12}}$$

$$+ \frac{Z}{R_{AB}} + \frac{Z}{R_{AC}} + \frac{Z^2}{R_{BC}}. \quad (3.1)$$

The first term in (3.1) is the kinetic energy operator and the others represent the electron-nuclear attraction, the electron-electron and nuclear-nuclear repulsion terms respectively.

The approximate total wave function for the $k$-th energy state of the system is expressed as

$$\psi(x_1, x_2) = \sum_{i} c_i \psi_i(x_1, x_2), \quad (3.2)$$

where the $\{c_i\}$ are coefficients to be determined and the $\{\psi_i\}$ are linearly independent determinantal wave functions. The energy $E_k$
of this state, is defined by

\[ E = \frac{\langle \psi | h | \psi \rangle}{\langle \psi | \psi \rangle}, \tag{3.3} \]

Application of the variation method, which demands that

\[ \frac{\delta E}{\delta c_i} = 0, \]

to (3.3) leads to a system of linear equations which may be written as

\[ (H - ES)C = 0, \tag{3.4} \]

where \( H \) and \( S \) are matrices with elements:

\[ H_{ij} = \langle \psi_i | h | \psi_j \rangle \]

and

\[ S_{ij} = \langle \psi_i | \psi_j \rangle \]

respectively, and \( C \) is a column vector with elements \{\psi_1\}. Once the forms of the two-electron configurations \{\psi_1\} are specified, the total electronic energy and corresponding wave function may be obtained by the solution of the pseudo-eigenvalue problem of (3.4).

(A detailed account of the CI method is given in part 2.)

With two-electron systems, such as \( \text{HZ}_2^2 \), it is possible to factorize the configuration \( \psi_i \) into a spatial part and a spin part. The spin factor, which is antisymmetric, because the ground state is a singlet, can be integrated out of the problem; thus:

\[ \psi_i(\overline{x}_1, \overline{x}_2) = \frac{1}{\sqrt{2}} (\alpha(s_1)\beta(s_2) - \alpha(s_2)\beta(s_1))\phi_i(\overline{r}_1, \overline{r}_2), \]
so that we may write

\[ \Phi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i} c_i \phi_i(\mathbf{r}_1, \mathbf{r}_2) \]  

(3.5)

\[ \Psi \] and \[ \Phi \] are both normalized to unity. The functions \( \{ \phi_i \} \) are formed from linear combinations of products of symmetry-adapted molecular orbitals which are constructed from a basis set of Slater-type atomic orbitals. The normalized form of these orbitals is

\[ \varphi(n, l, m) = \left[ \frac{(2l+1)^{2n+1}}{(2n)!} \right]^{1/2} r^{n-1} \exp(-ir) S_{lm} (\theta, \phi), \]

where \( l \) is a variational parameter and \( S_{lm} (\theta, \phi) \) is a normalized surface harmonic.

In order to examine the ZHZ ions the basis set was limited to three 1s functions, one on each nucleus with the designations 1s\(_A\), 1s\(_B\), and 1s\(_C\) respectively. Inspection of the Hamiltonian shows it to be invariant under the symmetry-operations of the point group \( C_{2v} \), consequently it is possible to generate three symmetry-adapted molecular orbitals from the limited basis set:

\[ \phi_1(t) = 1s_B(t) + 1s_C(t) \quad A_1 \]

\[ \phi_2(t) = 1s_A(t) \quad A_1 \quad (3.6) \]

\[ \phi_3(t) = 1s_B(t) - 1s_C(t) \quad E_1 \]

where \( t = \mathbf{r}_1 \) or \( \mathbf{r}_2 \). The irreducible representation to which each of the \( \phi_i(t) \) belongs is shown to the right of (3.6). From a similarity with \( H^+_3 \) only those configurations which transform according to the \( A_1 \)
irreducible representation of $C_{2v}$, will contribute to the ground state wave function and energy of $\text{ZH}_Z^{2Z-1}$. The fully symmetry-adapted space configurations are:

$$
\Phi_1(\overline{r}_1, \overline{r}_2) = 2\Phi_1(\overline{r}_1)\Phi_1(\overline{r}_2)
$$

$$
\Phi_2(\overline{r}_1, \overline{r}_2) = 2\Phi_2(\overline{r}_1)\Phi_2(\overline{r}_2)
$$

$$
\Phi_3(\overline{r}_1, \overline{r}_2) = 2\Phi_3(\overline{r}_1)\Phi_3(\overline{r}_2)
$$

$$
\Phi_4(\overline{r}_1, \overline{r}_2) = \Phi_1(\overline{r}_1)\Phi_2(\overline{r}_2) + \Phi_2(\overline{r}_1)\Phi_1(\overline{r}_2)
$$

Thus each of the calculations on the $\text{ZH}_Z^{2Z-1}$ ions may be regarded as a complete CI treatment within the limited basis set. The symmetry of the system requires that the orbital exponents $\ell_B$ and $\ell_C$ of the atomic orbitals $1s_B$ and $1s_C$ are equal. The orbital exponents were optimized to give a minimum value to the electronic energy, $E$, for each of a pre-selected set of values of $\theta$, $Z$ and the internuclear distance $Z-H$.

Energies and wave functions were obtained for $Z = 0.8 (0.2) 2.2$ for various values of $\theta$ in the range $30^\circ \leq \theta \leq 180^\circ$. For most values of $Z$ the bond length $R (= R_{AB})$ was taken as 1.66 bohr. This was the optimum bond length obtained by Christoffersen ($22$) for the ground state of $H_3^+$, consequently it was possible to compare the analysis of the results of the $H_3^+$ calculation obtained when $Z = 1.0$, with his results and so some knowledge of the effect of increasing the size of the basis set was obtained. For the case of $Z = 1.8$ two additional values of $R$ were used and, consequently an indication of the dependence on the bond length of the observed effects was obtained.
Preliminary results of the natural spin orbital analysis indicated that a large volume of results would be obtained, and that a correspondingly large amount of computing time would be required if each of the systems and geometries available were to be studied in detail. The natural spin orbital analysis, the concomitant electron population and energy analysis were restricted to the systems for which \( Z = 1.0 \ (0.4) \ 2.2 \) for all bond angles. But the two additional values of \( R \) for \( Z = 1.8 \) were included. Details of wave functions, orbital exponents, and energies for all of the geometries of the systems examined are presented in Tables 1.1-1.6.
### Table 1.1. Wave Function Coefficients, Orbital Exponents, and Energies for Z=1.00 a.u., r=1.66 bohr.

<table>
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<tr>
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<th>C3</th>
<th>C4</th>
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<th>Ω_B</th>
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### Table 1.3. Wave Function Coefficients, Orbital Exponents, and Energies for Z=1.30 a.u., r=1.66 bohr.

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### Table 1.4. Wave Function Coefficients, Orbital Exponents, and Energies for \( z = 2.50 \text{ a.u.}, \ R = 1.50 \text{ bohr} \)

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### Table 1.5. Wave Function Coefficients, Orbital Exponents, and Energies for \( z = 1.80 \text{ a.u.}, \ R = 1.50 \text{ bohr} \)

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### Table 1.6. Wave Function Coefficients, Orbital Exponents, and Energies for \( z = 1.30 \text{ a.u.}, \ R = 1.50 \text{ bohr} \)

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<td>-2.21513</td>
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<td>-0.10450</td>
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CHAPTER 4
ANALYSIS OF SYSTEMS

One of the difficulties encountered in the interpretation of a CI wave function arises from the arbitrary nature of the basis set. For the system under examination it was decided to construct the configurations from a set of symmetry-adapted molecular orbitals. Equally, it would have been feasible to orthonormalize this set, or merely to have used the atomic orbitals from which the molecular orbitals were constructed. In each case the energies obtained would have been the same, since each basis set is related to the others by a unitary transformation, but the coefficients in the series of configurations would differ, making it difficult to interpret wave functions presented in this way. In order to try to obviate this problem Löwdin(8) has shown that it is possible to select a set of one-electron functions which have characteristic properties belonging to the system and state under consideration. The components of this set are called natural spin orbitals. The set of natural spin orbitals, \( \{ \chi_k \} \), are defined as forming the set which diagonalizes the generalized first order density matrix. For a two-electron system it is possible to introduce many simplifications into the general theory of the natural spin orbital analysis, even when the orbitals are not orthonormal. An important simplification is the removal of electron spin from the problem, this leads to the natural orbital analysis for two electron systems. Introduction of the natural spin orbitals facilitates the interpretation of the wave functions, and also assists in the understanding of the behaviour of the electron density distribution.

Useful information about the behaviour of the electron density within a molecular system may often be gained by examining the behaviour
of the individual terms which contribute to the one particle density function. Such an examination of the systems discussed here has shown that it is possible to divide the electron distribution into two components which may be associated with Banyard and Shull's "local" and "shared" densities. Further insight into the behaviour of the systems under consideration may be gained from electron density contours, and these also provide a link between the natural spin orbital analysis and the analysis of the components of the total energy.

A. Natural Spin Orbital Analysis

The orthonormal formulation of the natural spin orbital analysis of two-electron systems has been discussed extensively in the literature and is a special case of the non-orthonormal formalism which will be developed in this section. In the two-electron case the wave function is equivalent to a real quadratic form and the spatial part may be written as

$$\phi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{ij} f_{ij} \varphi_i(\mathbf{r}_1) \varphi_j(\mathbf{r}_2), \quad (4.1)$$

in matrix notation this is

$$\Phi = \Phi \Phi^t,$$

where $\Phi$ is a row vector with the basis orbitals $\{\varphi_i\}$ as its elements. The first order density matrix is defined by

$$\gamma(\mathbf{r}_1; \mathbf{r}_1) = 2\phi^*(\mathbf{r}_1, \mathbf{r}_2)\phi(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2.$$
After substitution for $\phi$ from (4.1) and integration over $r_2$, this expression becomes

$$
\gamma(r_1; r_1') = 2 \sum_{i,j} f^*_{ij} \sum_{lm} s_{ijlm} \phi_i(r_1) \phi_j(r_1) \delta_{jm}, \quad (4.2)
$$

where $s_{jm} = \langle \phi_j | \phi_m \rangle$, and is, in general, non-zero. Using (4.2) it is possible to define $\gamma(1|1)$, the elements of the first order density matrix, as

$$
\gamma(1|1) = \sum_{jm} f^*_{jm} \delta_{jm} f_{ml},
$$

since $f_{ml} = f^*_{lm}$. In matrix notation this simply

$$
\gamma = F \Delta F^+, \quad (4.3)
$$

$\Delta$ being the overlap matrix between the basis (spatial) orbitals, that is, its elements are $s_{jm}$; the first order density matrix is now given as

$$
\gamma(r_1; r_1') = 2\phi \gamma \phi^+. \quad (4.4)
$$

The natural orbitals are defined as that set of orthonormal orbitals which diagonalizes the (spinless) first order density matrix. Thus if $\chi$ represents the natural orbital basis, then since

$$
\chi = \phi \Delta, \quad (4.4)
$$

$$
\gamma(r_1; r_1') = \chi A^{-1} \gamma (A^{-1})^+ \chi^+, \quad (4.4)
$$
\[
A^{-1} \gamma (A^{-1})^+ = \text{diag}(n_1, n_2, \ldots) \, . \tag{4.5}
\]

Since the \(\{\chi_i\}\) must be orthonormal then

\[
\gamma^+ \Delta A = I \tag{4.6}
\]

\((I)\) is the identity matrix). Equations (4.5) and (4.6) are the standard natural orbital equations, which define the matrix \(A\). (In the \(N\)-electron case these equations become the natural spin orbital equations, as both \(\gamma\) and \(\Delta\) are formed from the basis spin orbitals. This form of \(\gamma\) is considerably more difficult to construct than in the two-electron case.) However, in the two-electron problem it is possible to obtain the matrix \(A\) without constructing the first order density matrix; a tedious operation even for small basis sets. The procedure is as follows; let

\[
\chi = \Phi B \, , \tag{4.7}
\]

such that

\[
\Phi = \chi \text{diag}(g_1, g_2, \ldots) \chi^+ \, ,
\]

and

\[
<\chi_i|\chi_j> = \delta_{ij} \, .
\]
It is easily seen that the transformation matrix $B$ is defined by the conditions

$$B^+ \Delta B = I \quad ,$$  \hspace{1cm} (4.8)

and

$$B^{-1} F (B^{-1})^+ = \text{diag}(g_1, g_2, \ldots) \quad .$$  \hspace{1cm} (4.9)

Equations (4.8) and (4.9) may be solved as follows: perform a unitary transformation on $\Delta$ so that

$$U^+ \Delta U = \text{diag}(d_1, d_2, \ldots) \quad ,$$

where the eigenvectors of $\Delta$ are the columns of $U$. Now define a matrix $W$ with elements

$$W_{ij} = U_{ij} (d_j)^{-1/2} \quad .$$

Hence

$$W^+ \Delta W = I \quad .$$  \hspace{1cm} (4.10)

A comparison of (4.8) and (4.10) leads to the erroneous conclusion that $B$ and $W$ are identical. That this is not so may be shown by writing $B$ as the product of $W$ and another matrix $X$, i.e.

$$B = WX \quad \text{and} \quad B^+ = X^+ W^+ \quad .$$  \hspace{1cm} (4.11)
Substitution for $B$ and $B^+$ from (4.11) into (4.8) and use of (4.10) yields the result

$$X^+ X = I$$

Thus $B$ and $W$ are related by the unitary matrix $X$. This matrix may be determined by substitution for $B$ and $B^+$ from (4.11) into (4.9), this gives

$$X^{-1} M (X^{-1})^+ = \text{diag}(g_1, g_2, \ldots) \quad (4.12)$$

where

$$M = W^{-1} \mathcal{F} (W^{-1})^+$$

Equation (4.12) may be written in a more convenient form using the knowledge that as $X$ is a unitary matrix, $X^{-1} = X^*$, thus

$$X^+ M X = \text{diag}(g, g, \ldots) \quad .$$

Therefore $W$, $X$, and hence the transformation matrix $B$ may be determined.

Now consider the transformation

$$B^{-1} y (B^{-1})^+$$

Using (4.3) and (4.11) this becomes

$$X^{-1} W \mathcal{F} \Delta \mathcal{F}^+ (W^{-1})^+ (X^{-1})^+ \quad (4.13)$$
This equation may be greatly simplified by using (4.8), (4.10), and the fact that $X$ is unitary. The steps involved are not obvious and are shown in full, thus (4.13) is firstly rewritten as

$$X^{-1} W^{-1} P (W^{-1})^+ (W^+ A W) W^{-1} P^+ (W^{-1})^+ (X^{-1})^+$$

$$= X^{-1} M I M^+ X$$

$$= X^+ M M^+ X$$

$$= X^+ M X X^+ M^+ X$$

$$= \text{diag}(g_1, g_2, \ldots) \text{diag}(g_1, g_2, \ldots)$$

$$= \text{diag}(g_1^2, g_2^2, \ldots)$$

(4.15)

The conclusion is obvious; not only does the transformation matrix $B$ give a diagonal form to the wave function (called the natural expansion wave function), but the first order density matrix corresponding to this form is also diagonal. The orbitals defined by (4.7) are the natural orbitals, $B$ is the transformation matrix $A$ of (4.4), the diagonal elements of $\text{diag} (g_1, g_2, \ldots)$ are the natural expansion coefficients, and the occupation numbers of the natural orbitals are the diagonal elements of $\text{diag} (g_1^2, g_2^2, \ldots)$.

In summary, if

$$X = \phi B$$
and $B$ satisfies (4.8) and (4.9) then

$$
\phi(\mathbf{r}_1, \mathbf{r}_2) = \sum_k n_k \chi_k(\mathbf{r}_1) \chi_k(\mathbf{r}_2),
$$

(4.16)

$$
\gamma(\mathbf{r}_1, \mathbf{r}_1') = 2 \sum_k n_k \chi_k(\mathbf{r}_1) \chi_k(\mathbf{r}_1'),
$$

(4.17)

and

$$
n_k = \varepsilon_k^2
$$

Equation (4.16) represents the natural expansion wave function for a two-electron system. Introduction of the singlet spin function produces the natural expansion of the complete wave function:

$$
\psi(\mathbf{x}_1, \mathbf{x}_2) = 2^{-1/2} \left[ \alpha(s_1)\beta(s_2) - \beta(s_1)\alpha(s_2) \right] \sum_k \varepsilon_k \chi_k(\mathbf{r}_1) \chi_k(\mathbf{r}_2).
$$

(4.18)

It is possible to derive a form similar to (4.18) for the triplet state. Integration of (4.17) over $\mathbf{r}_1$ gives the expected result,

$$
\sum_k n_k = 1.
$$

(4.19)

If the basis orbitals were orthonormal then

$$
\Delta = I
$$

and from (4.3)

$$
\gamma = F F^T.
$$
and the treatment is then analogous to that of Löwdin and Shull[28].

It is known that the approximate wave function for a two-electron system is equivalent to a real finite quadratic form. A quadratic form is characterized by its rank \(r\) and its signature \(s\), two integers which are invariant under non-singular linear transformations[28, 29].

The rank of the quadratic form is defined as the rank of the determinant of its coefficients\(\{f_{ij}\}\) (see (4.1)), and the quadratic form is reducible by a non-singular linear transformation to a sum of "squares" which contains \(r\) terms. The number \(p\) of positive terms in this sum is the index of the quadratic form and if \(q\) is the number of negative terms, then

\[
 r = p + q
\]

and

\[
 s = p - q
\]

This implies that each approximate two-electron wave function of finite order has a rank and signature and that it may be reduced to a sum of "squares"; this explains the simple form of (4.16) and (4.18).

An important theorem due to Löwdin and Shull[28] states that if \(\Psi\) is an exact two-electron eigenfunction and \(\Psi_R\) an arbitrary two-electron wave function of rank \(r\), then

\[
\int |\Psi(x_1, x_2) - \Psi_R(x_1, x_2)|^2 dx_1 dx_2 =
\]

\[
2(1 - \int \Psi^*(x_1, x_2)\Psi_R(x_1, x_2) dx_1 dx_2)
\]

has a minimum value if the function \(\Psi_R\) is obtained by interrupting the natural expansion after the first \(r\) terms and renormalizing the finite series to unity. It is important to note that in the natural expansion

\[|g_1| > |g_2| > \ldots > |g_r|\]  

The theorem is also true if \(\Psi\) is
not an exact eigenfunction but an approximation of rank greater than \( r \).

Application of the natural orbital analysis to the \( ZH_2 \) problem is straightforward. The elements \( \{ f_{ij} \} \) of the coefficient matrix \( F \) are simply

\[
\begin{align*}
 f_{11} &= 2c_1, \\
 f_{22} &= 2c_2, \\
 f_{33} &= 2c_3, \\
 f_{12} &= f_{21} = c_4, \\
 f_{13} &= f_{31} = f_{23} = f_{32} = 0.
\end{align*}
\]

The quantities \( \{ c_4 \} \) are the coefficients in (3.2) and are given in Tables 1.1 to 1.6. The elements of the overlap matrix \( \Delta \), are easily seen to be

\[
\begin{align*}
 \Delta_{11} &= 2(1 + <1s_b|1s_c>) \\
 \Delta_{22} &= 1.0 \\
 \Delta_{33} &= 2(1 - <1s_b|1s_c>) \\
 \Delta_{12} &= \Delta_{21} = 2<1s_a|1s_b> \\
 \Delta_{13} &= \Delta_{31} = \Delta_{23} = \Delta_{32} = 0.
\end{align*}
\]

Equation (4.19) has been evaluated for each system examined. In some instances it was found that the sum of the occupation numbers differed from unity by as much as \( \pm 10^{-4} \); a significant difference. Examination of the original wave functions showed that if the normalization integral differed significantly from unity then a similar error appeared in (4.19).
| Table 2.1: Natural Expansion Coefficients (First Row) and Transformation Matrices for \( z = 1.00 \text{ a.u.} \) and \( R = 1.66 \text{ bohr} \). |
|---------------------------------|---------------------------------|
| \( 0.99499 \)     \(-0.08370\)    \(-0.04613\)                          | \( 0.99421 \)     \(-0.03928\)    \(-0.05895\)                          |
| \( 0.42233 \)     \(-0.44059\)    \(0.00000\)                          | \( 0.41613 \)     \(-0.43728\)    \(0.00000\)                          |
| \( 0.33163 \)     \(1.08361\)     \(0.00000\)                          | \( 0.36076 \)     \(1.11519\)     \(0.00000\)                          |
| \( 0.00000 \)     \(0.00000\)     \(1.46034\)                          | \( 0.00000 \)     \(0.00000\)     \(1.22370\)                          |
| \( \theta = 30.00 \)                                           | \( \theta = 40.00 \)                                           |
| \( 0.99347 \)     \(-0.08331\)    \(-0.07220\)                          | \( 0.99270 \)     \(-0.08529\)    \(-0.08529\)                          |
| \( 0.41335 \)     \(-0.53323\)    \(0.00000\)                          | \( 0.40793 \)     \(-0.57826\)    \(0.00000\)                          |
| \( 0.33540 \)     \(1.13810\)     \(0.00000\)                          | \( 0.40793 \)     \(1.15652\)     \(0.00000\)                          |
| \( 0.00000 \)     \(0.00000\)     \(1.08836\)                          | \( 0.00000 \)     \(0.00000\)     \(1.00158\)                          |
| \( \theta = 50.00 \)                                           | \( \theta = 60.00 \)                                           |
| \( 0.99137 \)     \(-0.08773\)    \(-0.05151\)                          | \( 0.98100 \)     \(-0.10925\)    \(-0.07731\)                          |
| \( 0.40154 \)     \(0.00000\)     \(-0.63243\)                          | \( 0.39435 \)     \(0.00000\)     \(-0.66539\)                          |
| \( 0.42975 \)     \(0.00000\)     \(1.17851\)                          | \( 0.45033 \)     \(0.00000\)     \(1.20144\)                          |
| \( 0.00000 \)     \(0.33991\)     \(0.00000\)                          | \( 0.00000 \)     \(0.39509\)     \(0.00000\)                          |
| \( \theta = 70.00 \)                                           | \( \theta = 80.00 \)                                           |
| \( 0.96929 \)     \(-0.12600\)    \(-0.06866\)                          | \( 0.96787 \)     \(-0.14300\)    \(-0.06651\)                          |
| \( 0.37345 \)     \(0.00000\)     \(-0.74456\)                          | \( 0.36089 \)     \(0.00000\)     \(-0.81242\)                          |
| \( 0.48833 \)     \(0.00000\)     \(1.24523\)                          | \( 0.52426 \)     \(0.00000\)     \(1.23309\)                          |
| \( 0.00000 \)     \(0.53437\)     \(0.00000\)                          | \( 0.00000 \)     \(0.79834\)     \(0.00000\)                          |
| \( \theta = 100.00 \)                                         | \( \theta = 120.00 \)                                         |
| \( 0.95664 \)     \(-0.15473\)    \(-0.05105\)                          | \( 0.95633 \)     \(-0.15759\)    \(-0.04719\)                          |
| \( 0.33793 \)     \(0.00000\)     \(-0.87294\)                          | \( 0.32756 \)     \(0.00000\)     \(-0.90220\)                          |
| \( 0.56569 \)     \(0.00000\)     \(1.31632\)                          | \( 0.58346 \)     \(0.00000\)     \(1.32319\)                          |
| \( 0.00000 \)     \(0.76931\)     \(0.00000\)                          | \( 0.00000 \)     \(0.76029\)     \(0.00000\)                          |
| \( \theta = 150.00 \)                                         | \( \theta = 180.00 \)                                         |
### TABLE 2.2. NATURAL EXPANSION COEFFICIENTS (FIRST ROW) AND TRANSFORMATION MATRICES FOR Z=1.40Å U. AND R=1.66Å NR.

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<th>Natural Expansion Coefficients</th>
<th>Transformation Matrices</th>
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TABLE 2.5. NATURAL EXPANSION COEFFICIENTS (FIRST ROW) AND TRANSFORMATION MATRICES FOR Z=1.80A,U, AND B=1.50BOHR.

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* Values for $\theta = 52.15$

+ Values for $\theta = 50.50$
The explicit forms and symmetries of the natural orbitals obtained in the ZHZ \(^{22-1}\) calculations are

\[
\chi_1(t) = [A_{11}(1s_B + 1s_C) + A_{21}1s_A(t)] , \quad A_1
\]

\[
\chi_2(t) = [A_{32}(1s_B - 1s_C)(t)] , \quad B_1
\]

\[
\chi_3(t) = [A_{13}(1s_B + 1s_C) + A_{23}1s_A(t)] , \quad A_1 \quad (4.20)
\]

where \( t \) is \( r_1 \) or \( r_2 \). This order assumes that \( n_1 > n_2 > n_3 \), but in some cases \( \chi_2 \) and \( \chi_3 \) must be reversed to preserve this order.

The results of the analysis for each of the systems examined are shown in Tables 2.1 to 2.6 and in Table 3.

**B. Electron Population Analysis**

Several approaches to this problem are possible\(^{27,30}\), but all depend on the expression for the one-particle density, and its division into component quantities. The expression for the one-particle density has the general form

\[
\gamma(x_1 : x_1') = N \int |\psi(x_1', x_2, \ldots x_N)|^2 dx_2 dx_3 \ldots dx_N ,
\]

where the integration is over the space-spin co-ordinates of all the particles except those of the primed quantity. The spinless one-particle density \( \gamma(r_1 : r_1') \) is obtained by integrating \( \gamma(x_1 : x_1') \) over the remaining spin co-ordinate. The result may then be rearranged so that, for example, all of the terms containing the orbital product \( \psi_{iA}^*(r_1) \psi_{jB}(r_1) \) are grouped together. \( \psi_{iA}(r_1) \) and \( \psi_{jB}(r_1) \) are the \( i \)-th orbital centred on nucleus A and the \( j \)-th orbital centred on nucleus B respectively.
The expression for the one-particle density may thus be written as a sum of terms, each of the form \( t_{ij} \phi^*_{1A}(r_i) \phi_{jB}(r_j) \), where \( t_{ij} \) is a coefficient determined by the integrations indicated. The electron distribution may then be broken down into parts, which are associated with the various nuclei and overlap regions between each pair of nuclei, by defining the atomic population associated with nucleus A as:

\[
N(A) = \sum_{ij} t_{ij} \langle \phi_{1A} | \phi_{jA} \rangle,
\]

and the overlap population of the region between nuclei A and B as:

\[
S(AB) = \sum_{kl} t_{kl} \langle \phi_{kA} | \phi_{1B} \rangle.
\] (4.21)

Equation (4.21) refers to pairs of nuclei so that \( \langle \phi_{1B} | \phi_{kA} \rangle \) is included in the sum and the quantity \( S(BA) \) does not arise.

Obviously

\[
\int \gamma(x_i : x_i) dx_i = \sum_A N(A) + \sum_{AB} S(AB).
\]

However, the appropriate integration of \( |\psi|^2 \) to obtain the expression for the one-particle density often presents difficulties. In the case of a CI wave function the off-diagonal elements of the first order density matrix are not necessarily zero, so that a very unwieldy expression results.

The difficulties that arise in the approach described can be circumvented by employing a method similar to the "Electronic Population Analysis" of Mulliken\(^{(27)}\). Direct application of Mulliken's theory is not possible since it demands a knowledge of the number of electrons occupying each of the symmetry-adapted molecular orbitals. Specifically, in the case of the \( \text{ZH}^{2Z-1} \) ions there are two electrons distributed between three molecular
orbitals, and it is obvious from the results to be presented that the occupation of each of the molecular orbitals changes significantly as the nuclear charges and geometry vary. We are thus led to the choice of using the natural orbitals since both their form and occupation numbers are clearly defined for each of the systems under consideration. As was shown in the previous section, the expression for the one-particle density in terms of the natural orbitals is simply,

\[ \rho(r) = \gamma(\mathbf{r}_1; \mathbf{r}_1') = 2\sum_{k} \chi^*_k(\mathbf{r}_1') \chi_k(\mathbf{r}_1) \]

In general,

\[ \chi_k(\mathbf{r}_1') = \sum_{A_1} \varphi_{iA}(\mathbf{r}_1') a_{iAk} \]

where \( \varphi_{iA} \) is the i-th orbital on centre A. The coefficients \( a_{iAk} \) may be obtained from the transformation matrix by inspection. The following breakdown of the electron distribution may be made:

(i) partial atomic population \( N_k(A) \) of nucleus A;

\[ N_k(A) = 2n_k \sum_{i,j} \langle \varphi_{iA} | \varphi_{jB} \rangle^* a_{iAk}^* a_{jAk} \]

(ii) atomic population \( N(A) \) of nucleus A;

\[ N(A) = \sum_k N_k(A) \]

(iii) partial overlap population \( S_k(AB) \) of the overlap region A-B;

\[ S_k(AB) = 2n_k \sum_{i,j} \langle \varphi_{iA} | \varphi_{jB} \rangle^* a_{iAk}^* a_{jAk} \]
(iv) overlap population $S(AB)$ of the overlap region $A-B$;

$$S(AB) = \sum_k S_k(AB) ,$$

(v) total atomic (or local) population $N_L$:

$$N_L = \sum_A N(A) ,$$

(vi) total overlap (or shared) population $S_S$:

$$S_S = \sum_{\text{pairs}(AB)} S(AB) ,$$

and obviously

$$N_L + S_S = N ,$$

the number of electrons.

The natural orbitals of the $\text{ZH}^{2+}$ ions are few in number, and of a relatively simple form. From (4.20) we have,

$$\chi_1^2 = A_{11}^2 (1s_B^1s_B^1 \text{ or } 2 \cdot 1s_B^1s_C^1 \text{ or } 1s_C^1s_C^1) + A_{21}^2 (1s_A^1s_A^1)$$

$$+ 2A_{11}A_{21}^2 (1s_B^1s_A^1 + 1s_C^1s_A^1) ,$$

$$\chi_2^2 = A_{32}^2 (1s_B^1s_B^1 - 2 \cdot 1s_B^1s_C^1 + 1s_C^1s_C^1) ,$$

$$\chi_3^2 = A_{13}^2 (1s_B^1s_B^1 + 2 \cdot 1s_B^1s_C^1 + 1s_C^1s_C^1) + A_{23}^2 (1s_A^1s_A^1)$$

$$+ 2A_{13}A_{23}^2 (1s_B^1s_A^1 + 1s_C^1s_A^1) .$$
The atomic populations are:

\[ N_1(A) = 2n_1A_{21}^2 \quad ; \quad N_1(B) = N_1(C) = 2n_1A_{11}^2 \]

\[ N_2(A) = 0 \quad ; \quad N_2(B) = N_2(C) = 2n_2A_{32}^2 \]

\[ N_3(A) = 2n_3A_{23}^2 \quad ; \quad N_3(B) = N_3(C) = 2n_3A_{13}^2 \]

\[ N(A) = 2(n_1A_{21}^2 + n_3A_{23}^2) \]

and

\[ N(B) = N(C) = 2(n_1A_{11}^2 + n_2A_{32}^2 + n_3A_{13}^2) \]

The overlap populations are:

\[ S_1(AB) = S_1(AC) = 4n_1A_{11}A_{21}S_{AB} \quad ; \quad S_1(BC) = 4n_1A_{11}^2S_{BC} \]

\[ S_2(AB) = S_2(AC) = 0 \quad ; \quad S_2(BC) = -4n_2A_{32}^2S_{BC} \]

\[ S_3(AB) = S_3(AC) = 4n_3A_{13}A_{23}S_{AB} \quad ; \quad S_3(BC) = 4n_3A_{13}^2S_{BC} \]

\[ S(AB) = S(AC) = 4S_{AB}(n_1A_{11}A_{21} + n_3A_{13}A_{23}) \]

and

\[ S(BC) = 4S_{BC}(n_4A_{11}^2 - n_2A_{32}^2 + n_3A_{13}^2) \]

\[ S_{AB} \] and \[ S_{BC} \] are the overlap integrals \( <1s_A|1s_B> \) and \( <1s_B|1s_C> \) respectively. \( A_{ij} \) are the elements of the transformation matrix.
Variations of the atomic and overlap populations as functions of $Z$ and $\theta$ are shown in Figs. 4 to 7. Population analyses for optimized wave functions with $R = 1.5$ bohr and $1.8$ bohr were performed for $Z = 1.8$ and the results permitted the study of the variation of the electron populations as a function of the Z-H bond length.

C. Electron Density Contours

The interpretation of the results of the natural orbital and electron population analyses proved difficult because of the large volume of results. It was felt that a quantitative description of the behaviour of the systems would greatly assist in the interpretation of the numerical quantities. Such a description is provided by the electron density contours.

From $(4.17)$, values of the electron density were obtained for each system in the plane of the nuclei, and contour maps were drawn for each system. A selection of these maps is shown in Fig. 8. Each map is symmetric about the line $XX'$, which bisects the bond angle $\theta$ (see Fig. 3). Changes in the contours, as $\theta$ and $Z$ vary, are clearly illustrated. A general feature of all the contour diagrams is shown by tracing the line of maximum density, i.e. minimum slope, between centres B and C. This line is such that the density always decreases in magnitude, when evaluated at adjacent spatial co-ordinates along its normal. These curves, which are also symmetric about the line $XX'$, are shown collectively in Fig. 9. They indicate specifically whether or not centre A is contained within the density contour of highest value which mutually embraces centres B and C. In some instances, the line of minimum slope is seen to divide, so that B is joined to A and C. The significance of this situation, indicated in Fig. 9 by the dotted lines, will be discussed in Chapter 5.
FIG. 4. The atomic population for centres A, B, and C as a function of the bond angle $\Theta$. The dotted lines are for centre A and the solid lines for centres B or C.
FIG. 5. The atomic population for centres A, B, and C as a function of \( Z \). The dotted lines are for centre A and the solid lines for centres B or C.
FIG. 6. The overlap population for A–B, A–C, and B–C as a function of the bond angle. The dotted lines are for B–C and the solid lines for A–B or A–C.
FIG. 7. The overlap population for A-B, A-C, and B-C as a function of Z. The dotted lines are for A-B or A-C and the solid lines for B-C.
FIG. 8. Contour diagrams of the electron density in the plane of the molecule for selected values of $Z$ and $\theta$. The diagrams are symmetric about the line $XX'$ which bisects the bond angle $\theta$. In (a) the density at D is less than 0.1764.
FIG. 9. The trace of points, between the centres B and C, with minimum slope in the electron-density surface when evaluated in the plane of the 2Z ions for Z = 1.0, 1.4, 1.8, and 2.2, see diagrams a, b, c, and d respectively. For each value of Z, the trace is shown for various values of the bond angle \( \theta \). The centre A is located about XX', which bisects \( \theta \). Each set of diagrams is symmetric.
FIG. 10. The atomic and overlap populations for \( Z = 1.8 \) as a function of \( R \). In the left-hand diagram the dotted lines are for \( A \) and in the right-hand diagram for \( B-C \). The solid lines represent \( B \) or \( C \) in the left-hand diagram and \( A-B \) or \( A-C \) in the right-hand diagram.
FIG. 11. The kinetic energy as a function of the bond angle $\theta$. 
FIG. 12. The electron repulsion energy as a function of the bond angle $\theta$. 
FIG. 13. The nuclear attraction energy as a function of the bond angle $\theta$. 
FIG. 14. The nuclear repulsion energy as a function of the bond angle $\theta$. 
D. Energy Analysis

As stated in Chapter 2, the behaviour of the electron energy of the ZHz²⁻¹ systems was unexpected, and it was thought that an investigation of the individual components of the total energy might provide an insight into this behaviour. The results of this investigation are displayed graphically in Figs. 11 to 14.
CHAPTER 5

DISCUSSION OF RESULTS

Certain general trends are immediately observable from the tables and diagrams presented. Inspection of the natural orbitals given in (4.20) indicates that $\chi_1$ and $\chi_3$ are bonding-type orbitals whereas $\chi_2$ is of an anti-bonding form. It is seen from the occupation numbers presented in Table 3 that for all values of $\theta$, $\chi_1$ predominates in the natural expansion of the wave function for $Z \leq 1.4$. Although a large occupation number for a bonding orbital does not necessarily guarantee the stability of the $ZH_2Z^{-1}$ ion for any choice of $Z$ and $\theta$, it is of interest to note, from the work of Banyard and Shull\(^{(25)}\), that for $Z < 1.3$ the ions are stable with respect to dissociation. Another obvious trend is the increase in electron density in the region of the nuclei B and C as the effective nuclear charge is increased. The significance of the way in which this increase occurs will be discussed in the following paragraphs.

For $Z = 1.0$, when $ZH_2Z^{-1}$ becomes $H_3^+$, $n_1$ and $n_3$ shown in Table 3 decrease and $n_2$ becomes larger as the bond angle increases from $30^\circ$ to $180^\circ$. The results for $H_3^+$ may be placed in perspective by referring to the occupation numbers of the natural orbitals of $a_1^-$ and $e_1^-$ type symmetry determined by Christoffersen and Shull\(^{(31)}\) for the united atom Li$^+$ and the dissociation products H + H + H$^+$. For Li$^+$ they quote total occupation numbers of 0.998121 and 0.001223 for the $a_1^-$ and $e_1^-$ type natural orbitals respectively. For the dissociation products of $H_3^+$, the total occupation numbers for the orbitals of $a_1^-$ and $e_1^-$ type symmetry are 0.666667 and 0.333333 respectively. When $Z$ is large, the dissociation products of minimum energy will have corresponding natural orbitals with occupation numbers of 0.5. Thus, the united atom character
is seen to feature strongly in the description of $H_{3}^{+}$ for all values of $\theta$. Table 3 shows that this conclusion is valid as far as $Z \leq 1.4$. When $Z \geq 1.8$ it is seen that, as $\theta$ increases, the occupation number associated with $X_2$ increases greatly at the expense of $n_1$. This would seem to indicate that, when $Z$ and $\theta$ are large, the electron density begins to concentrate predominately around the nuclei B and C at the expense of the proton at A and the internuclear regions. This conclusion is supported by noting that, as $Z$ and $\theta$ increase, the occupation numbers for $X_1$ and $X_2$ are both approaching 0.5. Quantitative evidence is also provided by both the electron population analysis (Figs. 4 to 7) and by the electron density contour maps (Fig. 8).

The results of the electron population analysis illustrated in Figs. 4 to 7 indicate that when the overlap population between centres B and C is greater than that of the region A-B, the $ZH_{2}^{Z-1}$ ions may be regarded as two-centre systems plus a strongly perturbing proton. However, when $S(BC)$ is less than $S(AB)$ the ion may be thought of as forming a three-centre system. Such an interpretation is strongly supported by the evidence shown in the diagrams of Fig. 9. The "divided" trace, i.e. the dotted lines of Figs. 9a, 9b, and 9c, is particularly interesting since it only occurs when $S(AB) \approx S(BC)$. The depression in the electron density surface of $H_{3}^{+}$ at its equilibrium bond angle (see Fig. 8a), centred at the centroid of the triangle ABC, was not observed by either Christoffersen and Shull$^{32}$ or by Schwartz and Schaad$^{32}$; this may be a consequence of our minimal basis set.

For $Z = 1.0$, it is seen from Fig. 4 that, as $\theta$ gets larger, $N(A)$ increases fairly sharply, but $N(B)$ and $N(C)$ become smaller; correspondingly the overlap populations $S(AB)$ and $S(AC)$ shown in Fig. 6 increase but the value of $S(BC)$ decreases considerably. This behaviour is partly illustrated by the contour maps a, d, and g of Fig. 8.
A similar situation occurs for \( Z = 1.4 \). However, for \( Z = 1.8 \), Fig. 4 shows that the atomic population for each nuclear centre increases as the bond angle is enlarged. The overlap population \( S(AB) \) also increases as \( \theta \) increases, but the magnitude of \( S(BC) \) is seen to decrease rapidly. Thus, as \( \theta \) varies from \( 30^\circ \) to \( 180^\circ \), a value of \( Z \geq 1.8 \) is capable of causing electron charge cloud to move from the internuclear region B-C towards the centres B and C, whereas when \( Z = 1.0 \) the charge cloud is moved from B and C towards centre A.

Fig. 7 reveals that, for any fixed bond angle, \( S(AB) \) decreases in value as \( Z \) is increased, this indicates the diminishing influence of the proton on the system. This conclusion is substantiated by the fact that \( N(A) \) tends to zero for all angles as \( Z \) becomes large. Fig. 7 also shows that when \( \theta < 100^\circ \), \( S(BC) \) increases initially and then decreases as \( Z \) continues to increase. This effect is greatest for small angles. For \( \theta \geq 100^\circ \), \( S(BC) \) shows no initial increase as a function of \( Z \). Hence as \( Z \) is increased for a fixed bond angle, the charge cloud is drawn away from A into the regions associated with B, C, and B-C. A further increase in \( Z \) removes the charge cloud from the internuclear region B-C and localizes it about the nuclei B and C.

For \( Z = 1.8 \), the electron population analysis was performed for wave functions corresponding to \( R = 1.50 \) a.u., \( 1.66 \) a.u., and \( 1.80 \) a.u. The results are shown in Fig. 10. For constant \( \theta \), as expected \( N(A) \) decreases in value and \( N(B) \) increases as \( R \) becomes larger, both \( S(AB) \) and \( S(BC) \) decrease.

Changes in the above results caused by extending the basis set may be examined most readily by studying the \( H_3^+ \) molecular ion, this is made possible by the analysis of the configuration interaction wave function of Christoffersen which involved a basis set of twelve real Slater-type orbitals. The occupation number of 0.98487 which
Christoffersen and Shull obtained for the first natural orbital $\chi_1$ differs from the value obtained in this calculation by only 0.00059 (see Table 3, $Z = 1.00$, $\theta = 60^\circ$, $R = 1.66$). The virtual independence of the occupation numbers with respect to the size and nature of the basis set has been commented on by Shull (26). Due to its large occupation number, the form of $\chi_1$ for $H_3^+$ will govern the essential features of the electron population analysis. Thus the evaluation of $N(A)$ and $S(AB)^*$ derived from $\chi_1$, taken in the first instance from the work of Christoffersen and Shull, and secondly from Table 2.1 for $\theta = 60^\circ$, should indicate the general effect of an extended basis set. In both cases we have in fact considered the "best" wave functions of rank 1. For the minimal basis set $N(A)$ and $S(AB)$ were found to be 0.33282 and 0.33386 respectively, while the extended basis set gave values of 0.30113 and 0.36554. Thus, an extension of the basis set causes a lowering of the atomic population of each nucleus with a corresponding increase in the overlap populations. Such changes in the electron population analysis are not too surprising since the 1$s$ minimal basis set could only be extended by the inclusion of higher orbitals which, by virtue of their more diffuse nature, provide a greater two-centre overlap. It is reasonable to expect that an extension of the basis set for the remaining $ZH_2Z^{-1}$ ions will have a similar effect, although this should become less marked as $Z$ is increased.

Hopton and Linnett (33) have discussed the structure of the linear $H_3^+$ molecular ion in terms of various approximations to a simple CI wave function obtained by Hirschfelder, Eyring and Rosen (34). As these latter authors did not allow the orbital exponents to vary, their wave functions

* For $H_3^+$ with $\theta = 60^\circ$, $N(A) = N(B) = N(C)$ and $S(AB) = S(AC) = S(BC)$
was not the best obtainable with their limited basis set (three 1s orbitals, one on each nucleus) and fixed geometry. The calculations of Hopton and Linnett have been repeated using the wave function obtained for Z = 1.0 at \( \theta = 180^\circ \) as the "best" wave function.

The approximations to the wave function \( \Phi \) (see (3.5)) are the valence bond (\( \Phi_{\text{VB}} \)), the molecular orbital (\( \Phi_{\text{MO}} \)), and three non-pairing of electrons forms (\( \Phi_A, \Phi_B, \text{ and } \Phi_C \)). Using the notation of the ZHZ\(^{2Z-1} \) work, these functions may be defined thus:

\[
\Phi_{\text{VB}}(\overline{r}_1, \overline{r}_2) = N_{\text{VB}}[ (1s_B(\overline{r}_1) + k \cdot 1s_A(\overline{r}_1))(1s_B(\overline{r}_2) + k \cdot 1s_A(\overline{r}_2)) \\
+ (k \cdot 1s_B(\overline{r}_1) + 1s_A(\overline{r}_1))(1s_B(\overline{r}_2) + k \cdot 1s_A(\overline{r}_2)) \\
+ (1s_C(\overline{r}_1) + k \cdot 1s_A(\overline{r}_1))(k \cdot 1s_C(\overline{r}_2) + 1s_A(\overline{r}_2)) \\
+ (k \cdot 1s_C(\overline{r}_1) + 1s_A(\overline{r}_1))(1s_C(\overline{r}_2) + k \cdot 1s_A(\overline{r}_2)) ]
\]

\[
= N_{\text{VB}}[0.5k\Phi_1(\overline{r}_1, \overline{r}_2) + 2k\Phi_2(\overline{r}_1, \overline{r}_2) + 0.5k^2\Phi_3(\overline{r}_1, \overline{r}_2) \\
+ (k^2 + 1)\Phi_4(\overline{r}_1, \overline{r}_2)]
\]

\[
\Phi_{\text{MO}}(\overline{r}_1, \overline{r}_2) = N_{\text{MO}}[ (1s_B(\overline{r}_1) + k \cdot 1s_A(\overline{r}_1) + 1s_C(\overline{r}_2)) \\
\cdot (1s_B(\overline{r}_2) + k \cdot 1s_A(\overline{r}_2) + 1s_C(\overline{r}_2)) ]
\]

\[
= N_{\text{MO}}[0.5\Phi_1(\overline{r}_1, \overline{r}_2) + 0.5k^2\Phi_2(\overline{r}_1, \overline{r}_2) + k\Phi_4(\overline{r}_1, \overline{r}_2)]
\]

\[
\Phi_A(\overline{r}_1, \overline{r}_2) = N_A \left[ (1s_B(\overline{r}_1) + 1s_A(\overline{r}_1))(1s_C(\overline{r}_2) + 1s_A(\overline{r}_2)) \\
+ (1s_C(\overline{r}_1) + 1s_A(\overline{r}_1))(1s_B(\overline{r}_2) + 1s_A(\overline{r}_2)) \right]
\]
\[ N_A \left[ 0.25 \Phi_1(\overline{r}_1, \overline{r}_2) + \Phi_2(\overline{r}_1, \overline{r}_2) - 0.25 \Phi_3(\overline{r}_1, \overline{r}_2) + \Phi_4(\overline{r}_1, \overline{r}_2) \right], \]

\[ \Phi_B(\overline{r}_1, \overline{r}_2) = N_B \left[ (1s_B(\overline{r}_1) + k \cdot 1s_A(\overline{r}_1))(1s_C(\overline{r}_2) + k \cdot 1s_A(\overline{r}_2)) \right. \]

\[ + (1s_C(\overline{r}_1) + k \cdot 1s_A(\overline{r}_1))(1s_B(\overline{r}_2) + k \cdot 1s_A(\overline{r}_2)) \]

\[ = N_B \left[ 0.25 \Phi_1(\overline{r}_1, \overline{r}_2) + k^2 \Phi_2(\overline{r}_1, \overline{r}_2) - 0.25 \Phi_3(\overline{r}_1, \overline{r}_2) + k \Phi_4(\overline{r}_1, \overline{r}_2) \right], \]

\[ \Phi_C(\overline{r}_1, \overline{r}_2) = N_C \left[ (1s_B(\overline{r}_1) + k \cdot 1s_A(\overline{r}_1))(1s_A(\overline{r}_2) + k \cdot 1s_C(\overline{r}_2)) \right. \]

\[ + (1s_A(\overline{r}_1) + k \cdot 1s_C(\overline{r}_1))(1s_B(\overline{r}_2) + k \cdot 1s_A(\overline{r}_2)) \]

\[ + (k \cdot 1s_B(\overline{r}_1) + 1s_A(\overline{r}_1))(k \cdot 1s_A(\overline{r}_2) + 1s_C(\overline{r}_2)) \]

\[ + (k \cdot 1s_A(\overline{r}_1) + 1s_C(\overline{r}_1))(k \cdot 1s_B(\overline{r}_2) + 1s_A(\overline{r}_2)) \]

\[ = N_C \left[ 0.5k \Phi_1(\overline{r}_1, \overline{r}_2) + 2k \Phi_2(\overline{r}_1, \overline{r}_2) - 0.5k \Phi_3(\overline{r}_1, \overline{r}_2) \right. \]

\[ + (k^2 + 1) \Phi_4(\overline{r}_1, \overline{r}_2) \]
The parameter \( k \) was chosen so as to maximise the overlap between each approximation \( \phi_{\text{APP}} \) and \( \phi \). The general form of each approximation is the same as that of \( \phi \), i.e.

\[
\phi_{\text{APP}}(\vec{r}_1, \vec{r}_2) = \sum_i c_i \phi_i(\vec{r}_1, \vec{r}_2) \tag{5.1}
\]

with the coefficients \( c_i \) suitably calculated. Each approximation was normalized to unity. Two further approximate wave functions were introduced into the present work; these were the "best" rank 1 and 2 wave functions \( \phi_I \) and \( \phi_{\text{II}} \), namely

\[
\phi_I(\vec{r}_1, \vec{r}_2) = \chi_1(\vec{r}_1)\chi_1(\vec{r}_2)
\]

\[
= 0.5A_1^2\phi_1(\vec{r}_1, \vec{r}_2) + 0.5A_2^2\phi_2(\vec{r}_1, \vec{r}_2)
\]

\[
+ A_{11}A_{21}\phi_4(\vec{r}_1, \vec{r}_2)
\]

\[
\phi_{\text{II}}(\vec{r}_1, \vec{r}_2) = (n_1 + n_2)^{-1/2}\left[g_1\chi_1(\vec{r}_1)\chi_1(\vec{r}_2) + g_2\chi_2(\vec{r}_1)\chi_2(\vec{r}_2)\right]
\]

\[
= (n_1 + n_2)^{-1/2}\left[0.5g_1A_1^2\phi_1(\vec{r}_1, \vec{r}_2) + 0.5g_2A_2^2\phi_2(\vec{r}_1, \vec{r}_2)
\]

\[
+ 0.5g_2A_{32}^2\phi_3(\vec{r}_1, \vec{r}_2) + g_1A_{11}A_{21}\phi_4(\vec{r}_1, \vec{r}_2)\right].
\]

These are the natural expansions truncated after 1 and 2 terms and renormalized to unity. Since \( \phi \) is of rank 3 it is the "best" rank 3 wave function. Obviously \( \phi_I \) and \( \phi_{\text{II}} \) are expressible in the form of (5.1). The overlap between each approximation and \( \phi \),
\begin{table}
\centering
\caption{Approximations to $\Phi$ Each wavefunction expressed as $\Phi_{AP}=\sum c_i \Phi_i$}
\begin{tabular}{cccccccc}
\hline
 & $\Phi$ & $\Phi_I$ & $\Phi_{II}$ & $\Phi_{VB}$ & $\Phi_{MO}$ & $\Phi_A$ & $\Phi_B$ & $\Phi_C$ \\
\hline
Rank & 3 & 1 & 2 & 3 & 1 & 2 & 2 & 3 \\
\hline
$k$ & - & - & - & -0.02 & 1.781 & - & 0.93 & 2.55 \\
$c_1$ & 0.03371 & 0.05365 & 0.05298 & -0.00396 & 0.05365 & 0.04645 & 0.05035 & 0.03793 \\
$c_2$ & 0.12658 & 0.17021 & 0.16808 & -0.01583 & 0.17021 & 0.18582 & 0.17420 & 0.15173 \\
$c_3$ & -0.04555 & 0.00000 & -0.04560 & -0.00396 & 0.00000 & -0.04645 & -0.05035 & -0.03793 \\
$c_4$ & 0.24485 & 0.19111 & 0.18873 & 0.39600 & 0.19111 & 0.04645 & 0.18731 & 0.22327 \\
$\langle \phi \mid \phi_{AP} \rangle$ & 1.00000 & 0.98638 & 0.99888 & 0.98010 & 0.98638 & 0.99835 & 0.99867 & 0.99936 \\
Overlap & 1.00000 & 1.00000 & 1.00000 & 0.98010 & 1.00000 & 0.99948 & 0.99979 & 0.99936 \\
\hline
\end{tabular}
\end{table}
together with the overlap with the "best" wave function of the same rank are shown in Table 4.

Hopton and Linnett conclude that the non-pairing forms are the best because they have higher overlaps with $\phi$ than either $\phi_{VB}$ or $\phi_{MO}$. If this were so the occupation numbers of linear H$_3^+$ would be much closer to those of the dissociation products than to those of the united atom, since the non-pairing form implies a degree of spatial correlation. The atomic population $N(A)$ for nucleus A is almost three times that of centres B or C; this would seem unusual if there were a high degree of spatial correlation between the electrons.

The key to the misleading high overlaps of the non-pairing approximations with $\phi$ (a result preserved in this calculation) lies in the fact that the five approximate forms are of different rank. The theorem stated in Chapter 4 implies that there is an upper bound to the overlap integral $\int \phi^* \phi_{APP} dr_1 dr_2$ which is determined by the rank of $\phi_{APP}$. A comparison of greater validity than the straightforward comparison of values of this integral for different approximations is to determine the rank of $\phi_{APP}$ and then compare the overlap integrals between $\phi_{APP}$ and the "best" function of the same rank, since this then accounts for the mathematical limitation of the approximation as well as the chemical limitation. It is seen from Table 4 that $\phi_I$ and $\phi_{MO}$ are identical; a result suspected by Shull$^{35}$. This evidence confirms the conclusion that linear H$_3^+$ may be regarded as a three centre system because $\phi_{MO}$ is the best approximation to $\phi$.

As $\theta$ increases the kinetic energy undergoes an initial decrease for all values of $Z$ (Fig. 11). The decrease becomes greater as $Z$ is increased. When $Z = 1.0$, the kinetic energy becomes constant for $\theta > 90^\circ$, however, the curve for $Z = 2.2$ shows a pronounced
minimum when \( \theta \approx 60^\circ \), and a constant value is attained only when \( \theta > 140^\circ \). Figs. 12, 13, and 14 show that, for \( Z = 1.0 \), the other energy contributions are virtually constant when \( \theta > 90^\circ \). This lack of angular dependence indicates that, when \( \theta > 90^\circ \), the proton at centre A tends to dominate the \( H_3^+ \) system.

Ruedenberg\(^{(36)}\) has shown that a lowering of the kinetic energy may be associated with an increased "smoothness" of the electron density surface throughout the molecule. It is related in character to the lowering of the kinetic energy of potential free electrons when the volume containing them is increased. Thus the kinetic energy curves shown in Fig. 11 may be interpreted as a measure of the relative freedom of the electrons within the ions as \( \theta \) is increased. For example, when \( Z = 2.2 \) and \( \theta = 30^\circ \), the charge cloud is localized about the B-C region of the ion; hence the value of the kinetic energy is high. As \( \theta \) is increased to a value of 60°, the kinetic energy suffers a decrease, suggesting that the larger value for the B-C separation allows the charge cloud to become more diffuse. However, for a further increase in \( \theta \), the kinetic energy is seen to increase; this is consistent with the observation that, for \( Z = 2.2 \) the charge cloud will divide and become localized about the separate centres B and C, as approaches 180°. For \( Z = 1.0 \), a similar situation will occur, namely, as B and C separate, the charge cloud will become more diffuse, and the value of the kinetic energy will therefore decrease for an initial increase in \( \theta \). However, a continued increase of \( \theta \) causes the charge cloud to contract towards centre A instead of dividing and localizing it about each of the centres B and C, as was the case for \( Z = 2.2 \). Thus, for \( H_3^+ \) it is not surprising that the kinetic energy remains virtually constant for \( \theta > 90^\circ \). The curves for \( Z = 1.4 \)
and 1.8 shown in Fig. 11 are clearly states of transition between the
two cases already discussed. Additional support for the above inter­
pretation is gained by noting that, for each value of Z, the
dependence of the electron density evaluated at centre B (or C) has
the same form as the corresponding curve for the kinetic energy shown
in Fig. 11.

From Figs. 12, 13, and 14 we see that the electron repulsion energy,
nuclear attraction, and nuclear repulsion energies become slightly more
\( \theta \)-dependent as Z becomes larger. This is quite reasonable since
the foregoing analysis has shown that, as Z increases, the tendency for
the charge cloud to contract around the centres B and C will also increase
as \( \theta \) approaches 180°. Hence when the division of the charge cloud
becomes more effective, the drop in electron repulsion energy will become
greater, as shown in Fig. 12. For a fixed value of Z, Fig. 13 shows that
the nuclear attraction energy will increase for an increase in \( \theta \),
presumably related to the fact that the charge cloud will be influenced
less by the combined effect of the nuclei at B and C. The nuclear
repulsion energy curves shown in Fig. 14 are simply dependent on Z and
the geometry of the \( \text{ZH}_{Z}^{2Z-1} \) system.

The comparison of the results of the analysis for the \( \text{ZH}_{Z}^{2Z-1} \) ions
with the \( H_{3}^{+} \) calculation of Christoffersen is very valuable. However it
is rather limited because \( H_{3}^{+} \) is a member of the \( \text{ZH}_{Z}^{2Z-1} \) systems, and
the comparison does not indicate whether or not the unexpected behaviour
(the initial decrease in the optimum bond angle as Z increases from 0.8),
is simply a feature of these systems. Recent work (37) on a four-centre
four-electron system of the form \( \text{ZH}_{Z}^{2(Z-1)} \) shows that this behaviour is
not confined to the \( \text{ZH}_{Z}^{2Z-1} \) pseudomolecular ions. In the \( \text{ZH}_{Z}^{2(Z-1)} \)
system four electrons are associated with a planar nuclear framework of
four nuclei, and as the nuclear charge Z is increased from 0.8 to 2.4
the optimum ZHZ bond angle decreases. As Z becomes very large this angle goes through a minimum and approaches $180^\circ$ asymptotically. This seems to imply that the electron density of the four-centre system will behave in a way similar to that of the three-centre system; for a given ZHZ bond angle in the four-centre system, the increasing nuclear charges will firstly draw the charge cloud away from the protons towards the geometric centre of the system, and then the charge cloud will divide into two parts, each localized about the variable nuclear charges Z.

The detailed analysis of the wave functions for the four-centre four-electron systems is awaited with interest.
The wave functions of a series of pseudomolecular ions of the form $\text{ZH}^2\text{Z}^{-1}$, where $Z = 1.0 (0.4) 2.2$ were reformulated in terms of their natural expansions. Consequently it was possible to investigate changes in the one-particle density due to variations of $Z$ and the bond angle $\text{ZH} (\theta)$, by means of an electron population analysis similar to that of Mulliken. Contour diagrams were constructed for the one-particle density in the plane of the nuclei. In addition the behaviour of the kinetic energy, the nuclear attraction energy, the electron and nuclear repulsion energies as functions of $Z$ and $\theta$ were also examined.

For $Z \leq 1.4$, the first natural orbital in the natural expansion of the wave function was found to have a large occupation number for all values of $\theta$. Such a feature is essential, although by itself no guarantee, for obtaining molecular stability with respect to dissociation; nevertheless the results obtained here are in accord with the observation\textsuperscript{(25)} that the ions are energetically stable for $Z < 1.3$.

The occupation numbers of the natural orbitals for $\text{H}_3^+$ were placed in perspective by making a comparison with similar quantities for the united atom $\text{Li}^+$ and the dissociation products $\text{H} + \text{H} + \text{H}^+$. Such a comparison clearly reveals that $\text{H}_3^+$ possesses a strong united atom character. The contour diagrams also showed that, when $\theta = 60^\circ$, the "bonds" in $\text{H}_3^+$ were directed towards the centroid of the positive charges. The elaborate wave function of Christoffersen\textsuperscript{(22)}, analysed by Christoffersen and Shull\textsuperscript{(31)}, also revealed this "bonding" arrangement. For fixed bond lengths $\text{BA}$ and $\text{CA}$ (Fig. 3), as $\theta$ was increased, the charge moved from the centres B and C towards A, indicating that the proton dominates the linear $\text{H}_3^+$ system. These results do not support the conclusion that
non-pairing description is applicable to the linear $H_3^+$ ion; Shull\(^{(35)}\) has described it as "a relatively normal (albeit lengthened) single bond in which is embedded an additional proton", a description supported by the present analysis.

When $Z$ is large, the dissociation products of minimum energy have natural orbitals with occupation numbers of 0.5. This situation is most closely represented when $Z = 2.2$ and $\theta = 180^\circ$. The contour diagrams and electron population analysis show that, at large values of $Z$, the electron density in the region of centre A is small and, as $\theta$ increases, the charge cloud flows from the internuclear region B–C towards the "outer" nuclei. The diagrams and analysis also show that, as $Z$ increases and $\theta$ decreases, the $ZH_{Z-1}^{2Z}$ ions change from a three-centre system to what is essentially a two-centre system plus a strongly perturbing proton.

Of the various components of the energy of the $ZH_{Z-1}^{2Z}$ ions, the $\theta$ dependence of the kinetic energy is most striking. As emphasised by Ruedenberg, a decrease in magnitude of the kinetic energy may be associated with an increase in the spatial freedom of the electrons. This interpretation assisted not only with the understanding of the kinetic energy curves but also permitted variations in the remaining energy components to be understood.

The $ZH_{Z-1}^{2Z}$ calculation was originally conceived as a model of one of the bridge bonds of diborane. The unusual behaviour of the system, which precludes its use as such a model, is not, however, confined to this system. The initial results of a calculation on $ZH_{ZH}^{2(Z-1)}$\(^{(37)}\) indicate that its behaviour is somewhat similar to that of $ZH_{Z-1}^{2Z}$ but further detailed analysis will be required to determine the extent of the similarity. The results discussed here cast some doubt on the validity of the molecular fragment model as an indicator of the nature of the bonds
in a complete molecule; nevertheless, the analysis has afforded considerable insight into the energy changes and accompanying changes in electron density as $Z$ and $\theta$ vary within the simply $\text{ZH}_2^{2Z-1}$ pseudomolecular system.
PART II
CHAPTER 7
INTRODUCTION - THE METHOD OF CONFIGURATION
INTERACTION

The theoretical methods for constructing a Configuration Interaction (CI) wave function are reviewed in this chapter and their application to homonuclear diatomic molecules is described. Because of the ambiguity of the description of CI wave functions, the terminology used in Part II of this thesis is now defined:

(i) DETERMINANT: An antisymmetrized product of occupied spin-orbitals. It is an eigenfunction of the $S_z$ operator.
(ii) DETOR: A determinant constructed from a set of orthonormal spin-orbitals.
(iii) CONFIGURATION: A linear combination of determinants which is an eigenfunction of the total spin operator $S^2$; it is also a basis for an irreducible representation of the molecular symmetry group.
(iv) CODETOR: A configuration in which the determinants are detors.

It must be emphasised that although these definitions are adhered to in both Parts I and Part II of this thesis there is no generally accepted usage of the name configuration and some authors use it synonymously with determinant.

The positions of the nuclei within a molecule are fixed with respect to some co-ordinate system, referred to as the global co-ordinate system. The origin of this set of co-ordinates is chosen to be at some convenient point; for a homonuclear diatomic molecule the origin is at the mid-point of a line joining the nuclei. The global co-ordinate system will be a right-handed set of co-ordinates.

The atomic orbitals are defined with respect to local co-ordinate systems which have their origins are the nuclei. The local co-ordinate
systems are chosen to be parallel to the global co-ordinate system.

Both systems to be used for the homonuclear diatomic molecules are shown in Fig. 15; the internuclear axis OZ passes through the two nuclei A and B whose co-ordinates with respect to the global co-ordinate system are \((0,0,-R/2)\) and \((0,0,R/2)\) respectively.

![Diagram](image)

**FIG. 15.** The co-ordinate systems for a homonuclear diatomic molecule, OX, OY and OZ define the global co-ordinate system.

The general form of the atomic orbitals will be a product of a radial factor \(R(r)\) and an angular factor \(\Theta(\theta, \phi)\), where the co-ordinates \((r, \theta, \phi)\) refer to a local co-ordinate system:

\[
\omega_i(r, \theta, \phi) = R_i(r)\Theta_i(\theta, \phi) . \quad (7.1)
\]

It is usual to construct the molecular orbitals as linear combinations of atomic orbitals which transform according to an irreducible representation of the molecular symmetry group. This is achieved by use of the projection operator (see, for example Hammersmesh\(^{39}\)). In general, the projection operator may be written as:

\[
P(\mu) = \frac{n_\mu}{g} \sum_R \chi^{(\mu)*}(R)O_R . \quad (7.2)
\]
In (7.2) the superscript $\mu$ refers to a particular irreducible representation. $\chi(\mu)R$ is the character of the element $R$ in the $\mu$ irreducible representation, and $O_R$ is the operator corresponding to the element $R$. $\eta_\mu$ is the degree of the irreducible representation and $g$ the order of the group. The usual technique for obtaining the 'symmetry adapted' molecular orbitals (SAMOs) is to apply the projection operator for each irreducible representation to each of the members of the chosen set of atomic orbitals. The result is a number of linear combinations of atomic orbitals each of which transforms according to one of the irreducible representations of the molecular symmetry group, these combinations are the SAMOs.

Homonuclear diatomic molecules have an axis of symmetry of infinite order (the axis of the molecule, OZ in Fig. 15) and a centre of symmetry. Their symmetry group is $D_{\infty h}$, generated by the operations:
(i) the rotations $C_\eta$ about the axis of symmetry by an angle $\eta$ ,
(ii) the inversion $i$ in the centre of symmetry,
(iii) a reflection $\sigma$ in the plane of symmetry containing the internuclear axis.

Because the axis of symmetry is of infinite order it is necessary to replace the summation in (7.2) by an integration with limits $0$ and $2\pi$ , the integrand being $\eta$ . The projection operator for the group $D_{\infty h}$ has the form

$$P(\mu) = \frac{x}{2\pi} \left[ \int_0^{2\pi} \chi(\mu)^*(C_\eta) O_{C_\eta} d\eta + \int_0^{2\pi} \chi(\mu)^*(iC_\eta) O_{iC_\eta} d\eta ight] + \int_0^{2\pi} \chi(\mu)^*(\sigma C_\eta) O_{\sigma C_\eta} d\eta + \int_0^{2\pi} \chi(\mu)^*(i\sigma C_\eta) O_{i\sigma C_\eta} d\eta ] \quad (7.3)$$
### Table 5. The Character Table of $D_{\infty h}$

<table>
<thead>
<tr>
<th>$\mu$</th>
<th>$E$</th>
<th>$C_\eta$</th>
<th>$iC_\eta$</th>
<th>$\sigma C_\eta$</th>
<th>$i\sigma C_\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Sigma^+ g$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\Sigma^+ u$</td>
<td>1</td>
<td>1</td>
<td>$-1$</td>
<td>1</td>
<td>$-1$</td>
</tr>
<tr>
<td>$\Sigma^- g$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>$-1$</td>
<td>$-1$</td>
</tr>
<tr>
<td>$\Sigma^- u$</td>
<td>1</td>
<td>1</td>
<td>$-1$</td>
<td>$-1$</td>
<td>1</td>
</tr>
<tr>
<td>$\Pi g$</td>
<td>2</td>
<td>$2\cos \eta$</td>
<td>$2\cos \eta$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\Pi u$</td>
<td>2</td>
<td>$2\cos \eta$</td>
<td>$-2\cos \eta$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\Delta g$</td>
<td>2</td>
<td>$2\cos 2\eta$</td>
<td>$2\cos 2\eta$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\Delta u$</td>
<td>2</td>
<td>$2\cos 2$</td>
<td>$-2\cos 2$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\Gamma g$</td>
<td>2</td>
<td>$2\cos 4\eta$</td>
<td>$2\cos 4\eta$</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
The character table for $D_{\infty h}$ is given in Table 5 and the specific application of the operator to complex Slater-type orbitals is given in Appendix II.

The construction of the secular equation is greatly simplified if the basis set of molecular orbitals is orthonormal. This may be achieved in two basic ways. The first method is to compute the overlap matrix for the non-orthonormal SAMOs. Let this matrix be $S$. The elements of $S$ are

$$s_{ij} = \int \varphi_i^* \varphi_j \, dr, \quad (7.4)$$

$\varphi_i$ and $\varphi_j$ are members of the set of non-orthonormal SAMOs. $S$ has the property of being real symmetric positive definite matrix so that it is possible to Choleski decompose it into the product of a lower triangular matrix $L$ and its transpose $L^T$:

$$S = LL^T, \quad (7.5)$$

and

$$L^{-1}S(L^T)^{-1} = I \quad (7.6a)$$

where $I$ is the identity matrix. The inverse of a lower triangular matrix is also lower triangular and $(L^T)^{-1}$ will be upper triangular. Let

$$U = (L^T)^{-1}$$

$$U^T = L^{-1}$$
(7.6a) may be written

\[ U^T S U = I \]  \hspace{1cm} (7.6b)

The set \( \{ \varphi_i \} \) of orthonormal SAMOs is now defined by

\[ \varphi_i = \sum_{j=1}^{1} \varphi_j^I u_{ji} \]  \hspace{1cm} (7.7)

where \( u_{ji} \) is an element of \( U \). It is immediately obvious from (7.7) that the orbital \( \varphi_i \) has the form produced by the technique known as the Schmidt orthogonalization process \(^{(40)}\). It has been found that the approach described leads to more stable numerical results than the straightforward application of the Schmidt procedure \(^{(40, 41)}\). The second method is that of simultaneous orthonormalization in which the eigenvectors of \( \mathbf{S} \) are divided by the square root of the corresponding eigenvalue; the resulting matrix may then be used as in (7.7), but the summation runs over all possible values of \( j \). A set of orthonormal symmetry adapted molecular spin orbitals may then be constructed according to (1.5).

A detor is defined as an antisymmetrized product of occupied spin-orbitals. The antisymmetrizer \( \mathbf{a} \) \(^{(12)}\) is a permutation operator which commutes with the Hamiltonian \( \mathbf{H} \), \( \mathbf{S}^2 \), \( \mathbf{S}_z \), and the group theoretical operators. Consequently a detor may be specified by defining the appropriate product of occupied spin-orbitals. For this purpose an 'ordered product' \( P_K \) of occupied spin orbitals is employed. If \( \psi_{k1}, \psi_{k2}, \ldots, \psi_{kn} \) are members of the chosen set of molecular spin-orbitals, then

\[ P_K = \psi_{k1}^{(1)} \psi_{k2}^{(2)} \cdots \psi_{kn}^{(n)} \]
where the spin-orbital identifiers $k_1, k_2, \ldots, k_n$ satisfy the condition

$$k_1 < k_2 < k_3 < \ldots < k_n \quad . \tag{7.8}$$

The corresponding detor $D_K$ is then given by

$$D_K = \mathcal{A} P_K$$

$$\quad = (n!)^{-1/2} \begin{vmatrix} \psi_{k_1(1)} \psi_{k_2(1)} & \cdots & \psi_{k_n(1)} \\ \psi_{k_1(2)} \psi_{k_2(2)} & \cdots & \psi_{k_n(2)} \\ \cdots & \cdots & \cdots \\ \psi_{k_1(n)} \psi_{k_2(n)} & \cdots & \psi_{k_n(n)} \end{vmatrix} \quad . \tag{7.9}$$

Obviously $P_K$ represents the diagonal of $D_K$, and the detor is an 'ordered detor'. The selection of the detors is equivalent to the choice of the $P_K$s. A basis set of $N$ molecular spin-orbitals gives rise to $N! / (N-n)! n!$ different ordered products of molecular spin-orbitals in an $n$-electron problem. For a sixteen electron system a minimal basis set of twenty spin-orbitals produces 4845 ordered products of spin-orbitals. This large number is drastically reduced by considerations of electron spin and molecular symmetry. A further reduction in the number of detors contributing to the wave function for a given state may be achieved by an artifact, employed Meckler\(^{42}\), Kotani and his colleagues\(^{43}\); Harris and Michels\(^{44}\) call it the 'Valence Configuration Interaction' (VCI) method. In the VCI method detors are constructed from valence shell orbitals; Meckler's CI on Oxygen uses the detors derived from the assignment of eight electrons to twelve SAMOs constructed from six p-type Gaussian-type orbitals, three on each nucleus. Kotani et alia\(^{43}\) extended the approach to include the 2$s$ orbitals. Thus in the former
calculation each detor had a closed shell or 'frozen core' of electrons occupying the 1s and 2s orbitals, and in the latter only the 1s shell was frozen. The drastic freezing of the core by Meckler reduced the total number of detors to 495, of which only 31 had the correct symmetry and electron spin properties. The results of the calculations of Kotani et alia are in good agreement with experimental results. It is concluded \((44,45)\) that to cause the orbitals, with principle quantum numbers less than that of the valence shell, to be occupied in every detor is a restriction of almost negligible effect.

The selection of the \(P_x\)'s is a simple process. The frozen core is assumed to consist of the first \(m\) orbitals in each detor, and the process begins by selecting the first \((n - 1)\) spin-orbitals with the lowest identifiers and allowing the \(n^{th}\) spin-orbital to take the values of the remaining \((N-n)\) identifiers. The identifier of spin-orbital \((n-1)\) is increased by one and the process is repeated, working along the ordered product until the \(m^{th}\) spin-orbital is reached. As an example consider the basis set of \(\psi_1, \psi_2, \psi_3, \psi_4, \psi_5,\) and \(\psi_6\) for a four electron system with two frozen orbitals; six \(P_x\) are generated,

\[
\begin{align*}
P_1 &= \psi_1(1)\psi_2(2)\psi_3(3)\psi_4(4) \\
P_2 &= \psi_1(1)\psi_2(2)\psi_3(3)\psi_5(4) \\
P_3 &= \psi_1(1)\psi_2(2)\psi_3(3)\psi_6(4) \\
P_4 &= \psi_1(1)\psi_2(2)\psi_4(3)\psi_5(4) \\
P_5 &= \psi_1(1)\psi_2(2)\psi_4(3)\psi_6(4) \\
P_6 &= \psi_1(1)\psi_2(2)\psi_5(3)\psi_6(4) \\
\end{align*}
\]

The ordered products \(P_1, P_3, P_4,\) and \(P_6\) correspond to \(S_z = 0\), while \(P_2\) has \(S_z = 1\) and \(P_5\) has \(S_z = -1\). In the construction of codetors with a total spin eigenvalue of 0, \(P_2\) and \(P_5\) would be omitted because \(S \neq |S_z|\). The construction of the eigenfunctions of \(S^2\) is more
difficult and several approaches are possible. Because of its computational simplicity, the method selected in the present work is based on the diagonalization of the operator $S_i^2$ over the chosen set of detors. The matrix involved has $\langle D_k | S_i^2 | D_L \rangle$ as its elements and as the antisymmetrizer commutes with $S_i^2$, these elements may be calculated as $\langle P_k | S_i^2 | P_L \rangle$.

The total spin operator may be written

$$S_i^2 = S_+ S_- + S_z^2 - S_z^2,$$  \hspace{1cm} (7.10)

where $S_+$ and $S_-$ are the 'step-up' and 'step-down' operators. The effect of $S_z^2$ and hence $S_z^2$ on a product of spin-orbitals is given by (1.9). $S_+$ and $S_-$ must be expanded as

$$S_+ = \sum_{i=1}^{n} S_{i+},$$ \hspace{1cm} (7.11a)

and

$$S_- = \sum_{i=1}^{n} S_{i-}.$$ \hspace{1cm} (7.11b)

The operators $S_{i+}$ and $S_{i-}$ are one-electron operators which act on the spin orbitals, defined according to (1.5), as shown in (7.12)

$$s_+ \psi_{2i-1} = s_+ \varphi_i \alpha = 0$$

$$s_- \psi_{2i-1} = s_- \varphi_i \alpha = \varphi_i \beta = \psi_{2i}$$

$$s_+ \psi_{2i} = s_+ \varphi_i \beta = \varphi_i \alpha = \psi_{2i-1}$$

$$s_- \psi_{2i} = s_- \varphi_i \beta = 0$$ \hspace{1cm} (7.12)
Applying $S^2$ to $P_3$:

\[ S^2 P_3 = S^2(\psi_1\psi_2\psi_3\psi_6) = S_+ S_- (\psi_1\psi_2\psi_3\psi_6) + 0 \cdot P_3 \\
= S_+ ((\psi_1\psi_2\psi_3\psi_6) + (\psi_1\psi_2\psi_4\psi_5)) \\
= (\psi_1\psi_2\psi_3\psi_6) + (\psi_2\psi_1\psi_3\psi_6) + (\psi_2\psi_2\psi_3\psi_5) \\
+ (\psi_1\psi_1\psi_4\psi_6) + (\psi_1\psi_2\psi_3\psi_6) + (\psi_1\psi_1\psi_4\psi_5) \cdot (7.13) \]

There are six terms in (7.13); the first is $P_3$, the second $P_3$ since $\psi_1$ and $\psi_2$ have to be interchanged to produce an ordered product, the third and fourth terms are zero because of the double occupancy of a spin-orbital which causes the corresponding detor to vanish, the fifth term is $P_3$ and the last $P_4$. Thus,

\[ S^2 P_3 = P_3 + P_4 \cdot (7.14) \]

It is seen from (7.12) and (7.13) that (7.14) can be obtained simply by applying the $S^2$ operator to the unfrozen orbitals $\psi_3$ and $\psi_6$. This is because the frozen core is an eigenfunction of $S^2$ with $S = 0$.

The final step of evaluating $\langle P_X | S^2 | P_L \rangle$ is achieved using the knowledge that

\[ \langle P_X | P_L \rangle = \delta_{KL} \]

where the integration is performed over the spin co-ordinates. Using the approach described in the next chapter it is possible to ensure that the resulting matrix is block diagonal, and it may be diagonalized by any suitable method\(^{13}\). The foregoing remarks concerning the construction
of spin eigenfunctions apply equally well to determinants.

The detors are constructed from an orthonormal set of symmetry adapted molecular spin-orbitals. The most suitable atomic orbitals for problems concerning diatomic molecules are complex Slater-type orbitals; the normalized form of these is

\[ \omega(n,l,m) = R_n(r)Y_{lm}(\theta,\phi) \quad , \quad (7.15a) \]

where

\[ R_n(r) = \left[ \frac{(2l)^{2n+1}}{(2n)!} \right]^{1/2} \frac{1}{r^{n-1}} \exp(-lr) \quad , \quad (7.15b) \]

and

\[ Y_{lm}(\theta,\phi) = \frac{(-1)^{1+m}}{2^{1+1}!} \left[ \frac{(2l+1)(1-|m|)!}{4\pi (1+|m|)!} \right]^{1/2} \sin^{|m|}\theta \]

\[ \left[ \frac{d}{d\cos\theta} \right]^{1+|m|} \sin2\theta \exp(jm\phi) \quad . \quad (7.15c) \]

The orbital is defined with respect to a local co-ordinate system, \( R_n(r) \) is a normalized radial function, \( Y_{lm}(\theta,\phi) \) is a spherical harmonic and \( j = \sqrt{-1} \). The SAMOs for a diatomic molecule are characterized by the component of the orbital angular momentum in the z-direction (the axial angular momentum and equal to \( m \) in primary units) of their constituent orbitals (see Appendix II). The axial angular momentum \( \Lambda \) of an orbital product and its corresponding detor may be obtained simply by summing the values of the magnetic quantum number \( m \) (7.15) of the constituent molecular spin orbitals, i.e.

\[ \Lambda = \sum_{i=1}^{n} m_i \quad . \quad (7.16) \]
The corresponding irreducible representation is partly determined by the value of $\Lambda$; $\Lambda = 0, 1, 2, \ldots$ gives rise to the $\Sigma$, $\Pi$, $\Delta$, $\ldots$ states of diatomic molecules. Under the operation of inversion the detor either remains unchanged (gerade or $g$) or changes sign (ungerade or $u$). The orbital product is gerade if it contains an even number of gerade spin orbitals, otherwise it is ungerade. Thus a detor may be characterized by the symbol $\Lambda^i$, where $i$ is replaced by $g$ for gerade detors and $u$ for ungerade detors. The $\Sigma$ detors are also characterized by their behaviour under the reflection $\sigma$ in the plane containing the internuclear axis. The operation $\sigma$ is most conveniently considered in one of the co-ordinate planes of the global co-ordinate system (i.e. the $xz$- or $yz$- planes [14, 40]). The result of such a reflection on each individual spin-orbital may be easily obtained. The reflection operator is applied simultaneously to each orbital in the ordered product; there are four possible results, summarized in (7.17).

$$\sigma P_L = \pm P_L \quad (7.17a)$$
$$\sigma P_L = \pm P_K \quad (7.17b)$$

If the wave function changes sign the superscript $-$ is added to $\Sigma$ and if the sign is unchanged the superscript $+$ is added. Thus, (7.17a) produces either a $+$ or $-$ state, while (7.17b) gives both.

When the total spin eigenfunctions have been obtained it is a simple matter to combine them to form codetors. In matrix notation the codetors are defined as

$$\psi_{\Sigma \sigma} = DT \Sigma \sigma \quad (7.18)$$
\[ \psi_{S\sigma} \] is a row vector with elements that are simultaneously eigenfunctions of \( S^2 \) and \( \sigma \). \( D \) is a row vector of detors, each corresponding to the same values of \( S_z \) and \( \Lambda_1 \). The matrix \( T_{S\sigma} \) can be regarded as a projection matrix which projects \( \psi_{S\sigma} \) from \( D \). The elements of \( T_{S\sigma} \) are determined by the methods previously described.

Having obtained the codetors which transform according to the molecular state being investigated, it is possible to proceed with the evaluation of the matrix elements:

\[ H_{IJ} = \langle \psi_I | \hat{H} | \psi_J \rangle \tag{1.13a} \]

and

\[ S_{IJ} = \langle \psi_I | \psi_J \rangle \tag{1.13b} \]

From (7.18)

\[ \psi_I = \sum_K D_K t_{KI} \tag{7.19} \]

Substitution of (7.19) into (1.13) gives

\[ H_{IJ} = \sum_K \sum_L t_{IK} t_{LJ} \langle D_K | \hat{H} | D_L \rangle \tag{7.20a} \]

and

\[ S_{IJ} = \sum_K \sum_L t_{IK} t_{LJ} \langle D_K | D_L \rangle \tag{7.20b} \]

The problem reduces to the evaluation of \( \langle D_K | \hat{H} | D_L \rangle \) and \( \langle D_K | D_L \rangle \), the elements of two matrices \( H_D \) and \( S_D \). In matrix notation (7.20) becomes

\[ H = T_{S\sigma}^T H D T_{S\sigma} \tag{7.21a} \]
and

\[ S = T_{S\sigma}^T S_{D\sigma} T_{S\sigma} \]  \hspace{1cm} (7.21b)

\( T_{S\sigma} \) is the transpose of \( T_{S\sigma} \). Löwdin\(^{(8)}\) has given general formulae for evaluating the elements of \( H_D \) and \( S_D \) in terms of integrals over basis orbitals when determinants are used. Evaluation of these formulae requires a considerable computational effort, and a simpler form produced for detors will be employed. Before evaluating the elements of \( H_D \) and \( S_D \) each pair of detors must be brought into maximum coincidence, this means that those spin-orbitals common to both detors must occupy the same columns in both. For each pair of detors

\[ <D_K|D_L> = \delta_{KL} \]  \hspace{1cm} (7.22)

The evaluation of \( <D_K|\bar{\Psi}|D_L> \) is split into two parts as shown in (7.23)

\[ <D_K|\bar{\Psi}|D_L> = <D_K|\sum_{\mu=1}^{n} h_\mu |D_L> \]

\[ + <D_K|\sum_{\mu<\nu} g_\mu \nu |D_L> \]  \hspace{1cm} (7.23)

There are four cases to be considered in the evaluation of the two terms in (7.23):

(i) \( D_K \) and \( D_L \) are identical,

(ii) \( D_K \) and \( D_L \) differ by one spin-orbital, \( \psi_m \) entering \( D_K \) where \( \psi_p \) enters \( D_L \);

(iii) \( D_K \) and \( D_L \) differ by two spin-orbitals, \( \psi_m \) and \( \psi_n \) entering \( D_K \) where \( \psi_p \) and \( \psi_q \) enter \( D_L \), and

(iv) \( D_K \) and \( D_L \) differ by more than two spin-orbitals
The following notation will be used:

\[ h_{ij} = \int \psi_i^*(1) h_1 \psi_j(1) dx_1 \, , \quad (7.24) \]

\[ [ij|kl] = \int \int \psi_i^*(1) \psi_k^*(2) (1/r_{12}) \psi_j(1) \psi_2(2) dx_1 dx_2 \, , \quad (7.25) \]

\[ J_{ij} = [i i | j j] \, , \quad (7.26) \]

\[ K_{ij} = [i j | j i] \, . \quad (7.27) \]

Thus,

\[ \langle D_K | \sum_{\mu=1}^{n} h_{\mu i} | D_L \rangle \begin{cases} = \sum_{i} h_{ii} \text{ for case (i)} \\ = h_{mp} \text{ for case (ii)} \\ = 0 \text{ for cases (iii) and (iv)}, \end{cases} \quad (7.28) \]

and

\[ \langle D_K | \sum_{\mu<\nu} g_{\mu \nu} | D_L \rangle \begin{cases} = \sum_{i j} (J_{ij} - K_{ij}) \text{ for case (i)} \\ = \sum_{i \neq m} ([i i | m p] - [i p | m i]) \text{ for case (ii)} \\ = [m p | n q] - [m q | n p] \text{ for case (iii)} \\ = 0 \text{ for case (iv)} \end{cases} \quad (7.29) \]
In (7.28) the summation is over all the occupied orbitals in $D_k$ for case (i) and in (7.29) the double summation for case (i) is over all the occupied orbitals in $D_k$; the single summation of case (ii) excludes the orbital $\psi_m'$ in $D_k$ and $\psi_p'$ in $D_L'$. The integrals of (7.24) to (7.27) can be reduced to integrals over spatial orbitals using the relation of (1.5) and the knowledge that the spin functions may be factored off and integrated separately. The integrals are normally computed over the basis atomic orbitals, and are then transformed directly into integrals over the orthonormal SAMOs. For the diatomic molecules this procedure is as follows:

\[ \varphi_i' = \sum_j \omega_i' \sigma_j' \]  
\[ \text{(7.30a)} \]

or in matrix form

\[ \varphi' = \omega \sigma' \]  
\[ \text{(7.30b)} \]

The $\varphi_i'$ are non-orthonormal SAMOs, which are then orthonormalized by one of the methods described, so that

\[ \varphi_k = \sum_i \varphi_i' \sigma_{ik} \]  
\[ \text{(7.31a)} \]

or in matrix form

\[ \varphi = \varphi' \sigma \]  
\[ \text{(7.31b)} \]

Combining (7.30) with (7.31) gives

\[ \varphi = \omega \varphi' \sigma = \omega \sigma \]  
\[ \text{(7.32)} \]
The integrals $h_{ij}$ are the elements of the one-electron Hamiltonian matrix $H$, hence the transformation to integrals over the set $\{\phi_i\}$ takes the form of a matrix product

$$h = C^T \bar{h} \omega C,$$  \hspace{1cm} (7.33)

where the elements of $\bar{h}$ are the integrals

$$\int \omega_i^*(\mathbf{r}) h_{ij} \omega_j(\mathbf{r}) d\mathbf{r}.$$  

Because of the large number of two-electron integrals the transformation of these integrals requires special consideration. The total number of two-electron integrals is equal to the fourth power of the number of basis atomic orbitals. For integrals yielding real results the following relations hold

$$[ij|kl] = [kl|ij] = [ji|lk] = [lk|ji] \quad (7.34a)$$

and

$$[ji|kl] = [kl|ji] = [ij|lk] = [lk|ij]. \quad (7.34b)$$

In (7.34) the integrals are over spatial orbitals, but the electron ordering is as in (7.25);

For diatomic molecules integration over the azimuthal angle gives a non-zero result only if the magnetic quantum numbers of the orbitals involved satisfy the condition

$$m_j - m_i = m_k - m_l \quad . \hspace{1cm} (7.35)$$

The transformation of the two-electron integrals for a diatomic molecule can be speeded up if the transformed orbitals have values of $m$ in the same order as the original atomic basis set, because (7.35) can be applied at each stage of the transformation. The inference of (7.35) is that in general either (7.34a) or (7.34b) is zero, or both are zero for one- and
two-centre two-electron integrals.

It is possible to index the integrals according to the scheme

\[ n_r = \frac{1}{2}(\max(i,j)(\max(i,j) - 1)) + \min(i,j) \]

\[ n_e = \frac{1}{2}(\max(k,l)(\max(k,l) - 1)) + \min(k,l) \]  \hspace{1cm} (7.36)

The two electron integrals are generated (see Chapter 8) according to the rules that \( i \geq j \), \( k \geq l \), and \( n_r \geq n_e \). The actual transformation proceeds in two stages. The first stage is

\[ [\omega_\mu \omega_\nu | \psi_i \psi_j] = \sum_{\lambda} \sum_{\sigma} c_{\lambda k} c_{\sigma l} [\omega_\mu \omega_\nu | \psi_k \psi_l] \hspace{1cm} (7.37a) \]

where \( \mu \), \( \nu \), \( k \), and \( l \) take all possible values, whilst \( \lambda \) and \( \sigma \) are subject to the condition \( \lambda \geq \sigma \). The second stage is

\[ [\psi_i \psi_j | \psi_k \psi_l] = \sum_{\mu} \sum_{\nu} c_{\mu i} c_{\nu j} [\omega_\mu \omega_\nu | \psi_k \psi_l] \hspace{1cm} (7.37b) \]

Once the matrix elements between the detors have been computed, the transformation of (7.21a) is performed to obtain the matrix elements \( H_{ij} \) \hspace{1cm} (1.13a). As a consequence of (7.22), the matrix \( S \) of (7.21b) is the identity matrix, since the columns of \( T_{\sigma \sigma} \) are of necessity orthonormal.

Kotani et alia\(^{(12)}\) have proposed an alternative method for computing the matrix elements \( H_{ij} \). Their method, based on the idea of representation matrices, appears to suffer from two disadvantages. Firstly it is desirable to know the wave function \( \Psi \) \hspace{1cm} (1.1) as a linear combination of detors since the first order density matrix, used to compute molecular properties, can most easily be computed from a wave function in the form of (1.7). Extracting this form from the method described is almost a trivial
exercise; to obtain it from the method of Kotani, although feasible, is far from easy, as the actual detors are never defined. Secondly, once the matrix elements between detors for a given $\Lambda_1$ and $S_Z$ have been evaluated, it is possible to set up matrix elements between codetors belonging to several 'reflection' and total spin states merely by changing the projection matrix $T_{S\sigma}$. This in itself represents a considerable saving in computer time as Kotani's method demands searches of the integral files (see Chapter 8) for each molecular state.

The final step in the method of Configuration Interaction is the solution of the secular equation which may be written as

$$
(H - E_1)A = 0 \quad .
$$

The energies $E_1$ are the eigenvalues of $H$, $A$ is a column vector, an eigenvector of $H$ corresponding to a particular $E_1$. Two possible methods of solving (7.38) are the method of Jacobi and the QR-Algorithm, both described by Wilkinson. The latter method is preferred, since it is currently the fastest method available for finding the eigenvalues and eigenvectors of a real symmetric matrix.

At this point it is convenient to discuss the construction of the first order density matrix, as all of the information required is available. For the $I$-th energy of a given molecular state the wave function $\Psi$ is

$$
\Psi = \sum_L \Psi_L a_{LI} \quad .
$$

where the $a_{LI}$ are the elements of the eigenvector corresponding to the energy $E_1$ of this level. The codetors $\Psi_L$ may be replaced by a sum of detors according to (1.10), so

$$
\Psi = \sum_K D_k \sum_L t_{KL} a_{LI} \quad .
$$
The coefficient of $D_k$ may be simply written as $b_{KI}$,

$$b_{KI} = \sum_L t_{KL} a_{LI} \quad (7.40)$$

According to Löwdin\(^8\) the elements $\gamma(l|k)$ of the first order density for the $I$-th energy level are given by

$$\gamma(l|k) = \sum_K \sum_L b_{KI} b_{LI} D_{KL}(k|l) \quad (7.41)$$

where $D_{KL}(k|l)$ is the cofactor of the term due to $\int \psi_k^*(1) \psi_l(1) dx_1$ in the integral $\langle D_K | D_L \rangle$. The summation over $K$ is over those determinants $D_K$ which contain spin-orbital $\psi_k$ and that over $L$ is over those determinants $D_L$ which contain $\psi_l$. If the determinants are in fact detors (7.41) is easily evaluated, because there are only two conditions under which $D_{KL}(k|l)$ is non-zero. The first is when $K = L$ in which case $D_{KL}(k|l) = \delta_{kl}$. The second is when $D_K$ and $D_L$ differ by one spin-orbital, $\psi_k$ appears in the $i$-th column of $D_k$ and $\psi_l$ appears in the $j$-th column of $D_L$, in this case

$$D_{KL}(k|l) = (-1)^{i+j} \quad (7.42)$$

and all other cofactors are zero. The first order density matrix so obtained is in terms of the orthonormal molecular spin-orbitals and may be used in the calculation of molecular properties (see Chapter 11). The first order density matrix may also be diagonalized to provide occupation numbers and the transformation matrix which carries the set $\{\psi_i\}$ into the natural spin-orbitals $\{x_k\}$ \(^8\).
CHAPTER 8

COMPUTATIONAL METHODS

The philosophy behind the programming of the methods described in the previous chapter has been to generalize wherever possible: a program capable of computing one- and two-centre integrals is not used if only one-centre integrals are required because the more general program is extremely inefficient if used in this way. Only one integral transformation program is used because the process is the same for both types of integrals. With one exception all subprograms are written in the FORTRAN V language\(^{(49)}\) for the ICL Atlas Computer. The one exception is a function subprogram, the body of which is written in Atlas Basic Language (ABL)\(^{(50)}\). Several distinct programs were written because some of the results produced at each stage may be used for other purposes; the integrals may be used in both CI and SCF programs. A set of subprograms used by more than one of the programs is listed in Appendix III under the heading of 'Utility Routines'. Considerable use of facilities not provided in other implementations of FORTRAN is made and, as a result, easier checking and correction of programs and greater efficiency has been achieved. The Atlas AMPEX one inch tape system uses pre-addressed tapes with numbered blocks, each of which store 512 words of Atlas information\(^{(51)}\). The Atlas disc store is used in exactly the same way. The programs to be described use these tapes and disc areas in the variable length mode and information from a particular run of a program constitutes a 'file' which may be placed anywhere on the tape or disc area merely by positioning the appropriate device at the block and word at which the file is to begin. As a safeguard no two programs may write on the same tape or disc area. The programming problem breaks down into four distinct parts:
(a) Generation of the codetors,
(b) Evaluation of the integrals over the atomic orbital basis set,
(c) Transformation of the integrals to an orthonormal basis set, and
(d) Construction and solution of the secular equation.

A. Generation Codetors

The program which generates the detors is called GENDET and is listed in Appendix IV. This program generates the ordered spin orbital products \( P_k \) of (7.9). These products are eigenfunctions of the operator \( S_z \) corresponding to an eigenvalue \( S_z \), they possess a given axial angular momentum \( \Lambda \), and are of either gerade or ungerade symmetry. The required values of \( S_z \) and \( \Lambda \) together with the inversion symmetry are specified in the data. Facilities are provided for freezing the inner-shell electrons. The data also contains the total number of electrons, the number in the frozen shell, and the number of spin-orbitals. The magnetic quantum number, inversion symmetry and the identifier of the orbital resulting from a reflection in the XZ-plane must be provided for each spin-orbital. The spatial parts of the orbitals are identified by use of (1.5). The calculation begins with the generation of all possible ordered spin orbital products. This is essentially the selection of \( n \) spin-orbitals from a total of \( N \) spin-orbitals where \( n \) is the number of electrons outside the frozen shell, and \( N \) the number of unfrozen spin-orbitals. This is accomplished by the subroutine COMBIN. The parameter list of this subroutine contains a logical variable which causes the first spin-orbital product \( P_1 \) to be generated when set equal to TRUE,

\[
P_1 = 1, 2, 3, \ldots, n - 1, n
\]

\[
= \psi_1 \psi_2 \psi_3 \cdots \psi_{n-1} \psi_n
\]
and the logical variable is set equal to FALSE. The subprogram then uses \( P_1 \) to generate \( P_2 \), \( P_2 \) to generate \( P_3 \), and the process continues until the last one is reached, this has the form

\[
P_{\text{LAST}} = N - n, N - n + 1, \ldots, N - 1, N
\]

\[
\equiv \psi_{N-n} \psi_{N-n+1} \ldots \psi_{N-1} \psi_N
\]

On encountering the final ordered product \( \text{COMBIN} \) will regenerate \( P_1 \), but the logical variable is reset to TRUE, and if this value is returned from the subprogram control passes to the next stage. As each \( P_K \) is generated it is tested in the subroutine SETUP to see if it has the correct values of \( S_z \), \( \Lambda \), and the required inversion symmetry. If it satisfies these requirements it is stored as a row of the two-dimensional array \( IS^\phi \). The number of entries is \( IS^\phi \) and the total number of \( P_K \) generated is counted.

The next step in the program is a call of the subroutine SPINIR which checks the inversion symmetry of each \( P_K \) and evaluates the matrix elements \( \langle P_L | \mathcal{S}^2 | P_K \rangle \). For \( \Lambda = 0 \), i.e. \( \sum \) products, SPINIR computes the effect on \( P_K \) of a reflection in the \( XZ \)-plane. Any one of these operations must produce a linear combination of the entries in \( IS^\phi \). In general the process proceeds as follows: consider an operator \( \mathcal{O} \) which may be either \( \sigma, \mathcal{S}^2 \), or \( i \), then

\[
\mathcal{O} P_K = \sum_{L} P_L^\dagger L K
\]

In (8.1) \( P_L^\dagger \) is a spin-orbital product which may not be ordered; therefore the elements of \( P_L^\dagger \) are permuted by the subroutine PERMUT to produce an ordered spin-orbital product \( P_L \), and the parity of the permutation is also obtained. \( P_L \) is then identified with an entry in \( IS^\phi \) by the subroutine \( \text{C\O LATE} \). If \( P_L \) cannot be found in \( IS^\phi \) an error message is printed and
execution ceases. The evaluation of \( \langle P_L | S^2 | P_K \rangle \) begins with
the application of the \( S^+ \) operator to the singly occupied orbitals of
\( P_K \). For the purpose of this operation the spins of the spin-orbitals in
\( P_K \) are identified as \( \alpha \), if the entry in the row of \( I S^\# \) corresponding
to \( P_K \) is odd, and \( \beta \) if the entry is even (this is in accordance with
(1.5)). The result of this operation is similar to (8.1), and the products
\( P_L \) are entered in a two-dimensional array \( I S^\# P \). The \( S^+ \) operator is then
applied to the entries in \( I S^\# P \) and the resulting spin-orbital products
are held as rows in the array \( I S^\# P \). By use of the subroutines PERMUT and
C\#LATE the values of \( C_{LX} \) in (8.1) are determined. For each \( P_K \) the values
of \( L \) for which \( C_{LX} \) is non-zero after the operation \((S^2_{Z} - S^2_{Z})\) are stored
in the array \( C^\#L \), and the non-zero value of \( C_{LX} \) is stored in the array
\( C^\#E \), since \( \langle P_L | S^2 | P_K \rangle = \langle D_L | S^2 | D_K \rangle = C_{LX} \). As each \( P_K \)
is processed the results are written onto a disc or tape file. The rows
of \( I S^\# \) are not processed sequentially. At the start of the process the
elements in a one-dimensional array \( INDEX \) are all zero, each element
corresponding to a row of \( I S^\# \). \( S^2 \) is applied to \( P_1 \) first, and the next
product examined is the first one in (8.1), for which \( C_{L} \), is non-zero and
has a non-zero entry in \( INDEX \). If there are no zero entries in \( INDEX \) and
\[ \Lambda = 0, \] the next product processed is the one resulting from the application
of the reflection operator to the \( P_K \) to which \( S^2 \) was applied, provided
that the entry in \( INDEX \) is zero. However if a non-zero entry is encountered
or \[ \Lambda \neq 0 \] the array \( INDEX \) is searched from the beginning for the next
zero element, and the process is operated until all the \( P_K \) have been examined.
This approach ensures that the matrix of the \( S^2 \) operator is block
diagonal, and makes interpretation of the results easier. The \( P_K \) are
numbered according to the order in which \( S^2 \) is applied. The output from
GENDET comprises:

(i) \( P_K \) on cards,
(ii) $K$, $iP_K$, $\sigma P_K$ (zero if $\Lambda = 0$), $L$ and $C_{LK}$ if non-zero.

(iii) Eigenvalues and eigenvectors of the blocks on the diagonal of the $S^2$ matrix. The card output is used as data for the program SECS$\phi$L (Appendix VII), which constructs and solves the secular equation.

B. Evaluation of Integrals over the atomic orbital basis set

This is one of the more difficult aspects of quantum molecular calculations. If the atomic orbitals are of the Slater-type, then the two-electron integrals may only be evaluated in 'closed form' when the constituent orbitals are on the same centre. These are the one-centre two-electron integrals. Although closed form expressions exist for two-centre two-electron integrals they are notoriously unstable and the integrals are usually evaluated by numerical integration. For integrals involving more than two centre various techniques are employed; the most favoured being some form of expansion in terms of Gaussian-type orbitals\(^{(52)}\). An alternative is to use the Gaussian orbitals by themselves (see for example Clementi and Davis\(^{(53)}\)), the disadvantage being the vast number of integrals involved and the length of time required to transform to an orthonormal SAMO basis.

The choice of complex Slater-type orbitals was made early in the project because of the availability of several diatomic integral programs based on these orbitals. As it is inefficient to use such programs for atomic calculations, a short program for evaluating all one-centre one- and two-electron integrals over complex Slater-type orbitals was written. This has been used both to check the transformation program and SECS$\phi$L. This program called $\phi$NECEN is listed in Appendix V, and the non-zero Clebsch-Gordon coefficients\(^{(41)}\) $C_{\ell_1 m_1 \ell_2 m_2}^{\ell m}$ used in the expansion of a product of spherical harmonics are also given. The method of indexing $C_{\ell_1 m_1 \ell_2 m_2}$ is easily determined by examination of the sub-program INDEX 1 and the coefficients are limited to the range $0 \leq \ell \leq 3$. 
with \( i = 1 \) or \( 2 \).

\textsc{phcen} uses the function subprogram \textsc{ipar} listed in Appendix III. The parameter list of \textsc{ipar} consists of a single integer variable name. On being called \textsc{ipar} is set equal to zero if this integer is even, and equal to unity if it is odd. The current method of representing decimal integers as binary integers is such that, if the decimal integer is even, the contents of the least significant bit of the word containing its binary equivalent is zero, whereas if the decimal integer is odd this bit contains a one. \textsc{ipar} is set equal to the contents of the least significant bit of the word containing the variable in the parameter list. The subprogram is of necessity written in ABL. An alternative to \textsc{ipar} is the use of the intrinsic function \textsc{mod}(\text{\texttt{N}}, \text{\texttt{2}}). A call of \textsc{mod}(\text{\texttt{N}}, \text{\texttt{2}}) has the same effect as \textsc{ipar}(\text{\texttt{N}}), but has been shown to take 50\% longer, even when used as a statement function.

The overlap and one-electron Hamiltonian integrals are stored in the two-dimensional arrays \( S \) and \( H \) in \textsc{phcen}. These arrays are written onto a magnetic tape (or disc area) referred to as the Master Integral Tape. The file begins at word zero of a block specified in the data. The two-electron integrals are generated in accordance with the rules given in Chapter 7. The storage of these integrals is such that the integral \( [\omega_\mu \omega_\nu | \omega_\lambda \omega_\sigma] \) (\( \mu \geq \nu \) and \( \lambda \geq \sigma \), \( \mu \geq \lambda \) and if \( \mu = \lambda \), \( \nu \geq \sigma \)) will be word number \( n_e \) of record number \( n_r \), where \( n_r \) and \( n_e \) (\( \leq n_r \)) are given by (7.36). The first record containing two-electron integrals follow immediately after \( S \) and \( H \). \textsc{phcen} computes all the integrals arising from a basis set of \( 1s \), \( 2s \), \( 2p_- \), \( 2p_+ \), and \( 2p_\pm \) complex Slater-type orbitals in less than two seconds.

The integrals required for the calculation of wave functions for diatomic molecules are computed using a modified version of a program written by Miller and Browne (54). The modifications consist of the removal of the facility by which the integrals over the complex Slater-type orbitals are transformed to integrals over real Slater-type orbitals. As this program
generates the integrals in a form incompatible with the input requirements of the transformation program, an interface between the two programs was written which produces a master integral tape of the same form as is produced by ŽNECEEN. The modifications to the Miller-Browne program and the interface were implemented by Dr M. Dixon and the author gratefully acknowledges his assistance in this respect.

C. Transformation of the integrals to an orthonormal basis set.

The transformation of the integrals over the atomic orbital basis into integrals over an orthonormal basis is a relatively simple process. The integral transformation program is called INTRA and is listed in Appendix VI. There are three essential parts to INTRA:

(i) the extension of the two-electron integral records to cover all values of $n_e$ (7.36),

(ii) the computation of the Schmidt orthonormalization coefficients (the elements of $U$ in (7.7)) and transform the one-electron Hamiltonian integrals,

(iii) the transformation of the two-electron integrals. As a preliminary to the transformation the integrals generated by either ŽNECEEN (for atomic systems) or by the Miller-Browne program (for diatomic systems) are copied from the Master Integral Tape onto a common disc area. This ensures that the Master Integral Tape cannot be corrupted by the transformation, as INTRA may only read this tape.

The two-electron integrals can be regarded as the elements of a real symmetric matrix $I$ with elements $I_{nrn_e}$, where $n_r$ and $n_e$ are defined by (7.36). Only the lower triangle of $I$ is computed by the integral generation programs and it is necessary to complete the upper triangle. This operation is the first stage of INTRA. It is complicated by the fact that $I$ is generally too large for more than a few rows to be in the core store at any one time.
This stage is contained within the subprogram called SETERI. The algorithm begins by reading each row of the matrix from the appropriate device (the number of elements in each row beginning equal to the number of the record). As each row is read it is packed out with zeros and the whole row written onto another device. The resulting matrix has a lower triangle equal to that of and an upper triangle of zeros. The matrix is then transposed by the subroutine BIGTRA. The lower triangle of is then merged with the transpose of to give the complete matrix.

The subprogram BIGTRA transposes a large matrix which is written on a disc or tape, in this case, by rows. It makes optimal use of the available core store by reading as many complete records (rows) as possible into the available space. Let this number by . The process in the Nth pass over the matrix to be transposed consists of the following sequence of operations: read first records into a two-dimensional array A, transpose the square matrix beginning at column of A, and enter this into the first block of the two-dimensional array B. The next records are read into A, transposed as before and entered into the second block of B. This procedure is repeated until B is full and it is then written onto a tape or disc by rows representing columns to of the original matrix. The sequence is repeated until the whole of the original matrix has been transposed, taking into account the fact that the number of rows of the original matrix may not be an integral multiple of . At the end of each pass over the original matrix, the appropriate device is rewound and at the end of the routine the original matrix is overwritten by its transpose.

For small basis sets the whole of this part of INTRA is performed in core.

The transformation of the one-electron integrals is performed by the subroutines GTH and TRANSH. Firstly the matrix of (7.30) is used to
transform the overlap matrix of the atomic orbitals into integrals over a SAMO basis. If the calculation is on an atomic system $A'$ is the identity matrix. The resulting overlap matrix $S$ overwrites the original one. The subroutine $\text{ORTHON}$ obtains the matrix $U$ of (7.7) by Choleski decomposition of $S$. The matrix $L^T$ of (7.5) is held in the array $QU$, which is then inverted to give the matrix $U$ which is stored in the array $QC$. The one-electron Hamiltonian matrix $h_\omega$ is transformed by the matrix product

$$h = C^* U^T C$$

where $C = C' U$. The transformed overlap matrix (i.e. $U^T S U$) is printed as a check on the orthogonality of the final set of orbitals.

The approach just described for obtaining the Schmidt orthonormalization coefficients was shown to produce better results in single precision arithmetic than the recursive approach suggested by Todd\(^{40}\) and Harris\(^{41}\) does in double precision arithmetic. It is also a much faster method.

The transformation of the two-electron integrals is carried out by the subprogram $\text{TWTRA}$ and its control routine $\text{CONTRA}$. If the $i$-th transformed orbital has the same axial angular momentum as the $i$-th atomic orbital, then the transformation of integrals not satisfying (7.35) is suppressed. Use of this feature is optional (see Appendix VI), and it can reduce the transformation time for the two-electron integrals by almost 50%. This option will enable the program to be used for the transformation of multi-centre integrals. The transformation proceeds in two stages. The first stage sets up the partially transformed integrals $[\omega_{\mu}^\omega \omega_{\nu}^\nu \varphi_{k} \varphi_{l}]$ according to (7.37a) and it is seen from (7.36) that for a given set of $\mu$ and $\nu$ all the integrals over the atomic orbitals appear in the same record. The partially transformed integrals are obtained for all possible values of $\mu, \nu, k, \text{and } l$. Partially transformed integrals for which
are actually computed, the remainder one set equal to zero and the transformation process suppressed. The partially transformed integrals form the elements of a two dimensional array, which is written onto a disc area, with each row corresponding to a record, the number of the row being given by

$$P_r = \mu_{\text{max}} (\nu - 1) + \mu \quad , \quad (8.4a)$$

and the position of the element in the record by

$$P_e = k_{\text{max}} (l - 1) + k \quad . \quad (8.4b)$$

(Obviously $\mu_{\text{max}} = k_{\text{max}} = \text{number of basis orbitals}$). Inspection of (7.37b) shows that the $[\omega_1 \omega_\nu | \phi_k \phi_1]$ appear as columns of this matrix, which is not symmetric. To avoid unnecessary searching of the disc file this matrix is transposed either in core or if it is too large by the subprogram BIGTRA.

The second stage of the two-electron transformation proceeds with the evaluation of (7.37b) using the condition of (7.35) wherever possible to speed the process. The complete file of transformed integrals consists of $[\phi_i \phi_j | \phi_k \phi_1]$ written in records with

$$P_c = i_{\text{max}} (j - 1) + i \quad (8.4c)$$

identifying the record, and $P_e$ of (8.4b) identifying the element in the record. The transformed two-electron integrals are followed by a single record containing the transformed one-electron Hamiltonian integrals. The

* FOOTNOTE: setting $m = 0$ for all the orbitals is equivalent to suppressing this test (see Appendix VI)
complete file begins at word zero of a block on the Master Transformed
Integral Tape as specified in the data. Thus for a basis set of \( n \) orbitals
the output to this tape will consist of \( (n^2 + 1) \) records, each containing
\( n^2 \) elements.

D. Construction and Solution of the Secular Equation

This is the final part of the CI method. The program SECS\( \Phi \) listed
in Appendix VII constructs and solves the secular equation for a CI
calculation on molecules of general geometry, the limit being twenty nuclei.
An option is provided to enable the user to compute the first order density
matrix, which is then diagonalized to give occupation numbers and natural
spin-orbitals. It is convenient to discuss SECS\( \Phi \) in terms of the functions
of the following three groups of subprograms,

(i) computation of the matrix elements \( \langle D_L | J | D_K \rangle \)
between detors,

(ii) construction and solution of \( (H - E^\Phi) A = 0 \),

and (iii) the optional natural spin-orbital analysis in which the first
order density matrix over the orthonormal SAMO is computed.

Computation of the \( \langle D_L | J | D_K \rangle \) requires the specification of
the ordered spin-orbital products, and for homonuclear diatomic molecules
the cards output by GENDET provide this information. As the matrix with
elements \( \langle D_L | J | D_K \rangle \) is symmetric only the lower triangle is
evaluated and stored in a one-dimensional array \( G \), where

\[
G(KL) = \langle D_L | J | D_K \rangle , \quad (K \leq L)
\]

(8.5)

and

\[
KL = (L^*(L - 1))/2 + K
\]

(8.6)
Before evaluating $G(KL)$ it is necessary to bring $D_L$ and $D_K$ into the condition of maximum coincidence. The subroutine $\text{MAXCORN}$ brings each pair of off-diagonal detors (i.e. $K < L$) into maximum coincidence, by permuting the elements of the ordered spin-orbital product defining one of them. The parity of the permutation is determined. Those pairs in which the detors differ by more than two spin-orbitals are ignored, because the corresponding matrix element is zero. For each of the remaining pairs the following information is entered as a row in the two-dimensional array $\text{IDIFF}$,

(i) the number of spin-orbitals by which the pair $(K, L)$ differs,
(ii) the identifiers of the spin-orbitals not common to both,
(iii) the parity of the permutation required to satisfy the condition of maximum coincidence,
(iv) the value of $KL$ given by (8.6).

The number of entries in $\text{IDIFF}$ are counted, and the array may be dumped on a disc file if it is too small for the current problem.

The actual evaluation of $G(KL)$ is in two steps and the first involves the computation of the two-electron contribution. The contribution of a frozen shell of electrons represents a constant which may be computed separately, and then added to the frozen shell-valence and valence-valence electron interactions for the diagonal terms $< D_K | I | D_K >$. This constant is computed in the subprogram $\text{PAS\kern-.1emO}$. The remaining interaction for the diagonal elements, and the values of the off-diagonal elements are computed in the subroutine $\text{PASTW\kern-.1emO}$.

In $\text{PASTW\kern-.1emO}$ the two electron integrals $[\phi_i \phi_j | \phi_k \phi_l]$ are read into core for all values of $k$ and $l$, for a given pair of values of $i$ and $j$, according to (8.4b) and (8.4c). Each record is examined to determine whether or not it contains integrals that will contribute to the diagonal elements (see 7.29); integrals which make a contribution are added or
subtracted, as appropriate, to the correct element of $G$. Next, by searching the array IDIFF, those integrals which contribute to the off-diagonal elements are found. As the detors are in terms of spin-orbitals and the integrals over (spatial) orbitals, it is necessary to use (1.5) to identify the correct integrals and to determine whether or not the integration over the spin co-ordinates produces zero. PASTWO makes considerable use of the function subprogram IPAR.

The final step is evaluating the matrix elements between the detors is the evaluation of the one-electron contribution. The transformed one-electron Hamiltonian matrix is read into core by the subprogram HPASS. The contribution from the frozen shell is evaluated once and added to the remaining contributions to the diagonal elements. For the off-diagonal elements there will only be one non-zero contribution which is added to $G(KL)$; $G(KL)$ is then multiplied by the appropriate parity factor ($\pm 1$).

Once the matrix elements between the detors have been evaluated the program proceeds to compute the matrix elements of the secular equation as indicated in (7.21). For homonuclear diatomic molecules the projection matrix $T_{SO}$ can be obtained by inspection of the output from GENDET. The evaluation of (7.21a) is the basis of the subroutine SECSOL (not to be confused with the program of the same name of which it is a part), its eigenvalues and corresponding eigenvectors are determined by the QR-Algorithm. The eigenvalues are the energies of the state projected by $T_{SO}$ and each eigenvector defines a wave function for this state.

Finally the program SECSOL will perform a natural spin orbital analysis on the $i$-th level of the state given by $T_{SO}$. The first order density matrix is computed from a wave function expanded as a sum of detors rather than as a sum of codetors. The coefficients $b_{\mathbf{k}l}$ are obtained using (7.40). The first order density matrix is computed by the method
indicated at the end of Chapter 7. It is diagonalized by the QR-Algorithm, and the subprograms NATORB and FRODNA4 constitute this section of SECSOL.

By use of the projection matrix $T_{\sigma S}$ it is possible to construct the secular equation for several molecular and spin states from a given array $G$. This fact and the desire to preserve many of the results produced by the program SECSOL led to the writing of subroutine TDFILE. This subprogram handles all transfers of preserved information, whether the transfers be between peripheral devices or between a peripheral device and core store. All the results obtained for a particular molecule will be held in a file which will also contain all of the transformed integrals used in the calculations. This file is kept on a magnetic tape called the Master Results Tape. TDFILE sets up a table of contents for this file. The entries in this table define the position of a particular set of results, the type of results, and the data required to enable information to be read from the file. The user may identify each entry in the contents table by providing a 32 character title in the data for SECSOL (see Appendix VII). A similar table is also kept for a private disc area on which all results currently being used, or generated, by the program is held. The master results tape is updated from this disc area; this has advantages in that the current set of results cannot be lost through machine faults, unless, of course, the disc actually fails during a transfer. Both contents tables are written on a small private disc area. TDFILE is written in such a way that it is virtually impossible for the user to accidently corrupt or over-write the master results tape or the master transformed integrals tape; the program SECSOL can only assess these tapes by a call of TDFILE.

Each program described has a 'multiple run' facility, which permits the processing of several sets of data in any one run. In the case of SECSOL both the specification of the detors and $T_{\sigma S}$ may be read in the first set of data and used in subsequent runs. This substantially reduces the number
of data cards required. SECSFIL may also be re-entered at the start of any section.

Once written each subprogram was thoroughly checked and rigourously tested (all test runs were in the FORTRAN V test mode\(^{49}\)). The final test of the programs was their ability to reproduce published results. The calculation chosen for this test was based on the CI calculations on the diatomic oxygen molecule of Meckler\(^{42}\), Kotari et alia\(^{43}\), and Schaefer and Harris\(^{45}\).

Meckler's calculation is a CI in which the SAMOs arising from the 1s and 2s atomic orbitals are frozen; the codetors arise from the 2p atomic orbitals. There are 31 detors with \(\Lambda = 0\) and \(S_z = 0\) which are tested by Meckler. From these detors it is possible to project 9 \(3\Sigma^-\) codetors and 12 \(1\Sigma^+\) codetors; the corresponding projection matrices \(T_{1-}\) and \(T_{0+}\) are also given. The calculation of Kotani et alia is based on the codetors arising from the 2s and 2p atomic orbitals, the 1s shell is frozen. It is possible to determine the specification of the detors and the projection matrix \(T_{1-}\) that they used for their \(3\Sigma^-\) wave function. The detors have \(S_z = 1\). This particular paper also contains the elements of the matrix \(U\) ((7.6) and (7.7)) which orthonormalizes the SAMOs. The most stringent test of both the programs GENDET and INTRA is the successful reproduction of the results published by Meckler and Kotani. Both programs performed satisfactorily. The paper by Schaefer and Harris\(^{45}\) contains the energies for 62 low-lying states of \(O_2\) at nine internuclear distances, and also values for the \(3\Sigma, 1\Delta,\) and \(1\Sigma\) states of the oxygen atom. Test runs for the \(3\Sigma^-\) and \(1\Sigma^+\) states of the molecule, at the same internuclear distances used by Schaefer and Harris, and for the three states of the atom, produced results which are in agreement with the published values to within machine accuracy. This final test also provided a check on the program \(\text{ONEGEN}.\) This program also produced integrals which agree with
those given in references (12) and (41). As a check on the accuracy of
the QR-Algorithm, the secular equation was also solved using a routine
based on the method of Jacobi (13).

The natural spin-orbital analysis was checked against the results
obtained from a general program, which will produce natural spin-orbitals
from a wave function expressed as a sum of determinants. This program
has reproduced various published results (20, 31, 37). Wherever possible test
calculations were checked on a desk calculator.

The results of the test calculations on O2 are given in Chapter 10,
together with the spectroscopic constants and molecular properties computed
using the methods described in Chapter 9.
In the Born-Oppenheimer approximation the separation of the electronic and nuclear motions leads to two equations, one describing the electronic behaviour and the other the nuclear motion. The solution of the first of these equations has been the subject of the preceding chapters and the electronic energy $E_e$ corresponding to this solution is a function of the nuclear co-ordinates. The electronic energy and the energy $V_N$ due to the electrostatic repulsion of the nuclei, together form the potential function $V$ used in the second equation. For a diatomic molecule this equation is similar to that of the rotating vibrator, and it has been solved by Dunham, who expanded the potential function about the equilibrium nuclear separation $R_e$ in a power series:

$$V(R) = V(R_e) + a_0 \xi^2 (1 + a_1 \xi + a_2 \xi^2 + ... ) \quad (9.1)$$

where

$$\xi = (R - R_e)/R_e,$$
$$a_0 = \omega_e^2/4B_e,$$

and

$$B_e = \hbar/(8\pi^2 c \mu R_e^2) \quad (9.2)$$

In (9.2) $\omega_e$ is the classical frequency of small oscillations, assuming the system is a harmonic oscillator, and $\mu$ is the reduced mass of the
Using the Wentzel-Kramers-Brillouin method Dunham obtained the equation

\[ E_{vJ} = \sum_{l,j} Y_{lj} (v + 1/2)^l j (j + 1)^j \]  \hspace{1cm} (9.3)

for the energy level of a rotating vibrator associated with a rotational quantum number \( J \) and a vibrational quantum number \( v \). The coefficients \( Y_{lj} \) (9.3) may be expressed in terms of \( \omega_e \), \( B_e \) and the coefficients \( a_j \) of (9.1). The appropriate formulae are to be found in Dunham's paper.

The connection between the \( Y_{lj} \) of (9.3) and the observed spectroscopic constants is easily determined. From (9.3) the energy of a vibrational level is

\[ E_{v0} = Y_{00} + Y_{10} (v + 1/2) + Y_{20} (v + 1/2)^2 \]
\[ + Y_{30} (v + 1/2)^3 + Y_{40} (v + 1/2)^4 + \ldots \] \hspace{1cm} (9.4)

This leads to the following expressions for the separations between the lowest vibrational levels,

\[ E_{10} - E_{00} = Y_{10} - 2Y_{20} + 13Y_{30}/4 + 5Y_{40} + \ldots \],
\[ E_{20} - E_{10} = Y_{10} - 4Y_{20} + 49Y_{30}/4 + 34Y_{40} + \ldots \] \hspace{1cm} (9.5)

The energy levels of the anharmonic oscillator are given by the expression

\[ E_{v0} = \omega_e (v + 1/2) - \omega_e x_e (v + 1/2)^2 \]
\[ + \omega_e y_e (v + 1/2)^3 + \omega_e z_e (v + 1/2)^4 + \ldots \] \hspace{1cm} (9.6)
(9.6) is obtained (55) by solving the appropriate Schrödinger equation using a potential function of the form

\[ V(R) = V(R_e) + f \xi^2 - g \xi^3 \]

with \( g \ll f \) which is a simplified form of (9.1). The separations between the lowest energy levels obtained from (9.6) are

\[ E_{10} - E_{00} = \omega_e - 2 \omega_e x_e + 13 \omega_e y_e / 4 + 5 \omega_e z_e + \ldots \]

\[ E_{20} - E_{10} = \omega_e - 4 \omega_e x_e + 49 \omega_e y_e / 4 + 34 \omega_e z_e + \ldots \] (9.7)

Comparison of (9.5) and (9.7) gives

\[ Y_{10} \approx \omega_e \]

\[ Y_{20} \approx - \omega_e x_e \]

\[ Y_{30} \approx \omega_e y_e \]

\[ Y_{40} \approx \omega_e z_e \] (9.8)

\( Y_{10} \) is not exactly equal to \( \omega_e \) because it contains terms in \( B_e^2 / \omega_e^2 \) which arise from the more general form of the potential function used by Dunham. Similar corrections appear in the other \( Y_{10} \).

For the rotational motion of the molecule the experimental expression for the difference in energy between rotational levels \( J \) and \( 0 \) in the same vibrational state is (56)

\[ E_{vJ} - E_{v0} = B_v J(J + 1) - D_v J^2(J + 1)^2 + H_v J^3(J + 1)^3 + \ldots \] (9.9)
The rotational constants $B_v$, $D_v$ and $H_v$ in the vibrational state considered are expressed in terms of $B_e$, $D_e$ and $H_e$ which are the rotational constants at $R_e$. The usual expressions are

$$B_v = B_e - \alpha_e (v + 1/2) + \gamma_e (v + 1/2)^2 + \delta_e (v + 1/2)^3 + \ldots,$$

$$D_v = D_e + \beta_e (v + 1/2) + \ldots,$$

$$H_v = H_e + \ldots. \quad (9.10)$$

Expansion of (9.3) gives

$$E_vJ - E_{v0} =$$

$$\left( Y_{01} + Y_{11}(v + 1/2) + Y_{21}(v + 1/2)^2 + \ldots \right)J(J + 1)$$

$$+ \left( Y_{02} + Y_{12}(v + 1/2) + Y_{22}(v + 1/2)^2 + \ldots \right)J^2(J + 1)^2$$

$$+ \left( Y_{03} + Y_{13}(v + 1/2) + \ldots \right)J^3(J + 1)^3$$

$$+ \left( Y_{04} + \ldots \right)J^4(J + 1)^4. \quad (9.11)$$

Comparison of (9.9), (9.10), and (9.11) yields the approximate relations

$$Y_{01} \approx B_e,$$

$$Y_{11} \approx -\alpha_e,$$

$$Y_{21} \approx \gamma_e,$$

$$Y_{31} \approx \delta_e,$$

$$Y_{02} \approx D_e,$$

$$Y_{03} \approx H_e. \quad (9.12)$$
Once again the \{ Y_{1j} \} differs from the "classical" values by terms in \( B_e^2/\omega_e^2 \), which are usually less than \( 10^{-6} \) (55).

The value of \( \omega_e \) is in \( \text{cm}^{-1} \), and the reduced mass \( \mu \), used to calculate \( B_e \) and hence \( \omega_e \), is measured in atomic mass units on the unified scale(57). The value of \( R_e \) is in bohrs so that

\[
B_e = 60.2014/(\mu R_e^2) \quad (9.13)
\]

The probable radius of convergence of (9.1) is \( 0 \leq R \leq 2R_e \) (58) and because the series is truncated, the actual region where it may reasonably be applied is close to \( R_e \) (59).

The computation of the spectroscopic constants is achieved by expressing the potential curve \( V(R) \) as a power series in \( R \). This series is then transformed into the form of (9.1) by using the method of synthetic division(40) (Horner's method) and the \( Y_{1j} \) are determined by using the appropriate formulae (55).

The coefficients of the power series in \( R \) are found by the method of least squares(40). Suppose

\[
V(R_i) = \sum_{j=1}^{n+1} R_i^{j-1} p_j \quad , \quad (9.14a)
\]

or in matrix notation

\[
A \ p = V \quad . \quad (9.14b)
\]

In (9.14b) the elements of the matrix \( A \) are \( A_{ij} = R_i^{j-1} \), \( p \) is a column vector of the unknown coefficients, \( V \) a column vector of the energies, and \( R_i \) is the \( i \)-th value of the internuclear distance. A unique vector which minimizes the Euclidean (or \( L_2 \)) norm of \( V - A \ p \), only exists when the columns of \( A \) are linearly independent (60). By taking powers of \( R_i \)
accuracy is reduced and the columns of $A$ may be nearly linearly dependent. These difficulties can be avoided if $R_j$, the independent variable, is transformed into the normalized independent variable $X_j$ where

$$X_j = \frac{2R_j - (R_1 + R_{n+1})}{(R_1 - R_{n+1})}, \quad (9.15)$$

and

$$|X_j| \leq 1.$$

In (9.15) $R_j$ is the minimum value of $R_i$ and $R_{n+1}$ the maximum value. $A_{ij}$ is now $X_j^{i-1}$ and the solution of the least squares problem results in the coefficients $q_j$ of the polynomial

$$V(X_j) = \sum_{j=1}^{n+1} X_j^{i-1} q_j. \quad (9.16)$$

Use of an algorithm by Mackinney (62) permits the direct transformation of (9.16) into (9.1). This algorithm transforms a polynomial in $X$ into one in $\xi$ where $X = a \xi + b$. In the present case $a = X_e + (R_1 + R_{n+1})/(R_1 - R_{n+1})$ and $b = X_e$. The minimum of $V(X)$ occurs at $X = X_e$; it may be found by using the Newton procedure (40) and the fact that $(dV/dR)_X = X_e = 0$. The Newton procedure is initiated with an approximation $X_k$ to $X_e$ where $X_k$ satisfies the condition $V(X_k) < V(X_j)$ for all $i \neq k$, $V(X_k)$ is a data point. The value of $R_e$ is simply $\frac{1}{2}(X_e (R_1 - R_{n+1}) + (R_1 + R_{n+1}))$. The solution of the least squares problem is further assisted by initially subtracting the mean value of $V(R_i)$ from each value of $V(R_i)$.

The foregoing analysis forms the basis of the program SPECTRO which is listed in Appendix VIII. The program is completely self contained and the Dunham analysis is performed by the subroutine DUNHAM. The solution of the least squares problem is performed by subroutine SLRIN2 which is a FORTRAN V translation of Bauer's algorithm (60). The program is so written
TABLE 6 Theoretical and Experimental Spectroscopic

constants for H₂

<table>
<thead>
<tr>
<th></th>
<th>McLean</th>
<th>Spectro</th>
<th>Experimental</th>
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</thead>
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<td>$ω_e$</td>
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<td>$7.9529 \times 10^4$</td>
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<td>$a_7$</td>
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</tr>
<tr>
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</table>
that several energy levels of the same symmetry, spin, and covering the
same range of $R$ may be processed in each run.

The results of the Dunham analysis are invariably compared with
experimental values and it is for this reason that the values of $V(R)$
are converted in the program from hartrees to $\text{cm}^{-1}$ using the conversion
factor given in Appendix I. The value of $V(R_e)$ in both $\text{cm}^{-1}$ and hartrees
is given in the program output.

McLean\textsuperscript{(63)} published a comprehensive set of results for the Dunham
analysis of a wave function for $H_2$ obtained by Kolos and Roothaan\textsuperscript{(19)}.
McLean's results, the experimental values\textsuperscript{(56,64)} and those obtained by
SPECTR\textsuperscript{6} are given in Table 6. As far as the $a_i$ s of (9.1) are concerned
the results given by SPECTR\textsuperscript{6} are in complete agreement with those of McLean.
Some discrepancies arise both in the classical and corrected spectroscopic
constants. This is due to the slight differences in the factors used to
convert primary units to secondary units as McLean used an older set\textsuperscript{(63)}. 
The diatomic oxygen molecule has been thoroughly studied by spectroscopists\(^1\) and the extensive theoretical study of Schaefer and Harris\(^2\) is in excellent agreement with experimental results. The work of these authors provided a valuable means of checking the accuracy of the programs described in the previous chapters.

Schaefer and Harris examined 62 low-lying states of the oxygen molecule at up to eight internuclear separations, and obtained values of the energies at an infinite separation by the appropriate combinations of the energies of the \(^3P\), \(^1D\) and \(^1S\) states of the separated atoms. Their approach to the programming problem is similar to the one used here\(^3\), although there are important differences in technique. The most significant of these differences is the evaluation of the one- and two-electron integrals which employs a method evolved by Harris\(^4\). Two other differences worth noting are the use of the recursive form of the Schmidt orthonormalization process \((40,41,60)\) and the use of Givens' method for diagonalizing a real symmetric matrix. Finally an important computer hardware aspect of the calculation of Schaefer and Harris is the fact that the Univac 1108 computer, which they used\(^5\), gives only 8 decimal digits accuracy for real arithmetic, consequently their results are probably only accurate to 5 or 6 decimal digits although they quote 7. Atlas gives 11 decimal digits\(^6\) so that a 5 or 6 figure agreement between the present results and those given in reference 45 is acceptable. The details of their calculation differ slightly from that described here. The detors of Schaefer and Harris are chosen so that \(S_z = S\) and the configuration are classified according to the value of \(\Lambda\) and \(S\). Thus, for example, the secular equation they solve contains all variants of \(^3\Sigma\) symmetry, and the \(g\), \(u\), \(+\), or \(-\) subspecies is sorted out by the diagonalization process. Naturally this leads to secular equations...
of large dimensions (110 x 110 for the $3\Sigma$ states). However, the present programs are designed to avoid this situation (see chapters 7 and 8). The program GENDET, apart from reproducing the results previously quoted, also confirms the number of configurations given in Table I of Schaefer and Harris.

Unlike diatomic oxygen, diatomic sulphur has not received much attention from the spectroscopists. The lack of experimental data is due to the difficulty in setting up long-path absorption experiments in $S_2$ vapour at temperatures around 650°C. This, combined with the large number (32) of electrons involved, and the fact that the ground state of the molecule is a triplet, probably accounts for the non-existence of theoretical work.

Oxygen and sulphur are both Group VI elements; oxygen being in the first row of the periodic table and sulphur in the second row. So far as is known the general pattern of the electronic states of $S_2$ resembles that of $O_2$.

The programs described in the preceding chapters have been used to obtain VCI wave functions for the following atomic and molecular systems:

(i) $3\Pi$, $1D$, and $1S$ states of atomic oxygen and sulphur.

(ii) $3\Sigma_g^-$ and $1\Sigma_g^+$ states of diatomic oxygen at fifteen internuclear distances.

(iii) $3\Sigma_g^-$, $1\Delta_g$, and $1\Sigma_g^+$ states of diatomic sulphur at seventeen internuclear distances. The orbital occupancy of the electrons in atomic oxygen is $(1s)^2(2s)^2(2p)^4$ and in sulphur it is $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^4$. The valence shell for both atoms is of the form $(ns)^2(np)^4$ with $n = 2$ for oxygen and $n = 3$ for sulphur. By arranging the six valence shell electrons in the eight available spin-orbitals it is possible to obtain two $P$-type, one $D$-type, and four $S$-type detors, in which $S_z = 0$ and $L_z = L$, where $L_z$ is the $Z$ component of the total orbital angular momentum $L$. From these detors it is possible to obtain one $3\Pi$ codetor, one $1D$ codetor, and two $1S$ codetors. The wave functions for the $3\Pi$ and $1D$ states are not really VCI wave functions at all because they consist of a single term and not a sum of terms. They are
<table>
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<tr>
<th>Type</th>
<th>Detors</th>
<th>Codetors</th>
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<tr>
<td><strong>P-type detors</strong></td>
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<tr>
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<td>$(1)(2)(3)(4)(7)(8)$</td>
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<td><strong>S-type detors</strong></td>
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<td></td>
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<tr>
<td>$D_4$</td>
<td>$(1)(2)(3)(4)(5)(8)$</td>
<td></td>
</tr>
<tr>
<td>$D_5$</td>
<td>$(1)(2)(3)(4)(6)(7)$</td>
<td></td>
</tr>
<tr>
<td>$D_6$</td>
<td>$(1)(2)(5)(6)(7)(8)$</td>
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<td>$D_7$</td>
<td>$(3)(4)(5)(6)(7)(8)$</td>
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</tr>
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<td>$D_3$</td>
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<td><strong>$^1D$ codetor</strong></td>
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<tr>
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<td>$D_7$</td>
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### TABLE 8. ORBITAL EXPONENTS

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<td>15.5409</td>
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<tr>
<td>2s</td>
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</tr>
<tr>
<td>2p</td>
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<tr>
<td>3s</td>
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</tr>
<tr>
<td>3p</td>
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### TABLE 9. ELECTRONIC ENERGIES OF ATOMIC STATES (HARTREES)

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<th>State</th>
<th>Oxygen</th>
<th>Sulphur</th>
</tr>
</thead>
<tbody>
<tr>
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<td>Ref. 45</td>
</tr>
<tr>
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<td>1D</td>
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<td>1S</td>
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<tr>
<td>Atomic States</td>
<td>Oxygen</td>
<td>Sulphur</td>
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<tr>
<td>---------------</td>
<td>------------</td>
<td>------------</td>
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<td>$^3!P + ^3!P$</td>
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<td>-793.1872</td>
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<tr>
<td>$^3!P + ^1!D$</td>
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<td>-793.1277</td>
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<tr>
<td>$^3!P + ^1!S$</td>
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<td>-793.1223</td>
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<td>$^1!D + ^1!D$</td>
<td>-149.8928</td>
<td>-793.0682</td>
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<td>$^1!D + ^1!S$</td>
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<td>$^1!S + ^1!S$</td>
<td>-149.7326</td>
<td>-793.0574</td>
</tr>
</tbody>
</table>
"single configuration" wave functions and, as the orbitals from which they are constructed are not optimized, the resulting energies will probably be poorer than the corresponding SCF energies. The detors are specified in Table 7 where only the identifiers of the valence shell spin-orbitals are given, these conform to the rule:

\[
\begin{align*}
ns & \alpha = 1, \quad ns \beta = 2, \\
np_0 & \alpha = 3, \quad np_0 \beta = 4, \\
np_\sigma & = 5, \quad np_\sigma \beta = 6, \\
np_+ & \alpha = 7, \quad np_+ \beta = 8.
\end{align*}
\]

The orbital exponents used in all the oxygen calculations were those of Schaefer and Harris\(^{(45)}\). For sulphur the atomic SCF exponents obtained by Clementi and Raimondi\(^{(73)}\) were used. All exponents are given in Table 8. The electronic energies of the three states of each atom are given in Table 9. The agreement between the present results for atomic oxygen and those of reference 45 is excellent. The SCF energy for the \(^3P\) state of sulphur\(^{(73)}\) is much better than that obtained by the VCI method. This result indicates a possible limitation imposed on the wave function by the VCI treatment. It was felt that a complete CI within the minimal basis set employed would provide valuable results. The energy of the \(^3P\) atomic ground state of sulphur given by this CI was found to be \(-396.6277\) hartrees: which is slightly better than SCF value. As the wave function only consists of four codetors (including that given in Table 7) it is not very extensive. Each of the additional codetors is a result of an excitation of one or more electrons from the \(2p\) shell into the \(3p\) shell, the \(3s\) shell always remaining doubly occupied. The value of the complete minimal basis set CI is that it shows that the interaction between the \(2p\) and \(3p\) shells cannot be ignored in the sulphur atom.

The energies of the atomic states which represent the dissociation limits of the low-lying molecular states are given in Table 10.

The minimal basis set of orbitals used for the atoms are utilized in the construction of the molecular orbitals for the molecular studies. The rules for forming the molecular orbitals are given in Appendix II. For
The molecular orbitals for sulphur include the orbitals

\[(3s\sigma_u)(3s\sigma_u)(3p\sigma_g)(3p\sigma_u)(3p\pi_g)(3p\pi_u)\]

in addition to those given for diatomic oxygen. In the studies of oxygen, the \((1s\sigma_g)\) and \((1s\sigma_u)\) orbitals were assumed to be always occupied by a total of four electrons, and the detors were obtained by arranging the remaining twelve electrons in the sixteen available molecular spin-orbitals. A set of 118 \(\Sigma_g^\pm\) detors was obtained with \(S_z = 0, 30\) \(3\Sigma_g^-\) codetors and 37 \(1\Sigma_g^+\) codetors were projected from this set. The set of valence shell molecular orbitals for sulphur differs from that of oxygen only by the value of the principle quantum number. In studies of \(S_2\) the whole of the oxygen set of molecular orbitals was assumed to be occupied by 20 electrons and the detors were obtained by arranging the twelve remaining electrons in the sixteen available molecular spin-orbitals. Obviously the number of \(\Sigma_g^\pm\) detors is the same for oxygen and sulphur, the numbers of codetors for the \(3\Sigma_g^-\) and \(1\Sigma_g^+\) states will also be the same. In addition a set of 44 \(\Delta_g\) detors was obtained with \(S_z = 0, 22\) \(1\Delta_g\) codetors were projected from this set. The detors and codetors are listed in Appendix IX, this appendix also contains a list of the "spatial orbital" configurations or "primative functions".

The energies of the five lowest levels of each state investigated are given in Tables 11 to 15 for each of the chosen internuclear separations. The corresponding potential curves are shown in Figs. 16 to 20. The results
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FIG. 16. Potential curves for the five lowest $\Sigma_g^-$ levels of $O_2$. 
FIG. 17. Potential curves for the five lowest $^1\Sigma_g^+$ levels of $O_2$. 
FIG. 18. Potential curves for the five lowest $^3\Sigma_g^-$ levels of $S_2$. 

The diagram shows various potential energy curves as a function of internuclear separation (Bohr radii). The curves are labeled with different quantum states, such as $^3\Sigma_g^-$, $^3\Sigma_g^-$, $^3\Pi$, and $^1S + ^1S$, $^1D + ^1D$, $^3P + ^3P$. The energy levels are plotted in units of energy (hartrees).
FIG. 19. Potential curves for the five lowest $^1\Sigma^+_g$ levels of $S_2$. 
FIG. 20. Potential curves for the five lowest \( ^1\Delta_g \) levels of \( S_2^* \).
TABLE 16 Spectroscopic Constants

(Units are cm\(^{-1}\) unless explicitly given, and \(a_1\) to \(a_6\) are dimensionless)

\[ \text{O}_2 \text{x}^2 \Sigma^{-I} \]

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| \(Y_{00}\) | -1.4979 | 1.6796 |
| \(Y_{10}\) | 1607.56 | 1580.36 | 1251.04 | 1432.69 |
| \(Y_{30}\) | 0.1539 | 0.0546 | -0.2558 | -0.0108 |
| \(Y_{40}\) | 0.0066 | -0.0003 |
| \(Y_{01}\) | 1.2422 | 1.4457 | 1.1636 | 1.4004 |
| \(Y_{11}\) | -0.0129 | -0.0158 | -0.0016 | -0.0182 |
| \(Y_{21}\) | \(7.9 \times 10^{-5}\) | 0.0003 |
| \(Y_{31}\) | \(9.3 \times 10^{-6}\) | \(-6.5 \times 10^{-5}\) |
| \(Y_{02}\) | \(-3.0 \times 10^{-6}\) | \(-4.0 \times 10^{-6}\) |
| \(Y_{12}\) | \(-1.1 \times 10^{-7}\) | \(1.3 \times 10^{-7}\) |
| \(Y_{22}\) | \(<10^{-8}\) | \(*\) |
| \(Y_{03}\) | \(<10^{-9}\) | \(*\) |
| \(Y_{13}\) | \(<10^{-8}\) | \(*\) |
| \(Y_{04}\) | \(<10^{-8}\) | \(*\) |
| \(a_0\) | \(5.2006 \times 10^5\) | \(3.3651 \times 10^5\) |
| \(a_1\) | -3.2487 | -3.4206 |
| \(a_2\) | 2.9408 | 10.6683 |
| \(a_3\) | 14.4668 | -31.0388 |
| \(a_4\) | -54.2388 | 20.5180 |
| \(a_5\) | 68.5968 | 84.8957 |
| \(a_6\) | -29.7533 | -113.0302 |

* Absolute value + Reference 28
TABLE 16 Spectroscopic Constants

(Units are cm\(^{-1}\) unless explicitly given, and \(a_1\) to \(a_6\) are dimensionless)

\[
\begin{align*}
S_2X^2 \Sigma_g^+ & \quad S_2a^1 \Delta_g & \quad S_2b^1 \Sigma_g^+ \\
\text{calc} & \quad \text{Expr}^+ & \quad \text{calc} & \quad \text{Expr}^+ & \quad \text{calc} & \quad \text{Expr}^+
\end{align*}
\]

| \(a_1\), bohrs | 3.9761 | 3.5754 | 3.9962 | 3.5905 | 4.0243 |
| \(V(\text{g}_\text{e})\) hartrees | -793.2757 | -793.2565 | -793.2472 |
| \(V(R_\text{e})\) \(10^{-7}\) | 2 | 3 \times 10^{-7} | 3.2 \times 10^{-6} |
| \(\rho\) hartrees | 0.0885 | 0.0693 | 0.0600 |
| \(\rho_0\) hartrees | 0.0869 | 0.1610 | 0.0147 | 0.0588 |
| \(\rho_{(0)}\) hartrees | 0.0016 | 0.0016 | 0.0546 | 0.0012 |
| \(Y_{10}\) | 703.4343 | 714.29 | 689.87 | 691.0864 | 693 ? |
| \(Y_{20}\) | -61.1530 | 2.844 | 3581.93 | 3.02 | 123.0598 | 3.4 ? |
| \(Y_{30}\) | 117.2205 | -387.0931 | -164.2823 |
| \(Y_{40}\) | 110.0365 | 1667.08 | 1.5303 |
| \(Y_{50}\) | 0.2371 | 0.2945 | 0.2318 | 0.2922 | 0.2310 |
| \(Y_{11}\) | 0.0021 | 0.0016 | 0.0452 | -0.0094 |
| \(Y_{21}\) | -0.0007 | -0.0670 | -0.0186 |
| \(Y_{31}\) | -0.0155 | -0.0853 | -0.0231 |
| \(Y_{02}\) | -6.9 \times 10^{-8} | -7.7 \times 10^{-7} | -2.4 \times 10^{-7} |
| \(Y_{12}\) | -2.2 \times 10^{-7} | -1.9 \times 10^{-6} | -4.4 \times 10^{-7} |
| \(Y_{22}\) | 2.7 \times 10^{-7} | -1.0 \times 10^{-5} | -1.3 \times 10^{-6} |
| \(Y_{03}\) | <10^{-8} * | <10^{-8} * | <10^{-8} * |
| \(Y_{13}\) | <10^{-8} * | <10^{-8} * | <10^{-8} * |
| \(Y_{04}\) | <10^{-8} * | <10^{-8} * | <10^{-8} * |
| \(a_0\) | 4.0375 \times 10^5 | 2.0498 \times 10^5 | 3.7238 \times 10^5 |
| \(a_1\) | 18.1835 | -34.6309 | -22.2509 |
| \(a_2\) | 80.4469 | 195.7953 | -127.9481 |
| \(a_3\) | 2.399.01 | 1.0117 \times 10^4 | 6036.38 |
| \(a_4\) | 5.2347 \times 10^4 | 4.2089 \times 10^4 | 8.2559 \times 10^4 |
| \(a_5\) | 3.9409 \times 10^5 | -8.1705 \times 10^5 | -4.5959 \times 10^4 |
| \(a_6\) | 5.5152 \times 10^6 | -7.4275 \times 10^6 | -6.6482 \times 10^6 |

* absolute value + Reference 68
for oxygen are in good agreement with those of Schaefer and Harris\(^{(45)}\),
and those for sulphur give the correct ordering of the lowest states;
\[ X^3\Sigma^-_g < a^1\Delta^+_g < b^1\Sigma^+_g \]
the separation of these states is 4500 cm\(^{-1}\) and 6000 cm\(^{-1}\) respectively, experimental
separations are 4500 cm\(^{-1}\) and 8000 cm\(^{-1}\). The prefix X, a, or b before
\(2S+1\) \(\Lambda^\(\sigma\)\) is the spectroscopic notation indicating the ground
state, first excited state, and second excited state respectively. The
suffix I, II, ... indicates the relative level of the symmetry species.
For example, \(3\Sigma^-_g\) is energetically lower than \(3\Sigma^-_{II}\)

Spectroscopic constants for the \(X^3\Sigma^-_g\) (i.e. ground state)
and \(b^1\Sigma^+_g\) states of diatomic oxygen were calculated using the
program listed in Appendix VIII. Similar calculations were performed for
the \(X^3\Sigma^-_g\), \(a^1\Delta^+_g\), and \(b^1\Sigma^+_g\) states of diatomic sulphur.
The results for both molecules are given in Table 16. The agreement between
the calculated values and the experimental values of the spectroscopic
constants is not too good for the two states of oxygen. Nor do these
results agree with those of Schaefer and Harris\(^{(45)}\). (The present results
were obtained by fitting a polynomial through the \(V(R_i)\) at the values of \(R_i\)
used by Schaefer and Harris.) The exact reason for the latter discrepancy
is difficult to determine with certainty but is probably an example of the
phenomenon noted by Beckel and Sattler\(^{(49)}\). They found that the values of
the spectroscopic constants, determined from a given set of values of the
total electronic energy, were very susceptible to changes in the number of
points to which the curve was fitted, to the degree of the polynomial
employed and to the accuracy of the actual energy values. Their criterion
for choosing the degree of the polynomial and radius of convergence was that
\[
|R - R_e| \leq \left|t/3A_{n-1}\right|^{1/n+1}
\]
All values of \( R_1 \) must lie in the range prescribed, \( t \) is the estimated machine error in each \( V(R_1) \) and \( n \) is the degree of the fitted polynomial. \( V(R) \) is expressed as a power series in \((R-R_e)\) rather than \( t \) (see Chapter 9) and \( A_{n-1} \) (the coefficient of \((R-R_e)^{n+1}\)) is the last significant term in the power series. The choice of this criterion seems rather arbitrary; Beckel and Sattler only managed to obtain two or three decimal digit consistency in the coefficients of the Dunham expansion. In the present calculations the value of \( t \) is extremely difficult to estimate as it depends on so many parameters. As \( R_e \) for both of the oxygen states considered here is about 2.5 bohr, it may well be argued that only energies corresponding to values of \( R \) in the range 2.0 \( \leq R \leq 3.0 \) should be used. In the case of Schaefer and Harris their published results only include five energies which satisfy this condition. This means that if \( t \) is \( 10^{-6} \) and as \( n \) is at most 4 then \( A_2 = 2.7 \times 10^{-7} \). Effectively this means that the potential curve must be almost parabolic over a substantial part of its range. It can be seen from Fig. 16 that the \( X^3 \Sigma^+ \) state is certainly not parabolic over the range 2.0 \( \leq R \leq 3.0 \). Obviously it is important when calculating spectroscopic constants to take great care over the mathematical methods and numerical techniques involved.

In calculating the spectroscopic constants for diatomic sulphur greater freedom was allowed in the choice of values of \( V(R) \) to which the curves were fitted. This process used was in two stages. Firstly a polynomial was fitted to all of the available points for each state. The \( L_2 \) norm of this solution for each problem was about \( 10^{-4} \) and was rather poor. The next step involved fitting a polynomial through those points which were most accurately represented in the first stage. The accuracy with which each point is represented may be obtained from SPECTRO by setting the variable \( N\theta \) equal to 1 in the data (see Appendix VIII). The results of this second stage are usually very good from the numerical analysis aspect,
as the \( L_2 \) norm rarely exceeds \( 10^{-11} \). The results obtained for sulphur using this technique are quite good, although in every case the vibrational constants \( \omega_x, \omega_y, \) and \( \omega_z \) are rather large. This suggests that either the system may not be represented by a simple rotating vibrator or that the VCI method gives a poor description of the state. There are no experimental results with which these values may be compared.

The dissociation of diatomic oxygen into atomic states is clearly defined and is amply discussed in the literature\(^{(45, 56, 65)}\). The \( \chi^3 \Sigma^-_g \) ground state of \( \text{O}_2 \) dissociates into the \( \chi^3 \Phi + \chi^3 \Phi \) states of the atoms as does the \( \chi^1 \Sigma^+_g \) state. The problem of the dissociation of \( \text{S}_2 \) has been discussed by many authors\(^{(56, 65, 69)}\). Agreement has only recently been reached on the value of the dissociation energy of the \( \chi^3 \Sigma^-_g \) state. The accepted value is 0.161 hartree\(^{(65, 69)}\) and the dissociation products are atoms in the \( \chi^3 \Phi \) state. The dissociation energy \( D_0 \) is measured from the lowest vibrational level and it is this value that is quoted experimentally. The dissociation energy \( D_B \), measured from the minimum of the potential curve differs from \( D_0 \) by the zero-point energy \( G(0) \).

\[
D_B = V(R_e) - V(\infty) = D_0 + G(0)
\]

\( D_B \) and \( G(0) \) are given by the program SPECTR\( \& \) (In the computer output the symbol 20 is used for \( G(0) \)). \( G(0) \) is calculated by putting \( V = 0 \) in (9.4), so that

\[
G(0) = Y_{00} + Y_{10}/2 + Y_{20}/4 + Y_{30}/8 + Y_{40}/16
\]

The value of \( D_0 \) for the ground state of diatomic sulphur is 54% of the experimental value and that of the oxygen ground state 70% of the experimental value.
TABLE 17. VCI, \( \pi \)-ORBITAL VCI, AND SCF ENERGIES FOR THE LOWEST STATES OF \( \text{O}_2 \) (HARTREES)

<table>
<thead>
<tr>
<th>R Bohrs</th>
<th>( X^3 \Sigma_g^- I )</th>
<th>( b^4 \Sigma_g^- I )</th>
<th>SCF*</th>
<th>37 TERM</th>
<th>12 TERM</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>-149.1407</td>
<td>-149.0598</td>
<td>-149.0521</td>
<td>-149.0712</td>
<td>-148.9792</td>
</tr>
<tr>
<td>2.3</td>
<td>-149.2031</td>
<td>-149.1411</td>
<td>-149.0912</td>
<td>-149.1480</td>
<td>-149.0797</td>
</tr>
<tr>
<td>2.5</td>
<td>-149.2151</td>
<td>-149.1702</td>
<td>-149.0743</td>
<td>-149.1680</td>
<td>-149.1188</td>
</tr>
<tr>
<td>2.7</td>
<td>-149.1996</td>
<td>-149.1674</td>
<td>-149.0281</td>
<td>-149.1637</td>
<td>-149.1295</td>
</tr>
<tr>
<td>2.9</td>
<td>-149.1741</td>
<td>-149.1514</td>
<td>-149.9679</td>
<td>-149.1487</td>
<td>-149.1261</td>
</tr>
<tr>
<td>3.1</td>
<td>-149.1465</td>
<td>-149.1311</td>
<td>-149.9024</td>
<td>-149.1307</td>
<td>-149.1166</td>
</tr>
<tr>
<td>3.3</td>
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<td>-149.1112</td>
<td>-148.8372</td>
<td>-149.1156</td>
<td>-149.1073</td>
</tr>
<tr>
<td>3.5</td>
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<td>-149.0961</td>
<td>-148.7744</td>
<td>-149.1032</td>
<td>-149.0986</td>
</tr>
<tr>
<td>4.0</td>
<td>-149.0838</td>
<td>-149.0826</td>
<td>-148.6413</td>
<td>-149.0883</td>
<td>-149.0873</td>
</tr>
</tbody>
</table>

* Reference 71. The author is grateful to Dr M. Dixon for permission to include these results.
### TABLE 18. VCI, \( \pi \)-ORBITAL VCI, AND SCF ENERGIES

FOR LOW-LYING STATES OF \( S_2 \) (HARTREES)

<table>
<thead>
<tr>
<th>( R ) Bohrs</th>
<th>30 TERM</th>
<th>9 TERM</th>
<th>SCF*</th>
<th>37 TERM</th>
<th>12 TERM</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>-793.0255</td>
<td>-792.9955</td>
<td>-793.0624</td>
<td>-792.9770</td>
<td>-792.9401</td>
</tr>
<tr>
<td>3.2</td>
<td>-793.1473</td>
<td>-793.1176</td>
<td>-793.1798</td>
<td>-793.1004</td>
<td>-793.0645</td>
</tr>
<tr>
<td>3.4</td>
<td>-793.2303</td>
<td>-793.2024</td>
<td>-793.2646</td>
<td>-793.1894</td>
<td>-793.1562</td>
</tr>
<tr>
<td>3.6</td>
<td>-793.2563</td>
<td>-793.2303</td>
<td>-793.2760</td>
<td>-793.2193</td>
<td>-793.1889</td>
</tr>
<tr>
<td>3.8</td>
<td>-793.2732</td>
<td>-793.2499</td>
<td>-793.2830</td>
<td>-793.2394</td>
<td>-793.2127</td>
</tr>
<tr>
<td>4.0</td>
<td>-793.2756</td>
<td>-793.2550</td>
<td>-793.2750</td>
<td>-793.2472</td>
<td>-793.2244</td>
</tr>
<tr>
<td>4.2</td>
<td>-793.2698</td>
<td>-793.2520</td>
<td>-793.2573</td>
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<td>-793.2266</td>
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<td>4.6</td>
<td>-793.2458</td>
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<td>-793.2326</td>
<td>-793.2208</td>
</tr>
<tr>
<td>4.8</td>
<td>-793.2341</td>
<td>-793.2242</td>
<td>-793.1802</td>
<td>-793.2250</td>
<td>-793.2161</td>
</tr>
</tbody>
</table>

* See footnote to Table 17.
The greatest contributory factor to the discrepancy between theory and experiment for S\textsubscript{2} lies in the use of the minimal basis set VCI method. Since the complete minimal basis set CI on the sulphur atom lowers the energy by 0.034 hartrees, it is reasonable to assume that the use of a more extensive CI for S\textsubscript{2} will lower the energy by almost twice this amount. A VCI calculation in which the nσ\textsubscript{g} and nσ\textsubscript{u} valence shell molecular orbitals are full is conveniently called a σ-orbital VCI and in the present work is easily obtained. In Appendix IX it is seen that the first 31 detors of \( \Sigma^+_g \) symmetry have the valence shell nσ\textsubscript{g} and nσ\textsubscript{u} orbitals doubly occupied. The \( 3 \Sigma^-_g \) and \( 1 \Sigma^+_g \) codetors arising from these detors are components of the σ-orbital VCI wave functions (see Chapters 7 and 8, also Meckler\textsuperscript{42}) for these states. There are 9 \( 3 \Sigma^-_g \) codetors and 12 \( 1 \Sigma^+_g \) codetors in the σ-orbital VCI. The results of these investigations are summarized in Tables 17 and 18, where the 9-term VCI represents the σ-orbital VCI for the \( 3 \Sigma^-_g \) state, the 30-term VCI is the current \( 3 \Sigma^-_g \) VCI result, the 12-term VCI is the σ-orbital VCI for the \( 1 \Sigma^+_g \) state and the 37-term VCI the current VCI result for this state. The difference in energy between the σ-orbital VCI energy and the complete VCI energy decreases as the internuclear separation increases. This result is expected as in the \( 3P \) ground state of the atoms only the p-type orbitals of the valence shell contribute to the wave function, and the s-type are always occupied. A similar effect should be seen in a more extensive CI on S\textsubscript{2}, which includes detors corresponding to excitations from the inner shell σ-orbitals. The present result for \( R = 2.3 \) in the ground state of O\textsubscript{2} is in good agreement with that of Kotani et alia\textsuperscript{43}, who give the energy of the 9-term VCI as -149.1332 and that of the complete VCI as -149.1911 hartree. They used different values for the orbital exponents to those used here.

An interesting feature of Figs. 16-20 is the existence of a number of
avoided crossings of the potential curves. The wave functions of the two energy levels \( 2S+1 \left( \sigma \right)_I \) and \( 2S+1 \left( \sigma \right)_II \) may be written

\[
\psi_I = \sum_i \psi_i c_{iI}, \quad (10.1a)
\]

and

\[
\psi_{II} = \sum_k \psi_k c_{kII}, \quad (10.1b)
\]

respectively. In (10.1) \( \psi_i \) and \( \psi_k \) are codetors of \( 2S+1 \left( \sigma \right)_I \) symmetry. Let

\[
V_{ik} = \langle \psi_I | J | \psi_k \rangle,
\]

\( V_{ii} \) is the total energy of the codetor \( \psi_i \) and the off-diagonal elements \( V_{ik} \) are very small. The energies corresponding to \( \psi_I \) and \( \psi_{II} \) are

\[
V_I = \sum_{ik} c_{iI} c_{kI} V_{ik},
\]

and

\[
V_{II} = \sum_{ik} c_{iII} c_{kII} V_{ik}.
\]

The conventional notation implies that \( V_I < V_{II} \), and as \( |V_{ik}| \ll |V_{ii}| \), both \( V_I \) and \( V_{II} \) are dominated by the energy corresponding to the codetors with the absolutely largest coefficient in \( \psi_I \) and \( \psi_{II} \). As the internuclear distance varies \( V_{ii} \) will also vary and its value relative to other diagonal terms will change. The "non-crossing" rule \( (70) \) may be interpreted as the statement that the potential energy curves of two electronic states of the same symmetry species cannot cross. If \( V_I \) is to remain below \( V_{II} \),
<table>
<thead>
<tr>
<th>( \psi_i )</th>
<th>( R = 2.1 )</th>
<th>( R = 2.3 )</th>
<th>( R = 2.5 )</th>
<th>( R = 2.7 )</th>
<th>( R = 2.9 )</th>
<th>( R = 3.1 )</th>
<th>( R = 4.0 )</th>
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<tbody>
<tr>
<td>1</td>
<td>0.00620</td>
<td>-0.01029</td>
<td>-0.04302</td>
<td>0.96567*</td>
<td>0.98217*</td>
<td>0.98062*</td>
<td>0.93752*</td>
</tr>
<tr>
<td>2</td>
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<td>0.01725</td>
<td>0.01794</td>
<td>-0.01579</td>
<td>-0.01454</td>
<td>-0.01397</td>
<td>-0.01158</td>
</tr>
<tr>
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<td>0.02600</td>
<td>0.02367</td>
<td>0.05256</td>
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<td>0.03404</td>
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</tr>
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<td>0.06357</td>
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<td>7</td>
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<td>-0.03906</td>
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<td>0.03098</td>
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</tr>
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<td>0.65834*</td>
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<td>-0.00439</td>
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<td>0.00032</td>
</tr>
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<td>0.24529</td>
<td>0.21333</td>
<td>-0.07919</td>
<td>-0.02513</td>
<td>-0.01326</td>
<td>0.00216</td>
</tr>
<tr>
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<td>0.00274</td>
<td>0.00635</td>
<td>0.00716</td>
<td>0.00592</td>
<td>0.00465</td>
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<td>15</td>
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<td>-0.17224</td>
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<td>-0.02205</td>
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</tr>
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<tr>
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<td>0.01539</td>
<td>0.01298</td>
<td>-0.07651</td>
<td>0.07443</td>
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<td>0.02339</td>
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</tr>
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<td>0.01452</td>
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* Absolutely largest value
the dominant codetor in \( \Psi \) must always be that with the lowest energy. If some of these energies are degenerate the coefficients of the appropriate detors will be nearly equal. A rapid variation of the coefficients defining a wave function with respect to the codetors is a consequence of the non-crossing rule. In Table 19 the coefficients of the \( ^3\Sigma_g^{-} \) and \( ^3\Sigma_g^{+} \) states are seen to vary rapidly as \( R \) varies. The distortion of the potential curves (fig. 16) in the region of \( R = 2.6 \) bohr indicates an avoided crossing. The distortion of the upper curve at about 2.5 bohr indicates an avoided crossing with a higher level not shown in the diagram. Several other examples are evident in Figs. 17 to 20.

The initial results from the natural spin-orbital analysis option of SECSII (Appendix VII) indicated that, for the atomic and molecular states examined, the VCI wave functions produced a set of natural spin-orbitals which was identical to the set of orthonormal symmetry adapted molecular spin-orbitals. The occupation numbers of the natural spin-orbitals forming the frozen shell were unity, and the values for the remaining natural spin-orbitals could easily be estimated by inspection of the wave function. Only with the complete CI atomic wave function was the natural spin-orbital basis different from the orthonormal spin-orbital basis. Little use was made of the natural spin-orbital analysis option because the time taken to construct and diagonalize the first order density matrix for a given energy level was almost as great as that taken to construct and solve the secular equation for which the energy level was a solution. It was felt that use of this option would add little to the present investigation of the VCI method.

A valuable indication of the merits of the VCI method can be made in view of some recent work by Dixon(71). Using the integrals output by the program INTRA (Appendix VI) he calculated the open-shell SCF energies of the \( O_2 \) and \( S_2 \) molecules in their \( X^3\Sigma_g^{-} \) ground state at a number of internuclear separations. The VCI method produces much better results than the
SCF method for oxygen at each bond length (see Table 17) and also predicts the dissociation products correctly, whereas the SCF energies indicate dissociation products of atoms in the \(^1S\) state. This is yet another example of the failure of the SCF method to predict correct dissociation products. The electron correlation introduced by even the \(\pi\)-orbital VCI is sufficient in the case of \(O_2\) to cause a significant drop in the total energy at each bond length compared with the SCF value. Examination of the results for \(S_2\) given in Table 18 show that the SCF gives better results than the VCI for bond lengths less than 4.0 bohr. The potential curve for the SCF results is a little deeper and rather more steep than the VCI curve but, as in the \(O_2\) calculation, the dissociation products are incorrect as, even at \(R = 4.8\) bohr, the energy of the \(X^3\Sigma_g^-I\) state is above that of the \(3P + 3P\) energy of the separated atoms. A single configuration wave function lacks electron correlation and in general this deficiency can be partly remedied by using a CI. The CI will cause a lowering of the electronic energy with respect to the single configuration value. In the case of the VCI wave function the amount of electron correlation introduced is restricted by excluding codetors which represent excitations from the inner shell \(\pi\)-orbitals. As was mentioned earlier the VCI for the sulphur atom produced an energy inferior to that of the SCF, but a complete minimal basis set CI was slightly better. The improvement in the energy in the atomic case is due entirely to the inclusion of excitations from the inner shell \(p\)-orbitals in the wave function. It may be reasonably assumed that the inclusion of excitations from the inner shell \(\pi\)-orbitals in \(S_2\) will cause a substantial decrease in the total energy in the correct part of the potential curve, this may also improve the values of the spectroscopic constants. The inference is that whilst the VCI method is rather good at describing states of the first row molecules, it may not be quite so good for other diatomic molecules. An examination of the VCI method in greater
detail for $S_2$ must wait until SECSØL has been modified to handle a far greater number of detors than the present limit of 120.
In the preceding chapters of Part II, the method of configuration interaction has been examined in detail. Methods for calculating CI wave functions and the less accurate valence configuration interaction wave functions of atomic and molecular systems have been described. It has been shown that the VCI method produces results which are in good agreement with experimental values when small atoms and molecules such as oxygen and $O_2$ are examined. Whilst the absolute values of the energies of the various states of $S_2$ calculated by means of the VCI method are not too good, the relative positions of the low-lying energy levels are in good agreement with the experimental values$^{(68)}$. A disappointing result of the work on both atomic and diatomic sulphur is that the SCF energies are slightly better than those for the VCI. The calculation of the VCI and complete minimal basis set CI energies, for the $^3P$ ground state of the sulphur atom clearly indicate that the contributions from delsors corresponding to excitations from inner shell 2p-orbitals cannot be neglected. This neglect may also explain why the $^1D$ and $^1S$ levels of the sulphur atom are close together in comparison with experimental values$^{(68)}$. If the delsors which correspond to excitations from the inner shell $\pi$-orbitals were to be included in the $S_2$ wave functions a lowering of the energy of at least twice the amount calculated in the atomic system could be expected. The poor agreement of the $S_2$ spectroscopic constants can be attributed to the VCI method, although difficulties can arise in the numerical analysis involved in the calculation of these quantities.

A very favourable aspect of the CI method in general is the ease with which it may be implemented on a digital computer, and the flexibility of
the method which, by its very nature, permits the examination of various low-lying excited states in addition to the ground state. The present implementation is designed to achieve flexibility with minimum effort. Consequently, it is possible to perform complete minimal basis set CI calculations. Having calculated the matrix elements between the appropriate detors for the complete CI, the energies corresponding to various groups of detors in the complete wave function can be obtained with ease. Similarly it is possible to perform an extensive VCI calculation and to then examine the effects of keeping certain of the valence shell molecular orbitals frozen. The $\pi$-orbital VCI calculations discussed in Chapter 10 illustrate the use of this feature.

The SCF calculations of Dixon $(71)$ took slightly longer than the VCIs for both oxygen and sulphur, so that the return in information from a VCI calculation is much greater. It is surprising that so few $(10)$ large VCI calculations have been attempted. There are problems in performing any type of CI calculation, but these problems are really no different from those encountered in SCF calculations which employ large bases of Gaussian-type orbitals.

The performance of the programs listed in the appendices is highly satisfactory. In the light of experience minor improvements were introduced into most of the programs during the production of the results quoted in Chapter 10. These made the programs easier to use and some resulted in a reduction of the amount of data supplied on punched cards.

The calculations on $S_2$ were almost at the limit of the range of SECSUL (Appendix VII) and certain major improvements, not apparent with the smaller $O_2$ molecule, have become obvious during the course of the $S_2$ work. These improvements will necessitate some considerable rewriting of the program. Perhaps the most pressing requirement is to make more efficient use of the array IDIFF (see Chapter 8), which is used in the
evaluation of the off-diagonal matrix elements between detors. In the present program this array has to be constructed each time the bond length of the molecule or the symmetry species of the detors is changed. This process can occupy more than 50% of the total CPU time for a given problem, which consists of the computation of the matrix elements between detors, construction of the secular equation and its solution. The array IDIFF does not depend on the bond length of a diatomic molecule. The present version of the program only dumps IDIFF on disc if it is too big for the available core store; it is overwritten later in the calculation. Without substantial rewriting and increasing the current storage requirements it is not possible to dump the array unconditionally and read it into core when required later. Naturally this improvement will speed the natural spin-orbital analysis since the array IDIFF, in a shortened form may be used there. This will then make the construction of the first order density matrix less expensive in terms of CPU time. A result of this improvement will be the relative ease of computation of molecular properties, such as dipole moments, since \( \langle 0 \rangle = \text{Tr}(\gamma P) \), where 0 is a one-electron operator, \( \gamma \), the first order density matrix and \( P \) the matrix of integrals of the one-electron property over the same orbital basis as \( \gamma \).

The ease with which the matrix elements between codetors of the same symmetry species may be projected from the matrix elements over the appropriate detors, compensates for the time required to evaluate the latter. Certainly in \( O_2 \) this feature reduced the CPU time by about \( \frac{1}{3} \).

In order to increase the number of detors that can be included in a CI wave function, a scheme in which only the non-zero matrix elements are stored is being investigated. At the same time, the possibility of only storing a list of non-redundant non-zero integrals over the orthonormal molecular orbitals is being considered. The integral generation programs produce non-redundant lists of integrals over the atomic orbitals, but the
lists contain zeros. However, the very rapid access to all of the integrals required in the calculation, which is necessary in the SCF procedure, is not so important in the CI process, since the list need only be scanned once or twice.

Even without the improvements mentioned in the preceding paragraphs, SECSOL may be used to provide many more useful results. In addition to the work reported here, calculations on other excited states of $S_2$ are in progress. The triplet and singlet $\Pi_g$ states are of particular interest, as the lowest levels of both states lie close to the $^3P + ^3P$ energies of the separated atoms. Since the relative positions of many of the states of $S_2$ are not known with any certainty this invites further study. Calculations of the wave functions for the diatomic molecules $F_2$ and $O_2^{3-}$ are in progress, and a calculation on CN is being considered. The possible use of Gaussian type orbitals, rather than the Slater-type so far used, is being investigated in connection with work on polyatomic molecules. The general theme of the proposed research is to evaluate the VCI method. The full potential of both the VCI and CI methods remains to be examined and exploited.
APPENDIX I

ATOMIC UNITS AND CONVERSION FACTORS

For atoms and molecules the Hamiltonian is made up from terms which represent the electrostatic interactions of the particles and the kinetic energy of the electrons. Since the nuclear motion may often be regarded as a quasi-static process as far as the electrons are concerned, it is justifiable to disregard the kinetic energy of the nuclei, and hence their Laplacian operators. The Schrödinger equation for a system of \( N \) electrons moving in the potential field of a fixed framework of \( M \) nuclei may then be written

\[
\left( \frac{\hbar^2}{2m_e} \sum_{i=1}^{N} \nabla_i^2 + (E_E - V_E) \right) \Psi = 0 \quad (I.1)
\]

In (I.1) \( V_E \) is the potential energy operator:

\[
V_E = - \sum_{K=1}^{M} \sum_{i=1}^{N} \frac{Z_K e^2}{r_{ik}} + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{e^2}{r_{ij}}
\]

The first term in \( V_E \) represents the nuclear-electron attraction energy and the second the electron-electron repulsion energy. In (I.1) \( E_E \) is the electronic energy and the first term is the kinetic energy operator for all the electrons. Both the value of \( E_E \) and its units will depend on,

(a) the units of \( \hbar \), Planck's constant divided by \( 2\pi \), \( m_e \) the electron rest mass, and \( e \) the electron charge, and

(b) the currently accepted values of these quantities.

Shull and Hall\(^{(75)} \) proposed the system of primary units in which \( m_e, e, \) and \( \hbar \) have the value unity. In the system of primary units the unit of energy is the hartree:

\[
1 \text{ hartree} = \frac{m_e e^4}{\hbar^2}
\]
and the unit of length is the bohr:

\[ 1 \text{ bohr} = \frac{\hbar^2}{m_e e^2} \]

Rewriting (I.1) in these units gives

\[
(\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 + (E_E + \sum_{K=1}^{M} \sum_{i=1}^{N} \frac{Z_K}{r_{iK}} - \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{1}{r_{ij}}) ) \Psi = 0.
\]

This form of Schrödinger's equation is used throughout this thesis, and is independent of the vagaries in measurement of \( m_e \), \( e \), and \( \hbar \).

For purposes of comparison with experimental results it is necessary to convert from the system of primary units to some system of secondary units, such as SI units. The values of the fundamental physical constants used in the conversion factors are given in Table I-1, and are taken from a more complete table of fundamental constants compiled by Cohen and DuMond\(^\text{(74)}\). The conversion factors for various units of energy are given in Table I-2. All masses are measured on the unified nuclidic mass scale\(^\text{(57)}\), in which the mass of the \(^{12}\)C nucleus is taken to be 12 atomic mass units (sometimes abbreviated amu, but the symbol u is used to indicate values on the unified nuclidic mass scale).
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<tr>
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<td>$1.2472 \times 10^{-13}$</td>
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<td>$1.251 \times 10^{-13}$</td>
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APPENDIX II

MOLECULAR ORBITALS FOR THE GROUP $D_{\infty h}$

The complex Slater-type orbitals defined in (7.16) are suitable basis atomic orbitals for the group $D_{\infty h}$ because the factor $\exp(j\eta \phi)$ is an eigenfunction of the rotation operator of the group (39). For the purposes of this appendix the notation $\varphi(a(n, l, m, \ell))$ will be used to denote a complex Slater-type orbital defined with respect to a nucleus C in the co-ordinate system of Fig. 15. By consideration of the effect of each of the four basic operations of the group (see Table 5) on a point it is easily shown that

$$
0_{C_{\eta}} \varphi_A(n, l, m, \ell) = \varphi_A(n, l, m, \ell) \exp(jm\eta),
$$

$$
0_{c_{\eta}} \varphi_A(n, l, m, \ell) = (-1)^{\frac{1}{2}} \varphi_B(n, l, m, \ell) \exp(jm\eta),
$$

$$
0_{\sigma C_{\eta}} \varphi_A(n, l, m, \ell) = \varphi_A(n, l, m, \ell) \exp(-jm\eta),
$$

and

$$
0_{\sigma C_{\eta}} \varphi_A(n, l, m, \ell) = (-1)^{\frac{1}{2}} \varphi_B(n, l, m, \ell) \exp(-jm\eta).
$$

A similar set of results is obtained for $\varphi_B(n, l, m, \ell)$. Using these relations and the projection operator defined in (7.4) the following SAMOs are obtained:

$$
\sigma_{\varepsilon} : \varphi_A(n, l, -0, \ell) + (-1)^{\frac{1}{2}} \varphi_B(n, l, 0, \ell),
$$

$$
\sigma_u : \varphi_A(n, l, 0, \ell) - (-1)^{\frac{1}{2}} \varphi_B(n, l, 0, \ell),
$$

$$
\pi_{\varepsilon} : \varphi_A(n, l, \pm 1, \ell) + (-1)^{\frac{1}{2}} \varphi_B(n, l, \pm 1, \ell),
$$

$$
\pi_u : \varphi_A(n, l, \pm 1, \ell) - (-1)^{\frac{1}{2}} \varphi_B(n, l, \pm 1, \ell),
$$

$$
\delta_{\varepsilon} : \varphi_A(n, l, \pm 2, \ell) + (-1)^{\frac{1}{2}} \varphi_B(n, l, \pm 2, \ell).
$$
\[ \delta_{\pm}^{\pm} : \varphi_A(n, 1, \pm 2, \ell) - (-1)^{l} \varphi_B(n, 1, \pm 2, \ell) , \]
\[ \gamma_{\pm}^{\pm} : \varphi_A(n, 1, \pm 3, \ell) + (-1)^{l} \varphi_B(n, 1, \pm 3, \ell) , \]
\[ \gamma_{\pm}^{\pm} : \varphi_A(n, 1, \pm 3, \ell) - (-1)^{l} \varphi_B(n, 1, \pm 3, \ell) . \]

The symbol to the left of each molecular orbital is the usual spectroscopic notation: if the modulus of the angular momentum \( m \) is 0, 1, 2, 3, ... then the orbital is designated \( \sigma, \pi, \delta, \gamma, ... \) and each orbital transforms according to the \( \Sigma^+_{\pm}, \Pi^+_{\pm}, \Sigma^0_{\pm}, \Pi^0_{\pm}, \ldots \) irreducible representation depending on the parity under the operation of inversion. The symmetry species of a molecular orbital is defined by \( m \) and the subspecies by the sign of \( m \) and the inversion parity. Within a given subspecies the molecular orbitals are not orthogonal, but orbitals belonging to different subspecies are orthogonal. To identify specific molecular orbitals an additional notation may be used and it is best illustrated by some examples:

\[ 1s\sigma_g = \varphi_A(1, 0, 0, \ell) + \varphi_B(1, 0, 0, \ell) , \]
\[ 1s\sigma_u = \varphi_A(1, 0, 0, \ell) - \varphi_B(1, 0, 0, \ell) , \]
\[ 2p_0\sigma_g = \varphi_A(2, 1, 0, \ell) - \varphi_B(2, 1, 0, \ell) , \]
\[ 2p_+\pi_g = \varphi_A(2, 1, 1, \ell) - \varphi_B(2, 1, 1, \ell) , \]
\[ 2p_-\pi_u = \varphi_A(2, 1, -1, \ell) + \varphi_B(2, 1, -1, \ell) . \]
In calculations on the electronic structure of homonuclear diatomic molecules it is assumed that the basis atomic orbitals defined for one nucleus have a one to one correspondence with those on the other.

To determine the linear combinations of determinants which are eigenfunctions of the reflection operator \( \sigma_{xz} \), it is necessary to know the effect of this operator on the SAMOs. Since any plane of reflection containing the internuclear axis is equally possible, choice of a particular plane will not alter the final result; the \( xz \)-plane (Fig. 15) was chosen for the present calculations. The properties of the SAMOs under reflection in this plane are easily determined since this operation merely changes the sign of \( m \), for example

\[
\sigma_{xz} \pi_{\pm}^{\pm} = \pi_{\mp}^{\pm}
\]

and

\[
\sigma_{xz} \pi_{\pm}^{-} = \pi_{\pm}^{-}
\]

The symmetry properties of the molecular orbitals are invariant under a unitary transformation so that the properties of an orthonormal set of SAMOs may be obtained by inspection of the non-orthonormal set. As an example, consider the orbital

\[
\varphi = c_1(1s\sigma_g) + c_2(2s\sigma_g) + c_3(2p\sigma_g)
\]

reflection in the \( xz \)-plane leaves this orbital unchanged as each of the \( \sigma \)-molecular orbitals is invariant under \( \sigma_{xz} \) however the orbital

\[
\varphi_+ = c_1(2p_+\pi_g) + c_2(3d_+\pi_g)
\]
is carried into

$$\varphi_\downarrow = c_1(2p_\pi g) + c_2(3d_\pi g)$$

since the sign of $m$ is changed by $\sigma_{xz}$.
APPENDIX III
UTILITY ROUTINES

The subprograms listed in this appendix are used by several of the programs listed in Appendices IV-VIII. The subroutines TQL2 and TRED2 constitute the QR-Algorithm\(^{(47, 48)}\) and are FORTRAN V versions of routines written, in FORTRAN IV by the staff of the University of Leicester Computer Laboratory. The author expresses his thanks to the Director for permission to include these routines.
*FORTRAN LIB
SUBROUTINE ENTR(PRNAME,NO)
C.....VERSION 3.
    TEXT PRNAME
    DATA LP/0/
    IF(NO) 1,3,1
    1 CALL CNTR(I)
    WRITE(LP,2) PRNAME,1
    2 FORMAT("NUMBER OF INSTRUCTIONS USED ON ENTRY TO SUBPROGRAM ",A6,
        1=",I5)
    3 RETURN
END

*FORTRAN LIB
SUBROUTINE ERROR(A)
    DATA LDN02/0/
    TEXT A
    WRITE(LDN02,1) A
    1 FORMAT(LIN1,ISAS)
    CALL EXIT
    RETURN
END

*FORTRAN LIB
FUNCTION IPAR(N)
    INTEGER N
    C.....IF N IS EVEN THEN IPAR = 0,
    C.....IF N IS ODD THEN IPAR = 1.
    C.....*** ATLAS BASIC LANGUAGE ***
    101,41,1,-0.4
    101,41,41,0.4
    121,32,0,1
    137,32,41,0
    113,32,0,IPAR+0.4
    121,32,0,*G3000000
    113,32,0,IPAR
    RETURN
END

*FORTRAN LIB
SUBROUTINE QUIT(PRNAME,NO)
C.....VERSION 2.
    TEXT PRNAME
    DATA LP/0/
    IF(NO) 1,3,1
    1 CALL CNTR(I)
    WRITE(LP,2) PRNAME,1
    2 FORMAT("NUMBER OF INSTRUCTIONS USED ON EXIT FROM SUBPROGRAM ",A6,
        1=",I5)
    3 RETURN
END

*FORTRAN LIB
SUBROUTINE TQL2(N,EPS,NZ,Z,D,E,NN)
    DIMENSION Z(NZ,NZ),D(NZ),E(NZ)
    C THIS SUBROUTINE GIVES ALL THE EIGENVALUES AND EIGENVECTORS OF A
    C TRIDIAGONAL MATRIX
    CLEAR NN
    IF ( N .LT. 2 ) GOTO 1
    DO 10 I = 2,N
    10 E(I-1) = E(I)
    END
CLEAR F,B,E(N)
DO TO L = 1,N
CLEAR J
I = I * (ABS(B(L)) + ABS(E(L)))
IF ( I .GE. N ) GOTO 2
B = H
2 DO 50 J = L,N
50 IF ( I .GT. B ) GOTO 3
3 IF ( J .LE. L ) GOTO 4
5 IF ( J .NE. L ) GOTO 6
J = J + 1
P = (P(L+1) - E(L))/2*E(L)
R = SQRT(P**2 + 1)
IF ( P .LT. 0 ) GOTO 7
H = D(L) - S(L)/(P+R)
GOTO 111
7 H = P(L) - S(L)/(P-R)
111 DO 40 I = L,N
40 D(I) = D(I) - H
F = F + H
P = P + H
C = 1
CLEAR S
IF ( I .LE. L ) GOTO 3
KK = -(K-1)
KKK = -L
DO 50 II = KK,KKK
I = -II
G = C*3(I)
H = C*P
IF ( ABS(P) .LT. ABS(E(I))) GOTO 9
C = E(I)/P
R = SQRT(C**2 + 1)
S(I+1) = S*P*R
S = S/R
C = 1/R
GOTO 111
9 C = P/E(I)
R = SQRT(C**2 + 1)
S(I+1) = S*P*R
S = S/R
C = C/R
110 D(I+1) = H - S*(C*G + S*D(I))
DO 50 K = 1,N
H = Z(K,I+1)
Z(K,I+1) = S*Z(K,I) + C*H
Z(K,I) = C*Z(K,I) - S*H
50 CONTINUE
3 D(L) = S*P
D(L) = C*P
IF ( ABS(S(L)) .GT. B ) GOTO 5
4 D(L) = D(L) + F
5 CONTINUE
DO 70 I = 1,N
K = I
P = D(I)
IF ( I .EQ. N ) GOTO 11
II = I + 1
DO 60 J = II,N
IF ( J(J) .GE. P ) GOTO 30
K = J
P = J(J)
30 CONTINUE
11 IF ( K .LT. I ) GOTO 13
I(K) = D(I)
P(I) = P
DO 50 J = 1,N
P = Z(J,I)
Z(J,I) = A(J,K)
50 Z(J,K) = P
13 CONTINUE
70 CONTINUE
600 RETURN
11(I) = Z(I,1)
Z(1,1) = 1.0
GOTO 600
6 NN = 1
RETURN
END

*FORTRAN LIB
SUBROUTINE TR3D2(N,TOL,NA,A,Z,D,E)
C THIS SUBROUTINE TRIDIAGONALISES A SYMMETRIC MATRIX
DIMENSION A(NA,NA),Z(NA,NA),D(NA),E(NA)
DO 10 I = 1,N
DO 20 J = 1,I
Z(I,J) = A(I,J)
20 CONTINUE
10 CONTINUE
IF ( N .LT. 2 ) GOTO 1
M = -N
MM = -2
DO 30 II = M ,MM
I = -II
L = I-2
F = Z(I,I-1)
CLEAR G
IF ( I .EQ. 2 ) GOTO 2
DO 40 K = 1,L
40 G = G + Z(I,K)*Z(I,K)
2 H = G - F*F
IF ( G .GE. TOL ) GOTO 3
3 L = L + 1
IF ( F .GE. 0 ) GOTO 4
Z(I) = SQRT(H)
G = Z(I)
GOTO 7
4 Z(I) = -SQRT(H)
G = Z(I)
7 H = H-F*G
Z(I,I-1) = F-G
CLEAR F
DO 50 J = 1,L
CLEAR G
Z(J,I) = Z(I,J)/H
DO 60 K = 1,J
60 CONTINUE
G = G + Z(J,K) * Z(I,K)
IF ( J = K, L ) GOTO 5
JJ = J + 1
DG 70 K = JJ, L
70 G = G + Z(K,J) * Z(I,K)
5 E(J) = G/H
50 F = F + G * Z(J,I)
III = F/(H+II)
DG 80 J = 1, L
F = Z(I,J)
E(J) = X(J) - III*F
G = E(J)
L0 120 K = 1, J
Z(J,K) = Z(J,K) - F*E(K) - G*Z(I,K)
140 CONTINUE
30 CONTINUE
111 F(I) = H
30 CONTINUE
CLEAR D(I), Z(I)
LD 100 I = 1, N
L = I-1
IF ( D(I) .EQ. 0 ) GOTO 6
IF ( I .EQ. 1 ) GOTO 6
DD 110 J = 1, L
CLEAR G
DG 120 K = 1, L
120 G = G + Z(I,K) * Z(K,J)
DD 130 J = 1, L
K(J,K) = Z(K,J) - G*Z(I,K)
130 CONTINUE
110 CONTINUE
6 F(I) = Z(I,I)
K(I,I) = 1
IF ( I .EQ. 1 ) GOTO 100
DD 130 J = 1, L
CLEAR Z(J,I), Z(I,J)
130 CONTINUE
100 CONTINUE
1 CONTINUE
1 RETURN
END

*FORTRAN LIB
SUBROUTINES WRITEK(A,NCOL,NROW,MRKW,MCOL,LP)
C.....OUTPUT OF REAL MATRIX TO DEVICE NUMBER LP.
DIMENSION A(NROW,NCOL)
DO 4 I=1, NCOL, 5
J=I-1
IF(J-MCOL) 2,2,1
1 J=MCOL
2 WRITE(LP,3) I,J
3 FORMAT(6",5EX,2X,"COLUMNS",I3," TO ",I3)
DO 4 K=1, NROW
WRITE(LP,5) (A(K,L),L=I,J)
4 CONTINUE
5 FORMAT(" "*,1P5E24.10)
RETURN
END
GENDET is described in Chapters 7 and 8 and, although specifically designed for the \( \text{D}_{\infty h} \) symmetry group, can be easily adapted to work for both \( \text{D}_{\infty h} \) and \( \text{C}_{\infty v} \). As stated in Chapter 7 each detor is characterized by its axial angular momentum \( \Lambda \) and the value of the \( Z \)-component \( S_z \) of the electron spin. This program also computes the effect of an inversion on each detor and, for \( \Sigma \) detors the effect of a reflection in the \( xz \)-plane. The matrix elements \( \langle D_\| | S^2 | D_j \rangle \) are computed (\( D_\| \) and \( D_j \) are detors) and the corresponding matrix is diagonalized to provide eigenfunctions of \( S^2 \). The program outputs the detors on cards in the form of spin-orbital identifiers for each detor. The spin-orbitals are numbered from 1 to \( N_{\text{KEEP}} \), and an inversion or reflection on each spin-orbital produces another spin-orbital with an identifier in this range.

This program uses two common disc areas, each of 200 blocks in length and these are devices 58 and 59. The line printer is stream 0 and the card punch stream 5. GENDET requires the subprograms IPAR, TQL2, TRED2, and WRITMX from Appendix III. The store requirements are standard.

Data Specification for GENDET

Card 1. \( N_{\text{KEEP}}, N_{\text{FULL}}, M_{\text{KEEP}}, \text{INVERS, MREQ, SREQ} \)

FORMAT (515, F10.5)

\[
N_{\text{KEEP}} \quad \{
\begin{array}{c}
= 0 \text{ to stop execution,} \\
= \text{number of spin-orbitals}
\end{array}
\}
\]
NFULL = number of spin orbitals frozen
(1ST. NFULL orbitals in each detor will be the same).
MKEEP = number of electrons
INVERS = 0 if gerade detors are required
         = 1 if ungerade detors are required.
MREQ = required value of axial angular momentum, \( \Lambda \)
SREQ = required value of z-component of electron spin, \( S_z \).

Card 2 (I)  IREF(I), INVR(I), M\( \Psi \)(I)

FORMAT (3I5)

IREF(I) = signed identifier of the spin-orbital resulting from the reflection of the
         I-th spin-orbital in the XZ-plane
INVR(I) = signed identifier of the spin-orbital resulting from the inversion of the
         I-th spin orbital
(1 \( \leq \) I \( \leq \) NKEEP)

Card 3  F

FORMAT (9A8)

F is an array which defines the output format of the detors on the lineprinter; it has the form

\(((\text{'b'}, I3, LX, mI3, nX, I4, 6X, I4))\)
or\(((1Hb, I3, LX, mI3, nX, I4, 6X, I4))\)
b is a blank; l, m and n have the following numerical values:

\[
m = NKEEP \\
n = l + 3 \\
2l = 3(21 - m)
\]

Variations are possible.

**Restrictions**

\[
NKEEP \leq 30 \\
0 \leq NFULL \leq 8
\]

The program will stop if the number of detors generated for a given set of \( A \) and \( S_z \) exceeds 200. At the end of a set of data the first card of the next set is read, execution ceases if \( NKEEP = 0 \).
--- FORTRAN LIB 4,142,168 ---

C.....DETERMINANT GENERATOR. THIS PROGRAM GENERATES ALL POSSIBLE
C.....M-ELECTRON DETERMINANTS OBTAINABLE FROM N-SPIN ORBITALS.
C.....THE AXIAL ANGULAR MOMENTUM AND Z-COMPONENT OF ELECTRON SPIN ARE
C.....DETERMINED AND ONLY THOSE DETERMINANTS WITH REQUIRED VALUES ARE
C.....OUTPUT TOGETHER WITH INFORMATION ABOUT THE BEHAVIOUR OF THE
C.....DETERMINANT UNDER THE OPERATIONS OF INVERSION, REFLECTION AND S**2

COMMON IC,INVERS,L,P,M,MKEEP,MM1,MREQ,NC,NFULL,NKEEP,MP,SREQ,
1ISO(200,30),IFU(30),IGU(30),IREF(30),INVR(30),MCM(30),F(9),LI(30)

TEXT F
DIMENSION I CLEAR (6171)
EQUIVALENCE (IC,ICLEAR)
TEXT TEMP,SPIN
LOGICAL FIRST
DATA ICR/0/

C.....READ DATA.
C.....NKEEP=NUMBER OF SPIN-ORBITALS.
C.....NFULL=NUMBER OF SPIN ORBITALS FROZEN.
C.....MKEEP=NUMBER OF ELECTRONS.
C.....MRQ=REQUIRED VALUE OF AXIAL ANGULAR MOMENTUM(MZ).
C.....SREQ=REQUIRED VALUE OF Z-COMPONENT OF ELECTRON SPIN(SZ).
C.....IGU(I)=0 IF ORBITAL I IS GERADE AND 1 IF ORBITAL I IS UNGERADE.
C.....IREF(I)=RESULT OF AXIAL REFLECTION ON ORBITAL I.
C.....INVR(I)=RESULT OF INVERSION ON ORBITAL I.
C.....MOM(I)=AXIAL ANGULAR MOMENTUM OF ORBITAL I.
C.....ISERS=0 FOR GERADE DETERM. AND 1 FOR UNGERADE DETERM.

1000 CLEAR ICLEAR
READ (ICR,1) NKEEP,NFULL,MKEEP,INVERS,MREQ,SREQ
1 FORMAT(515,F10.5)
   IF(NFULL.EQ.0) GO TO 109
READ (ICR, 2) (IREF(I),INVR(I),MOM(I),I=1,NKEEP)
2 FORMAT(315)

C.....F IS A VARIABLE FORMAT STATEMENT - SEE SUBROUTINE SPINIR(OUTPUT OF
C.....RESULTS).
READ (ICR,999) F
999 FORMAT(9A8)
DO 997 I=1,NKEEP
   IF(INVR(I)) 9,3,9
997 CONTINUE
998 IGU(I)=1

C.....F IS A VARIABLE FORMAT STATEMENT - SEE SUBROUTINE SPINIR(OUTPUT OF
C.....RESULTS).
READ (ICR,999) F
999 FORMAT(9A8)
DO 997 I=1,NKEEP
   IF(INVR(I)) 9,3,9
997 CONTINUE
998 IGU(I)=1

3 TEMP='UNGERADE'
   GO TO 5
4 TEMP='GERADE'
   WRITE(LP,6) NKEEP,NFULL,TEMP,MRQ,SREQ
6 FORMAT(1x,34X,'M-ELECTRON DETERMINANTS FROM',13,' SPIN-ORBITALS
   (FIRST',I3,' ARE FROZEN')/','10X,'DETERMINANTS ARE: ','AS',
   'WIT 2H','12,' UNITS OF AXIAL ANGULAR MOMENTUM AND ','F4.1,
   'UNITS OF SPIN IN Z-DIRECTION'/)
   WRITE(LP,7)
7 FORMAT(1x,34X,'ORBITALS HAVE FOLLOWING PROPERTIES'/' ','4X,'ORBITA
   1L','10X,'INVERSION','10X,'REFLECTION','10X,'INVERSION SYMMETRY',
   2 'SPIN','10X,'AXIAL MOMENTUM')
   TO 15 I=1,NKEEP
   IF(IGU(I)) 2,3,9
2 TEMP='GERADE'
   GO TO 10
9 TEMP='UNGERADE'

10 IF(MOD(I,2)) 12,11,12
11 SPIN=' BETA'
   GO TO 13
12 SPIN='ALPHA'
13 WRITE(LP,14) I,INVR(I),IREF(I),TEMP,SPIN,MOM(I)
14 FORMAT( ''18,13X,I5,14X,I5,20X,A3,14X,A3,7X,I7)
15 CONTINUE
   WRITE(LP,16)
16 FORMAT(''1/'' NO.'',26X,''DETERMINANT'',26X,''REFLECTION INVERSION'',14X
1,'''S**2'')
   N=NKEEP-NFULL
   M=MKEEP-NFULL
   MM=M-1
   NP=NFULL+1
   X DISPLAY(LP,13) /N,M,NP
   FIRST=.TRUE.
   CLEAR IC
17 CALL CCMBIN(IFU,N,M,FIRST)
   IF(FIRST) GO TO 15
   CALL SETUP
   GO TO 17
18 CALL SPINIR
   WRITE(LP,103) NC,MKEEP,NFULL,IC
108 FORMAT(0', 4X,214,'-ELECTRON DETERMINANTS WITH FIRST ',14,' SPIN
1 ORBITALS FROZEN- ',14, ' HAVE REQUIRED SYMMETRY AND SPIN VALUES')
   GO TO 1000
109 STOP
END

*FORTRAN LIB
   SUBROUTINE CCMBIN(J,N,K,FIRST)
   DIMENSION J(30)
   LOGICAL FIRST
   IF(FIRST) GO TO 5
NMK=N-K
I=K+1
1 I=I-1
   IF(J(I)-NMK-I) 2,4,4
2 E=J(I)
   DO 3 I=I,K
   M=M+1
3 J(L)=M
   CONTINUE
   GO TO 7
4 IF(I-1) 5,5,1
5 FIRST=.NOT.FIRST
   DO 6 I=1,K
   J(I)=I
   6 CONTINUE
7 RETURN
END

*FORTRAN LIB
SUBROUTINE OUTDET(INDEX,COE,ICOL,ID,F,IC,MKEEP)
   C......OUTPUTS RESULTS.
   COMMON KC,INVERS
   DIMENSION INDEX(200),COE(252),ICOL(252),ID(30)
   DIMENSION LIMSET(200,2),OP(20,20),EV(20),VR(20)
   DATA ICP,IDISC,JDISC,LP/5,5S,59,0/
   TEXT F(9)
   TEXT TEMP/'SINGLET'/
   WRITE(ICP,14) IC
   CLEAR NBLOCK
   TOL=2**(-347)
   X WRITE(LP,141) (I,INDEX(I),I=1,IC)
   X 141 FORMAT(2H ,14)
   EPS=2.0**(-35)
   DO 21 NIM=1,IC
   READ(IDISC) I,(ID(J),J=1,MKEEP),IRS,IVR,K,IALPHA,(ICOL(J),COE(J),U=1,1/
   LPILA)
   IF(IRE) 12,13,12
   12 IRE=ISIGN(INDEX(IABS(IRE)),IRS)
   13 IVR=ISIGN(INDEX(IABS(IVR)),IVR)*(-1)**INVERS
   X DISPLAY(LP,5) /I,INDEX(I),IALPHA,K,ICOL(I)
   I=IND2X(I)
   VRITE(LP,2) TEMP
   2 FORMAT(2H ,99X,AS>
   GO TO 9
   3 DO 4 J=1,IALPHA
   ICOL(J)=IND2X(ICOL(J))
   4 CONTINUE
   C......RE-ORDER ICOL SO THAT CONTENTS ARE IN ASCENDING ORDER.
   IRE=IALPHA-1
   IF(IRE) 71,71,41
   41 DO 7 J=1,IRE
   JMIN=ICOL(J)
   IVR=J+1
   DO 6 JJ=IVR,IALPHA
   IF(JMIN-ICOL(JJ)) 6,6,5
   6 JMIN=ICOL(JJ)
ICOL(JJ) = ICOL(J)
ICOL(J) = JMIN
CMIN = COE(JJ)
COE(JJ) = COE(J)
COE(J) = CMIN
6 CONTINUE
7 CONTINUE
71 WRITE(LP,8) (ICOL(J),COE(J),J=1,IALPHA)
8 FORMAT((' ',I9X,I10,4X,F7.3))
9 WRITE(ICP,10)(ID(J),J=1,MINSEP)
10 FORMAT(3212)
11 TRACEx MAX,MIN
WRITE(JDISC) K,IALPHA,(ICOL(J),COE(J),J=1,IALPHA)
MIN=ICOL(1)
MAX=MIN
IF(K) 17,17,11
11 IF(IALPHA=1) 17,17,15
15 DO 16 J=2,IALPHA
MIN=MINO(MIN,ICOL(J))
MAX=MAXO(MAX,ICOL(J))
16 CONTINUE
17 IF(NBLOCK) 19,18,19
18 NBLKX=NBLK+1
LIMSET(NBLK,1)=MIN
LIMSET(NBLK,2)=MAX
GO TO 21
19 IF(MIN-LIMSET(NBLK,2)) 20,20,18
20 LIMSET(NBLK,1)=MINO(MIN,LIMSET(NBLK,1))
LIMSET(NBLK,2)=MAXO(MAX,LIMSET(NBLK,2))
21 CONTINUE
22 READ IDISC
23 CONTINUE
C.....DIAGONALIZATION OF SPIN OPERATOR MATRIX.
WRITE(LP,22) NBLK
22 FORMAT('0',36X,'SPIN OPERATOR MATRIX HAS',14,' BLOCKS ON DIAGNAL'
1)
X WRITE(LP,220)
X 220 FORMAT('0',51X,'CONTENTS OF LIMSET'/''
X WRITE(LP,221)((1,J,LIMSET(I,J),J=1,2),I=1,NBLK)
X 221 FORMAT((' ',40X,2('LIMSET(',I3,'-',I1,')=',I4,4X))
DO 36 NLM=1,NBLK
MIN=LIMSET(NLM,1)
MAX=LIMSET(NLM,2)
IVR=MIN-1
IRE=MAX-IVR
CLEAR JMIN
CLEAR OP,EV,WK
DO 23 IVAL=MIN,MAX
READ (JDISC) K,IALPHA,(ICOL(J),COE(J),J=1,IALPHA)
JMIN=JMIN+1
DO 23 JVAL=1,IALPHA
IVX=ICOL(JVAL)-IVR
OP(JMIN,IVAL)=COE(JVAL)
23 CONTINUE
X CALL WRITEX(OP,20,20,IRE,IRE,LP)
CALL TRED2(IRE,TOL,20,OP,EV,WK)
CALL TQL2(IRE,EPS,20,OP,EV,WK,NFAIL)
C.....OUTPUT RESULTS FOR CURRENT BLOCK.
WRITE(LP,24) MIN,MAX
24 FORMAT('1'/'0',27X,'DETERMINANTS',14,' TO ',14,' FORM TOTAL SPIN E
IIGENFUNCTIONS AS F0LLCTr7S'
DO 25 IVAL=1,IRE
EV(IVAL)=SQRT(1.0+4.0*EV(IVAL))
25 CONTINUE
DO 29 IVAL=1,IRE,5
JVAL=IVAL+4
IF(JVAL.GT.IRE) JVAL=IRE
WRITE(LP,26) IVAL,JVAL,(EV(KVAL) ,KVAL=IVAL,JVAL)
26 FORMAT('0',33X, 'MULTIPICITIES (=2*S+1) FOR EIGENFUNCTIONS’,I4,’ T10 ’,I4/(’,1P5E24.10))
WRITE(LP,27) IVAL,JVAL
27 FORMAT('0',43X, 'EIGENVECTORS’,I4,’ TO ',I4/’ ’)
DO 29 KVAL=1,IRE
WRITE(LP,23) (CP(KVAL,JMIN),JMIN=IVAL,JVAL)
23 FORMAT(’,1P5E24.10)
29 CONTINUE
36 CONTINUE
REI7IND IDISC
REI7IND JDISC
RETURN
END

FORTRAN LIB
SUBROUTINE PERMUT(IOTA,IE,M,MI1,MAX)
C ....PERMUTES ELEMENTS (KI) OF IOTA SO THAT RESULT IS AN ORDERED
C ....CONFIGURATION WITH K1.K2.K3...LE.KM.
C ....IE=PARITY OF PERMUTATION.
DIMENSION IOTA(MAX)
IE=0
DO 3 J1=1,M
K1=I1+1
DO 2 J=I1,M
IF(IABS(IOTA(J1))-IABS(IOTA(I1))1,2,2
1 I2=IOTA(I1)
IOTA(I1)=IOTA(J1)
IOTA(J1)=I2
IE=IE:-1
2 CONTINUE
3 CONTINUE
IE=(-1)**IE
RETURN
END

FORTRAN LIB
SUBROUTINE SETUP
C  COMPUTES MZ AND SZ FOR DETERMINANT NC+1 AND DETERMINES SYMMETRY.
C ICN IC, INVERS,LP,M ,IC=KEEP,mil ,MRSQ,NC,NFULL,NR3EP,NP,SR3Q,
!ISA(200, 30) ,IFU(30) ,IGU(30) ,IREF(30) ,INVR(30) ,MOM(30),F(9)
TEXT F
NC=NC-1
IC=IC+1
CLEAR ISZ,MZ,INVERT
IC 4 I=1,M
J=IFU(I)+NFULL
ISO(IC,I)=J
IF(MOD(J,2)) 1,2,1
1 ISZ=ISZ+1
GO TO 3
SUBROUTINE SPINIR
C  DETERMINES RESULT OF INVERSION, REFLECTION AND TOTAL SPIN
C  OPERATIONS.

COMMON IC, INVERS, LP, M, NKEEP, MM1, MREQ, NC, NFULL, NKEEP, NP, SREQ,
ISO(200,30), IFU(30), IGU(30), IREF(30), INVR(30), MGM(30), F(9)
TEXT F
TEXT TEMP/

DIMENSION IUO(10,2), ISMOP(10,10), ISPOP(252,10), ICCEF(252), ID(30),
ICOL(252), ISOR(30), ISO(30), COS(252)
EQUIVALENCE (IFU, ID), (ICCEF, COS)

END
C. THESE CONTRIBUTE TO S**2.
   IF((ISO(I,1)+1)/2-(ISO(I,2)+1)/2) 2,3,2
   K=K+1
   IU0(K,1)=ISO(I,1)
   IU0(K,2)=1
   DO 6 J=2,NM1
   JCRB=(ISO(I,J)+1)/2
   IF((ISO(I,J-1)+1)/2-JCRB) 4,6,4
   4 IF((ISO(I,J-1)+1)/2-JCRB) 5,6,5
   5 K=K+1
   IU0(K,1)=ISO(I,J)
   IU0(K,2)=J
   6 CONTINUE
   IF(JCRB-(ISO(I,M)+1)/2) 7,8,7
   7 K=K+1
   IU0(K,1)=ISO(I,M)
   IU0(K,2)=M
   C. IF K=0 THIS DETERMINANT CONSISTS OF DOUBLY OCCUPIED SPATIAL
   C. ORBITALS AND S**2 PRODUCES ZERO - THUS IT IS A SINGLET.
   3 IF(K-1) 29,29,9
   C. S**2 OPERATOR
   9 CLEAR LSP,LSM
   DO 15 I=1,K
   IF(IPAR(IU0(I,IALPHA))) 10,15,10
   C. OPERATE ON ALPHA SPIN WITH S-.
   10 LSP=LSP+1
   DO 11 J=1,K
   ISMOP(LSM,J)=IU0(J,1)
   11 CONTINUE
   ISMOP(LSM,IALPHA)=IU0(IALPHA,1)
   DO 14 IBETA=1,K
   IF(IPAR(ISMOP(LSM,IBETA))) 14,12,14
   C. OPERATE ON BETA SPINS WITH S+.
   12 LSP=LSP+1
   DO 13 J=1,K
   ISPOP(LSP,J)=ISMOP(LSM,J)
   13 CONTINUE
   ISPOP(LSP,IBETA)=ISMOP(LSM,IBETA)-1
   14 CONTINUE
   15 CONTINUE
   C. COMPARE DETERMINANTS RESULTING FROM APPLICATION S+S- WITH ORDERED
   C. DETERMINANTS TO IDENTIFY THEM AND DETERMINE COEFFICIENTS.
   16 CONTINUE
   LSP=LSP-1
   DO 21 IOUTER=1,LSM
   INLIM=IOUTER+1
   DO 20 INNER=INLIM,LSP
   CLEAR IBETA
   DO 13 J=1,K
   IF(ISPOP(IOUTER,J)-ISPOP(INNER,J)) 17,13,17
   17 IBETA=1
   18 CONTINUE
   IF(IBETA) 20,19,20
   ICOEF(INNER)=ICOEF(INNER)+ICOEF(IOUTER)
   CLEAR ICOEF(IOUTER)
   19 CONTINUE
   20 CONTINUE
   21 CONTINUE
C.....DETERMINE IDENTIFIERS OF DETERMINANTS THAT RESULT FROM S**2.
C.....REASSIGN OCCUPIED ORBITALS.
211 DO 23 IALPHA=1,LSP
   IF(ICOE(IALPHA)) 22,23,22
22 DO 23 J=1,M
   ID(J)=ISC(I,J)
23 CONTINUE
   DO 24 J=1,K
   ID(J)=RSP(I,J)
24 CONTINUE
C.....RE-ORDER ID AND COLLATE WITH ISO.
   CALL PERMUT(ID,ID,M,MM,30)
   CALL COLATE(ISO,ID,M,200,30,IC,ICO)
   ICCL(IALPHA)=ICO
   COE(IALPHA)=ICOEF(IALPHA)
C.....OPERATE ON I-TH. DETERMINANT WITH S**2*(S**2-1).
   IF(I-ICO) 26,25,26
   COE(I)=FLOAT(ICOEF(IALPHA))+SREQ*(SREQ-1.0)
   COE(I)=SIGN(COE(I),IE)
25 CONTINUE
C.....OUTPUT RESULT.
C.....DETERMINANTS TO BE OUTPUT WITH FIRST NFULL ORBITALS.
29 DO 30 J=1,NFULL
   ID(J)=J
30 CONTINUE
   DO 31 J=MKEEP,NFULL+1
   ID(J)=RSP(I,J-NFULL)
31 CONTINUE
   CLEAR IALPHA
   IF(K-1) 32,311,33
311 COE(1)=1.0+SREQ*(SREQ-1.0)
   ICCL(1)=I
   GO TO 36
31 CLEAR COE(I)
   IALPHA=I
   ICCL(1)=INDEX(I)
   GO TO 36
32 CLEAR COE(I)
   IALPHA=I
   ICCL(1)=INDEX(I)
   GO TO 36
33 DO 35 J=1,LSP
   IF(COE(J)) 34,35,34
34 IALPHA=IALPHA+1
   ICCL(IALPHA)=ICCL(J)
   COE(IALPHA)=COE(J)
35 CONTINUE
36 WRITE(IDISC) I,(ID(J),J=1,M),(RE,IVR,K,IALPHA,(ICCL(J),COE(J),
   J=1,IALPHA)
   X DISPLAY(IP,10) /K,IALPHA
   X WRITE(IP,95) (J,ICCL(J),J,COE(J),J=1,IALPHA)
   X 95 FORMAT(12,'1C13=',13,'1C13','=13,F7.3)
   IF(K) 361,371,361
361 DO 37 J=1,LSP
   IF(COE(J)) 371,37,37
371 IF(MREQ) 30,372,33
372 IF(INDEX(IABS(RE))) 33,373,33
373 I=IABS(RE)
   GO TO 43
37 CONTINUE
371 IF(MREQ) 33,372,33
372 IF(INDEX(IABS(RE))) 33,373,33
373 I=IABS(RE)
   GO TO 43
33 CONTINUE
   ENDFILE IDISC
   REWIND IDISC
42 FORMAT(‘ ’,32I2)
   CALL OUTDET(INDEX,COE,ICOL,ID,F,IC,MKESP)
39 RETURN
END
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16-electron determinants from 20 spin-orbitals (first 4 are frozen)
Determinants are gerade with 3 units of axial angular momentum and 0.0 units of spin in Z-direction

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8 1.0
Determinants 1 to 2 form total spin eigenfunctions as follows

\[ \begin{align*}
\text{Multiplicities} (\pm 2, \pm 1) & \\
1,000,000,000,000 \times 0 & \\
7 \times 7 \times \text{matrix} = 0.071067619 E-01 \\
7 \times 7 \times \text{matrix} = 0.071067619 E-01
\end{align*} \]
DETERMINANTS 3 TO 4 FORM TOTAL SPIN EIGENFUNCTIONS AS FOLLOWS

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EIGENVECTORS 1 TO 2

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Determinants 5 to 6 form total spin eigenfunctions as follows:

Multiplicities ($\tilde{2s}\times1$) for eigenfunctions 1 to 2:

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Eigenvalues 1 to 2:

$-7.0710678119E-01$  $7.0710678119E-01$  $-7.0710678119E-01$  $7.0710678119E-01$
DETERMINANTS 7 TO 8 FORM TOTAL SPIN EIGENFUNCTIONS AS FOLLOWS

MULTIPLICITIES (E-2S+1) FOR EIGENFUNCTIONS 1 TO 2

1.0000000000E+00
3.0000000000E+00

EIGENVECTORS 1 TO 2

7.0710678119E+01  7.0710678119E+01
=7.0710678119E-01  7.0710678119E-01

1820 16-ELECTRON DETERMINANTS WITH FIRST 4 SPIN ORBITALS FROZEN HAVE REQUIRED SYMMETRY AND SPIN VALUES
APPENDIX V

 giorno. A PROGRAM FOR COMPUTING ONE-CENTRE
ONE- AND TWO-ELECTRON INTEGRALS OVER COMPLEX
SIATER-TYPE ORBITALS

Analytical expressions are used for the integrals. The indexing
scheme for the two-electron integrals is described in Chapter 7. This
program computes all the distinct one- and two-electron integrals which
arise from a basis set consisting of any combination of s, p, d, or f
orbitals on a single centre.

giorno uses one magnetic tape on which the integrals will be written.
This tape is device number 1 and the lineprinter is device number 0. The
version of giorno listed in this appendix reads the Clebach-Gordon
coefficients from a private disc area which is device number 2. The non­
zero values of these coefficients are listed after the data specification.
In addition to the subprograms listed the subprogram IPAR (Appendix III)
is also required. The storage requirements are standard.

Data Specification for giorno

Card 1

I
F\texttt{ORMAT} (I5)

\begin{align*}
I &= 0 \text{ to stop execution} \\
I &= 1 \text{ to continue execution}
\end{align*}

Card 2

\texttt{NXBLGC}
F\texttt{ORMAT} (I5)

\texttt{NXBLGC} = \text{number of block at which the integral
file is to begin on device number 1.}
Card 3, 4. **TITLE**

**FORMAT (9A8/6A8)**

**TITLE** is an array of 15 elements (120 characters) which is used to identify the run.

Card 5 **NBASIS, CH**

**FORMAT (I5, F10.5)**

- **NBASIS** = number of basis orbitals
- **CH** = nuclear charge (a.u.)

Card 6(I) **N(I), L(I), M(I), Z(I)**

**FORMAT (3I5, F10.5)**

- **N(I)** = principle quantum number (q.n.) of orbital I.
- **L(I)** = angular momentum q.n. of orbital I
- **M(I)** = magnetic q.n. of orbital I
- **Z(I)** = exponent of orbital I

(1 ≤ I ≤ NBASIS)

**Restrictions**

1 ≤ NBASIS ≤ 30
1 ≤ N(I) ≤ 12
0 ≤ L(I) ≤ 3 and L(I) < N(I)
|M(I)| ≤ L(I)

At the end of a set of data the first card of the next set is always read. The last card of the data check should have I = 0.
### Non-Zero Values of Clebsch-Gordan Coefficients

#### Number of Non-Zero Coefficients = 152

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**Formula:**

\[ C_{\ell_{1}\ell_{2} \ell_{3}}^{\ell_{4}\ell_{5}\ell_{6}} = \text{Non-Zero Values} \]
*FORTRAN LIB 3,1,0
C.....MAIN PROGRAM FOR SINGLE CENTRE INTEGRAL PROGRAM.
C.....VERSION 2. 12/05/71.
C. COMMON /TOALL/ CH, DEV, DIV, I, IA, IB, IC, ICR, ID, J, K, KK, LP, MTD25, NB,
      1NBASIS, NI, NP, N2, T1, T2, ZK, ANORM(30), CG(440), ERI(465), FCTRL(25),
      2H(30, 30), IN(455, 2), L(30), M(30), N(30), S(30, 30), TITL(15), Z(30)

C....DEFINE DEVICE NUMBERS,
C....ICR = CARD READER,
C....LP = LINE PRINTER,
C....MTD25 = INTEGRAL OUTPUT DEVICE NUMBER (TAPE OR DISC),
C....ID = DEVICE NUMBER FOR CONSTANTS TABLE.
      CLEAR ICR, LP
      MTD25=1
      ID=2
      READ(ID) (CI(I), I=1, 440)
      UNLOAD ID
      FCTRL(1)=1.0
      DO 1 I=2, 25
          K=I-1
          FCTRL(I) = IC*FCTRL(K)
      CONTINUE
      READ(ICR, 33) NBASIS
      CALL SEARCH(MTD25, NBASIS, 0)
      READ(ID) (CI(I), I=1, 440)
      CALL ALLOC
      GO TO 2
      END

*FORTRAN LIB
SUBROUTINE ILLONE
C.....ONE-CENTRE ONE- AND TWO- ELECTRON INTEGRALS.
C. COMMON /TOALL/ CH, DEV, DIV, I, IA, IB, IC, ICR, ID, J, K, KK, LP, MTD25, NB,
      1NBASIS, NI, NP, N2, T1, T2, ZK, ANORM(30), CG(440), ERI(465), FCTRL(25),
      2H(30, 30), IN(455, 2), L(30), M(30), N(30), S(30, 30), TITL(15), Z(30)
      READ(ICR, 33) NBASIS
      CALL SEARCH(MTD25, NBASIS, 0)
      READ(ICR, 1) TITLE
      READ(ICR, 2) NBASIS, CH, (NI(I), LI(I), M(I), Z(I), I=1, NBASIS)
      WRITE(LP, 3) TITLE
      WRITE(LP, 35) CH
      WRITE(LP, 4) (NI(I), LI(I), M(I), Z(I), I=1, NBASIS)
      1 FORMAT(9(3, 8E3), 7(5F12.5))
      2 FORMAT(15, F10.5/(315, F10.5))
      3 FORMAT(1H/1H, 15A3)
      4 FORMAT(1H, 4DX, 23HN L M EXPONENT/(1H, 4DX, 315, F12.5))
      NB=(NBASIS*(NBASIS+1))/2
      NI=(NB*(NB+1))/2
      WRITE(LP, 33) NI
      WRITE(LP, 37) NBASIS
      DO 16 I=1, NBASIS
          NI=2*NI+1
          ANORM(I)=SQRT(2.0*Z(I)**2/FCTRL(NI))
      DO 16 I=1, I
          S(I, K)=0.0
          M(I, K)=0.0
          IF(L(I)-L(K)) 13, 11, 15
      11 IF(N(I)-K(K)) 15, 12, 15
      12 ZK=2.0*Z(K)
CLEAR T1
DIV=1.0/(Z(I)+Z(K))
DEV=1.0/SQRT(2.0*N(K)*(2.0*N(K)-1.0))
1F(N(K)=L(K)-1) 14,14,13
13 N2=N(I)+N(K)-1
NP=2*N(K)-1
T1=ANORM(I)*FCTRL(N2)*DIV**N2*SQRT(ZK**NP/FCTRL(NP))*4.0*(N(K)+
1L(K))*(N(K)-L(K)-1)*DEV/SQRT((2.0*N(K)-2.0)*(2.0*N(K)-3.0))
14 N2=N(I)+N(K)
NP=2*N(K)-1
T2=ANORM(I)*FCTRL(N2)*DZV**N2*SQRT(ZK**NP/FCTRL(NP))
N2=N2+1
S(I,K)=ANORM(I)*ANORM(K)*DZV**N2*FCTRL(NP)
H(I,K)=Z(K)*(-0.5*Z(K)*((T1+S(I,K))+2.0*T2*DEV*(N(K)*Z(K)-CH))
15 S(K,I)=S(I,K)
H(K,I)=H(I,K)
16 CONTINUE
WRITE(LP,17)
17 FORMAT(1HL/1H ,43X,34XOVERLAP MATRIX FOR ATOMIC ORBITALS/)
DO 21 I=1,NBASIS,5
K=I+4
IF(K-NBASIS) 19,19,18
18 K=NBASIS
19 WRITE(LP,32) I,K
20 FORMAT((1H ,1PS25.10))
21 CONTINUE
WRITE(LP,22)
22 FORMAT(1H0,34X,51HONE-ELECTRON HAMILTONIAN MATRIX FOR ATOMIC ORBIT
ALS/)
DO 25 I=1,NBASIS,5
K=I+4
IF(K-NBASIS) 24,24,23
23 K=NBASIS
24 WRITE(LP,32) I,K
DO 25 J=1,NBASIS
WRITE(LP,20) (H(J,KK),KK=I,K)
25 CONTINUE
WRITE(NTD25) I
WRITE(NTD25) TITLE,J
DO 26 I=1,NBASIS
WRITE(NTD25) (S(I,J),J=1,NBASIS)
WRITE(NTD25) (H(I,J),J=1,NBASIS)
26 CONTINUE
WRITE(LP,34)
IF(NBASIS.GT.5) WRITE(LP,35)
DO 27 I=1,NBASIS
J=(I*(I-1))/2
DO 27 K=I,J
KK=I+J
IN(KK,1)=I
IN(KK,2)=K
27 CONTINUE
DO 31 I=1,NB
IC=IN(I,2)
IA=IN(I,1)
KK=IABS(M(IA)-M(IC))
DO 29 J=1,I
IB=IN(J,1)
ID=IN(J,2)
CLEAR ERI(J)
IF(KK-IABS(M(IB)-M(ID))) 29,28,29
28 ERI(J)=SC(IA,IC,IB,ID)
29 CONTINUE
WRITM25) (ERI(J),J=1,I)
IF(NBASIS.GT.5) GO TO 31
WRITM25) (ERI(J),J=1,I)
30 CONTINUE
31 CONTINUE
32 FORMAT(1HO,49X,19HCONTENTS OF RECORD ,12/
33 FORMAT(1HO,32X,51HNUMBER OF TWO-ELECTRON INTEGRALS TO BE CALCULATE
34 I=17/
35 FORMAT(1HO,49X,22HTWO-ELECTRON INTEGRALS)
36 FORMAT(IHO,45X,17HNUCLEAR CHARGE = ,F10.5/
37 FORMAT('0',33X,'INTEGRALS BEGIN AT BLOCK',I4,' OF MASTER FILE')
38 FORMAT('0',37X,'PRINTING OF TWO-ELECTRON INTEGRALS SUPPRESSED')
39 RETURN
END
*FORTRAN LIB
INTEGER FUNCTION INDEX1(MM,M1,M2,LL,L1,L2)
C.....EVALUATION OF CLEBSCH-GORDON INDICES. VERSION 2. 09.04.69 ADT.
IM1=IABS(M1)
IM2=IABS(M2)
I1=(L1*(L1+1))/2+IM1+1
I2=(L2*(L2+1))/2+IM2+1
IZ=4*MAX0(I1,I2)*(MAX0(I1,I2)-1)+8*MINO(I1,I2)+LL/2
IF(IA3S(MM)-IM1-IM2) 2,1,2
1 I7=7
GO TO 3
2 I3=3
3 INDEX1=IZ-I
RETURN
END
*FORTRAN LIB
FUNCTION SC(IA,IC,IB,ID)
COMMON /TOALL/ KEEP(22),ANORM(30),CG(460),ERI(465),FCTRL(25),
LH(30,30),IN(465,2),L(30),M(30),N(30),S(30,30),TITLE(15),Z(30)
CLEAR SC
LGWAC=IABS(L(IA)-L(IC))
LG=IABS(L(IB)-L(ID))
IF(IGK-LGWAC-IGK-LGWAC)) 4,1,4
1 FCURLP=1.2566370614E-K1
LGH=MAX0(LGWAC,LGWAC)+1
IGH=MINO(L(IA)+L(IC),L(IB)+L(ID))+1
IF(IGH-LGH) 4,2,2
2 IM=M(IC)-M(IA)
Z1=Z(IA)+Z(IC)
Z2=Z(ID)+Z(IC)
N1=N(IA)+N(IC)
N2=N(IB)+N(ID)
LC 3 IMP=LGH,IGH,2
LI=IMP-1
JA=IND(X1(NU-1),NU,LU(LA),LU(LIC))
JE=IND(X1(-1),LU(IS),LU(ID),LU(LB),LU(LIB))
SC=SC+SCADD(FLOAT(JA)*CG(JA)*CG(JD)*N(NU,NU1,N2,Z1,Z2)
3 CONTINUE
SC=SC-NRM(ID)*NRM(IDC)*NRM(ID)*SC
4 RETURN
END

FUNCTION W(INU,N1,N2,Z1,Z2)
CALL /TOALL/ KEXP(Z2),NRM(30),CG(440),JRI(465),FCTRL(G5),
IN(30,30),IN(460,2),L(30),L(30),S(30,30),TITL(15),Z(30)
NU=NU+1
X=1
X2=2
X=NU-NU1
M=NU+M2
IF (JUMP) 4,3,4
3 JUMP=1
W=X2*IP*X1
NU=NU1-1
X1=X2
X2=Z1
GO TO 1
4 W=W-X2*IP*X1
RETURN
END
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<thead>
<tr>
<th>Statement Number</th>
<th>FORTRAN Statement</th>
</tr>
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<tbody>
<tr>
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<td>OXGEN TEST DATA - INTEGRALS FOR ATOMIC OXYGEN (SCHEFFER AND HARRIS'S EXPONENTS).</td>
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ONEGEN TEST DATA - INTEGRALS FOR ATOMIC OXYGEN (SCHAEFER AND HARRIS'S EXONENTS).

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<thead>
<tr>
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<tr>
<td>2</td>
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NUMBER OF TWO-ELECTRON INTEGRALS TO BE CALCULATED = 120
INTEGRALS BEGIN AT BLOCK 50 OF MASTER FILE
### Overlap Matrix for Atomic Orbital

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### One-Electron Hamiltonian Matrix for Atomic Orbital

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### Two-Electron Integrals

**Contents of Record 1:**

- 47855000002E-00
- 67428461270E-01
- 1116172056E+00

**Contents of Record 2:**

- 12109572047E-01
- 2466514040E-01
- 0.0000000000E+00

**Contents of Record 3:**

- 31839582301E-01
- 0.0000000000E+00
- 0.0000000000E+00

**Contents of Record 4:**

- 12853982402E-01
- 2465810266E-01
- 0.0000000000E+00

**Contents of Record 5:**

- 12809832402E-01
- 2467584665E-02
- 0.0000000000E+00

**Contents of Record 6:**

- 12853982402E-01
- 2465810266E-01
- 0.0000000000E+00

**Contents of Record 7:**

- 36251260345E-02
- 1795763874E+01
- 0.0000000000E+00

**Contents of Record 8:**

- 12853982402E-01
- 2465810266E-01
- 0.0000000000E+00

**Contents of Record 9:**

- 36251260345E-02
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**Contents of Record 10:**

- 12853982402E-01
- 2465810266E-01
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**Contents of Record 11:**

- 36251260345E-02
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### Additional Values

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**Contents of Record 12**

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APPENDIX VI

INTRA. A PROGRAM FOR TRANSFORMING ONE- AND
TWO-ELECTRON INTEGRALS OVER AN ATOMIC ORBITAL
BASIS INTO INTEGRALS OVER AN ORTHONORMAL BASIS

The methods and indexing schemes employed by INTRA are described in chapters 7 and 8. The program is written so that it will be possible to implement restart facilities should these prove necessary for large basis sets. The program occupies about 1500 FORTRAN V source cards and its storage requirements are standard. In addition to the subprograms listed here, INTRA requires the routines ENTR, ERROR, QUIT, and WRITMX from Appendix III.

INTRA uses five magnetic tapes or disc areas, the actual requirements being dictated by the size of the basis set; for less than 24 basis orbitals the following assignment is possible:

<table>
<thead>
<tr>
<th>VARIABLE NAME</th>
<th>VALUE</th>
</tr>
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<tbody>
<tr>
<td>LDN03</td>
<td>3</td>
</tr>
<tr>
<td>LDN08</td>
<td>4</td>
</tr>
<tr>
<td>LDN09</td>
<td>5</td>
</tr>
<tr>
<td>LDN10</td>
<td>6</td>
</tr>
<tr>
<td>LDN11</td>
<td>Defined in Master transformed integral tape which will contain the file of transformed integrals.</td>
</tr>
</tbody>
</table>
This program will process several sets of integrals in each run. As a precaution against corruption of the tape on device LDN10 each set of integrals should be transferred to the beginning of the common disc area LDN03 at the start of each run. The user must normally specify seven of the eight possible sections of data.

Data specification for INTRA

Section 1 : Transfer untransformed integrals from device LDN10 to device LDN03

Card 1
NBASIS
FORMAT (15)
NBASIS = number of basis orbitals

Card 2
IWHERE, ISTART (15)
FORMAT (215)
IWHERE = 1
ISTART(15) \{ = 0 to suppress timing information
\} = 1 to obtain timing information

Card 3
NEXTBL
FORMAT (15)
NEXTBL = number of block at which the untransformed integral file begins on device LDN10

Section 2 : Read data required to start transformation

Card 1
IWHERE, ISTART(15)
FORMAT (215)
IWHERE = 2
ISTART(15) : see section 1 card 2

Card 2
JSER, ISTDP
FORMAT (215)
JSER = serial number given to the untransformed integral file by the integral generation program. If the program \texttt{NECEN} was used then JSER = 100000

\text{ISTOP} = 1

Card 3 \hfill (M(I), I = 1, \text{NBASIS})

\texttt{FORMAT (30I2)}

\begin{align*}
&= 0 \text{ if the magnetic quantum number of the } \\
&\quad \text{I-th atomic orbital and the I-th transformed orbital are different.} \\
M(I) &= \text{magnetic quantum number of the I-th atomic orbital if the magnetic quantum number of} \\
&\quad \text{the I-th transformed orbital is the same.}
\end{align*}

Section 3 : Complete the upper triangle of the distinct two-electron integral matrix

Card 1 \hfill \texttt{IWHERE, ISTART(15)}

\texttt{FORMAT (2I5)}

\begin{align*}
\text{IWHERE} &= 3 \\
&= 0 \text{ to suppress timing information and printing} \\
&\quad \text{of one-electron integrals (untransformed)} \\
\text{ISTART(15)} &= 1 \text{ to obtain timing information and printing} \\
&\quad \text{of untransformed one-electron integrals}
\end{align*}

Section 4 : Compute Schmidt orthonormalization coefficients and transform the one-electron integrals

Card 1 \hfill \texttt{IWHERE, ISTART(15)}

\texttt{FORMAT (2I5)}

\begin{align*}
\text{IWHERE} &= 4 \\
\text{ISTART(15)} &= \text{see section 1 card 2}
\end{align*}
Card 2  \(N_{\text{NO}}\)

**FORMAT (I5)**

\(N_{\text{NO}}\) = number of non-zero elements in the matrix which transforms the atomic orbitals into non-orthonormal symmetry adapted molecular orbitals (The 'Symmetry Transformation Matrix')

Card 3 \((k)\)  \(I, J, WSP2(I, J)\)

**FORMAT (2I3, F4.1)**

\(WSP2(I, J)\) is the \(I, J\)-th element of the symmetry transformation matrix and is written as an integer in real form; e.g. 1.0.

\((1 < k < N_{\text{NO}})\)

Card 4  \(\text{NIR}\)

**FORMAT (I5)**

\(\text{NIR} =\) number of different irreducible representations to which the transformed orbitals belong; subspecies are counted as different.

Card 5  \((\text{IRI}(I), I = 1, \text{NBASIS})\)

**FORMAT (16I5)**

\(\text{IRI}(I) =\) a number which identifies the irreducible representation to which the \(I\)-th orbital belongs. As long as these are different for different irreducible representations their value is only restricted to the range 1 \(<\ \text{IRI}(I) \< 10000\)

(continue onto successive cards if \(\text{NBASIS} > 16\))
Section 5 : Transformation of two-electron integrals

Card 1

```plaintext
IWHERE, ISTART(15)
FORMAT (2I5)
```

IWHERE = 5

- 0 to suppress timing information and the printing of the transformed two-electron integrals
- 1 to obtain timing information and the printing of the transformed two-electron integrals

Card 2

```plaintext
ISER
FORMAT (I10)
```

ISER = any integer > 0, it is a restart parameter which is not used by the current version of INTRA

Card 3

```plaintext
(ISSTART(I), I = 5, 12)
FORMAT (8I5)
```

- ISTART(5) = 1
- ISTART(6) = numerical value of NBASIS
- ISTART(7) = 1
- ISTART(8) = numerical value of NBASIS
- ISTART(9) = 1
- ISTART(10) = numerical value of NBASIS
- ISTART(11) = 1
- ISTART(12) = numerical value of NBASIS

Section 6 : Transfer transformed integrals from device LDN03 to device LDN11
Card 1
IWHERE, ISTART(15)
FORMAT(2I5)
IWHERE = 6
ISTART(15) : see section 1 card 2

Card 2, 3
TITLE
FORMAT (9A8/6A8)
TITLE is an array of 15 elements (120 characters) used to identify the transformed integrals output from this run.

Card 4
LDN11, NEXTBL
FORMAT (2I5)
LDN11 = numerical value of the device number for the final output to the Master Transformed integral tape.
NEXTBL = number of block at which the transformed integral file is to begin on device LDN11

Section 7 : End of program, this should not be used if section 8 is required.
Card 1
IWHERE, ISTART (15)
FORMAT (2I5)
IWHERE = 1
ISTART(15) = 0

Section 8 : Re-entry of program clearing workspace in process. This section should be used instead of section 7 if another set of data is to be processed.
Card 1

IWHERE, ISTART(15)

FÖRMAT (2I5)

IWHERE = 8

ISTART(15) = 0

Restrictions

1 \leq \text{NBASIS} \leq 30
*FORTRAN LIB 8,5,325

C.....MAIN ROUTINE FOR INTEGRAL TRANSFORMATION PROGRAM.
C COMMON /TCALL/,NBASIS, NB, 1ST0P, 1STRT(20), M(30), LDNO1, LDNO2, LDNO3,
1LDNO8, LDNO9, LDNO10, LDNO11
C COMMON /TOSUM/, AREA1(3469)
C COMMON AREA2(13530)
C.....DEFINE DEVICE NUMBERS,
C.....LDNO1=CARD READER,
C.....LDNO2=LINE PRINTER,
C.....LDNO3=INTEGRAL FILE,
C.....LDNO8=WORK FILE 1,
C.....LDNO9=WORK FILE 2,
C.....LDNO10=MASTER INTEGRAL FILE.
    CLEAR LDNO1, LDNO2
    LDNO3=3
    LDNO3=4
    LDNO9=5
    LDNO10=6
11 CLEAR 1STRT, M, AREA1, AREA2
    CALL CUTFRQ(LDNO2)
    REWIND LDNO3
    REWIND LDNO8
    REWIND LDNO9
    READ(LDNO1,1) NBASIS
    NB=(NBASIS*(NBASIS+1))/2
1 FORMAT(215)
2 READ(LDNO1,1) IWHERE, 1STRT(15)
   GO TO (3,4,5,6,7,8,9,11), IWHERE
C.....TRANSFER INTEGRALS FROM LDNO1 TO LDNO3 IF NECESSARY.
C.....READ DATA AND CHECK INTEGRAL FILE SERIAL NUMBER.
   CALL RSET
   GO TO 2
C.....SET UP COMPLETE MATRIX OF DISTINCT TWO-ELECTRON INTEGRALS.
6 CALL TRANSH
   GO TO 2
C.....TRANSFORM TWO-ELECTRON INTEGRALS.
7 CALL CNTER
   GO TO 2
C.....TRANSFER TRANSFORMED INTEGRALS FROM LDNO3 TO LDNO10 IF NECESSARY.
C.....JOB COMPLETE.
   CALL CNT(NB)
   WRITR(LDNO2,10) NB
10 FORMAT(,'B',30X,**** JOB COMPLETE -',15,' INSTRUCTIONS USED ****')
   STOP
   END

*FORTRAN LIB

SUBROUTINE BIGTRA(A,B,MTDO1,MTDO2,NCOL,NROW,NPAS)
C.....TRANSPOSE OF A LARGE MATRIX.
DIMENSION A(NROW,NCOL),B(NROW,NCOL)
REWCIND MTDO1
REWIND MTDO2
NCOR=NCOL-NRROW

SUBROUTINE BIGTRA(A,B,MTDO1,MTDO2,NCOL,NROW,NPAS)
C.....TRANSPOSE OF A LARGE MATRIX.
DIMENSION A(NROW,NCOL),B(NROW,NCOL)
REWCIND MTDO1
REWIND MTDO2
NCOR=NCOL-NRROW
DO 3 IPASS=1,NPASS
READ  (MTDO1) ISER
JK=(IPASS-1)*NROW
JR=NROW
IF(JK-NCON) 2,2,1
3 JR=NCL-JK
2 DO 6 IPART=1,NPASS
IK=(IPART-1)*NROW
IR=NROW
IF(IK-NCON) 4,4,3
3 IR=NCL-IK
4 DO 5 I=1,IR
READ(MTDO1) (A(I,J),J=1,NCOL)
5 CONTINUE
6 JC=I+JK
DO 5 J=1,IR
IC=J+IK
B(I,IC)=A(J,JC)
CONTINUE
DC 7 I=1,JR
WRITE(MTDO2) (B(I,J),J=1,NCOL)
7 CONTINUE
REWIND MTDO1
8 CONTINUE
REWIND MTDO2
REWIND MTDO2
WRITE(MTDO1) ISER
ENDFILE LTDO1
REWIND MTDO2
REWIND MTDO1
REWIND MTDO2
RETURN
END

SUBROUTINE CONTR
TEXT SUBRUTINE CONTR
SUBROUTINE FOR TWO-ELECTRON INTEGRAL TRANSFORMATION.
COMMON /TCALL/ NBASII,NE,ISTOP,ISTART(20),H(30),LONG1,LDNO1,LDNO2,LDNO3,
1LDNO4,LDNO5,LDNO6,LDNO7,
COMMON S(30,30),H(30,30),C(30,30),IDUM(4000),DUMY(4000)
EQUIVALENCE (IDUM(23),ISER),(IDUM(24),I),(IDUM(25),J),(IDUM(26),IP
1),(IDUM(27),II),(IDUM(28),I2)
EQUIVALENCE (DUMY(3),DUMY1),(DUMY(4),SMAT),(DUMY(5),ILMAT),(DUMY(6),
1SMAT)
CALL ENTR(6HCONTRA,ISTART(15))
C.....SKIP TITLE AND SERIAL NUMBER OF TAPE ON UNIT 03. SKIP UNTRANS-
C.....FORMED S AND H MATRICES.
READ(LDNO3) ISER
READ(LDNO3) UMEM
DC 1 I=1,NBASIS
READ(LDNO3) SMAT
READ(LDNO3) HILMAT
1 CONTINUE
C.....TAPE ON UNIT 03 CORRECTLY POSITIONED - SERIALIZE TAPE ON UNIT 04.
READ(LDNO1,3) ISER
3 FORMAT(I10)
   WRITE(LDNO2,301) ISER
301 FORMAT(I10,2X,74X,8HSENTINAL NUMBER OF TAPE CN UNIT 04 IS ,I10/)
WRITE(LDNO)
WRITE(LDNO2) ISER

C.....SET UP ISTART
READ(LDNO1,4) (ISTART(I),I=3,12)
4 FORMAT(I13)

C.....CHECK DATA. ISTOP=50 IF ISTART(I).LE.NBASIS.NE.ISTART(I).
J=1
10 J=I+1
IF(ISTART(I)-ISTOP(I)) 7,7,5
5 WRITE(LDNO2,5) I,IP
6 FORMAT(CH ISTART(I,I3,14H) .GT. ISTART(I,I3,1H))
J=0
7 CONTINUE
IP(J) 3,3,0
3 CALL EXIT
9 J=1
13 I=5,8,0
IF(ISTART(I)-NBASIS) 10,13,11
10 ISTOP=50
GO TO 13
11 WRITE(LDNO2,12) I
12 FORMAT(CH ISTART(I,I3,13H) .GT. NBASIS)
J=0
13 CONTINUE
IP(J) 13,3,15
15 J=1
19 I=16,12,2
IF(ISTART(I)-NBASIS) 17,19,18
16 WRITE(LDNO2,12) I
J=0
17 CONTINUE
IP(J) 13,3,13
18 CALL EXIT

C.....CHECK IF RESTART NECESSARY.
11=5
12=7
13 IF(ISTART(I2+1)-NBASIS) 20,21,21
20 ISTART(I2)=ISTART(I2+1)+1
GO TO 27
21 IF(ISTART(I2+1)-NBASIS) 22,23,23
22 ISTART(I2)=ISTART(I2+1)+1
23 CONTINUE
GO TO 15
24 I1=1
25 I3=11
27 WRITE(LDNO2,23) (I,ISTART(I),I=6,11,2)
28 FORMAT(I10,2X,74HRESTART IS NECESSARY IN THE TWO-ELECTRON INTEGRAL TRANSFORMATION ROUTINE/1H ,22X,20HRESTART VALUES ARE -4(CH IS START(I2,13I),I3))
GO TO 35
29 WRITE(LDNO2,30)
30 FORMAT(I10,33X,48HTRANSFORMATION OF TWO-ELECTRON INTEGRALS COMPLETED 1C/)

C.....CHECK FOR HALT AT THIS POINT.
IF((ISTOP-5) EQ 34,31,34)
31 WRITE(LDNO2,32)
32 FORMAT('IH0,2IX,7THUSER REQUEST - PROGRAM TO STOP AT END OF TWO-ELE
CTRON INTEGRAL TRANSFORMATION/)
33REWIND LDNO3
REWIND LDNO9
STOP
34 CALL QUIT(GHCONTRA, ISTART(15))
RETURN
END

*FORTRAN LIB
SUBROUTINE DUMPSH(S, H, NBASIS, NO)
C.....OPTIONAL OUTPUT OF OVERLAP AND ONE-ELECTRON HAMILTONIAN MATRICES.
COMMON /TCALL/ NBASIS, NB, ISTOP, ISTART(20), M(30), LDNO1, LDNO2, LDNO3,
1 LDNO3, LDNO9, LDNO10, LDNO11
DIMENSION S(30,30), H(30,30)
IF(NO) 1, 4, 1
1 WRITE(LDNO2, 2)
2 FORMAT('1'X53X,'OVERLAP MATRIX')
CALL WRITEM(S, 30, 30, NBASIS, NBASIS, LDNO2)
WRITE(LDNO3, 3)
3 FORMAT('0'X44X,'ONE-ELECTRON HAMILTONIAN MATRIX')
CALL WRITEM(H, 30, 30, NBASIS, NBASIS, LDNO2)
4 RETURN
END

*FORTRAN LIB
SUBROUTINE MFILE2
C.....TRANSFERS INTEGRALS IN MASTER FILE TO DISC FILE FOR TRANSFORMATION
COMMON /TCALL/ NBASIS, NB, ISTOP, ISTART(20), M(30), LDNO1, LDNO2, LDNO3,
1 LDNO3, LDNO9, LDNO10, LDNO11
COMMON S(30,30), H(30,30), SRI(900)
TEXT TITLE(15)
EQUIVALENCE (LDN20, NERI(E)) , (ERI, TITLE)
CALL ENTR('MFILE2', ISTART(15))
READ (LDNO1, 1) NEXTBL
1 FCRIVL\T(I5)
C...POSITION MASTER INTEGRAL FILE AT NEXTBL.
MTDRE=LDNO10
MTDR=LDNO3
CALL SEARCH(LDNO10, NEXTBL, 0)
WRITE(LDNO2, 2) NEXTBL
2 FORMAT('1'X53X,'INTEGRALS FOR THIS RUN ARE IN THE MASTER INTEG
RAL FILE STARTING AT BLOCK', 15)
READ (MTDRE) ISER
WRITE (MTDRE) ISER
READ (MTDRE) TITLE, IRUN
WRITE (MTDRE) TITLE, IRUN
DISPLAY /TITLE:
IF 3 I=1,NBASIS
READ (MTDRE) (S(J,I), J=1,NBASIS)
WRITE (MTDRE) (S(J,I), J=1,NBASIS)
READ (MTDRE) (H(J,I), J=1,NBASIS)
WRITE (MTDRE) (H(J,I), J=1,NBASIS)
3 CONTINUE
IF 4 I=1,NB
READ (MTDRE) (SRI(J), J=1,1)
WRITE (MTDRE) (SRI(J), J=1,1)
4 CONTINUE
**FORTRAN LIB**

**SUBROUTINE MFILE3**

C.....TRANSFERS TRANSFORMED INTEGRALS FROM DISC (LDNO3) TO MASTER

C.....(TRANSFORMED) INTEGRAL FILE (LDNO4).

C COMMON /TCAST/ NBASIS,NB,ISTCP,ISTART(20),M(30),LDNO1,LDNO2,LDNO3,
1 LDNO4,LEN2,LEN11,LEN12
C COMMON ERI(900),H(30,30)
C TEXT TITLE(15)
C EQUIVYLENCE (ERI,TITLE)

C.....TITLE IS 120 CHARACTERS (15 ATLAS WORDS) USED TO IDENTIFY THE
C.....INFORMATION IN EACH MASTER FILE.

READ (LDNO1,1) TITLE
1 FORMAT(9A3/GA3)
READ (LDNO1,12) LDNO4,NEXTBL
12 FORMAT(2I5)
WRITE (LDNO3,2) TITLE,NEXTBL
2 FORMAT(0,A/B0,15A3/' ',21X,'WILL BE FOUND IN THE MASTER (TRANSFORMED)
1 INTEGRAL FILE STARTING AT BLOCK',15)
CALL SEARCH(LDNO4,NEXTBL,0)
MTDRE=LDNO3
MTDV/R=LDNO4
CLEAR ERI
NSQRD=NBASIS*NBASIS
DO 3 I=1,NSQRD
READ (MTDRE) (ERI(J),J=1,NSQRD)
WRITE (MTDV/R) (ERI(J),J=1,NSQRD)
3 CONTINUE
READ (MTDRE) ((H(I,J),I=1,NBASIS),J=1,NBASIS)
WRITE (MTDV/R) ((H(I,J),I=1,NBASIS),J=1,NBASIS)
ENDFILE MTDWR

C.....DETERMINS POSITIONS OF ALL MAGNETIC DEVICES.

WRITE (LDNO4,5)
5 FORMAT('C',20X,'POSITIONS OF MAGNETIC DEVICES')
CALL WHIPS
RESEND MTDWR
RETURN
END

*FORTRAN LIB

**SUBROUTINE MXPROD(A,B,C,IA,IB)**

C.....PRODUCT OF TWO REAL SQUARE MATRICES - C=A*B.

DIMENSION A(IA,IA),B(IA,IA),C(IA,IA)
DO 1 I=1,IB
DO 1 J=1,IB
C(I,J)=0.0
1 CONTINUE
*FORTRAN-LIE
  SUBROUTINE MTRX(A,B,IA,IB)
  DIMENSION A(IA,IA),B(IA,IA)
  DO 1 J=1,IB
  RETURN
  END

*FORTRAN-LIE
  SUBROUTINE CRVTN
  DIMENSION BASIS
  COMMON /I/ N,NB,ISTOP,ISTART(20),M(30),LDNO1,LDNO2,LDNO3,
  LDNO4,LDNO5,LDNO6,LDNO7
  COMMON C(30,30),H(30,30),S(30,30)
  DIMENSION :C(30,30),Q(30,30),QV(30,30),QW(30,30),QX(30,30)
  DO 10 I=1,30
  CALL ENTR(CI3RTN,ISTART(15))
  10 CONTINUE

C....SET UP WORKSPACE.
  DO 1 I=1,N
  DO 1 J=1,N
  CALL G(I,J),QU(I,J),QV(I,J),QW(I,J)
  1 CONTINUE
  2 CONTINUE

C....CHOLESKY DECOMPOSITION OF QU.
  DO 11 I=1,N
  QA=G(I,I)
  IF(MM1) 5,3,3
  3 DO 3 J=1,IN
  QA=R(V(I,J),V(I,J))
  3 CONTINUE
  4 CONTINUE
  DO 10 J=1,N
  QA=G(I,J)
  IF(MM1) 9,3,7
  7 DO 9 K=1,IN
  QA=G(I,J)-G(V(J,K),V(I,K))
  9 CONTINUE
  10 CONTINUE
  11 CONTINUE

C.....QC = INVERSE OF QU.
  DO 12 I=1,N
  QA=1.0/QU(I,I)
  IF(MM1) 3,3,3
  3 DO 3 J=1,N
  QA=QU(I,J)/QU(I,I)
  3 CONTINUE
  12 CONTINUE

C.....SUBROUTINE MTRX
  DIMENSION A(IA,IA),B(IA,IA)
  DO 1 J=1,IB
  RETURN
  END
IP1=I1
CLEAR QA
EQ 111  J=I1,L
QA=QA-SU(I,J)*M(J)
11 CONTINUE
K(I)=SQRT(U(I,I))
C(I,L)=M(I)
12 CONTINUE
CC(I,J)=CC(I,J)
C...COMPUTE TRANSFORMED OVERLAP MATRIX.
CALL MATRN(QC,W,30,N)
CALL MATRC(QC,30,W,30,N)
CALL MATRN(W,30,30,N)
WRITE((LDNO2,20))
CALL WRTM(K,J,W,30,30,N,LDNO2)
DO 14 I=1,N
DO 14 J=1,N
C(I,J)=CC(I,J)
14 CONTINUE
20 PRINT((LDNO,55X,18CHGT3*C = 1/1I))
CALL QUIR(10,START(15))
RETURN
END

*FORTRAN LIB
SUBROUTINE RESSET
C...RESTART AT BEGINNING OF TRANSFORMATION SECTION.
CALL/(READ/NBASIS,ISTART,START(20),M(30),LDNO1,LDNO3,LDNO3,
1/10,10)
READ(LDNO1) JSER,ISTOP
READ(LDNO3) ISER
IF(JSER-ISER) 2,3,2
2 CALL IVRNP(I3ER,I3ER,3)
3 READ(LDNO3) TITLE,IRUN
WRITE(LDNO3,3) TITLE
4 PRINT((LDNO2,3))
CALL HISTRES3ET,ISTART(15))
READ(LDNO2,2)
IF(J1,J) 4,5,3
5 READ(LDNO3) TITLE,IRUN
WRITE(LDNO3,3) TITLE
C...READ AND CHECK DATA.
READ(LDNO3,6) M(I),I=1,NBASIS)
3 FORMAT(30I2)
C...CHECK J-VALUES.
WRITE(LDNO2,6) M(I),I=1,NBASIS)
6 FORMAT(30I2)
CLEAR J
IF(IABG0(I)) 3,9,7
7 WRITE(LDNO2,3) I
3 FORMAT(30I2)
J=1
9 CONTINUE
IF(J) 10,11,10
10 CALL EXIT
11 CALL QUIR("RESET",START(15))
SUBROUTINE SETERI
C ....SETS UP COMPLETE MATRIX OF DISTINCT TWO-ELECTRON INTEGRALS FROM
C ....LOWER TRIANGLE. VERSION 3. 06/09/71.
COMMON /TOALL/ NIS, NB, ISTOP, ISTART(20), M(30), LDN01, LDN02, LDN03,
LDN08, LDN09, LDN10, LDN11
COMMON A(5000), B(5000)
DIMENSION C(66,66), ERI(3000), H(30,30), S(30,30)
EQUIVALENCE (A, ERI), (A(901), H), (A(1301), S), (B, C)
ON ERROR KB, KV, NB, I, J
CALL ENTRY("SETERI", ISTART(15))
C....SKIP OVER SERIAL NUMBER, TITLE, AND ONE-ELECTRON INTEGRALS.
REWIND LDN03
READ(LDNO3) I
READ(LDNO3) I
CALL TPPOSN(LDNO3, KB, KW)
DISPLAY(LP, 5) /KB, KW
DO 1 I = 1, NBASIS
READ(LDNO3) J
READ(LDNO3) J
1 CONTINUE
CALL TPPOSN(LDNO3, KB, KW)
IF(NBASIS-11) 2, 2, 5
2 DO 3 I = 1, NB
CALL TPPOSN(LDNO3, KB, KW)
DISPLAY(LP, 5) /1, KB, KW
READ(LDNO3) (C(I, J), J = 1, I)
DO 3 J = 1, I
C(J, I) = C(I, J)
3 CONTINUE
CALL SEARCH(LDNO3, KB, KW)
WRITE(LDNOS) (C(I, J), J = 1, NB)
4 CONTINUE
GO TO 12
5 DO 6 I = 1, NB
CLEAR ERI(I)
6 CONTINUE
DO 7 I = 1, NB
READ (LDNO3) (ERI(J), J = 1, I)
WRITE (LDNO3) (ERI(J), J = 1, I)
7 CONTINUE
REWIND LDNO3
NRCW=5000/12
NPASS=1
IF(NCB(NB, NRCW)) 9, 3, 9
8 CLEAR NPASS
9 NPASS=NPASS+NB/NRCW
CALL BIGTRA(A, B, LDN09, LDN06, NB, NRCW, NPASS)
CALL SEARCH(LDNO3, KB, KW)
DO 10 I = 1, NB
READ (LDNO3) (ERI(J), J = 1, NB)
READ (LDNO3) (ERI(J), J = 1, I)
WRITE (LDNO3) (ERI(J), J = 1, NB)
10 CONTINUE
CALL SEARCH(LDNO3, KB, KW)
REWIND LDNO3
RETURN
END
DO 11 I=1,NB
READ (LDNO3) (ERI(J),J=1,NB)
WRITE(LDNO3) (ERI(J),J=1,NB)
11 CONTINUE
12 REWIND LDNO3
REWIND LDNO3
REWIND LDNO3

C......READ OVERLAP AND ONE-HAMILTONIAN MATRICES.
READ(LDNO3) I
READ(LDNO3) I
DO 13 I=1,NBASIS
READ(LDNO3) (S(J,I),J=1,NBASIS)
READ(LDNO3) (H(J,I),J=1,NBASIS)
13 CONTINUE

C......CALL 3EALINES(LDNO3,KB,IC)
C......PRINT S AND H IF REQUIRED.
RETURN

END

*FORTRAN LIB

SUBROUTINE TRANSH
C......VERSION 5.26/03/71.
C......TRANSFORMS ONE-ELECTRON INTEGRALS OVER ATOMIC ORBITALS INTO
C......INTEGRALS OVER A SET OF CINCHOCORIAL ATOMIC OR MOLECULAR ORBITALS
C......AS REQUIRED. CONTROL IS IN ISTART(19). TRANSFORMATION MATRIX C IS
C......OBTAINED BY THE DIAGONALIZATION OF THE OVERLAP MATRIX S.
C.
CALL/READ/NBASIS,NB,ISTOP,ISTART(20),M(30),LENO1,LDNO2,LDNO3,
LDNO3,LDNO9,LDNO10,LDNO11
CALL C(30,30),H(30,30),S(30,30),I(30),WP1(30,30),WP2(30,30),
WP3(30,30)
CALL ENTR("TRANSH",ISTART(15))
WRITE(LDNO2,1)
1 FORMAT(1HL110,40X,40HTRANSFORMATION OF ONE-ELECTRON INTEGRALS/)
C......TABLE ON UNIT 03 IS POSITIONED AT END OF DISTINCT ERI MATRIX.
C......READ NON-ZERO ELEMENTS OF SYMMETRY TRANSFORMATION MATRIX. NONO =
C......NUMBER OF NON-ZERO ELEMENTS.
2 CLEAR WP2
READ(LDNO1,30) NONO
30 FORMAT(16I5)
DO 32 K=1,NONO
READ(LDNO1,31) I,J,WP2(I,J)
31 FORMAT(3I3,F4.1)
32 CONTINUE
WRITE(LDNO2,40)
40 FORMAT(10%40X,"SYMMETRY TRANSFORMATION MATRIX")
CALL WRITE(WP2,30,30,NBASIS,NBASIS,LDNO2)

C......TRANSFORM OVERLAP MATRIX.
30 CALL MATRAN(WP2,WP1,30,NBASIS)
CALL MAFROM(WP1,S,C,30,NBASIS)
CALL MATRED(C,WP2,S,30,NBASIS)
X WRITE(LDNO2,40)
X CALL WRITH(S,30,30,NBASIS,NBASIS,LDNO2)
43 FORMAT(1PS524.10)
CALL ORTHON
X WRITE(LDNO2,43)
X CALL WRITH(C,30,30,NBASIS,NBASIS,LDNO2)
X 46 FORMAT(10%4X,"OVERLAP MATRIX FOR NON-CINCHOCORIAL M.O.s")
X 48 FORMAT(10%4X,"MATRIX WHICH ORTHOGNLIZES M.O.s")
**FORTRAN LIB**

**SUBROUTINE**

C....TRANSFORM TWO-ELECTRON INTEGRALS (TII).
C....TAPES ON UNIT 03 POSITIONED AT BEGINNING OF COMPLETE MATRIX
C....DISTINCT ERI, UNLESS THIS IS A RESTART. H-MATRIX IS OVERWRITTEN IN
C....THIS SUBPROGRAM.

**TEXT**

CCARDON /TCALL/ NBASIS,ND,ISTCP,IST(4),ISTAR,ISTARG,ISTARE,
1STAR9,ISTAR9,ISTAR9,ISTAR9,ISTAR9,ISTAR9,ISTAR9,ISTAR9,ISTAR9,
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EQUIVALENCE (DUMA,A,WSP1),(DUMB,WSP2),(C,H)
X 103 FORMAT(4H MU=,I2,4H NU=,I2,6H NGOT=,I4,7H NWANT=,I4)
X 104 FORMAT("DINTEGRAL(beit,413,)->") IS COMPOSED OF -")
X 105 FORMAT(" C(,213,)*INTEGRAL(4,413,)"). INTEGRAL INDEX IS ",I4)
X 106 FORMAT("OPARTIALLY TRANSFORMED INTEGRALS"/(" "03X,ERI(4,14,"="
X 1,1PE17.10))
X 107 FORMAT("0**** TRANSFORMED INTEGRALS ****/(" "03X,ERI(4,14,"="
X 1,1PE17.10))
ON ERROR/NSQRD,IJUMP,ISTAGE,NGOT,NWANT,MU,NU,MAX,MIN,NMOVE/,K1,LL
CALL ENTR(SHTWOTRA,15(3))
CALL WRTPS
NSQRD=NBASIS*NBASIS
1 ISTAGE=1
CLEAR NGOT
C ....COMMENCE TRANSFORMATION OF CHARGE DISTRIBUTION 2.
DO 22 MU=ISTAR5,ISTAR6
DO 21 NU=ISTART,ISTARS
C ....PICK UP REQUIRED BLOCK OF DISTINCT ERI,
MAX=MAXO(MU,NU)
NWANT=(MAX*(MAX-1))/2+MINO(MU,NU)
WRITE(LDNO2,103) MU,NU,NGOT,NWANT
NMOVE=NWANT-NGOT
IF(NMOVE) 2,2,4
2 NM0VE=1-NMOVE
DO 3 I=1,NMOVE
BACKSPACE LDNO3
3 CONTINUE
READ(LDNO3) (WSP2(J),J=1,NB)
GO TO 6
4 DO 5 I=1,NMOVE
READ(LDNO3) (WSP2(J),J=1,NB)
5 CONTINUE
6 NGOT=NWANT
IM=M(NU)-M(MU)
CLEAR WSPI
DO 13 LAMBDA=1,NBASIS
K1=NBASIS*(LAMBDA-1)
DO 12 U^1,NBASIS
C  CHECK PHI INTEGRATION GIVES NON-ZERO RESULT, THIS IS CHECK 1,
IF(IM-M(LAMBDA)+M(LL>) 12,9,12
9 K2=K1+LL
WRITE(LDNO2,104) MU,NU,LAMBDA,LL
DO 11 IS=1,NBASIS
C ....CHECK TRANSFORMATION COEFFICIENT IS NON-ZERO, THIS IS CHECK 2.
IF(C(IS,LL)) 10,11,10
10 MAX=MAXO(IS,LAMBDA)
J=(MAX*(MAX-1))/2+MINO(IS,LAMBDA)
WRITE(LDNO2,105) IS,LL,MU,NU,LAMBDA,IS,J
WSPI(K2)=WSPI(K2)+C(IS,LL)*WSP2(J)
11 CONTINUE
12 CONTINUE
13 CONTINUE
C ....TRANSFORMATION OF 4TH. ORBITAL COMPLETE FOR THIS MU AND NU.
CLEAR WSP2
DO 19 KK=1,NBASIS
KL=NBASIS*(KK-1)
DO 18 LL=1,NBASIS
C ....CHECK 1.
IF(IM-M(KK)+M(LL)) 18,15,18
15 K2=K1+LL
WRITE(LDN02,104) MU,NU,KK,LL
DO 17 LAMBDA=1,NBASIS
C.....CHECK 2.
IF(C(LAMBDA,KK)) 16,17,16
16 J=NBASIS*(LAMBDA-1)+LL
WRITE(LDN02,105) LAMBDA,KK,NU,NU,LAMBDA,LL,J
WSP2(K2)=WSP2(K2)+C(LAMBDA,KK)*WSP1(J)
17 CONTINUE
18 CONTINUE
19 CONTINUE
C.....TRANSFORMATION OF 3RD. ORBITAL COMPLETE FOR THIS MU AND NU.
WRITE(LDN09) (WSP2(K),K=1,NSQRD)
WRITE(LDN02,106) (K,WSP2(K),K=1,NSQRD)
21 CONTINUE
22 CONTINUE
ENDIF LDNO9
C.....THIS STAGE IS COMPLETE IF ISTAR6=ISTAR8=NBASIS.
IF(ISTAR6+ISTAR8-NBASIS-NBASIS) 23,25,23
23 ICD=4H2ND.
WRITE(LDN02,24) ICD
24 FORMAT(1HO,31X,18HTRANSFORMATION OF A4,35HCHARGE DISTRIBUTION IS
1NCOMPLETE/)
REWIND LDN03
REWIND LDNO9
GO TO 27
25 WRITE(LDN02,26)
26 FORMAT(1HO,34X,51HTRANSFORMATION OF 2ND. CHARGE DISTRIBUTION COMPL
1ET/)
C.....CHECK FOR HALT AT THIS POINT.
IF(ISTOP-50) 28,27,28
27 RETURN
28 REWIND LDNO9
C.....POSITION UNIT 03 AT END OF TRANSFORMED H-MATRIX, IF THIS IS NOT A
C.....RESTART AT THIS POINT, C AND H MATRICES MUST BE SKIPPED, OTHERWISE
C.....TAPE IS AT END OF PREVIOUSLY TRANSFORMED ERI. SKIP SERIAL NUMBER
C.....ON UNIT 04.
READ(LDN03) CMAT
READ(LDN03) HMAT
29 ISTALL=2
C.....TRANSPOSE PARTIALLY TRANSFORMED TWO-ELECTRON INTEGRALS ON DEVICE
C.....LDNO9, DEVICE LDNO8 IS USED AS TEMPORARY WORK SPACE.
IF(NBASIS-8) 300,300,290
290 NROW=5000/NSQRD
NPASS=1
IF(MOD(NSQRD,NROW)) 292,291,292
291 CLEAR NPASS
292 NPASS=NPASS+NSQRD/NROW
WRITE(LDN02,293) NROW,NSQRD,LDN09,LDNO8,NROW,NPASS,LDNO9
293 FORMAT(15X,"TRANSPOSE PARTIALLY TRANSFORMED TWO-ELECTRON INTEGRALS ON DEVICE"
1H-CLEAN")
WRITE(LDN02,294) SEC
294 FORMAT(33X,"TRANSPOSE TIME =","F10.2"," SECONDS")
GO TO 303
C....CCURRENCE TRANSFORMATION OF 1ST. CHARGE DISTRIBUTION.
DO 44 KK=1,ISTAR0,ISTAR1
K1=NBASIS*(KK-1)
DO 43 LI=ISTAR1,ISTAR2
NCOL=K1+LL
IN=M(LL)-M(KK)
WRITE(LDNO0) (#SP1(NRCW), NRCW=1, NSQRD)
CLEAR WSP2
DO 35 MU=1,NBASIS
K1=NBASIS*(MU-1)
DO 34 J=1,NBASIS
C....CHECK 1.
IF(IM=M(MU)+M(J)) 34,31,34
31 K2=K1+J
WRITE(LDNO2,104) MU,J,KK,LL
DO 33 NU=1,NBASIS
C....
C R j ' ] C K
2.
IF(C(NU,J)) 33,32,32
32 I=NU+I
WRITE(LDNO2,105) NU,J,MU,NU,KK,LL,I
WSP2(K2)=WSP2(K2)+C(NU,J)*WSP1(I)
33 CONTINUE
34 CONTINUE
35 CONTINUE
C....TRANSFORMATION OF 2ND. ORBITAL COMPLETE FOR THIS MU AND NU.
CLEAR WSP1
DO 41 I=1,NBASIS
K1=NBASIS*(I-1)
DO 40 J=1,NBASIS
C....CHECK 1.
IF(IM=M(I)+M(J)) 40,37,40
37 K2=K1+J
WRITE(LDNO2,104) I,J,KK,LL
DO 39 MU=1,NBASIS
C....CHECK 2.
IF(C(MU,I)) 33,39,33
38 II=NBASIS*(MU-1)+J
WRITE(LDNO2,105) MU,I,MU,J,KK,LL,II
WSP1(K2)=WSP1(K2)+C(MU,I)*WSP2(II)
39 CONTINUE
40 CONTINUE
41 CONTINUE
C....TRANSFORMATION OF 1ST. ORBITAL COMPLETE FOR THIS KK AND LL.
WRITE(LDNO3) (#SP1(K), K=1,NSQRD)
X WRITE(LDNO2,107) (K, #SP1(K), K=1,NSQRD)
43 CONTINUE
44 CONTINUE
ENDFILE LDNO3
C....TAPE ON UNIT 03 CONTAINS UNTRANSFORMED S AND H MATRICES, LOWER
C.....TRANSFORMED II MATRICES AND ALL OR PART OF THE TRANSFORMED ERI.
C.....THIS STAGE IS COMPLETE IF ISTAR0=ISTAR2=NBASIS.
 IF(ISTAR0.EQ.ISTAR2.AND.ISTAR2.EQ.NBASIS) 45,451,45
 45 ICD=IST,
   WRITE(LDN02,24) ICD
   REWIND LDN03
   REWIND LDN09
   GO TO 46
C.....OVER WRITE INTEGRALS ON DEVICE LDN03 WITH TRANSFORMED ERI AND
C.....TRANSFORMED H-MATRIX.
 451 REWIND LDN03
   READ(LDN09)
   READ(LDN03) IER
   READ(LDN03) ICD
   DO 452 I=1,NBAS
   READ(LDN03) GIMAT
   READ(LDN03) IMAT
   CONTINUE
   DO 453 I=1,NB
   READ(LDN03) ERIMAT
   CONTINUE
   READ(LDN03) ( (C(I,J),I=1,NBASIS),J=1,NBASIS)
   CLEAR H
   READ(LDN03) ( (H(I,J),I=1,NBASIS),J=1,NBASIS)
   CLEAR NBAS
   MTDRE=LDN03
   MTDWR=LDN09
   DO 455 I=1,NSQRD
   READ(MTDRE) (WSP1(J),J=1,NSQRD)
   WRITE(MTDWR) (WSP1(J),J=1,NSQRD)
   CONTINUE
   IF(NRO.V) 457,456,457
   NBAS1=1
   NPAS3=MTDRE
   MTDRE=MTDWR
   MTDWR=NPAS3
   REWIND MTDRE
   REWIND MTDWR
   GO TO 454
457 WRITE(MTDWR) ( (H(I,J),I=1,NBASIS),J=1,NBASIS)
   ENDFILE MTDWR
   REWIND MTDWR
   IF(I5(3)) 458,458,458
458 CALL CUTBK(LDN02)
   WRITE(LDN02,4536)
   DO 459 I=1,NSQRD
   WRITE(LDN02,4536) I
   READ(MTDWR) (WSP1(J),J=1,NSQRD)
   WRITE(LDN02,4533) (WSP1(J),J=1,NSQRD)
   CONTINUE
459 FORMAT("0",49X,"CONTENTS OF RECORD",4/
4533 FORMAT("1","3P224.10")
   RZAP(MTDWR) ( (H(I,J),I=1,NBASIS),J=1,NBASIS)
   WRITE(LDN02,4534)
4534 FORMAT("0",33X,"TRANSFORMED ONE-ELECTRON HAMILTONIAN MATRIX")
   CALL WRITEX(H,30,30,NBASIS,NBASIS,LDN02)
4535 CALL WRITEPS
   REWIND MTDWR
4536 FORMAT("1"/"0",43X,"TRANSFORMED TWO-ELECTRON INTEGRALS")
46 CALL QUIT(‘TWOTRA’,I5(3))
SUBROUTINE WRONTP(IWANT, IGOT, IUNIT)
C......CALLED WHEN TEST OF MAGNETIC TAPE SERIAL NUMBER INDICATES THAT THE
C......WRONG TAPE HAS BEEN MOUNTED.
   DATA LDNO2/0/
   WRITE(LDNO2,1) IUNIT, IWANT, IGOT
1 FORMAT(40HTHE WRONG TAPE HAS BEEN MOUNTED ON UNIT ,12/
   12S THE TAPE REQUIRED IS NUMBER,110/28H THE TAPE MOUNTED IS NUMBER
2R,110/29H CONTINUATION IS NOT POSSIBLE////)  
   CALL EXIT
   RETURN
END
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INTRA TEST DATA - INTEGRALS FOR ATOMIC OXYGEN (SCHAER AND HARRIS'S EXPONENTS)
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- 7.50
- 7.1
INTEGRALS FOR THIS RUN ARE IN THE NASTER INTEGRAL FILE STARTING AT BLOCK 50.
ONECEM TEST DATA - INTEGRALS FOR ATOMIC OXYGEN (SCHAEFER AND HARRIS'S EXPONENTS).

POSITIONS OF MAGNETIC DEVICES

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NUMBER OF INSTRUCTIONS USED ON EXIT FROM SUBPRCGRAM MFILE2 = 331
NUMBER OF INSTRUCTIONS USED ON ENTRY TO SUBPRCGRAM RESSET = 333
DIATOMIC CONFIGURATION INTERACTION PROGRAM
HOMONUCLEAR VERSION 1, 1/09/69.
A.D. TAIT
QUANTUM MOLECULAR PHYSICS GROUP,
DEPARTMENT OF PHYSICS,
UNIVERSITY OF LEICESTER,
LEICESTER, ENGLAND, LE1 7RH

ONEGEN TEST DATA - INTEGRALS FOR ATOMIC OXYGEN (SCHAEFER AND HARRIS'S EXPONENTS).

MAGNETIC QUANTUM NUMBERS

M(1) = 0
M(2) = 0
M(3) = 0
M(4) = -1
M(5) = 1

NUMBER OF INSTRUCTIONS USED ON EXIT FROM SUBPRGGRAM RESET = 346
NUMBER OF INSTRUCTIONS USED ON ENTRY TO SUBPRGGRAM SETER1 = 348
### Overlap Matrix

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### One-Electron Hamiltonian Matrix

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<td>0.000000000000E+00</td>
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</table>
TRANSFORMATION OF ONE-ELECTRON INTEGRALS

SYMMETRY TRANSFORMATION MATRIX

<table>
<thead>
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</tr>
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</tr>
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OF INSTRUCTIONS USED ON ENTRY TO SUBPROGRAM ORTHON = 457

C	S	C = 1

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OF INSTRUCTIONS USED ON EXIT FROM SUBPROGRAM ORTHON = 470

TRANSFORMED ORBITALS BELONG TO 4 DIFFERENT IRREDUCIBLE REPRESENTATIONS
(SUBSPECIES COUNTED AS DIFFERENT)

TRANSFORMED ORBITALS ARE ASSIGNED AS FOLLOWS
CRITICAL 1 BELONGS TO IR 1
CRITICAL 2 BELONGS TO IR 1
CRITICAL 3 BELONGS TO IR 2
CRITICAL 4 BELONGS TO IR 3
CRITICAL 5 BELONGS TO IR 4

TRANSFORMATION MATRIX
TRANSFORMATION MATRIX

<table>
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<tr>
<th>Columns 1 to 5</th>
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<th></th>
<th></th>
</tr>
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<td>0.0000000000E+00</td>
</tr>
<tr>
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</table>

TRANSFORMED ONE-ELECTRON INTEGRAL MATRIX

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NUMBER OF INSTRUCTIONS USED ON EXIT FROM SUBPROGRAM TRANSH = 504
NUMBER OF INSTRUCTIONS USED ON ENTRY TO SUBPROGRAM CONTRA = 506

NUMBER OF INSTRUCTIONS USED ON ENTRY TO SUBPROGRAM TWOTRA = 512

SERIAL NUMBER OF TAPE ON UNIT 04 IS 200000

TAPE POSITIONED AT NUMBER BLOCK WORD
3 1 79

TAPE POSITIONED AT NUMBER BLOCK WORD
4 1 0

TAPE POSITIONED AT NUMBER BLOCK WORD
5 1 2

TAPE POSITIONED AT NUMBER BLOCK WORD
6 50 0

TAPE POSITIONED AT NUMBER BLOCK WORD
7 1 0

TAPE POSITIONED AT NUMBER BLOCK WORD
8 20 0

END OUTPUT 3 BLOCKS

TRANSFORMATION OF 2ND. CHARGE DISTRIBUTION COMPLETE
<table>
<thead>
<tr>
<th>CONTENTS OF RECORD 13</th>
<th>CONTENTS OF RECORD 14</th>
<th>CONTENTS OF RECORD 15</th>
<th>CONTENTS OF RECORD 16</th>
<th>CONTENTS OF RECORD 17</th>
<th>CONTENTS OF RECORD 18</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.10579384558E+00</td>
<td>-9.0856167517E-03</td>
<td>6.0036016959E-01</td>
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<td>7.776378235E-01</td>
<td>7.774378136E-01</td>
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### CONTENTS OF RECORD 25

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### TRANSFORMED ONE-ELECTRON HAMILTONIAN MATRIX

#### COLUMNS 1 TO 3

<p>| | | | |</p>
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<thead>
<tr>
<th></th>
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</table>
NUMBER OF INSTRUCTIONS USED ON EXIT FROM SUBPROGRAM THQTRA = 972.

TRANSFORMATION OF TWO-ELECTRON INTEGRALS COMPLETE

NUMBER OF INSTRUCTIONS USED ON EXIT FROM SUBPROGRAM CONTRA = 974.

INTRA TEST DATA INTEGRALS FOR ATMOCIC OXYGEN (SCHAEFER AND HARRIS'S EXPONENTS); WILL BE FOUND IN THE MASTER (TRANSFORMED) INTEGRAL FILE STARTING AT BLOCK 50

POSITIONS OF MAGNETIC DEVICES:

<table>
<thead>
<tr>
<th>TAPE NUMBER</th>
<th>POSITIONED AT BLOCK</th>
<th>WORD</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>2</td>
<td>164</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>138</td>
</tr>
<tr>
<td>6</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>53</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>20</td>
<td>0</td>
</tr>
</tbody>
</table>

JOB COMPLETE = 1007 INSTRUCTIONS USED
APPENDIX VII

SECS\$L. A PROGRAM FOR THE CONSTRUCTION AND
SOLUTION OF THE SECULAR EQUATION IN THE
METHOD OF CONFIGURATION INTERACTION

This program computes the matrix elements of the secular equation using the methods described in chapters 7 and 8. The secular equation is solved using the QR-Algorithm and facilities are provided for computing and diagonalizing the first order density matrix if this is required. The program occupies about 1700 FORTRAN V source cards and its storage requirements are approximately 115 blocks of compilation store and 115 blocks of execution store. In addition to the subprograms listed here SECS\$L requires the routines ENTR, ERR\$R, IPAR, QUIT, and WRITMX from Appendix III.

SECS\$L uses two magnetic tapes and three disc areas which are assigned as follows:

<table>
<thead>
<tr>
<th>VARIABLE NAME</th>
<th>VALUE</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTD01</td>
<td>Defined in Private disc area of &gt; 150 blocks. Data Contains results of current run.</td>
</tr>
<tr>
<td>MTD02</td>
<td>Defined in Master results tape. Data</td>
</tr>
<tr>
<td>MTD</td>
<td>3 Private disc area of 30 blocks. Contains specification of detors and projection matrix $T_{S\sigma}$</td>
</tr>
<tr>
<td>IDISC</td>
<td>4 Private disc area of 3 blocks. Contains contents tables of MTD01, MTD02.</td>
</tr>
</tbody>
</table>
INTRA Defined in Master transformed integral tape-produced data by the program INTRA.

MTD 7 Common disc area of 100 blocks

The line printer is device 0.

The data provided by the user is divided into six sections. Once the detors have been specified this information is written onto MTD (= 3) followed by the projection matrix, this data may be used in a later run but only the last specifications read are available.

Data specification for SECSGL

Section 1 : Read data required to compute matrix elements between detors.

Card 1 IWHERE, N\$ F\$FORMAT (ZI5)

IWHERE = 1

$\{ N\$ = 0 to suppress timing information

$\{ = 1 to obtain timing information

Card 2, 3 TITLE

F\$FORMAT (9A8/6A8)

TITLE is an array of 15 elements (120 characters) used to identify the run.

Card 4 MTD01, MTD02, NBASIS, NDET, NELEC, NFULL

F\$FORMAT (6I5)

MTD01 = Device number of private disc area

MTD02 = Device number of master results tape

NBASIS = Number of basis orbitals

NDET = Number of detors

NELEC = Number of electrons

NFULL = Number of spin-orbitals frozen.
Card 5

\(N_{\text{NO}}\)

\text{FORMAT (I5)}

\[
\begin{align*}
N_{\text{NO}} = 0 & \text{ If the detors have to be specified} \\
N_{\text{NO}} = 1 & \text{ If the detors were specified in the previous run}
\end{align*}
\]

Card 6

\(F\)

\text{FORMAT (9A8)}

\(N_{\text{NO}} = 1\)

\(F\) is an array which defines the lineprinter format for the printing of the detor specifications. It has the form:

\[
((b, I8, mX, nI3))
\]

or \((1Hb, I8, mX, nI3))\),

where \(b\) is a blank, \(n\) = numerical value of \(NBASIS\), and \(m = \frac{1}{2} (112 - 3 n)\)

Variations are possible

Card 7(I)

\((\text{IDET}(I, J), J = 1, \text{NELEC})\)

\(\text{FORMAT (1X, 32I2)}\)

\(N_{\text{NO}} = 1\)

\(\text{IDET}(I, J)\) specifies the \(J\)th spin-orbital of the \(I\)th detor. These cards, of which there are \(N_{\text{DET}}\), will normally be these output by the program \(\text{GENDET}\).

\((1 \leq I \leq N_{\text{DET}})\).

Section 2 : Computation of \(G(k) = \left< \sum_{\mu} \left| D_{\mu} \right| \right| \mu \left| \sum_{\nu} \right| j \left| D_{\nu} \right>\), where \(k = (\mu(\mu - 1))/2 + \nu\) and \(\mu \geq \nu\). The transformed integrals must be on \(\text{MTDO1 at word 0, block 1}\).
Card 1

IWHERE, N\phi
FORMAT (2I5)
IWHERE = 2
N\phi : see section 1 card 1

Section 3 : Compute H and solve (H-EI) Q = 0
Card 1

IWHERE, N\phi
FORMAT (2I5)
IWHERE = 3
N\phi : see section 1 card 1

Card 2

NC\phiNF, N\phiNO
FORMAT (2I5)
NC\phiNF = number of codetors
N\phiNO = number of non-zero elements in the
projection matrix T_{50}

Card 3

IFILE
FORMAT (1I5)

IFILE = 0 If the projection matrix has to be defined
IFILE = 1 If the projection matrix was defined in the
previous run

Card 4(k)

I, J, T(I, J)
(Omitted if IFILE = 1)

FORMAT (2I5, F10.2)

T(I, J) is the I, J-th element of the projection
matrix T_{50}. It should be non-zero and
written as an integer in real form, e.g.
1.00. The program normalizes the columns
of T_{50}
(1 \leq k \leq N\phiNO)
Card 5  
NCEN  
FRMAT (I5)  
NCEN  = number of nuclei  

Card 6(I)  
CH(I), X(I), Y(I), Z(I)  
(Omitted if  
FRMAT (1P4E 20.10)  
NCEN = 1)  

CH(I)  = Charge on nucleus I (a.u.)  
X(I)  The cartesian co-ordinates \((x,y,z)\) of the  
Y(I)  I-th nucleus.  
Z(I)  

\((2 \leq I \leq \text{NCEN})\)

Section 4  ; Natural spin orbital analysis of a specified energy level.

Card 1  
IWHERE, NS  
FRMAT (2I5)  
IWHERE  = 4  
NO  : see section 1 card 1

Card 2  
ICNL  
FRMAT (I5)  
ICNL  defines the energy level for which the  
analysis is required  
\((1 \leq \text{ICNL} \leq \text{NCNF})\)

Card 3  
IFILE, JFILE  
FRMAT (2I5)  
IFILE  = 3  
JFILE  = 4

Card 4  
(DN(ENTRY, J), J = 1, 4)  
FRMAT (4A8)  
This card contains 32 characters used to  
identify the NS analysis, ENTRY is known  
to the program.
Section 5  Entries to the subprogram TDFILE: the data is divided into five sections.

Card 1  IWHEREno

FORMAT (2i5)

IWHEREno = 5

NO : see section 1 card 1

This card precedes the cards from one of the following subsections

A : Copy transformed integrals onto MTD01 and MTD02 from INTRA

Card 2A  IFILE, JFILE

FORMAT (2i5)

IFILE = 1

JFILE = 1

Card 3A  IENTRY, NXBLGC

FORMAT (2i5)

IENTRY = 2

NXBLGC = number of block at which transformed integral file will begin on MTD02

Card 4A  INTRA, IG0, NBLGC

FORMAT (3i5)

INTRA = device number for Master transformed integral tape.

IG0

= 0 To initialize the contents tables of MTD01 and MTD02

= 1 If the contents table of MTD02 contains entries

NBLGC = number of block at which transformed integral file begins on INTRA.
Card 5A  \((DN(1, k), k = 1, 4)\)

\texttt{FORMAT (4A8)}

This card contains 32 characters used to identify the integrals.

B : Copy selected entries from MTD02 onto MTD01

Card 2B  \(\text{IFILE, JFILE} \)

\texttt{FORMAT (2I5)}

\begin{align*}
\text{IFILE} & = 1 \\
\text{JFILE} & = 0
\end{align*}

Card 3B  \(\text{IENTRY, NXBL/C} \)

\texttt{FORMAT (2I5)}

\begin{align*}
\text{IENTRY} & = \text{number of entries to be copied from MTD02 onto MTD01 and must always include the last entry on MTD02.} \\
\text{NXBL/C} & = 0
\end{align*}

Card 4B  \((LD(I), I = 1, IENTRY)\)

\texttt{FORMAT (16I5)}

\(LD(I)\) is the subscript of an entry in the contents table of MTD02. The records corresponding to this entry are copied onto MTD01.

Continue on successive cards if IENTRY > 16)

C : Read data into core from MTD01

Card 2C  \(\text{IFILE, JFILE} \)

\texttt{FORMAT (2I5)}

\begin{align*}
\text{IFILE} & = 2 \\
\text{JFILE} & = 0
\end{align*}

Card 3C  \(\text{IENTRY} \)

\texttt{FORMAT (I5)}
IENTRY is the subscript of an entry in the contents table of MTDO1. The records corresponding to this entry will be read into the appropriate area of core.

D : Write results onto MTDO1

Card 2D IFILE, JFILE
FORMAT (2I5)

IFILE = 3

= 2 If matrix elements between detors are to be transferred
= 3 If the solution of the secular equation is to be transferred
= 4 If the first order density matrix is to be transferred

JFILE

Card 3D (DN(NENTRY, J), J = 1, 4)
FORMAT (4A8)

This card contains 32 characters used to identify the entry.

E : Update MTDO2 from MTDO1, entries on MTDO1, not already on MTDO2 will be added to MTDO2.

Card 2E IFILE, JFILE
FORMAT (2I5)

IFILE = 4
JFILE = 0

Section 6 : End of job

Card 1 IWHERE, NØ
FORMAT (2I5)

1
IWHERE = 6
NO : see section 1 card 1

Restrictions

1 \leq NB\text{BASIS} \leq 30
1 \leq NDET \leq 120
1 < NE\text{LEC} \leq 32
0 \leq N\text{FULL} \leq 8
1 \leq N\text{C\&N}\text{F} \leq 78
1 \leq NC\text{EN} \leq 20

The number of entries in the contents table of MTD02 must not exceed 158, and the number in that of MTD01 must not exceed 10.

Error Messages

Checks are made to see that the data does not violate the limits of the program. Certain violations give rise to the message ERR\text{R} \text{R} n, where n is a number in the list below:

\begin{align*}
\text{ERR}\text{R} n & \quad \text{CAUSE} \\
1 & \quad \text{NB\text{BASIS}} > 30 \\
2 & \quad \text{NE\text{LEC}} > 32 \\
3 & \quad \text{NDET} > 120 \\
4 & \quad \text{N\text{FULL}} > 8 \\
5 & \quad \text{N\text{C\&N}\text{F}} > 78
\end{align*}

Several other error conditions can arise which will terminate execution. In these circumstances the error messages are self-explanatory.

The following actions may cause termination as the subroutine TDFILE will interpret them as errors:

(i) attempting to read integrals into core,
(ii) attempting to read the first order density matrix into core,
(iii) attempting to read the 'next new record' into core
(iv) requesting more records from MTD02 than are actually present.
*FORTRAN LIB 6,19,302

C....MAIN PROGRAM FOR SECSOL - CONSTRUCTION AND SOLUTION OF THE SECULAR EQUATION WITH AN OPTIONAL NATURAL SPIN-ORBITAL ANALYSIS.

COMMON /SECSQN/ AA(33767),ICR,LP,MTD,NO,ANY0,ANY1,ANY2,ANY3,ANY4,
IGF,ICOL,IDOISC,IFILE,JFILE,LINK,MTDO1,MTDO2,NBASIS,NCONF,NDLT,NSLOC
2,NF,NSQRD,NXBLOC
EQUIVALENCE (NXBLOC,IWHERE)

C....DEFINE DEVICE NUMBERS,
C.....LP = LINE PRINTER,
C.....ICR = CARD READER,
C.....MTD = WORKFILE.
C.....IDOISC=CONTENT TABLES FILE.
CLEAR ICR,LP
MTD=3
IDOISC=4
1 READ (ICR, 2) IWHERE,NO
2 FORMAT (215)
GO TO (3,4,5,6,7,8),IWHERE

C....READ DATA FOR COMPUTING MATRIX ELEMENTS BETWEEN DETORS.
3 CALL SECDAT(1)
GO TO 1

C....COMPUTE MATRIX ELEMENTS BETWEEN DETORS.
4 MTD=7
CALL PASONE
CALL MAXCCN
CALL PASTWO
CALL HPASS
MTD=3
GO TO 1

C....COMPUTE H-MATRIX AND SOLVE (H-2*I)*C =0.
5 CALL SECSOL
GO TO 1

C....PERFORM NATURAL SPIN ORBITAL ANALYSIS.
6 CALL NATORB
GO TO 1

C....CORE/PERIPHERAL TRANSFER - MAKE SURE DATA IS CORRECT.
7 CALL TDFILE
GO TO 1

C....JOB COMPLETE.
8 CALL TIME(ANYO)
WRITE(LP,9) ANYO
9 FORMAT('O',3X, '**** JOB COMPLETE - TIME USED = ',F10,5,' SECONDS * 1***')
STOP
END

*FORTRAN LIB

SUBROUTINE ADDNRE(H,N,M,ICR,LP)
C....ADDS NUCLEAR REPULSION ENERGY TO SOLUTION OF SECULAR EQUATION.
C....VERSION 2. MAXIMUM NUMBER OF NUCLEI IS TWENTY.
DIMENSION H(N,N),X(20),Y(20),Z(20),CH(20)
SQRD(X,I,J)=(X(I)-X(J))**2
READ(ICR,1) NCEN
1 FORMAT(IS)
IF(20-NCEN) 10,2,2
2 IF(NCEN-1) 9,9,3
3 READ(ICR,4) (CH(I),X(I),Y(I),Z(I),I=1,NCEN)
4 FORMAT(1P4.20,10)
WRITE(LP,5) NCEN,(I,CH(I),X(I),Y(I),Z(I),I=1,NCEN)
5 FORMAT('O',3X,'GEOLOGY OF MOLECULE, I3, NUCLEI AS FOLLOWS/*'""
1,24X,'NUCLEUS NUCLEAR CHARGE X CO-ORDINATE Y CO-ORDINATE Z
2 CO-ORDINATE'/(',27X,12,1P319.7,1P316.6))
CLEAR ERN
NCEN=NCEN-1
DO 6 I=1,MCEN
K=I+1
DO 6 J=K,NCEN
ERN=ERN+CH(I)*CH(J)/SQRT(SQRD(X,I,J)+SQRD(Y,I,J)+SQRD(Z,I,J))
6 CONTINUE
WRITE(LP,7)ERN
7 FORI,IAT/0',38X,'NUCLEAR REPULSION ENERGY=',1PE17.10)
DO 8 I=1,M
H(I,I)=H(I,I)+ERN
8 CONTINUE
9 RETURN
10 WRITE(LP,11)NCEN
11 FORMAT('0',42X,'NCEN=',15,'. NCEN MUST NOT EXCEED 20')
CALL EXIT
STOP
END
*FORTRAN LIB
SUBROUTINE EA03A(A,B,N,ND,EPS)
C...REPLACES HARWELL LIBRARY VERSION OF JACOBI'S METHOD BY AN
C...INTERFACE WITH THE QR-ALGORITHM.
DIMENSION A(ND,ND),B(ND,ND),D(78),E(78)
EPS=2.0**(-35)
TOL=2.0**(-349)
CLEAR LP
DISPLAY(LP,20)/EPS,TOL
CALL TRED2(N,TOL,ND,A,B,D,E)
CALL TQL2(N,EPS,ND,B,E,E)
C...IF NN,NE,0 TQL2 HAS FAILED TO CONVERGE.
IF(NN)1,3,1
1 WRITE(LP,2)
2 FORMAT('0',120('**')/' */',118X,'**'/*',47X,'TQL2 FAILED TO CONVERG
12',46X,'**'/*',118X,'**'/*',120('**'))
C...ENTER EIGENVALUES IN DIAGONAL OF A.
3 DO 4 I=1,N
A(I,I)=D(I)
4 CONTINUE
RETURN
END
*FORTRAN LIB
SUBROUTINE F0DMA4
C...COMPUTES FIRST ORDER DENSITY MATRIX. VERSION 4. 03/05/71,
C...ASSUMES BASIS SPIN ORBITALS ARE ORTHONORMAL.
CC=NCHM/SRCBN/T(120,7S),AA(60,60),C(120),JD(1182,2),C,GAMMA(60,60)
1,IDENT(120,32),ID(843),KDET(32),EV(78,78),SP(3923),IR,MTrap,NO,
2ANY0,ANY1,ANY2,ANY3,ANY4,OF,ICOL,IDISC,IFILE,JFILE,LINK,MTDO,
3MTD02, NBAS IS, NCGNF, ITDET, NELEC, NFULL, NSQRD, NNBLOC
EQUIVALENCE (SP,FACTOR),(SP(2),I),(SP(3),ICRB),(3P(4),IR),(3P(5),
1IS),(3P(6),II),(3P(7),I2),(3P(8),J),(3P(9),JCRR),(3P(10),K),
2(3P(11),L)
CALL ENTR("FCDMA4",NO)
WRITE(LP,20)((IDENT(I,J),J=1,NBAS),I=1,NDSET)
X DISPLAY(LP,4)/NF,NFULL,NBAS,NDE
CLEAR LINK
NBAS IS=NBAS IS+NBAS
C.....IF DETORS K AND L DIFFER BY TWO OR MORE SPIN-ORBITALS THEN
C.....THE COFACTOR OF EVERY ELEMENT IN THE INTEGRAL OF THEIR PRODUCT IS
C.....ZERO. CONSTRUCT A TABLE CONTAINING THE INDEX (IS) OF PAIRS THAT
C.....DIFFER BY ONLY 1 SPIN-ORBITAL.

     DO 12 K=2,NDET
     IR=K-1
     I1=(K*IR)/2
     DO 11 L=1,IR
     CLEAR I2
     IS=I1+L
     DO 1 I=NF,NELEC
     KDET(I)=IDET(L,I)
     1 CONTINUE
     DO 5 I=NF,NELEC
     IF(IDET(K,I)-KDET(I)>2,5,2
     2 DO 3 J=NF,NELEC
     IF(IDET(K,I)-KDET(J))3,4,3
     3 CONTINUE
     GO TO 5
     4 IORB=KDET(I)
     KDET(I)=KDET(J)
     KDET(J)=IORB
     5 CONTINUE
     DO 3 I=NF,NELEC
     IF(IDET(K,I)-KDET(I))6,8,6
     6 I2=I-1
     IF(I2-1)7,7,11
     7 IGRB=ICDET(I)
     JORB=IDET(I)
     3 CONTINUE
     DO 9 I=NF,NELEC
     IF(IDET(L,I)-JORB)9,10,9
     9 CONTINUE
     DO S I=NF,NELEC
     IF(IDET(K,I)-KDET(I))12,12
     IF(I2-1)7,7,11
     7 IGRB=I
     JORB=KDET(I)
     3 CONTINUE
     DO 9 I=NF,NELEC
     J=I
     IF(IDET(L,I)-JORB)9,10,9
     9 CONTINUE
     X WRITE(LP,13) (ID(I),I=1,LINK)
     X WRITE(LP,14) ((JD(I,J),J=1,2),I=1,LINK)
     CLEAR GAMMA

C.....COMPUTES FIRST ORDER DENSITY MATRIX.
     X WRITE(LP,28) ((IDET(I,J),J=1,NELEC),I=1,NDET)
     DO 23 K=1,NDET
     DISPLAY(LP,5) K
     IF(C(K))141,141
     141 DO 22 L=1,NDET
     IF(C(L))142,143
     142 I2=K-L
     IF(I2)17,17
     C.....DETERS K AND L ARE IDENTICAL.
     15 FACTOR=C(K)*C(K)
     DO 16 I=1,N3LEC
     I1=IDET(K,I)
     GAMMA(I1,I1)=GAMMA(I1,I1)+FACTOR
     16 CONTINUE
GO TO 22
C.....DETECTORS K AND L ARE DIFFERENT - IF THEIR INDEX (IS) DOES NOT
C.....APPEAR IN ID THEY DIFFER BY 2 OR MORE SPIN-ORBITALS.
17 IF(LINK.eq.0) GO TO 22
IS=(MAXO(K,L)*MAXO(K,L)-1)/2+MINO(K,L)
DO 13 I=1,LINK
J=I
IF(IS-ID(I)) 18,19,18
13 CONTINUE
GO TO 22
19 IORB=JD(J,1)
JORB=JD(J,2)
IF(I2) 20,21,21
20 I0RB=JD(J,1)
J0RB=JD(J,2)
IDEB=IDET(K,IORB)
JDEB=IDET(L,JORB)
GA1A(J, I) =GA1A(J, I)+C(K)*C(L)*(-1.0)**(IORB+JORB)
22 CONTINUE
23 CONTINUE
C.....CHECK SYMMETRY OF GA1A
DO 27 I=1,NBASIS
II=I+1
DO 26 J=II,NBASIS
FACOR=ABS(GA1A(I,J)-GA1A(J,I))
IF(I2) 24,26,26
24 WRITE(LP,25) I,J,J,I,FACOR
25 FORMAT(35X, 'GA1A(',I2, I2),NE,GAMMA(',12, 'I2,') . DIFFERENCE=',1PE9.2)
26 CONTINUE
27 CONTINUE
23 CONTINUE
X 23 FORMAT(35X, 'GA1A(',I2, I2),NE,GAMMA(',12, 'I2,') . DIFFERENCE=',1PE9.2)
RETURN
END

FORTRAN LIB

SUBROUTINE HPASS

C.....COMPUTES ONE-ELECTRON CONTRIBUTION TO MATRIX ELEMENTS.
C.....READ ONE-ELECTRON HAMILTONIAN MATRIX.
CCBLOQ...G(7260),ERI(900),IDET(130,32),IDDIFF(3073,7),
1 IDUM(261),ANY1,ANY2,ANY3,ANY4,OF,ICOL,DISC,IFIL3,JFIL3,LINK,MTDC1
2,MTDO2,NBASIS,NCONF,NDST,NSECF,NF,NFULL,NSORD,NXBLOCK
EQUIVALENCE (IDUM(149) ,I),(IDUM(150) ,J) , (IDUM(151), FSU)
1(IDUM(152) ,I), (IDUM(153) ,K), (IDUM(154) ,L), (IDUM(155) ,LL),
2(IDUM(156) ,LM), (IDUM(157) ,KP), (ANY3, LNO), (ANY4, LQ), (IDUM(259) ,MTD)
DIMENSION H(30,30)
EQUIVALENCE (ERI,H)
CALL EITTR(" HPASS",IDUM(260))
READ(MTDO2) ((II(I,J) ,J=1,NBASIS) ,I=1,NBASIS)
CLEAR FSU
X 23 CONTINUE
C.....COMPUTE FROZEN CORE CONTRIBUTION TO DIAGONAL ELEMENTS.
IF(NFULL) 3,3,1
1 NF=NFULL/2
X WRITE(IDUM(258),11)
DO 2 I=1,NF
X WRITE(IDUM(258),12) I,I,H(I,I)
FSU=FSU+H(I,I)
2 CONTINUE
FSUM=2.0*FSUM
3 NF=NFULL+1

C....COMPUTE DIAGONAL ELEMENTS.
DO 5 L=1,NDET
KL=(L*(L+1))/2
DO 4 L1=NF,NFULL
LL1=(IDET(L,L1)+1)/2
G(KL)=G(KL)+H(LL1,LL1)
4 CONTINUE
G(KL)=G(KL)+FSUM+GF
5 CONTINUE

C....COMPUTE OFF-DIAGONAL ELEMENTS - IF DETORS L AND K DIFFER BY
C....MORE THAN ONE SPIN ORBITAL THE ONE ELECTRON CONTRIBUTION IS ZERO.
INC=3073
DO 13 LU=1,ICOL
IF(ICOL-l) 51,53,51
51 READ (MTD) IDIFF
IF(LU-ICOL) 54,52,54
52 IF(LINK) 53,13,53
53 LINK=LINK
54 DO 9 L=1,LNO
KL=IDIFF(L,2)
IF(IDIFF(L,1)-1) 6,G,8
C  DETORS L AND K DIFFER BY IM IN L AND KP IN K.
6 LM=IDIFF(L,3)
KP=IDIFF(L,4)
IF(IPAR(LM)-IPAR(KP)) 8,7,8
7 G(KL)=G(KL)+H((LM+1)/2,(KP+1)/2)
C  MULTIPLY BY APPROPRIATE PARITY FACTOR.
8 G(KL)=IDIFF(L,2)*G(KL)
9 CONTINUE
X DISPLAY(IDU(25S),12)/FSUM
X WRITE(IDU(25S),10) (KL,G(KL),KL=1,(NDET*(NDET+1))/2)
X 10 FORMAT(("G",I4,"=",1PE17.10))
X 11 FORMAT("",47X,"CONTRIBUTIONS TO FSUM")//
X 12 FORMAT("",47X,"H","12","12","=",1PE17.10)
X 13 CONTINUE:
REWIND MTD
CALL QUIT("HPASS",IDU(260))
RETURN
END

FORTRAN LIB
SUBROUTINE MAXCON
C....BRINGS DETORS INTO MAXIMUM COINCIDENCE, DETERMINES AND IDENTIFIES
C....THE SPIN-ORBITALS BY WHICH EACH PAIR OF DETORS DIFFER,
C....ONLY OFF-DIAGONAL ELEMENTS ARE TREATED AND RESULTS ARE STORED ONLY
C....IF TWO DETORS DIFFER BY NOT MORE THAN TWO SPIN-ORBITALS.
COMMON /SUCCON/ G(7260),THI(900),IDET(120,32),IDIFF(3073,7),
1 IDUM(261),ANY,ANY2,ANY3,ANY4,GF,ICOL,IPERM,INUM,IDC,LIN,J,
2 MTD,MTD02,NBASIS,NCONF,NDET,NFULL,NQRS1,NDI!D,NDX
DIMENSION KDET(32)
EQUIVALENCE (IDU(109),KDET),(IDUM(142),L),(IDUM(143),LM1),
1 (IDUM(144),I),(IDUM(145),IPERM),(IDUM(146),I),(IDUM(147),IT MP),
2 (IDUM(148),IDC),(IDUM(175),LIN),(IDUM(176),J),(IDUM(259),KTP)
IF(NDET.NEQ.1) RETURN
CALL ENTR("MAXCON",IDU(260))
CLEAR DIFF,LINK,LIN
ICOL=1
DO 11 L=2,NDET
IM1=L-1
DO 10 K=1,IM1
CLEAR IPERM,IDC
LINK=(L*IM1)/2+K
DO 1 I=1,NELEC
KDET(I)=IDET(K,I)
1 CONTINUE
DO 5 I=NF,NELEC
IF(IDET(L,I)-KDET(I)) 2,5,2
2 DO 3 J=NF,NELEC
IF(IDET(L,I)-KDET(J)) 3,4,3
3 CONTINUE
GO TO 5
4 ITMP=KDET(I)
KDET(I)=KDET(J)
KDET(J)=ITMP
IPERM=IPERM+1
5 CONTINUE
J=2
LIN=LIN+1
DO 3 I=NF,NELEC
IF(IDET(L,I)-KDET(I)) 6,8,6
6 IDC=IDC+1
IF(2-IDC) 9,7,7
7 J=J+1
IDIFF(LIN,J)=IDET(L,I)
J=J+1
IDDIFF(LIN,J)=KDET(I)
8 CONTINUE
IDIFF(LIN,2)=(-1)**IPERM
IDDIFF(LIN,1)=IDC
IDDIFF(LIN,7)=LINK
IF(LIN-3073) 10,81,10
81 ICOL=ICOL+1
WRITE(MTD) IDIFF
CLEAR LIN,IDIFF
GO TO 10
9 LIN=LIN-1
10 CONTINUE
11 CONTINUE
IF(ICOL-1) 12,14,12
12 IF(LIN) 13,14,13
13 WRITE(MTD) IDIFF
ICOL=ICOL+1
14 REWIND MTD
LINK=LIN
X WRITE(IDUM(353),15) (I,(IDIFF(I,J),J=1,7),I=1,LIN)
X 15 FORMAT(’ ’,6X,’CONTENTS OF IDIFF’/(’’,45X,’I=’,I,3X,7I3))
I=3073*(ICOL-1)+LIN
WRITE(16,1G) I
16 FORMAT(’ ’,26X,’NUMBER OF NON-ZERO OFF-DIAGONAL MATRIX ELEMENTS BETWEEN DETORS=’/,I5)
CALL QUIT(’MAXCON’,IDUM(260))
RETURN
END

*FORTRAN LIB
SUBROUTINE MULTRA(A,B,C,IP,IQ,IR,IA,IB,IC)
C PRODUCT OF MATRICES A AND B STORED IN C.
DIMENSION A(IA,IQ),B(IB,IR),C(IC,IR)
DO 1 I=1,IP
DO 1 J=1,IR
C(I,J)=0.0
DO 1 K=1,IQ
C(I,J)=C(I,J)+A(I,K)*B(K,J)
1 CONTINUE
RETURN
END

SUBROUTINE NATORB
C.....CONTROL ROUTINE FOR NATURAL SPIN ORBITAL ANALYSIS.
COMMON/SECHRN,T(120,73),AA(60,60),C(120),JD(1122,2),C,GAMMA(60,60)
1,IDET(120,32),ID(343),KDET(32),EV(75,73),SP(3923),ICR,LP,MTD,NG,
2ANY1,ANY2,ANY3,ANY4,GP,ICCL,IDS,ICF,IPF,JF,MAKE,LINK,MTDO1,
3MTDO2,NBASIS,NCONF,NDET,NELEC,NF,NFULL,NSQRD,NXBLCC
EQUIVALENCE (SP(l),I),(SP(2),J),(SP(3),K),(SP(4),L)
CALL ENTR('NATORB',NG)
C.....READ DATA FROM DEVICE MTD.
READ(MTD) ((IDET(I,J),J=1,NEL3C),I=1,NDET)
READ(MTD) ((T(I,J),J=1,NCONF),I=1,NDET)
READ(MTD) (0,1=1,NCONF)
C.....COMPUTE COEFFICIENTS OF INDIVIDUAL DETERMINANTS FOR LEVEL ICOL OF
C.....THIS STATE.
CLEAR C
READ(ICR,12) ICCL
WRITE(LP,13) ICCL
DO 11 I=1,NDET
DO 1 J=1,NCONF
X DISPLAY(LP,10) /I,J,T(I,J),ICCL,EV(J,ICOL)
C(I)=C(I)+T(I,J)*EV(J,ICOL)
1 CONTINUE
X DISPLAY(LP,10) /I,C(I)
11 CONTINUE
C.....COMPUTE FIRST ORDER DENSITY MATRIX - GAMMA-MATRIX.
WRITE(LP,14)
WRITE(LP,15) (I,C(I),I=1,NCONF)
CLEAR GAMMA
CALL FGDMA4
C.....WRITE FIRST ORDER DENSITY MATRIX ONTO MTDO1.
CALL TDFILE
C.....BEGIN ANALYSIS. SINCE THE BASIS ORBITALS ARE ORTHONORMAL THE
C.....SOLUTION TO THE NSO EQUATIONS IS THE UNITARY MATRIX WHICH
C.....DIAGONALIZES GAMMA.
CALL RQAGR(GAMMA,AA,NBASIS,30,GP)
C.....THE OCCUPATION NUMBERS ARE THE DIAGONAL ELEMENTS OF GAMMA, A IS
C.....THE TRANSFORMATION MATRIX.
WRITE(LP,2)
2 FORMAT('G',40X,'RESULTS OF NATURAL SPIN ORBITAL ANALYSIS')
CLEAR GF
DO 5 I=1,NBASIS,5
J=I+4
IF(J-NBASIS) 4,4,3
J=NBASIS
4 WRITE(LP,6) I,J
WRITE(LP,7) (GAMMA(K,K),K=1,J)
WRITE(LP,8) I,J
5 CONTINUE
WRITE(LP,7) (...(K,L),L=1,J)
*FORTRAN LIB
SUBROUTINE PASONE
C.....COMPUTES ELECTRON-ELECTRON INTERACTION BETWEEN FROZEN COR
C.....ELECTRONS. THIS IS ZERO IF NFULL IS ZERO.
C
DIMENSION KEEP(40,3)
EQUIVALENCE (IDUM,ICEEP) ,  (IDUM(121) ,IC) ,  (IDUM(122) ,L) ,  (IDUM(123) ,K)
1, (IDUM(124) ,LM1) ,  (IDUM(125) ,L2) ,  (IDUM(126) ,K1) ,  (IDUM(127) ,K2) ,
2,IDUM(128) ,IREC) ,  (IDUM(129) ,J) ,  (IDUM(130) ,ICOUNT) ,  (IDUM(131) ,LL)
3(IDUM(132),1CC), (IDUM(250),MTD)
CALL ENTR('PASONE',IDUM(2G0))
CLEAR GF
IF(NFULL) 11,11,1
1 NSQRD=NBASIS*NBASIS
CLEAR IC
DO 2 L=2,NFULL
LM1=L-1
L1=(L+1)/2
L2=(L1-1)*NBASIS
IC=IC+1
KEEP(IC,1)=L
KEEP(IC,2)=L
KEEP(IC,3)=L1+L2
DO 2 K=1,LM1
K1=(K+1)/2
IC=IC+1
KEEP(IC,1)=L
KEEP(IC,2)=K
KEEP(IC,3)=L1+L2
DO 2 K=1,LM1
K1=(K+1)/2
IC=IC+1
KEEP(IC,1)=L
KEEP(IC,2)=K
KEEP(IC,3)=L2+K1
X WRITE(IDUM(258),12) L,K
X WRITE(IDUM(258),13) (KEEP(IREC,J),J=1,3),IREC=1,IC)
2 CONTINUE
K2=KEEP(1,3)
DO 3 IRGC=2,IC
K2=MAX0(K2,KEEP(IRGC,3))
3 CONTINUE
X DISPLAY /K2
DO 10 IRGC=1,K2
READ(MTD01) (SRI(J),J=1,NSQRD)
X WRITE(IDUM(258),14) IRGC
X WRITE(IDUM(258),15) (SRI(J),J=1,NSQRD)
**FORTRAN LIB**

SUBROUTINE PASTA

C......COMPUTES CORR-VALENCE AND VALENCE-VALENCE ELECTRON INTERACTION
C......CONTRIBUTIONS TO MATRIX ELEMENTS.

COMMON /SECENA/ G(7260),ERI(900),IDET(120,32),IDIFF(3073,7),
1IDUM(261),ANY1,ANY2,ANY3,ANY4,GF,ICOL,IDISC,IFILE,JFILE,WBLOC
2MTDUL,MTDL2,NBASIS,MCYT,MTDO1,MTDO2,NF,NELEC,NFULL,NSQRD,NSRLC
EQUIV/ILDNCE (I,DUM(250),LP)

CALL ETRN("PASTWV",IDUM(260))

IF(NELEC.EQ.NFULL) GO TO 331

CLE/IR G
NXBLCC=NF
IF(NF.EQ.1) ILC3LGC=2
DO 37 J=1,NBASIS

WRITE(LP,39) I, J
R=AO(MTDUL) (ERI(L),L=1,NSQRD)

CALL ETRN("PASTWV",IDUM(260))

IF(NF,LJ,I1) NKBLOC=2
DO 37 L=1,NBASIS

WRITE(LP,33) L,J
R=AO(MTDUL) (ERI(L),L=1,NSQRD)

WRITE(LP,40) (ERI(L),L=1,NSQRD)

C......DIAGONAL ELEMENTS.

C......(II/ ) TYPE INTEGRALS.

C......SUM OVER VALENCE ELECTRONS.
\[ L_i = u_i \]

**SUM OVER CORE AND VALENCE ELECTRONS.**

\[ G(KL) = G(KL) + ERI(NBASI8*(LL2-1)+LL2) \]

\[ X \text{ WRITE}(LP,42) \text{ NBASI8*(LL2-1)+LL2}, ERI(NBASI8*(LL2-1)+LL2) \]

**TYPE INTEGRALS.**

\[ G(KL) = G(KL) - ERI(NBASI8*(LL2-1)+I) \]

**DIFF-DIAGONAL ELEMENTS.**

\[ L(i, j) = (i(i+1))/2 \]

**CHECK THAT SPINS DO NOT CAUSE THE INTEGRAL TO BE ZERO.**

\[ G(KL) = G(KL) + ERI(NBASI8*((KL)-1)/2+1, KL) \]

**DIFF-DIAGONAL ELEMENTS.**

\[ L(i, j) = (i(i+1))/2 \]

**CHECK THAT SPINS DO NOT CAUSE THE INTEGRAL TO BE ZERO.**

\[ G(KL) = G(KL) + ERI(NBASI8*((KL)-1)/2+1, KL) \]

**DIFF-DIAGONAL ELEMENTS.**

\[ L(i, j) = (i(i+1))/2 \]

**CHECK THAT SPINS DO NOT CAUSE THE INTEGRAL TO BE ZERO.**

\[ G(KL) = G(KL) + ERI(NBASI8*((KL)-1)/2+1, KL) \]

**DIFF-DIAGONAL ELEMENTS.**

\[ L(i, j) = (i(i+1))/2 \]

**CHECK THAT SPINS DO NOT CAUSE THE INTEGRAL TO BE ZERO.**

\[ G(KL) = G(KL) + ERI(NBASI8*((KL)-1)/2+1, KL) \]
X  I W S P = N B A S I S * ( ( I M + 1 ) / 2 - 1 ) + ( K P + 1 ) / 2
X  W R I T E ( L P , 4 2 ) I W S P , E R I ( I W S P )
   2 0  C O N T I N U E
X  W R I T E ( L P , 4 3 ) K L , G ( K L )
   G O  T O  3 6
C . . . . . . ( I P / M I )  T Y P E  I N T E G R A L S .
   2 1  K P = I D I F F ( L , 4 )
      I F ( J - ( K P + 1 ) / 2 ) 3 6 , 3 3 , 3 3
   2 2  D O  2 3  L I = 1 , N 3 L E C
      L I = I D S T ( L V A L , L I )
      I F ( I - ( L I + 1 ) / 2 ) 2 8 , 2 3 , 2 6
      2 3  I F ( I P A R ( K P ) - I P A R ( L I ) ) 2 6 , 3 2 , 3 6
   2 4  L I = I D I F F ( L , 3 )
      I F ( I P A R ( L I ) - I P A R ( L I ) ) 2 8 , 2 6 , 3 6
   2 5  G ( K L ) = G ( K L ) - E R I ( N B A S I S * ( ( I M + 1 ) / 2 - 1 ) + ( L I + 1 ) / 2 )
   X  I W S P = N B A S I S * ( ( I M + 1 ) / 2 - 1 ) + ( L I + 1 ) / 2
   X  W R I T E ( L P , 4 2 ) I W S P , E R I ( I W S P )
   2 5  C O N T I N U E
X  W R I T E ( L P , 4 3 ) K L , G ( K L )
   G O  T O  3 6
C . . . . . . ( K P , K Q  I N  K )
   2 7  L M = I D I F F ( L , 3 )
      I F ( J - ( L M + 1 ) / 2 ) 3 5 , 3 3 , 3 6
   2 8  K P = I D I F F ( L , 4 )
      I F ( J - ( K P + 1 ) / 2 ) 3 5 , 3 2 , 3 3
C . . . . . . ( K P / N Q )  T Y P E  I N T E G R A L S .
   2 9  I F ( I P A R ( L M ) - I P A R ( K Q ) ) 3 6 , 3 3 , 3 6
   3 0  L N = I D I F F ( L , 5 )
      K Q = I D I F F ( L , 6 )
      I F ( I P A R ( L M ) - I P A R ( K Q ) ) 3 6 , 3 3 , 3 6
   3 1  G ( K L ) = G ( K L ) + E R I ( N B A S I S * ( ( I N + 1 ) / 2 - 1 ) + ( K Q + 1 ) / 2 )
   X  I W S P = N B A S I S * ( ( I N + 1 ) / 2 - 1 ) + ( K Q + 1 ) / 2
   X  W R I T E ( L P , 4 2 ) I W S P , E R I ( I W S P )
   X  W R I T E ( L P , 4 3 ) K L , G ( K L )
   G O  T O  3 6
C . . . . . . ( K Q / N P )  T Y P E  I N T E G R A L S .
   3 2  K P = I D I F F ( L , 6 )
      I F ( J - ( K Q + 1 ) / 2 ) 3 3 , 3 3 , 3 6
   3 3  I F ( I P A R ( L M ) = I P A R ( K Q ) ) 3 6 , 3 4 , 3 6
   3 4  L K = I D I F F ( L , 3 )
      K P = I D I F F ( L , 4 )
      I F ( I P A R ( L M ) - I P A R ( K P ) ) 3 6 , 3 3 , 3 6
   3 5  G ( K L ) = G ( K L ) + E R I ( N B A S I S * ( ( I N + 1 ) / 2 - 1 ) + ( K P + 1 ) / 2 )
   X  I W S P = N B A S I S * ( ( I N + 1 ) / 2 - 1 ) + ( K P + 1 ) / 2
   X  W R I T E ( L P , 4 2 ) I W S P , E R I ( I W S P )
   X  W R I T E ( L P , 4 3 ) K L , G ( K L )
   3 6  C O N T I N U E
3 6 1  C O N T I N U E
R E / I N D  M T D
3 7  C O N T I N U E
X  W R I T E ( I D U M ( 2 5 3 ) , 3 6 ) ( K L , G ( K L ) , K L = 1 , ( M A T ( M A T + 1 ) ) / 2 )
X  3 3  I F C H K O R T ( " ^ G ( " , 1 4 , " ) = " , 1 6 , 1 6 ) )
3 3 1  C A L L  Q U I T ( ' P A S T W O ' , I D U M ( 2 5 0 ) )
SUBROUTINE SECDAT(JUMP)

C....READS AND CHECKS DATA.

C/...SEC/...JN/...TT(72,120),H(120,120),T(120,70),IDUM(652),ANY1,
1ANY2,ANY3,ANY4,GF,ICLE,IDISC,IFILE,FILE,LINK,MTDO1,MTDO2,NBAS,
2NCMP,NDEST,NBSLC,NF,NFULL,NSDND,NBLSNC

TEXT TITLE

1
2
2
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DIMENSION G(7260),ERI(600),IDET(120,32),IDIFF(3000,7),TITLE(15),
1(6)

EQUIVALENCE (TT,G,TITLE),(TT(G,94),ERI,P),(TT(49,105),IDET),
1(H1,23),IDIFF)

EQUIVALENCE (IDUM(520),1),(IDUM(521),J),(IDUM(522),MCX),
1(IDUM(523),K),(IDUM(334),L),(IDUM(G43),ICH),(IDUM(G49),LP),
1(IDUM(656),LTD)

CALL ENTR('SECDAT',IDUM(651))

GO TO (1,12),JUMP

C....READ DATA FOR MATRIX ELEMENTS BETWEEN DETORS.

1 READ(J,9) TITLE,MTDO1,MTDO2,NBASIS,NDEST,NBSLC,NFULL

2 NCMP,NBSLC*NBAS

2 CALL CUTBRK(LP)

WRITE(LP,3) TITLE,NDET,NELEC,NBAS15,NFULL,MTDO1,MTDO2

WRITE(LP,77) TITLE

3 FORMAT('F')

77 FORMAT('GENERAL CONFIGURATION INTERACTION PROGRAM',
1'0','3X','CONSTRUCTION AND SOLUTION OF THE SECULAR EQUATION','0','
256X,'QUANTUM MOLECULAR PHYSICS GROUP','0','48X,
3'UNIVERSITY OF LEICESTER','0','
486X,'LEICESTER, ENGLAND, LSI THM.],'0','15AS/8','3X','PRIVATE
5CONSTRUCTED FROM ',213,'ELECTRON ENERGIES','0','14K,BASED CONSTR
6GUCED FROM ',13,'SPATIAL CRISTALS WITH FIRST ',12,'SPIN-CRISTALS
7FROZEN','0','40X,'PRIVATE WORKFILE IS DEVICE NUMBER','17/0','5X,'H
8CASTER RESULTS FILE IS DEVICE NUMBER','14)

IF(NFULL=30) 4,4,21

IF(NBSLC=32) 5,5,22

IF(NDEST=120) 6,6,23

IF(NFULL=3) 7,7,24

10 DO 71 I=1,NDEST

11 DO 71 J=1,NBSLC

12 CLEAR IDST(I,J)

71 CONTINUE

READ(JCR,13) ICRO
IF(NCONF) 72,74,72

72 READ MTD
READ(MTD) ((IDET(I,J),J=1,NELEC),I=1,NDET)
WRITE(IP,73)

73 FORMAT("0",3X,"**** DETORS SPECIFIED IN A PREVIOUS RUN****"/0")
GO TO 201

74 WRITE(IP,8)
READ(1CR,11) F
3 FORMAT("1"/0",48X,"SPECIFICATION OF DETORS"/0 NUMBERS",55X,"DE
1TOR")
DO 10 I=1,NDET
READ(1CR,9) (IDET(I,J),J=1,NELEC)
WRITE(LP,F) I,(IDET(I,J),J=1,NELEC)
9 FORMAT(1X,32I2)
10 CONTINUE
11 FORMAT(3A3)
WRITE(MTD) ((IDET(I,J),J=1,NELEC),I=1,NDET)
GO TO 201

C..... READ PROJECTION MATRIX FOR WAVE FUNCTION.
12 READ(1CR,13) NCONF,NONO
READ(1CR,13) IFILE.
IF(IFILE) 121,130,121
121 READ(MTD) ((T(I,J),J=1,NCONF),I=1,NDET)
WRITE(LP,122)
122 FORMAT("0",33X,"**** PROJECTION MATRIX DEFINED IN A PREVIOUS RUN *
**"/0")
READ MTD
GO TO 201

13 FORMAT(2I5)
130 CLEAR T
IF(NCONF=73) 131,131,25
131 READ(1CR,14) (I,J,T(I,J),K=1,NCONF)
14 FORMAT(2I5,F10.2)
DO 143 J=1,NCONF
CLEAR ANY2
DO 141 I=1,NDET
ANY2=ANY2+T(I,J)*T(I,J)
141 CONTINUE
ANY2=1.0/SQRT(ANY2)
DO 142 I=1,NDET
T(I,J)=T(I,J)*ANY2
142 CONTINUE
143 CONTINUE
144 CONTINUE

C......CHECK ORTHONORMALITY OF CO-DETEORS.
CLEAR IFILE
NCNO=NCONF-1
DO 145 I=1,NCNO
J=I+1
DC 147 K=J,NCONF
CLEAR ANY2
DO 144 I=1,NDET
ANY2=ANY2+T(L,I)*T(L,K)
144 CONTINUE
145 CONTINUE
IF(ABS(ANY2)<1.0D-16) 147,147,145
IFILE=1
147 CONTINUE
143 CONTINUE
IP(IFILE,.3I0) G3 TO 149
CALL EXIT
149 WRITE(MTD) ((T(I,J),J=1,NCONF),I=1,NDET)
ENDFILE MTD
REWIND MTD
WRITE(IP,15) NCONF
15 FORMAT('1'/'0',34X,12, 'CO-DELTORS OF CORRECT SYMMETRY AND SPIN ARE 1 FORMED')
DO 20 K=1,NCONF
WRITE(LP,16) K
16 FORMAT('0',45X, 'CO-DELTOR(,I4,') =')
DO 19 L=1,NDET
IF(T(L,K)) 17,19,17
17 WRITE(LP,18) T(L,K),L
18 WRITE("",45X, 1PE17.10,"*DELTOR(',S-,I4,')")
19 CONTINUE
20 CONTINUE
201 CALL QUIT("SECDAT",IDUM(651))
RETURN
21 CALL ERROR("ERROR 1")
22 CALL ERROR("ERROR 2")
23 CALL ERROR("ERROR 3")
24 CALL ERROR("ERROR 4")
25 CALL ERROR("ERROR 5")
STOP
END

*Fortran Lib

SUBROUTINE SECSOL
C ....FORMS H-MATRIX AND SOLVES SECULAR EQUATION FOR THIS CASE.
COMMON /SECQNG/ TT(73,120),H(120,120),T(120,78),IDUM(652),ANY1,
1 ANY2,ANY3,ANY4,GF,ICOL,IDISC,IFILE,JFILE,LINK,MTD01,MTD02,NBASIS,
2 NCONF,NBASIS,NELEC,NFULL,NSQRD,NXBLK
DIMENSION G(7280),V(120,78),HM(78,78),EV(78,78)
EQUIVALENCE (TT,W,G),(H,HM),(T,EV)
EQUIVALENCE (IDUM(525),L),(IDUM(526),LK),(IDUM(527),IKL) ,  (IDUM(528),
1,NM1) ,(IDUM(530),AMIN) ,  (IDUM(531),MIN)
X 2,(IDUM(649),LP)
CALL ENTR("SECSOL",IDUM(651))
C ....SET UP H-MATRIX.
DO 1 L=1,NDET
LK=(L+(L-1))/2
DO 1 K=1,L
KL=LK+K
H(L,K),H(K,L)=G(KL)
1 CONTINUE
X WRITE(LP,11)
X CALL WRITMX(H,120,120,NDET,NCONF,LP)
X SECDAT(2)
X WRITE(LP,12)
X CALL WRITMX(T,120,78,NDET,NCONF,LP)
X CALL MXMUL(T,H,V,NCONF,NCONF,120,120,120)
DO 2 L=1,NDET
DO 2 K=1,NCONF
H(L,K)=V(L,K)
2 CONTINUE
X WRITE(LP,13)
X CALL WRITMX(H,120,120,NCONF,LP)
X CALL TRANS(T,TT,NCONF,120,78)
X WRITE(LP,14)
X CALL WRITMX(TT,78,120,NCONF,NDT,LP)
DO 3 L=1,NDET
DO 3 K=1,NCONF
T(L,K)=H(L,K)
3 CONTINUE
CALL REmult(TT,T,NCONF,NCONF,78,120,78)
C......ENERGIES ARE THE EIGENVALUES OF HM.
CALL EA03A(HM,EV,NCONF,78,AMIN)
C......ADD NUCLEAR REPULSION ENERGY TO EIGENVALUES IF SYSTEM IS NOT
C......SINGLE CENTRE.
CALL ADDNRE(HM,NCONF,IDUM(648),LP)
C......OUTPUT SOLUTION OF SECULAR EQUATION.
WRITE(LP,3)
3 FORMAT("1/0",46X,"SOLUTION OF SECULAR EQUATION/"")
DO 9 I=1,NCONF,5
J=I+4
IF(J-NCONF) 6,6,5
5 J=NCONF
WRITE(LP,7) I,J,(HM(K,K),K=I,J)
7 FORMAT("0",46X,"ENERGIES OF STATES",13," TO ",13/0",1P5E24.10)
WRITE(LP,8) I,J
8 FORMAT("0",43X,"EIGENVECTORS FOR STATES",13," TO ",13/"")
9 CONTINUE
X 91 FORMAT("0",1P5E24.10)
X 10 FORMAT("0",38X,"MATRIX ELEMENTS OF SECULAR EQUATION H-MATRIX")
X 11 FORMAT("0",42X,"MATRIX ELEMENTS BETWEEN DETERMINANTS")
X 12 FORMAT("0",44X,"SPACE-SPIN TRANSFORMATION MATRIX")
X 13 FORMAT("0",45X,"PARTIALLY TRANSFORMED H-MATRIX")
X 14 FORMAT("0",37X,"TRANSPOSE OF SPACE-SPIN TRANSFORMATION MATRIX")
X 15 FORMAT("0",37X,"EIGENVALUES OF HM")
CALL QUIT("SECQUAL",IDUM(651))
RETURN
END

*FORTRAN LIB
SUBROUTINE TDFILE
C......CONTROLS ALL TRANSFERS FROM CORE TO PERIPHERALS AND VICE VERSA.
COMMON /SECQKV/ AA(33767),ICR,LP,MTD,NO,AHY,AHY1,AHY2,AHY3,AHY4,
1GF,ICOL,IDISC,IFILE,JFILE,IFILE,LINK,MTDO1,MTDO2,NOBASIS,NCONF,NDET,NBSQ
2,NF,HQSQD,NXBLOC
DIMENSION HM(73,73),EV(73,73),GA(60,60),A(60,60),ERI(900)
1KT(153,4),IKT(153),KD(10,4),LD(10)
EQUIVALENCE (AA(7261),ERI),(AA(9361),HM,A),(AA(15443),GA),(AA(2376
11),EV)
TEXT TN(153,4),DN(10,4)
TEXT V<4/" NEXT NEW RECORD ",/CALL ENTRY("TDFILE","NO")
READ(ICR,2) IFIL3,JFILE
WRITE(LP,44) IFILE,JFILE
GO TO 1,13,25,32,IFILE
C......A DISC FILE IS TO BE CREATED.
1 READ(ICR,2) IENTRY,NXBLOC
2 FORMAT(1G15)
3 Rwind MTD01
4 Rwind MTD02
5 IF(NXBLOC) 2001,204,2001
C......COPY TRANSFORMED INTEGRALS INTO DISC AND MASTER RESULTS FILES.
READ(ICR,2) INTRA,IGO,NBLOC
CALL SEARCH(INTRA,NBLOC,0)
LD(1),LT(1),I,MENTRY=1
LD(2),LT(2),J,NENTRY=2

C......MASTER RESULTS FILE TABLE CONTAINS ENTRIES.
READ(IDISC) MENTRY,IENTRY,((TN(K,L),L=1,4),(KT(K,L),L=1,4),LT(K),
I=1,MENTRY)
REWIND IDISC
I=MENTRY
J=I+1
LD(1)=LT(I)
LD(2),LT(J)=LT(I)+1
IF(NXBLDC-ICR(I,1)) 2003,2003,2004

NXBLDC=ICT(I,1)+1
CALL SEARCH(MTD02,NXBLDC,0)
KT(I,1)=NXBLDC
KD(1,1),ICT(1,4),IE(1,4)=1
KT(J,3),KD(1,3)=NSQRD
KT(J,4),KD(2,4)=5
CLEAR KD(1,2),KD(1,3),KD(2,3),KT(J,3)
READ(ICR,26) (DN(1,K),K=1,4)
CONTINUE
I=NSQRD+1

CONTINUE
MENTRY=MENTRY+1
CALL TTPOSN(MTD01,KD(2,1),KD(2,2),MTD02,KT(MENTRY,1),KT(MENTRY,2))
GO TO 17

C......MASTER CONTENTS TABLE PRESENT.
READ (IDISC) MENTRY,IDSNTRY,((TN(I,J),J=1,4),(KT(I,J),J=1,4),LT(I),
I=1,MENTRY)
REWIND IDISC
IF(MENTRY-IENTRY) 3,5,5
WRITE(LP,4) IENTRY,MENTRY
WRITE(LP,47) ((TN(I,J),J=1,4),(KT(I,J),J=1,4),LT(I),I=1,MENTRY)
CALL EXIT

READ(ICR,2) (LD(I),I=1,IENTRY)

C......CHECK ENTRIES IN-ASCENDING ORDER.
DO I=2,IENTRY
IF(LD(I)-LD(I-1)) 6,6,8
WRITE(LP,7)
FORMAT(0,38X,"WHY ASK FOR",I4," ENTRIES WHEN YOU ONLY GOT",I3)
WRITE(LP,47) ((TN(I,J),J=1,4),(KT(I,J),J=1,4),LT(I),I=1,MENTRY)
CALL EXIT

WRITE(LP,7)
FORMAT(0,37X,"DISC TABLE ENTRIES MUST BE IN ASCENDING ORDER")
CALL EXIT

CONTINUE
DO I=2,IENTRY
DO J=1,4
DN(I,J)=TN(LD(I),J)
KD(J,3)=KT(LD(I),3)
KD(J,4)=ICT(LD(I),4)
CALL SEARCH(MTD02,KT(LD(I),1),KT(LD(I),2))
GO TO (10,12,13,14,15),KD(1,4)
C... INTEGRALS.
10  \text{I=KD(I,3)+1}

\text{DO 11 K=1,L}
\text{READ (MTD02) (ERI(M),M=1,\text{KD(I,3)})}
\text{WRITE(MTD01) (ERI(M),M=1,\text{KD(I,3)})}

11  \text{CONTINUE}
\text{GO TO 15}

C... G-VECTOR (MATRICES ELEMENTS BETWEEN DETERMINANTS).
12  \text{READ (MTD02) (AA(K),K=1,\text{KD(I,3)})}
\text{WRITE(MTD01) (AA(K),K=1,\text{KD(I,3)})}
\text{GO TO 15}

C... ENERGIES AND EIGENVECTORS.
13  \text{READ (MTD02) (HM(K,K),(EV(L,K),L=1,\text{KD(I,3)}),K=1,\text{KD(I,3)})}
\text{WRITE(MTD01) (HM(K,K),(EV(L,K),L=1,\text{KD(I,3)}),K=1,\text{KD(I,3)})}
\text{GO TO 15}

C... FIRST ORDER DENSITY MATRIX.
14  \text{READ (MTD02) (GA(K,L),L=1,\text{KD(I,3)}),K=1,\text{KD(I,3)})}
\text{WRITE(MTD01) (GA(K,L),L=1,\text{KD(I,3)}),K=1,\text{KD(I,3)})}

15  \text{CALL TPO3N(MTD01,\text{KD(I+1,1)},\text{KD(I+1,2)})}
\text{CONTINUE}
\text{KD(1,1)=1}
\text{CLEAR KD(1,2)}
\text{NENTRY=IENTRY}

17  \text{WRITE(IDISC) MENTRY,NENTRY,((TN(I,J),J=1,4),(KT(I,J),J=1,4),LT(I),NENTRY),
\text{((DN(I,J),J=1,4),(KD(I,J),J=1,4),LD(I),I=1,\text{NENTRY})}
\text{REWIND IDISC}
\text{REWIND MTD01}
\text{REWIND MTD02}
\text{CLEAR JUMP}
\text{GO TO 45}

C... DATA TO BE READ INTO CORE FROM DISK.
18  \text{READ (IDISC) MENTRY,NENTRY,((TN(I,J),J=1,4),(KT(I,J),J=1,4),LT(I),NENTRY),
\text{((DN(I,J),J=1,4),(KD(I,J),J=1,4),LD(I),I=1,\text{NENTRY})}
\text{REWIND IDISC}
\text{JUMP=1}
\text{GO TO 45}

C... READ SUBSCRIPT VALUE FOR ENTRY TO DISK CONTENTS TABLE.
19  \text{READ(ICR,2) IENTRY}
\text{WRITE(LP,20)}
\text{\text{FORMAT(0,43X,THE FOLLOWING IS REQUIRED IN CORE/)}}
\text{WRITE(LP,47) (DN(ENTRY,J),J=1,4),(KD(ENTRY,J),J=1,4),LD(ENTRY)}
\text{CALL SEARCH(MTD01,\text{KD(ENTRY,L)},\text{KD(ENTRY,2)})}
\text{GO TO (21,23,24,21,21),\text{KD(ENTRY,4)}}

C... IMPROPER REQUEST.
21  \text{WRITE(LP,22)}
\text{\text{\text{FORMAT(0,33X,IMPROPER REQUEST - CONTINUATION NOT POSSIBLE/)}}}
\text{CALL EXIT}

C... G-VECTOR.
23  \text{READ(MTD01) (AA(I),I=1,\text{KD(ENTRY,3)})}
\text{GO TO 49}

C... ENERGIES AND EIGENVECTORS.
24  \text{READ(MTD01) (HM(K,K),(EV(L,K),L=1,\text{KD(ENTRY,3)}),K=1,KT(ENTRY,3))}
\text{GO TO 49}

C... RESULTS TO BE ADDED TO DISK AND DISK CONTENTS TABLE UPDATED.
25  \text{READ (IDISC) MENTRY,NENTRY,((TN(I,J),J=1,4),(KT(I,J),J=1,4),LT(I),NENTRY),
\text{((DN(I,J),J=1,4),(KD(I,J),J=1,4),LD(I),I=1,\text{NENTRY})}
\text{REWIND IDISC}
\text{READ(ICR,26) (DN(ENTRY,J),J=1,4)}
\text{GO TO 49}

26  \text{FORMAT(14A3)}
\text{IENTRY=\text{ENTRY}-1}
CALL SEARCH(MTD01,KD(IENTRY,1),KD(IENTRY,2))
IF(KD(IENTRY,4)=1) 263,261,263
261 DO 262 I=1,KD(IENTRY,3)
READ(MTD01) ANY3
262 CONTINUE
263 READ(MTD01) ANY3
CALL TPPOSN(MTD01,KD(NENTRY,1),KD(NENTRY,2))
LD(NENTRY)=MAX0(LD(NENTRY),LT(MENTRY))
IF(JFILE-3) 27,28,29
C.....G-VECTOR
27 KD(NENTRY,3)=(NDET*(NDET+1))/2
KD(NENTRY,4)=2
WRITE(MTD01) (AA(I),I=1,KD(NENTRY,3))
GO TO 30
C.....ENERGIES AND EIGENVECTORS.
28 (NENTRY, 3)=NC0NF
KD(NENTRY,4)=3
WRITE(MTD01) (IM(K,K),EV(L,K),L=1,NC0NF),K=1,NC0NF)
GO TO 30
C.....FIRST ORDER DENSITY MATRIX.
29 (NENTRY, 3)=NBASIS
KD(NENTRY,4)=4
WRITE(MTD01) (GA(K,L),L=1,NBASIS),K=1,NBASIS)
30 NENTRY=NENTRY+1
CALL TPPOSN(MTD01,KD(NENTRY,1),KD(NENTRY,2))
CLEAR KD(NENTRY,3)
KD(NENTRY,4)=5
LD(NENTRY)=LD(NENTRY-1)+1
DO 31 I=1,4
DN(NENTRY,I)=V/(I)
31 CONTINUE
WRITE(IDISC) MENTRY,NENTRY,((TN(I,J),J=1,4),(KT(I,J),J=1,4),LT(I),
11=1,MENTRY),((DN(I,J),J=1,4),(KD(I,J),J=1,4),LD(I),I=1,MENTRY)
REWIND IDISC
CLEAR JUMP
GO TO 451
C.....UPDATE MASTER FILE AND CONTENTS TABLE.
32 READ (IDISC) MENTRY,NENTRY,((TN(I,J),J=1,4),(KT(I,J),J=1,4),LT(I),
11=1,MENTRY),((DN(I,J),J=1,4),(KD(I,J),J=1,4),LD(I),I=1,MENTRY)
REWIND IDISC
IENTRY=MENTRY
M=MENTRY-1
CALL SEARCH(MTD02,KT(M,1),KT(M,2))
IF(KT(M,4)=1) 323,321,323
321 DO 322 I=1,KT(M,3)
READ(MTD02) ANY3
322 CONTINUE
323 READ(MTD02) ANY3
CALL TPPOSN(MTD02,KT(IENTRY,1),KT(IENTRY,2))
DO 42 I=1,IENTRY
DISPLAY(LP,5)/I/
DO 33 J=1,1
IF(LD(I)-LT(J)) 33,42,33
33 CONTINUE
DISPLAY(LP,5) I
DO 34 K=1,4
TN(IENTRY,K)=DN(I,K)
34 CONTINUE
LT(IENTRY)=LD(I)
KT(IENTRY,3)=KD(I,3)
**Fortran Code**

```fortran
KT(ENTRY,4)=KD(I,4)
CALL SEARCH(MTD01,KD(I,1),KD(I,2))
GO TO (35,37,33,39,43),KD(I,4)

C....TRANSFORMED INTEGRALS.
35 IGO=NSQRD+1
DO 36 K=1,IGO
READ (MTDO1) (ERI(I),I=1,NSQRD)
WRITE(MTD02) (ERI(I),I=1,NSQRD)
36 CONTINUE
GO TO 40

C....G-VECTOR.
37 READ (MTDO1) (AA(K),K=1,KD(I,3))
WRITE(MTD02) (AA(K),K=1,KD(I,3))
GO TO 40

C....ENERGIES AND EIGENVECTORS.
38 READ (MTDO1) (HM(K,K),EV(L,K),K=1,KD(I,3)),(HM(K,K),EV(L,K),K=1,KD(I,3))
WRITE(MTD02) (HM(K,K),EV(L,K),L=1,NSQRD),K=1,KD(I,3))
GO TO 40

C....FIRST ORDER DENSITY MATRIX.
39 READ (MTDO1) ((GA(K,L),L=1,KD(I,3)),K=1,KD(I,3))
WRITE(MTD02) ((GA(K,L),L=1,KD(I,3)),K=1,KD(I,3))
GO TO 40

40 ENTRY=ENTRY+1
CALL TPPOSN(MTD02,ICT(ENTRY,1),ICT(ENTRY,2))
42 CONTINUE

43 ENTRY=ENTRY
WRITE(IDISC) ENTRY,ENTRY,((T1(I,J),J=1,4),(KT(I,J),J=1,4),LT(I),
I=1,ENTRY),((D1(I,J),J=1,4),(KD(I,J),J=1,4),LD(I),I=1,ENTRY)
REWND IDISC
CLEAR JUMP

C....PRINT CONTENTS TABLES.
44 FORMAT("
","12","FILE","PARA","M","VALUES",IFILE = ",I2," JFILE = ",I2)
45 WRITE(LP,47) ((T1(I,J),J=1,4),(KT(I,J),J=1,4),LT(I),I=1,ENTRY)
46 WRITE(LP,47) ((D1(I,J),J=1,4),(KD(I,J),J=1,4),LD(I),I=1,ENTRY)
1," RECORD TYPE =",I2," SEQUENCE NUMBER =",I3)
48 FORMAT("B",40X,"CONTENTS OF PRIVATE FILE FROM BLOCK",15")
IF(JUMP) 50,40,19
49 CALL QUIT("TDFILE",NO)
RETURN
50 STOP
END

*Fortran Lib

SUBROUTINE TRANS(A,AT,N1,N2,M1,M2)
C....TRANSPOSE OF MATRIX A STORED IN MATRIX AT.
DIMENSION A(M1,M2),AT(M2,M1)
DO 1 I=1,N1
DO 1 J=1,N2
AT(J,I)=A(I,J)
1 CONTINUE
RETURN
END
```
STATEMENT NUMBER  | FORTRAN STATEMENT                                                                 |
------------------|----------------------------------------------------------------------------------|
<pre><code>              | SECSP.L TEST DATA = TRIPLET P STATE OF ATOMIC OXYGEN (SC HAEFE F AND HARRIS'S EXPONENTS) |
              | 1 5 1 8, 1UX, 8 I3)                                                                 |
              | 1 2 3 4 5 8 9 10                                                                   |
              | 1 2 3 4 5 7 9 10                                                                   |
              | 1 5 1 2 1 0 0                                                                      |
              | 1 5 0 0                                                                         |
              | OXYGEN ATOM INTEGRALS                                                             |
              | 2 1                                                                           |
              | 5 1                                                                           |
              | 3 2                                                                           |
              | OXYGEN ATOM CI P DEPOR. HATREX                                                   |
              | 2 1                                                                           |
              | 1                                                                           |
              | 2                                                                           |
</code></pre>
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<th>CONF.</th>
<th>FORTRAN STATEMENT</th>
</tr>
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<td>1 2 3 4 5 6 7 8 9 10</td>
<td>1 2 3 4 5 6 7 8 9 10</td>
<td>OXYGEN ATOM CI 2 P SOLUTION</td>
</tr>
<tr>
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<td></td>
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<tr>
<td></td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>OXYGEN ATOM CI 3 P DENSITY MATRIX</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
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</tbody>
</table>
GENERAL CONFIGURATION INTERACTION PROGRAM
CONSTRUCTION AND SOLUTION OF THE SECULAR EQUATION
A. D. TAIT
QUANTUM MOLECULAR PHYSICS GROUP,
DEPARTMENT OF PHYSICS,
UNIVERSITY OF LEICESTER,
LEICESTER, ENGLAND, LE1 7RH.

SECSOL TEST DATA - TRIPLET P STATE OF ATOMIC OXYGEN (SCHAEFER AND HARRIS'S EXPONENTS).
WAVE FUNCTION CONSTRUCTED FROM 2 8-ELECTRON DETORS
DETORS CONSTRUCTED FROM 5 SPATIAL ORBITALS WITH FIRST 2 SPIN-ORBITALS FROZEN
PRIVATE WORKFILE IS DEVICE-NUMBER 1
MASTER RESULTS FILE IS DEVICE NUMBER 2
NUMBER

1

2

NUMBER OF INSTRUCTIONS USED ON EXIT FROM SUBPROGRAM TDFILE =

NUMBER OF INSTRUCTIONS USED ON ENTRY TO SUBPROGRAM TDFILE =

TDFILE PARAMETER VALUE

CONTENTS OF MASTER

OXYGEN ATOM INTEGRALS.

*** NEXT NEW RECORD ***

FROM BLOCK 100 WORD 0, L

FROM BLOCK 101 WORD 164, L

CONTENTS OF PRIVATE

OXYGEN ATOM INTEGRALS.

*** NEXT NEW RECORD ***

FROM BLOCK 1 WORD 0, L

FROM BLOCK 2 WORD 164, L

NUMBER OF INSTRUCTIONS USED ON EXIT FROM SUBPROGRAM TDFILE =

NUMBER OF INSTRUCTIONS USED ON ENTRY TO SUBPROGRAM PASONE =

NUMBER OF INSTRUCTIONS USED ON EXIT FROM SUBPROGRAM PASONE =

NUMBER OF INSTRUCTIONS USED ON ENTRY TO SUBPROGRAM MAXCON =

NUMBER OF NON-ZERO OFF-DIAGONAL M A

NUMBER OF INSTRUCTIONS USED ON EXIT FROM SUBPROGRAM MAXCON =

NUMBER OF INSTRUCTIONS USED ON ENTRY TO SUBPROGRAM PASTWO =

NUMBER OF INSTRUCTIONS USED ON EXIT FROM SUBPROGRAM PASTWO =

NUMBER OF INSTRUCTIONS USED ON ENTRY TO SUBPROGRAM HASS =

NUMBER OF INSTRUCTIONS USED ON EXIT FROM SUBPROGRAM HASS =

NUMBER OF INSTRUCTIONS USED ON ENTRY TO SUBPROGRAM TDFILE =

TDFILE PARAMETER VALUE

CONTENTS OF PRIVATE

OXYGEN ATOM INTEGRALS.

FROM BLOCK 1 WORD 0, L

OXYGEN ATOM CI P DETOR MATRIX.

FROM BLOCK 2 WORD 164, L

*** NEXT NEW RECORD ***

FROM BLOCK 2 WORD 165, L

NUMBER OF INSTRUCTIONS USED ON EXIT FROM SUBPROGRAM TDFILE =

NUMBER OF INSTRUCTIONS USED ON ENTRY TO SUBPROGRAM SESSOL =

NUMBER OF INSTRUCTIONS USED ON ENTRY TO SUBPROGRAM SE3DAT =
\[ n \text{ OF DETORS} \]

\[
\begin{array}{ccc}
  & 25 & 0 \\
 0 & 10 & 10 \\
 4287 & 4289 & \\
\end{array}
\]

\[ S, IFILE = 1 \text{ JFILE} = 1 \]

\[ FILE FROM BLOCK 100 \]

\[
\begin{array}{ccc}
  \text{OOP PARAMETER} & 25. & 0. \\
  \text{RECORD TYPE} & 1. & 5. \\
  \text{SEQUENCE NUMBER} & 1 & 2 \\
\end{array}
\]

\[ FILE FROM BLOCK 1 \]

\[
\begin{array}{ccc}
  \text{OOP PARAMETER} & 25. & 0. \\
  \text{RECORD TYPE} & 1. & 5. \\
  \text{SEQUENCE NUMBER} & 1 & 2 \\
\end{array}
\]

\[ TRIIX ELEMENTS BETWEEN DETORS = 1 \]

\[
\begin{array}{c}
  4335 \\
  4340 \\
  4342 \\
  4401 \\
  4406 \\
\end{array}
\]

\[ S, IFILE = 3 \text{ JFILE} = 2 \]

\[ FILE FROM BLOCK 1 \]

\[
\begin{array}{ccc}
  \text{OOP PARAMETER} & 25. & 3. \\
  \text{RECORD TYPE} & 1. & 2. \\
  \text{SEQUENCE NUMBER} & 1 & 2 \\
\end{array}
\]

\[
\begin{array}{ccc}
  \text{OOP PARAMETER} & 0. & 0. \\
  \text{RECORD TYPE} & 5. & 5. \\
  \text{SEQUENCE NUMBER} & 2 & 3 \\
\end{array}
\]

\[
\begin{array}{c}
  4425 \\
  4428 \\
  4429 \\
\end{array}
\]
1 CO-DETOURS OF CORRECT SYMMETRY AND SPIN ARE FORMED

\[
\text{CO-DETOUR}(1) = \\
+7.0710673119E+01\times\text{DETOUR}(1) \\
+7.0710673119E+01\times\text{DETOUR}(2)
\]

NUMBER OF INSTRUCTIONS USED ON EXIT FROM SUBPROGRAM SE3DAT = 4447
SOLUTION OF S

ENERGIES OF S

\[-7.4540361952E+01\]

EIGENVECTORS FOR

\[1.0000000000E+00\]

NUMBER OF INSTRUCTIONS USED ON EXIT FROM SUBPROGRAM SESSOL

NUMBER OF INSTRUCTIONS USED ON ENTRY TO SUBPROGRAM TDFILE

TDFILE PARAMETER VALU

CONTENTS OF PRIVATE

OXYGEN ATOM INTEGRALS.
OXYGEN ATOM CI P DETOR MATRIX.
OXYGEN ATOM CI 3 P SOLUTION.

FROM BLOCK 1 WORD 0.
FROM BLOCK 2 WORD 164.
FROM BLOCK 2 WORD 165.

*** NEXT NEW RECORD ***
FROM BLOCK 2 WORD 171.

NUMBER OF INSTRUCTIONS USED ON EXIT FROM SUBPROGRAM TDFILE
NUMBER OF INSTRUCTIONS USED ON ENTRY TO SUBPROGRAM NATORB
ECJLAR EQUATION

STATE 1 TO 1

STATE 1 TO 1

= 4455
= 4457

ES, IFILE = 3 JFILE = 3

FILE FROM BLOCK 1

LOOP PARAMETER = 25, RECORD TYPE = 1, SEQUENCE NUMBER = 1
LOOP PARAMETER = 3, RECORD TYPE = 2, SEQUENCE NUMBER = 2
LOOP PARAMETER = 1, RECORD TYPE = 3, SEQUENCE NUMBER = 3
LOOP PARAMETER = 0, RECORD TYPE = 5, SEQUENCE NUMBER = 4

= 4473
= 4475
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<th>Natural Spin Orbital Coefficients</th>
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<td>( C(1) = 7.0710678116 \times 10^{-9} )</td>
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<tr>
<td>( C(2) = 7.0710678119 )</td>
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<table>
<thead>
<tr>
<th>Number of Instructions</th>
<th>Used on Entry to Subprogram From</th>
<th>Used on Exit from Subprogram From</th>
<th>Used on Entry to Subprogram TDIFI</th>
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<tr>
<td><strong>TDFILE Parameter V</strong></td>
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<td><strong>Contents of PRIV</strong></td>
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<td>Oxygen Atom Integrals.</td>
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</tr>
<tr>
<td>FROM BLOCK 1 WORD</td>
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<tr>
<td>Oxygen Atom CI P Detor Matrix.</td>
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<tr>
<td>FROM BLOCK 1 WORD 16</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Oxygen Atom CI 3P Solution.</td>
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<td></td>
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</tr>
<tr>
<td>FROM BLOCK 2 WORD 16</td>
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<tr>
<td>Oxygen Atom CI 3P Density Matrix</td>
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<tr>
<td>FROM BLOCK 2 WORD 17</td>
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<td></td>
<td></td>
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<tr>
<td>**** Next New Record ****</td>
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<td></td>
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</tr>
<tr>
<td>FROM BLOCK 2 WORD 27</td>
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<table>
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<td>1.0000000000E+00</td>
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<tr>
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<tr>
<td>0.0000000000E+00</td>
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<tr>
<td>0.0000000000E+00</td>
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<tr>
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<td>5.0000000000E-01</td>
</tr>
<tr>
<td>5.0000000000E-01</td>
</tr>
<tr>
<td><strong>Transformation</strong></td>
</tr>
<tr>
<td>0.0000000000E+00</td>
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<tr>
<td>0.0000000000E+00</td>
</tr>
<tr>
<td>0.0000000000E+00</td>
</tr>
<tr>
<td>0.0000000000E+00</td>
</tr>
<tr>
<td><strong>Sum of Occupation Number of El</strong></td>
</tr>
<tr>
<td><strong>Number of Instructions Used on Exit from Subprogram NATRO</strong></td>
</tr>
</tbody>
</table>
TAL ANALYSIS OF LEVEL 1
INDIVIDUAL DETERMINANTS

FILE = 3 JFILE = 4

VALUES:

ATE FILE FROM BLOCK

0. LOOP PARAMETER = 25. RECORD TYPE = 1. SEQUENCE NUMBER = 1
4. LOOP PARAMETER = 3. RECORD TYPE = 2. SEQUENCE NUMBER = 2
5. LOOP PARAMETER = 1. RECORD TYPE = 3. SEQUENCE NUMBER = 3
1. LOOP PARAMETER = 10. RECORD TYPE = 4. SEQUENCE NUMBER = 4
3. LOOP PARAMETER = 0. RECORD TYPE = 5. SEQUENCE NUMBER = 5

AL SPIN ORBITAL ANALYSIS

RS OF ORBITALS 1 TO 5

MATRIX COLUMNS 1 TO 5

RS OF ORBITALS 6 TO 10

MATRIX COLUMNS 6 TO 10

NUMBERS = 8.0000000001E+00

ECTROWS = 8

RB = 4552
OXYGEN ATOM INTEGRALS. FROM BLOCK 100 WORD
OXYGEN ATOM CI 3 P DETOR MATRIX. FROM BLOCK 101 WORD 16
OXYGEN ATOM CI 3 P SOLUTION. FROM BLOCK 101 WORD 16
OXYGEN ATOM CI 3P DENSITY MATRIX FROM BLOCK 101 WORD 17
**** NEXT NEW RECORD **** FROM BLOCK 101 WORD 27

OXYGEN ATOM INTEGRALS. FROM BLOCK 1 WORD
OXYGEN ATOM CI 3 P DETOR MATRIX. FROM BLOCK 2 WORD 16
OXYGEN ATOM CI 3 P SOLUTION. FROM BLOCK 2 WORD 16
OXYGEN ATOM CI 3P DENSITY MATRIX FROM BLOCK 2 WORD 17
**** NEXT NEW RECORD **** FROM BLOCK 2 WORD 27

NUMBER OF INSTRUCTIONS USED ON ENTRY TO SUBPROGRAM TDFI

**** JOB COMPLETE - TIM
VALUES IF FILE = 4 JFILE = 0

ER FILE FROM BLOCK 100

0. LOOP PARAMETER = 25. RECORD TYPE = 1. SEQUENCE NUMBER = 1
4. LOOP PARAMETER = 3. RECORD TYPE = 2. SEQUENCE NUMBER = 2
3. LOOP PARAMETER = 1. RECORD TYPE = 3. SEQUENCE NUMBER = 3
1. LOOP PARAMETER = 10. RECORD TYPE = 4. SEQUENCE NUMBER = 4
3. LOOP PARAMETER = 0. RECORD TYPE = 5. SEQUENCE NUMBER = 5

ATE FILE FROM BLOCK 1

5. LOOP PARAMETER = 25. RECORD TYPE = 1. SEQUENCE NUMBER = 1
4. LOOP PARAMETER = 3. RECORD TYPE = 2. SEQUENCE NUMBER = 2
3. LOOP PARAMETER = 1. RECORD TYPE = 3. SEQUENCE NUMBER = 3
1. LOOP PARAMETER = 10. RECORD TYPE = 4. SEQUENCE NUMBER = 4
3. LOOP PARAMETER = 0. RECORD TYPE = 5. SEQUENCE NUMBER = 5

LE = 4592

E USED = 28.71875 SECONDS ****
APPENDIX VIII

SPECTRGF. A PROGRAM FOR COMPUTING THE
SPECTROSCOPIC CONSTANTS OF DIATOMIC MOLECULES

SPECTRGF is described in chapter 9 and requires only a card reader
(stream 0) for input of data and a lineprinter (also stream 0) for
output. The program is completely self contained. The storage requirements
are standard.

Data specification for SPECTRGF

Card 1  
NC\&NF, NDEG, NR, N\$

FORMAT (4I5)

NC\&NF = number of energy levels of the molecule to
be investigated for the symmetry and spin
defined by Card 4. If NC\&NF = 0 execution
ceases.

NDEG = degree of fitted polynomial

NR = number of values of the bond length to which
polynomial is to be fitted.

N\$ = 0 to suppress diagnostic output.

\$
\$ 0 to obtain diagnostic output, including
residuals

Card 2  
TITLE

FORMAT (9A8/6A8)

TITLE is an array of 15 elements (120 characters)
used to identify the run.

Card 3  
RMASS

FORMAT (1PE20.10)
RMASS = reduced mass of the molecule on the unified mass scale (see Appendix I and reference\(^{(57)}\))

Card 4

ISPIN, LAMBDA, INVERS, REFLEC

F\(\text{ORMAT}\) (2I5, 2A4)

ISPIN = value of total spin eigenvalue for this state
LAMBDA = value of axial angular momentum for this state

\[
\begin{align*}
\text{INVERS} & : \\
\text{Gbbb for gerade states} \\
\text{Ubbb for ungerade states} \\
\text{bbbb for heteronuclear diatomic molecules} \\
\text{+bbbb for } & \Sigma^+ \text{ states} \\
\text{−bbbb for } & \Sigma^- \text{ states} \\
\text{bbbb for all other states} \\
\end{align*}
\]

(Note: b = blank)

Card 6

\((R(I), I = 1, NR)\)

F\(\text{ORMAT}\) (1PE20.10)

\(R(I)\) is the value of the \(I\)-th bond length in bohrs.

\((1 \leq I \leq NR)\) Repeat, as required.

Card 7

\(((E(I,J), J = 1, NR), I = 1, NC\text{}\(\text{NF}\))\)

F\(\text{ORMAT}\) (1PE20.10)

\(E(I,J)\) is the energy at \(R(I)\) of the \(J\)-th energy level. Repeat as required.

As the program is re-entered at Card 1 after each run, it is necessary to terminate execution by setting \(NC\text{\(\text{NF}\)} = 0\).

Restrictions

\[
1 \leq NR \leq 20 \\
1 \leq NDEG \leq NR \\
1 \leq NC\text{\(\text{NF}\)} \leq 5 \\
0 \leq LAMBDA \leq 4
\]
*FORTRAN
C.....MAIN ROUTINE FOR SPECTROSCOPIC CONSTANTS PROGRAM.
C.....READS ALL DATA FOR EACH RUN.
LOGICAL LOGIC
COMMON /SPEC/ ICR,INVERS,ISPIN,LAMBDA,LOGIC,LP,NCONF,NDEG,NR,NO,
1,REFLEC,REMASS,TITLE(15),F(20),P(20),R(20),BE(5),DE(5),D0(5),PC(5),
2MINR(5),RMIN(5),RZ(5),X(20),XX(20,20),A(5,10),YLJ(5,15),E(5,20)
DIMENSION ANGM0M(5)
DATA ANGMOM/GH SIGMA,3H PI,3H DELTA,3H PHI,3H GAMMA
1/
 CLEAR ICR,LP
12 READ(ICR,3) NCONF,NDEG,NR,NO
 IF(NCONF.EQ.0) STOP
 READ(ICR,1) TITLE
 READ(ICR,2) REMASS
 READ(ICR,4) ISPIN,LAMBDA,INVERS,REFLEC
 READ(ICR,2) (R(I),I=1,NR)
 READ(ICR,2) ((E(I,J),J=1,NR),I=1,NCONF)
1 FGRA;AT(9A/CA)
2 FORI11T(1PE20 .10)
3 FGRA;AT(1GI5)
4 FGRA;AT(2I5,2A4)
C.....PRINT DATA
I=2*ISPIN+1
LAMBDA=LAMBDA+1
WRITE(LP,5) TITLE
WRITE(LP,6) REMASS
WRITE(LP,7) NCONF,NR
WRITE(LP,13) NDEG
WRITE(LP,3) I,ANGMOM(LAMBD/0,INVERS,REFLEC,(I,I=1,5)
5 FORMAT(1IH/1IO,4X,3HISPECTROSCOPIC CONSTANTS PROGRAM/1HO,15A8)
6 FORMAT(1H0,35X,1HREDUCED MASS =,1PE17.10,19HAI.IU (UNIFIED SCALE))
7 : ' IAT(1IH,32X,25HNUMBER OF ENERGY LEVELS =,I2,26H, NUMBER OF BOND
1 LENGTHS =,13)
2 FORMAT(1IH,41X,26HTHE SPECTROSCOPIC STATE IS,I2,A6,1X,2A1/1H0,47X,
125HENERGIES AND BOND LENGTHS/1H0,5X,6H (BOHRS),6X,5(9X,1HS,II,9X)
2)
DO 10 I=1,NR
 WRITE(LP,9) R(I),(E(J,I),J=1,NCONF)
9 FORMAT(1HO,F11.19X,1P5E20.10)
10 CONTINUE
13 FORMAT(1HO,44X,29HDEGREE OF FITTED POLYNOMIAL =,I3)
 CALL FINDRE
 CALL DUNHAM
 CALL RFILE
 GO TO 12
END

*FORTRAN
SUBROUTINE DUNHAM
C.....COMPUTES DIATOMIC SPECTROSCOPIC CONSTANTS USING DUNHAM'S ANALYSIS.
C.....VERSION 5.
LOGICAL LOGIC
COMMON /SPEC/ ICR,INVERS,ISPIN,LAMBDA,LOGIC,LP,NCONF,NDEG,NR,NO,
1,REFLEC,REMASS,TITLE(15),F(20),P(20),R(20),BE(5),DE(5),D0(5),PC(5),
2MINR(5),RMIN(5),RZ(5),X(20),XX(20,20),A(5,10),YLJ(5,15),E(5,20)
DIMENSION FL(20),FD(20)
1(P(8),A5),(P(9),A6),(P(10),A7)
DATA EPS/1.0E-10/
C. COMPUTE VALUES OF NORMALIZED INDEPENDENT VARIABLE X AND SET UP XX.
   DO 1 I=1,NR
   X(I)=(2.0*R(I)-BPA)*BMA
   XX(I,1)=1.0
   DO 1 J=2,NTERM
   XX(I,J)=XX(I,J-1)*X(I)
   1 CONTINUE
C. COMPUTE MEAN ENERGY FOR THIS LEVEL.
   SUM=E(ICONF,1)
   DO 2 I=2,NR
   SUM=SUM+E(ICONF,I)
   2 CONTINUE
   SUM=SUM/FLOAT(NR)
   IF(NO.NE.0) WRITE(LP,3) ICONF, SUM
   3 FORMAT(1H0,41X,5HLEVEL,12,14H MEAN ENERGY =,1PE17.10)
C. SUBTRACT MEAN FROM EACH ENERGY AND CONVERT TO CM**(-1).
   DO 4 I=1,NR
   F(I)=(E(ICONF,I)-SUM)*2.1947462E+05
   4 CONTINUE
C. FIT POLYNOMIAL TO F(X).
   CALL DRLIN2(XX,F,P,NR,NTERM,20,20,EPS,LOGIC)
   IF(LOGIC) WRITE(LP,5)
   5 FORMAT(1H0,40X,40HITERATIVE IMPROVEMENT OF SOLUTION FAILED)
C. COMPUTE L2 NORM OF SOLUTION.
   B=0.0
   DO 6 I=1,NR
   D=POLYVA(X(I),P,NDEG)
   IF(NO.NE.0) WRITE(LP,7) X(I), F(I), D, W
   6 CONTINUE
   7 FORMAT(1H0,13X,2HX=,1PE17.10,6H D(X)=,1PE17.10,6H F(X)-D(X)=,1PE17.10)
   WRITE(LP,8) B
   8 FORMAT(1H0,45X,21HL2 NORM OF SOLUTION =,1PE9.2)
C. FIND MINIMUM OF F(X).
   FL(I)=P(I)
   IM2=I-2
   FL(IM2)=IM2*FL(IM1)
   FD(IM2)=IM2*FD(IM1)
   DO 9 I=3,NTERM
   IM1=I-1
   FL(IM1)=IM1*FL(I)
   FD(IM2)=IM2*FD(IM1)
   9 CONTINUE
   DO 10 I=ICONF,NC0NF
   IF(NO.NE.0) WRITE(LP,19) ICONF, D
   10 CONTINUE
   IF(ABS(D)-EPS) 15,11,11
   11 FORMAT(1H0,12,13,13)
   12 R2=R2-D
   GC TO 10
   13 WRITE(LP,14) ICONF, D
C.. Transform Polynomial to Dunham Form.

D=RS+BPA*BMA
CALL POLYX(D,RE,P,FL,NDEG)
B=1.0/FL(3)
DO 161 I=4,NTERM
FL(I)=FL(I)*B
161 CONTINUE

C.. FL Contains Dunham Expansion Coefficients.

FL(1)=FL(1)+SUM*2.1947462E+05
IML=MILN(10,NTERM)
DO 17 I=1,IML
A(ICONF,I)=FL(I)
P(I)=FL(I)
17 CONTINUE

RE=0.5*(RS/BMA+BPA)
RMIN(ICONF)=RE

C.. Compute Spectroscopic Constants and YU.

BE(ICONF)=60.2014/(RIASS*RE*RE)
IF(BE(ICONF).LE.0.0.OR.AO.LE.0.0) GO TO 18
Y/E(ICONF)=2.0*SQRT(A0*BE(ICONF))
DE(ICONF)=4.0*(BE(ICONF)/1VE(ICONF))**2*BE(ICONF)
FC(ICONF)=5.891461E-02*RMASS*V/S(ICONF)**2

C.. Define B, W, and BY for ease of writing formulae.

B=BE(ICONF)
W=W2(ICONF)
BV=(B/W)**2
A1SQ=A1*A1
A2SQ=A2*A2
A3SQ=A3*A3

YU(ICONF, 1)=0.125*B*(3*A2-1.75*A1SQ)
YU(ICONF, 2)=W*(1.0+B*W*(25*A4-16.75*A2SQ-0.5*A1*(35*A3-0.25*A1
1 *(459*A2-144.375*A1SQ)))
YU(ICONF, 3)=0.5*B*(3*(A2-1.25*A1SQ)+0.5*BW*(0.5*A1*(-1365*A5+
1 3667.5*A2-300.25*A1*(3535*A4-15503.25*A2SQ+0.5*A1*
2 (-23365*A3-40.125*A1*(239985*A2-52263.75*A1SQ)))+
3 245*A6-0.5*A2*(335*A4-426.75*A2SQ-271.25*A3SQ))
YU(ICONF, 4)=0.5*W*B7*(10*A4-9.5*A2SQ-A1*(35*A3-0.25*A1*(225*A2-
1 83.125*A1SQ)))
YU(ICONF, 5)=5*W*B*(0.25*A1*(-33*A5+241.5*A2*A3-0.25*A1*(543*A4-
1 1247.25*A2SQ-0.5*A1*(-1053*A3+0.125*A1*(23285*A2-
2 5737.75*A1SQ))))-0.25*A2*(33*A4-13.75*A2SQ-3.5*(
3 2.25*A3SQ-A6))
YU(ICONF, 6)=B*(1.0+B*W*(15*(1+A3)-9*A2+A1*(14-23*A2+10.5*A1*(1+
1 A1))))
YU(ICONF, 7)=W*W*6*(1+A1)*BW*(A1*((235-455*A2+356.25*A3-397.5*A4+
1 +346.25*A2SQ-0.5*A1+(-1147.5-2409.75*A2+2572.5*A3+
2 A1*(1155-356.75*A2-974.53125*A1*(1+A1))))-0.5*A2*
3 (335+75*A3-251.25*A2+190*A3-112.5*A1+175*(1+A5)))
YU(ICONF, 8)=G*B*BW*(5*(1+A3)-3*A2+A1*(10-13*A2-7.5*A1*(1+A1))]
YU(ICONF, 9)=20*W*W*W*(A1*(-21-45*A2+26.25*A3-25.5*A4+51.75*
1 A23)-0.25*A1*(-112.5-236.25*A2+217.5*A3+A1*(141-
2 377.25*A2+113.3675*A1 *(1+A1)))-0.5*A2*(17+45*A3-
3 12.75*A4-14*A3-4.5*A1-7*(1+A5))
YU(ICONF,10)=4*B*W*(1+A1)*BW*(A1*(-125-237.12+102.5*A3+A1*(-A2*
1 165.5+173.25+126*A1*(1+0.5*A1))))-A2*(119-46*A2)+90*
2 \begin{align*}
2 & A_3 - 45 A_4 + 163) \end{align*}

\begin{align*}
2 & Y_U (ICONF, 11) = -12 B_W B_V B* (9.5 - 4 A_2 + 9 A_1 * (1.5 * A_1)) \\
2 & Y_U (ICONF, 12) = -24 B_W B_V B* (A_1 * (125 - 117 A_2 + 47.5 A_3 + A_1 * (123.75 - 103.51 A_2 + 90 A_1 * (1 + 0.5 A_1) - A_2 * (61 - 26 A_2) + 30 A_3 - 15 A_4 + 65) \\
2 & Y_U (ICONF, 13) = 16 B_W B_V B* (3 A_1) \\
2 & Y_U (ICONF, 14) = 12 B_W B_V B* (233 A_1 * (279 - 88 A_2 + A_1 * (139 - 63 A_1)) - 120 A_2 \\
2 & + 30 A_3 / 3) \\
2 & Y_U (ICONF, 15) = -64 B_W B_V B* (13 + 9 A_1 * (1 + 0.25 A_1) - A_2) \\
2 & DO (ICONF) = Y_U (ICONF, 1) - 0.5 * (Y_U (ICONF, 2) + 0.5 * (Y_U (ICONF, 3) + 0.5 * (Y_U (ICONF, 4) + 0.5 * Y_U (ICONF, 5))))
\end{align*}

13 CONTINUE

19 FORMAT (I1, 21X, 9H ITERATION, I4, 19H CURRENT ESTIMATE =, 1PE17.10, 11H INCREMENT =, 1PE17.10)

RETURN

END

**FORTRAN**

SUBROUTINE FINDRE

C..... DETERMINES WHICH LEVELS ARE BOUND.

COMMON /SPEC/ ICR, INVERS, ISPIN, LAMBDA, LOGIC, LP, NCONF, NDEG, NR, NO, 1REFLEC, RMASS, TITLE (15), F (20), P (20), B (5), E (5), D (5), D0 (5), FC (5), 2MINR (5), RMIN (5), W (5), X (20), XX (30, 20), A (5, 10), YLJ (5, 15), E (5, 20)

NR1 = NR - 1

DO 4 I = 1, NCONF

MINR (I) = NR

1 MIN = E (I, NR)

DO 3 J = 1, NR1

IF (MIN = E (I, J)) 3, 3, 2

2 MIN = E (I, J)

MINR (I) = J

R2 = R (J)

3 CONTINUE

RMIN (I) = R2

4 CONTINUE

C..... SET RESULTS VECTORS TO ZERO.

DO 6 I = 1, 5

BE (I) = 0.0

DE (I) = 0.0

WE (I) = 0.0

FC (I) = 0.0

EQ (I) = 0.0

DO 5 J = 1, 10

A (I, J) = 0.0

5 CONTINUE

DO 6 J = 1, 15

YLJ (I, J) = 0.0

6 CONTINUE

RETURN

END

**FORTRAN**

SUBROUTINE ORLIN2 (A, B, X, N, M, NRCH, NCCL, EPS, ITFAIL)

C..... ORLIN2 GIVES THE LEAST SQUARES SOLUTION FOR A SYSTEM OF N LINEAR

C..... EQUATIONS IN M UNKNOWNS. A IS THE N*M-MATRIX OF THIS SYSTEM, B THE

C..... CONSTANT VECTOR ON THE RIGHT SIDE, EPS THE MAXIMAL RELATIVE

C..... ROUNDING ERROR AND X THE SOLUTION VECTOR. ITFAIL IS SET EQUAL TO

C..... .TRUE. IF THE ITERATIVE IMPROVEMENT IS INEFFECTIVE.


DIMENSION A (NRCH, NCCL), B (NRCH), X (NRCH), U (20, 20), P (20), V (20), W (20)

1PP (20)
LOGICAL ITFAIL
ITFAIL=.FALSE.
DO 1 I=1,N
DO 1 J=1,M
U(I,J)=A(I,J)
1 CONTINUE
L=0
DO 51 I=1,M
S=0.0
DO 2 J=1,N
T=U(J,I)
P(J)=T
S=S+T*T
2 CONTINUE
L=L+1
Q(L)=S
T=0.0
C....ELEMENT OF V STORED IN X.
DO 3 J=1,N
T=T+P(J)*B(J)
3 CONTINUE
X(I)=T
IF(I-M) 31,51,51
31 IP=I+1
DO 5 IH=IP,M
T=0.0
DO 4 J=1,N
T=T+P(J)*U(J,IH)
4 CONTINUE
C....ELEMENT OF THE I-TH. ROW OF R STORED IN Q.
L=L+1
Q(L)=T
T=T/S
C....FORMATION OF A COLUMN OF THE I-TH. REMAINING MATRIX.
DO 5 J=1,N
U(J,IH)=U(J,IH)-P(J)*T
5 CONTINUE
C....END OF FORMATION OF THE MATRICES R AND U AND THE VECTOR V.
C....BACK SUBSTITUTION.
LL=L
LM=M+2
MP=M+1
DO 7 IS=1,M
I=MP-IS
IH=L-I
T=Q(L)
S=X(I)
IF(I-M) 52,61,61
52 IP=I+1
DO 6 J=IP,M
S=S-Q(J+IH)*X(J)
6 CONTINUE
61 X(I)=S/T
L=L-I-IS
7 CONTINUE
C....END OF BACK SUBSTITUTION.
C....INTERATIVE IMPROVEMENT OF THE SOLUTION.
EPS2=EPS*EPS
S0=0.0
C.....RESIDUAL VECTOR STORED IN P
DO 9 J=1,N
     P(J)=-SC Prod(-B(J),A,J,X,M,NCW,NCOL)
9 CONTINUE
C.....VECTOR ON THE RIGHT SIDE STORED IN PP.
   TO 11 J=1,M
     S=0.0
   DO 10 I=1,N
     S=S+U(I,J)*P(I)
   10 CONTINUE
   PP(J)=S
11 CONTINUE
C.....BACK SUBSTITUTION.
   DO 13 IS =1,M
     J=MP-IS
     IH=L-J
     S=PP(J)
     IF(J-M) 111,121,121
111 IP=J+1
   DO 12 I=IP,M
     S=S-Q(I+IH)*PP(I)
   12 CONTINUE
121 S=S/Q(L)
   PP(J)=S
   S1=S1+S*S
   T=X(J)
   S2=S2+T*T
   X(J)=S+T
   L=L+J+M
13 CONTINUE
C.....END OF BACK SUBSTITUTION.
IF(S1-0.25*S2) 14,16,16
14 IF(.NOT.(S1.GE.S2*EPS2.AND.(S0.EQ.0.OR.S1.LE.(S0*0.01))))GO TO 15
15 S0=S1
GO TO 8
16 ITFAIL=.TRUE.
GO TO 15
END

*FORTRAN
FUNCTION POLYVA(X,P,K)
C.....COMPUTES THE VALUE OF A POLYNOMIAL OF DEGREE K. THE COEFFICIENTS
C.....ARE IN P WITH THE CONSTANT TERM IN P(1). (K<20).
   DIMENSION P(20)
   DOUBLE PRECISION FOFX
   KP=K+1
   FOFX=DBLE(P(KP))
   DO 1 I=1,K
      FOFX=FOFX*DBLE(X)+DBLE(P(KP-I))
1 CONTINUE
POLYVA=FOFX
RETURN
END

*FORTRAN
SUBROUTINE POLYX(A,B,C,D,N)
C. FORTRAN V VERSION OF ACM ALGORITHM 29 "POLYNOMIAL TRANSFORMER".

DIMENSION C(20), D(20), Z(20), W(20)

C. POLYX COMPUTES THE COEFFICIENTS D0, D1, ..., DN OF THE TRANSFORMED
C. POLYNOMIAL P(T) GIVEN C0, C1, ..., CN CP P(X) WHERE X = A*T + B.

W(1) = 1.0
Z(1) = 1.0
D(1) = C(1)
NPl = N + 1
DO 1 I = 2, NPl
   W(I) = 1.0
   Z(I) = B * Z(I - 1)
   D(I) = D(I) + C(I) * Z(I)
1 CONTINUE

DO 2 J = 2, NPl
   W(1) = W(1) * A
   D(J) = C(J) * W(1)
   IF (J, EQ, NPl) RETURN

   K = 2
   JPl = J + 1
   DO 2 I = JPl, NPl
      W(K) = A * W(K) + 1.0 * (K - 1)
      D(J) = D(J) + C(I) * W(K) * Z(K)
      K = K + 1
2 CONTINUE
RETURN
END

FORTRAN

SUBROUTINE RFIL3

C.  OUTPUT OF RESULTS.

LOGICAL LOGIC

COMMON / SPEC/ ICR, INVERS, ISPIN, LAMBDA, LOGIC, LP, NCONF, NDEG, NR, NO,
1REFL, RMASS, TITLE(15), P(20), R(20), BS(5), DS(5), DO(5), FC(5),
2MINR(5), MIN(5), WS(5), X(20), XX(20, 20), A(5, 10), YJ(5, 15), E(5, 20)

DIMENSION T(31, 2)

DATA T / 8H , R3, 8HE(RE) (H, SH Y/E(AI, 3H ICE(DY, SH BE(CM
1 , 81 - 1 DE(CM, 31 - 1 Y00, SH Y10, SH Y20, SH Y30, SH Y40
2, 8H Y01, SH Y11, SH Y21, SH Y31, SH Y02, SH Y12
3, 8H Y22, SH Y03, SH Y13, SH Y04, SH B R, SH LIN
4, 8H A0, 8H A1, 8H A2, 8H A3, 8H A4, 8H A5
5, 8H A6, 8H A7, 8H (BOCHR), 3HARHRES), 8H - 1), (SHN2, CM - 1)
6, 8H - 1), (SH - 1), (SH - WE), 8H = -VE, (SH = WE
7, 8H = VEZ , 8H = BE , 3H = -ALPHA, 8H = GAMMA , 8H = DELTA, (SH = -DE
8, 8H = BETA, 8H = SH, 8H = FE, 8H = SH = HE, 3H(E)(CM - 1)
9, 8H SHEAR, 8H (CM - 1), 7*8H

DATA T1, T2/ 8H Z0(CM, SH - 1) /

DO 1 I = 1, NCONF
   X(I) = A(I, 1) + 4.5563354838E-06
1 CONTINUE

WRITE(LP, 2) TITLE
WRITE(LP, 3) (I, I = 1, NCONF)
WRITE(LP, 4) (T(I, 1), T(I, 2), (MIN(I, I = 1, NCONF)
WRITE(LP, 4) (T(2, 1), T(2, 2), (X(I), I = 1, NCONF)
WRITE(LP, 5)

WRITE(LP, 4) (T(3, 1), T(3, 2), (WE(I), I = 1, NCONF)
WRITE(LP, 4) (T(4, 1), T(4, 2), (FC(I), I = 1, NCONF)
WRITE(LP, 4) (T(5, 1), T(5, 2), (BE(I), I = 1, NCONF)
WRITE(LP, 4) (T(6, 1), T(6, 2), (DE(I), I = 1, NCONF)
WRITE(LP, 4) (T1, T2, (S(I), I = 1, NCONF)
WRITE(LP, 6)
2 FORMAT(1H1/1HO,15AS/1HO,48X,23HSPECTROSCOPIC CONSTANTS)
3 FORMAT(1HO,20X,5(6X,5HLEVEL,I3,6X))
4 FORMAT(1H ,4X,2A8,1P5E20.10)
5 FORMAT(1HO,43X,33HCALASSICAL SPECTROSCOPIC CONSTANTS/1H )
6 FORMAT(1HO,40X,40HCORRECTED SPECTROSCOPIC CONSTANTS (CM-1)/1H )

DO 7 I=1,15
   J=I+6
   WRITE(LP,4) T(J,1),T(J,2),(YIJ(K,I),K=1,NCONF)
7 CONTINUE

WRITE(LP,8)

8 FORMAT(1H0,41X,33HDUNHAM ANALYSIS EXPANSION COEFFICIENTS/1H )

DO 9 I=1,10
   J=I+21
   WRITE(LP,4) T(J,1),T(J,2),(A(K,I),K=1,NCONF)
9 CONTINUE

RETURN
END

*FORTRAN

FUNCTION SCPROD(S,A,I,P,N,NRCN,V,NCOL)
DIMENSION A(NRCN,NCOL),P(NRCN)
INTEGER PRECISION T

T=S
DO 1 J=1,N
   T=T+DBLE(A(I,J))*DBLE(P(J))
1 CONTINUE

SCPROD=T
RETURN
END
<table>
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<tr>
<th>STATEMENT NUMBER</th>
<th>FORTRAN STATEMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 2 3 4 5 6</td>
<td>SPECTRO TEST DATA - SPECTROSCOPIC CONSTANTS FROM KCL</td>
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<tr>
<td></td>
<td>S.R. ROFTMAN H2 HAVE FUNCTION.</td>
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<td>C STATEMENT NUMBER</td>
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SPECTROSCOPIC CONSTANTS PROGRAM
SPECTRO TEST DATA - SPECTROSCOPIC CONSTANTS FROM KOLOS-ROOÖHÅAN H2 WAVE FUNCTION.
REDUCED MASS = 5.6391261006E-01AMU (UNIFIED SCALE)
NUMBER OF ENERGY LEVELS = 1, NUMBER OF BOND LENGTHS = 8
DEGREE OF FITTED POLYNOMIAL = 7
THE SPECTROSCOPIC STATE IS 1 SIGMA G+.

ENERGIES AND BOND LENGTHS

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<thead>
<tr>
<th>R (DOHRS)</th>
<th>E1</th>
<th>E2</th>
<th>E3</th>
<th>E4</th>
<th>E5</th>
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</table>
LEVEL 1  MEAN ENERGY = -1.120331253E+00  
F(X) = 2.198150802E+04  D(X) = -9.1927920E+02  F(X)-D(X) = 1.78813933E-07  
X = -7.999999999E-01  F(X) = -9.189127992E+02  D(X) = -9.189127992E+02  F(X)-D(X) = 9.685754776E-08  
X = -6.000000000E-01  F(X) = -9.786546191E+03  D(X) = -9.786546191E+03  F(X)-D(X) = 5.960464775E-08  
X = -3.999999999E-01  F(X) = -1.187613520E+04  D(X) = -1.187613520E+04  F(X)-D(X) = 0.000000000E+00  
X = -2.000000000E-01  F(X) = -1.058040504E+04  D(X) = -1.058040504E+04  F(X)-D(X) = 5.960464775E-08  
X =  2.000000000E-01  F(X) = -3.877696280E+03  D(X) = -3.877696280E+03  F(X)-D(X) = 1.490116194E-08  
X =  6.000000000E-01  F(X) =  4.004561352E+03  D(X) =  4.004561352E+03  F(X)-D(X) = 0.000000000E+00  
X = 1.000000000E+00  F(X) =  1.105841942E+04  D(X) =  1.105841942E+04  F(X)-D(X) = 5.960464775E-08  

L2 VORM 0' SOLUTION = 5.22E-14
ITERATION 1 CURRENT ESTIMATE = -3.999999999E-01 INCREMENT = -1.264395835E-03
ITERATION 2 CURRENT ESTIMATE = -3.987356041E-01 INCREMENT = -2.685127708E-06
ITERATION 3 CURRENT ESTIMATE = -3.987329176E-01 INCREMENT = -1.211993481E-11

MINIMUM OF NORMALIZED POLYNOMIAL = -1.187624832E+04 AT X = 0.3907329176

SPECTRO TEST DATA - SPECTROSCOPIC CONSTANTS FROM KOLOSH-ROOHTAAN H2 WAVE FUNCTION.

SPECTROSCOPIC CONSTANTS

<table>
<thead>
<tr>
<th>LEVEL</th>
<th>RE (DOHRS)</th>
<th>E(RE) (HARTREES)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.4012670824E+00</td>
<td>-1.1744422967E+00</td>
</tr>
</tbody>
</table>

CLASSICAL SPECTROSCOPIC CONSTANTS

WE(CH-1) = 4.3994526819E+03  
KE(DYNE.CM-1) = 5.7461311684E+05  
BE(CH-1) = 6.0842846589E+01  
DE(CH-1) = 4.6546953692E+02  
Z0(CM-1) = 2.1809659866E+03
**CORRECTED SPECTROSCOPIC CONSTANTS (CH⁻¹)**

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<td>Y₁₃</td>
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<td>Y₀₄ = H₀E</td>
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**DUNHAM ANALYSIS EXPANSION COEFFICIENTS**

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APPENDIX IX

SPECIFICATION OF DETORS AND CODETORS FOR
THE $^3Σ^-_g$, $^1Σ^+_g$, AND $^1Δ_g$ STATES

The detors are specified by using the identifiers of the valence shell molecular spin-orbitals according to the rules

\[
\begin{align*}
ns \sigma_g \alpha &= 1 , & ns \sigma_g \beta &= 2 , \\
ns \sigma_u \alpha &= 3 , & ns \sigma_u \beta &= 4 , \\
np_0 \sigma_g \alpha &= 5 , & np_0 \sigma_g \beta &= 6 , \\
np_0 \sigma_u \alpha &= 7 , & np_0 \sigma_u \beta &= 8 , \\
np-\pi_g \alpha &= 9 , & np-\pi_g \beta &= 10 , \\
np-\pi_u \alpha &= 11 , & np-\pi_u \beta &= 12 , \\
np+\pi_g \alpha &= 13 , & np+\pi_g \beta &= 14 , \\
np+\pi_u \alpha &= 15 , & np+\pi_u \beta &= 16 .
\end{align*}
\]

In the oxygen molecule calculations $n = 2$, and for the sulphur molecule $n = 3$. To obtain the data required for SECSGAL the frozen inner shell spin orbitals must be specified in addition to those given in this appendix. Each codetor is written in the form

\[
\Psi_I = n_I \sum_J D_J t_{JI} ,
\]

where $t_{JI}$ is a non-zero element of the projection matrix $S_{\sigma\sigma}^T$ (chapters 7 and 8), and $n_I$ is the normalization factor for $\Psi_I$. The value of $n_I$ is calculated in the routine SECDAT (see Appendix VII), and

\[
n_I = \left( \sum_J t_{JI}^2 \right)^{-\frac{1}{2}}
\]
(In Tables IX.1 and IX.3, D₁ appears as D(I) because these tables are computer output and subscripting variables is not possible.) Finally the spatial orbital configurations are given in Table IX.5. A spatial orbital configuration merely gives the total number of electrons occupying each molecular orbital of a particular symmetry species.
TABLE IX. 1. \( \Sigma_g \) DETORS.

| \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) |
| \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) | \( \Sigma_g \) |
### TABLE IX. 1. DETORS (Continued).

|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
TABLE IX.2

$^3\Sigma^-$ Codetors constructed from detors in Table IX.1.

\[
\psi_1 = 2^{-1/2}(D_4 - D_7)
\]
\[
\psi_2 = 2^{-1/2}(D_5 - D_8)
\]
\[
\psi_3 = 2^{-1/2}(D_{11} + D_{12})
\]
\[
\psi_4 = 2^{-1/2}(D_{13} + D_{14})
\]
\[
\psi_5 = 8^{-1/2}(\ - D_{16} - D_{17} + D_{19} + D_{20}
+ D_{21} + D_{22} - D_{24} - D_{25})
\]
\[
\psi_6 = 24^{-1/2}(\ - 2D_{15} - D_{16} + D_{17} + D_{18} + D_{19} - D_{20}
- D_{21} + D_{22} + 2D_{23} + D_{24} + D_{25} - 2D_{26})
\]
\[
\psi_7 = 12^{-1/2}(\ - D_{15} + D_{16} - D_{17} + D_{18} - D_{19} + D_{20}
+ D_{21} - D_{22} + D_{23} - D_{24} + D_{25} - D_{26})
\]
\[
\psi_8 = 2^{-1/2}(D_{27} + D_{28})
\]
\[
\psi_9 = 2^{-1/2}(D_{29} + D_{30})
\]
\[
\psi_{10} = 12^{-1/2}(\ - 2D_{32} - D_{33} + D_{34} + 2D_{35} + D_{36} - D_{37})
\]
\[
\psi_{11} = 6^{-1/2}(\ - D_{32} + D_{33} - D_{34} + D_{35} - D_{36} + D_{37})
\]
\[
\psi_{12} = 12^{-1/2}(\ - 2D_{38} - D_{39} + D_{40} + 2D_{41} + D_{42} - D_{43})
\]
\[
\psi_{13} = 6^{-1/2}(\ - D_{38} + D_{39} - D_{40} + D_{41} - D_{42} + D_{43})
\]
\[
\psi_{14} = 8^{-1/2}(\ - D_{45} - D_{46} + D_{48} + D_{49}
+ D_{50} + D_{51} - D_{53} - D_{54})
\]
\[ \psi_{15} = 2^{1/2} \left( - D_{44} - D_{45} + D_{46} + 2D_{47} + D_{48} - D_{49} - D_{50} + D_{51} + 2D_{52} + D_{53} - D_{54} - 2D_{55} \right) \]

\[ \psi_{16} = 12^{-1/2} \left( - D_{44} + D_{45} - D_{46} + D_{47} - D_{48} + D_{49} + D_{50} - D_{51} + D_{52} - D_{53} + D_{54} - D_{55} \right) \]

\[ \psi_{17} = 2^{-1/2} (D_{58} + D_{59}) \]

\[ \psi_{18} = 2^{-1/2} (D_{60} + D_{61}) \]

\[ \psi_{19} = 8^{-1/2} \left( - D_{65} + D_{66} - D_{67} + D_{68} + D_{69} + D_{70} + D_{71} - D_{73} - D_{74} \right) \]

\[ \psi_{20} = 24^{-1/2} \left( - 2D_{64} - D_{65} + D_{66} + 2D_{67} + D_{68} - D_{69} - D_{70} + D_{71} + 2D_{72} + D_{73} - D_{74} - 2D_{75} \right) \]

\[ \psi_{21} = 12^{-1/2} \left( - D_{64} + D_{65} - D_{66} + D_{67} - D_{68} + D_{69} + D_{70} - D_{71} + D_{72} - D_{73} + D_{74} - D_{75} \right) \]

\[ \psi_{22} = 12^{-1/2} \left( - 2D_{76} - D_{77} + D_{78} + 2D_{79} + D_{80} - D_{81} \right) \]

\[ \psi_{23} = 6^{-1/2} \left( - D_{76} + D_{77} - D_{78} + D_{79} - D_{80} + D_{81} \right) \]

\[ \psi_{24} = 12^{-1/2} \left( - 2D_{82} - D_{83} + D_{84} + 2D_{85} + D_{86} - D_{87} \right) \]

\[ \psi_{25} = 6^{-1/2} \left( - D_{82} + D_{83} - D_{84} + D_{85} - D_{86} + D_{87} \right) \]

\[ \psi_{26} = 8^{-1/2} \left( - D_{91} - D_{92} + D_{94} + D_{95} + D_{96} + D_{97} - D_{99} - D_{100} \right) \]
TABLE IX.2 (continued)

\[ \psi_{27} = 24^{-1/2} \left( -2D_{90} - D_{91} + D_{92} + 2D_{93} + D_{94} - D_{95} - D_{96} + D_{97} + 2D_{98} + D_{99} - D_{100} - 2D_{101} \right) \]

\[ \psi_{28} = 12^{-1/2} \left( -D_{90} + D_{91} - D_{92} + D_{93} - D_{94} + D_{95} + D_{96} - D_{97} + D_{98} - D_{99} + D_{100} - D_{101} \right) \]

\[ \psi_{29} = 2^{-1/2} (D_{110} + D_{111}) \]

\[ \psi_{30} = 2^{-1/2} (D_{112} + D_{113}) \]

\[ \Sigma^+ \text{ Codetors constructed from detors in Table IX.1.} \]

\[ \psi_1 = D_1 \]

\[ \psi_2 = 2^{-1/2} (D_2 + D_3) \]

\[ \psi_3 = 2^{-1} (D_5 + D_6 - D_8 + D_9) \]

\[ \psi_4 = 12^{-1/2} (2D_4 - D_5 - D_6 + 2D_7 - D_8 - D_9) \]

\[ \psi_5 = D_{10} \]

\[ \psi_6 = 2^{-1/2} (D_{11} - D_{12}) \]

\[ \psi_7 = 2^{-1/2} (D_{13} - D_{14}) \]

\[ \psi_8 = 8^{-1/2} (D_{16} + D_{17} - D_{19} + D_{20} - D_{21} + D_{22} - D_{24} + D_{25}) \]

\[ \psi_9 = 24^{-1/2} (2D_{15} - D_{16} - D_{17} + 2D_{18} - D_{19} - D_{20} + D_{21} + D_{22} - 2D_{23} + D_{24} + D_{25} - 2D_{26}) \]

\[ \psi_{10} = 2^{-1/2} (D_{27} - D_{28}) \]
| \( \psi_{11} \) | \( = 2^{-1/2}(D_{29} - D_{30}) \) |
| \( \psi_{12} \) | \( = D_{31} \) |
| \( \psi_{13} \) | \( = 2^{-1}( - D_{33} + D_{34} - D_{36} + D_{37}) \) |
| \( \psi_{14} \) | \( = 2^{-1}( - D_{39} + D_{40} - D_{42} + D_{43}) \) |
| \( \psi_{15} \) | \( = 2^{-1/2}( - D_{45} + D_{46} - D_{48} + D_{49} - D_{50} + D_{51} - D_{53} + D_{54}) \) |
| \( \psi_{16} \) | \( = 24^{-1/2}( 2D_{44} - D_{45} - D_{46} + 2D_{47} - D_{48} - D_{49} + D_{50} + D_{51} - 2D_{52} + D_{53} + D_{54} - 2D_{55}) \) |
| \( \psi_{17} \) | \( = 2^{-1/2}( D_{56} - D_{57}) \) |
| \( \psi_{18} \) | \( = 2^{-1/2}( D_{58} - D_{59}) \) |
| \( \psi_{19} \) | \( = 2^{-1/2}( D_{60} - D_{61}) \) |
| \( \psi_{20} \) | \( = D_{62} \) |
| \( \psi_{21} \) | \( = D_{63} \) |
| \( \psi_{22} \) | \( = 2^{-1/2}( - D_{65} + D_{66} - D_{68} + D_{69} - D_{70} + D_{71} - D_{73} + D_{74}) \) |
| \( \psi_{23} \) | \( = 24^{-1/2}( 2D_{64} - D_{65} - D_{66} + 2D_{67} - D_{68} - D_{69} + D_{70} + D_{71} - 2D_{72} + D_{73} + D_{74} - 2D_{75}) \) |
| \( \psi_{24} \) | \( = 2^{-1}( - D_{77} + D_{78} - D_{80} + D_{81}) \) |
| \( \psi_{25} \) | \( = 2^{-1}( - D_{83} + D_{84} - D_{86} + D_{87}) \) |
TABLE IX.2 (continued)

\[ \psi_{26} = 2^{-1/2}(D_{88} - D_{89}) \]
\[ \psi_{27} = 8^{-1/2}( - D_{91} + D_{92} - D_{94} + D_{95} \]
\[ - D_{96} + D_{97} - D_{99} + D_{100}) \]
\[ \psi_{28} = 24^{-1/2}( 2D_{90} - D_{91} - D_{92} + 2D_{93} - D_{94} - D_{95} \]
\[ + D_{96} + D_{97} - 2D_{98} + D_{99} + D_{100} - 2D_{101}) \]
\[ \psi_{29} = 2^{-1}( - D_{103} + D_{104} - D_{106} + D_{107}) \]
\[ \psi_{30} = 12^{-1/2}( 2D_{102} - D_{103} - D_{104} + 2D_{105} - D_{106} - D_{107}) \]
\[ \psi_{31} = 2^{-1/2}( D_{108} - D_{109}) \]
\[ \psi_{32} = 2^{-1/2}( D_{110} - D_{111}) \]
\[ \psi_{33} = 2^{-1/2}( D_{112} - D_{113}) \]
\[ \psi_{34} = D_{114} \]
\[ \psi_{35} = D_{115} \]
\[ \psi_{36} = 2^{-1/2}( D_{116} - D_{117}) \]
\[ \psi_{37} = D_{118} \]
| \( D(1) \) | \( D(2) \) | \( D(3) \) | \( D(4) \) | \( D(5) \) | \( D(6) \) | \( D(7) \) | \( D(8) \) | \( D(9) \) | \( D(10) \) | \( D(11) \) | \( D(12) \) | \( D(13) \) | \( D(14) \) | \( D(15) \) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
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| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |

**Table IX.3. \( \Delta_g \) DETORS.**

\( \Delta_g \) DETORS represent a set of operations on a group that preserve certain properties. These tables list the operations for different values of \( \Delta_g \), showing how elements are transformed under each operation. Each row corresponds to a different \( \Delta_g \) value, and the columns list the transformed elements.
TABLE IX.4

$^1\Delta$ Codetors constructed from detors in Table IX.3.

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<thead>
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<th>Codetor</th>
<th>Expression</th>
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<td>$2^{-1/2}(D_1 - D_2)$</td>
</tr>
<tr>
<td>$\psi_2$</td>
<td>$2^{-1/2}(D_3 - D_4)$</td>
</tr>
<tr>
<td>$\psi_3$</td>
<td>$D_5$</td>
</tr>
<tr>
<td>$\psi_4$</td>
<td>$D_6$</td>
</tr>
<tr>
<td>$\psi_5$</td>
<td>$2^{-1}(-D_8 + D_9 - D_{11} + D_{12})$</td>
</tr>
<tr>
<td>$\psi_6$</td>
<td>$12^{-1/2}(2D_7 - D_8 - D_9 + 2D_{10} - D_{11} - D_{12})$</td>
</tr>
<tr>
<td>$\psi_7$</td>
<td>$D_{13}$</td>
</tr>
<tr>
<td>$\psi_8$</td>
<td>$D_{14}$</td>
</tr>
<tr>
<td>$\psi_9$</td>
<td>$2^{-1/2}(D_{15} - D_{16})$</td>
</tr>
<tr>
<td>$\psi_{10}$</td>
<td>$2^{-1/2}(D_{17} - D_{18})$</td>
</tr>
<tr>
<td>$\psi_{11}$</td>
<td>$2^{-1}(-D_{20} + D_{21} - D_{23} + D_{24})$</td>
</tr>
<tr>
<td>$\psi_{12}$</td>
<td>$12^{-1/2}(2D_{19} - D_{20} - D_{21} + 2D_{22} - D_{23} - D_{24})$</td>
</tr>
<tr>
<td>$\psi_{13}$</td>
<td>$D_{25}$</td>
</tr>
<tr>
<td>$\psi_{14}$</td>
<td>$D_{26}$</td>
</tr>
<tr>
<td>$\psi_{15}$</td>
<td>$2^{-1}(-D_{28} + D_{29} - D_{31} + D_{32})$</td>
</tr>
<tr>
<td>$\psi_{16}$</td>
<td>$12^{-1/2}(2D_{27} - D_{28} - D_{29} + 2D_{30} - D_{31} - D_{32})$</td>
</tr>
<tr>
<td>$\psi_{17}$</td>
<td>$2^{-1/2}(D_{33} - D_{34})$</td>
</tr>
<tr>
<td>$\psi_{18}$</td>
<td>$2^{-1/2}(D_{35} - D_{36})$</td>
</tr>
</tbody>
</table>
\[ \psi_{19} = 2^{-1}( -D_{38} + D_{39} - D_{41} + D_{42} ) \]
\[ \psi_{20} = 12^{-1/2}( 2D_{37} - D_{38} - D_{39} + 2D_{40} - D_{41} - D_{42} ) \]
\[ \psi_{21} = D_{43} \]
\[ \psi_{22} = D_{44} \]
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<th>Present Codetors</th>
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<td>h, i</td>
<td></td>
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<tr>
<td>8 2 2 - 2 4 2 2</td>
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<td>f</td>
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TABLE IX.5. PART 2, $\Delta_g$ SPATIAL ORBITAL CONFIGURATIONS.

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Quantum-Mechanical Study of Some Three-Center Two-Electron Systems. II. A Natural-Orbital, Electron-Population, and Energy Analysis

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(Received 6 May 1968)

Configuration-interaction wavefunctions for a series of pseudomolecular ions of the form \( ZH^+Z^+\), where \( Z = 1.0 \) (0.4) 2.2, were reformulated in terms of natural orbitals. Consequently, changes in the electron density could be investigated, as a function of \( Z \) and the bond angle \( ZHZ \), by means of the population analysis of Mulliken. Contour diagrams were also determined for the charge density evaluated in the plane of the molecule. The total energy for each system was analyzed in terms of the kinetic energy, nuclear attraction energy, and the electron and nuclear repulsion energies. The results are presented graphically as a function of the bond angle \( \theta \) for each value of \( Z \). For \( Z = 1.0 \), i.e., \( H^+ \), the occupation numbers for the natural orbitals revealed the united atom character of this system, and the contour diagrams indicated that, in the equilibrium configuration, the "bonds" were directed from each nucleus towards the centroid of the positive charges. As \( \theta \) was increased beyond 60°, it was found that the "central" proton within \( H^+ \) began to dominate the system. For \( Z = 2.2 \), the ions approach most closely to their separated systems of minimum energy as \( \theta \) tends to 180°. The contour diagrams and the electron-population analysis also show that the \( ZH^+Z^+ \) ions change from a three-center to, basically, a two-center system and a strongly perturbing proton as the values for \( Z \) and \( \theta \) increase and decrease, respectively. The \( \theta \) dependence of the kinetic energy is perhaps the most interesting of the energy curves. By associating a decrease in kinetic energy with an increase in spatial freedom for the electrons, it was possible to understand the \( \theta \) variations of all the energy components for each value of \( Z \). The present examination has allowed us to observe, in detail, changes which occur in the electron density and energy components for a series of three-center two-electron systems when \( \theta \) and \( Z \) are allowed to vary.

I. INTRODUCTION

In recent years considerable effort has been devoted to the study of the \( H^+ \) ion. This two-electron system constitutes a simple molecule with electron-deficient bonds. A similar kind of bonding among three attracting centers of charge is thought to exist in diborane in the form of a "bridge" or "banana" bond.^ In an effort to obtain some understanding of such bonds, energy changes with respect to noninteger variations of the nuclear charge were studied by extending the calculations for \( H^+ \) to a series of pseudomolecular ions of the form \( ZHZ^+Z^+ \). The results were reported in Part I of the present series. Several interesting features emerged from these calculations: first, we observed an initial decrease in the optimum value of the bond angle \( ZHZ \) as the effective nuclear charge \( Z \) was increased and, second, it was found that a double minimum occurred in the angular dependence of the molecular energy when \( Z \sim 1.8 \). Further, when \( Z = 0 \), the calculation predicted a pleasing degree of energy stability for the hydride ion.

In Part I it was tentatively suggested that the behavior of the energy of the \( ZHZ^+Z^+ \) ions might be explained by the existence of two variable components of the electron density. These components were referred to as the "shared" density and the "local" density: the former was associated with the internuclear regions and the latter was situated, primarily, about each of the \( Z \) nuclei. Clearly, such an interpretation called for a more detailed investigation.

In the present article the electron density and molecular energy for the \( ZHZ^+Z^+ \) ions, when \( Z = 1.0 \) (0.4) 2.2, are analyzed for various values of the bond angle \( ZHZ \) ranging from \( \theta = 30°-180° \). The wavefunction is reformulated in terms of natural spin orbitals and the occupation numbers are examined as a function of \( Z \) and \( \theta \). The NSO representation also permits us to perform an electron-population analysis in terms of definitions for "shared" and "local" densities. Contour maps of the total electron density for each \( ZHZ^+Z^+ \) configuration were also obtained. For completeness, the molecular energy \( E \) is analyzed in terms of its components. Thus, the kinetic energy of the electrons, the electron–nuclear attraction energy, the electron–electron and nuclear–nuclear repulsion energies are presented as a function of \( \theta \) for each value of \( Z \). By means of the above techniques, it was hoped to obtain insight into the behavior of the charge density within a three-center electron-deficient system with respect to variations of nuclear charge and bond angle.

II. ANALYSIS OF CALCULATIONS

At this point, it is appropriate to present a brief description of the wavefunction used in Part I. The ground-state wavefunction \( \Phi \) for the \( ZHZ^+Z^+ \) ions, 3050
where the bond length \( Z-H \) was denoted by \( R \), contained a normalized antisymmetric spin part which could be factorized out of the problem; therefore, the normalized symmetric space part of the wavefunction could be written as

\[
\Psi(1, 2) = \sum_i a_i \phi_i(1, 2),
\]

where the coefficients \( a_i \) were obtained by solving the appropriate secular equations. Each space configuration \( \phi_i(1, 2) \) was formed from a product of two one-electron symmetry-adapted molecular orbitals constructed from a minimal basis set of three 1s Slater-type atomic orbitals, one centered on each nucleus. Thus, we have

\[
\begin{align*}
\phi_1(1, 2) &= 2\gamma_1(1)\gamma_1(2), \\
\phi_2(1, 2) &= 2\gamma_2(1)\gamma_2(2), \\
\phi_3(1, 2) &= \left[\gamma_1(1)\gamma_2(2) + \gamma_1(2)\gamma_2(1)\right],
\end{align*}
\]

where

\[
\begin{align*}
\gamma_1(t) &= [\varphi'(1S_B) + \varphi'(1S_C)](t), \\
\gamma_2(t) &= [\varphi'(1S_B) - \varphi'(1S_C)](t), \\
\gamma_3(t) &= [\varphi'(1S_B) - \varphi'(1S_C)](t),
\end{align*}
\]

and \( t = 1 \) or 2. The 1s orbital exponents were optimized to give minimum energy \( E \) for each set of preselected values of \( Z \) and \( \theta \).

### A. Natural Spin Orbitals

Natural spin orbitals are defined as forming a basis set which diagonalizes the generalized first-order density matrix. Further, if a many-particle wavefunction \( \Phi \), expressed as a superposition of configurations over some arbitrary basis set, is reformulated in terms of configurations built up from natural spin orbitals, then this natural expansion of \( \Phi \) is distinguished as the superposition of configurations of most rapid convergence.

For the special case of two-electron systems, Löwdin and Shull showed that the natural expansion for the space part of the wavefunction could be expressed as

\[
\Psi(1, 2) = \sum_n c_n \chi_n(\tilde{r}_1)\chi_n(\tilde{r}_2),
\]

where the natural orbitals \( \chi_n(\tilde{r}_k) \) are defined such that the spinless first-order electron density matrix can be written as

\[
\gamma(\tilde{r}_k' | \tilde{r}_k) = 2 \sum_n n_n \chi_n^*(\tilde{r}_k')\chi_n(\tilde{r}_k).
\]

The occupation number of the \( k \)-th natural orbital is given by \( n_k = c_k^2 \) and satisfies the relation

\[
\sum n_n = 1.
\]

For the simple basis set employed in Part I, we obtained natural orbitals of the following form and symmetry

\[
\begin{align*}
\chi_1(t) &= [A_{1u}(b+c)+A_{1u}a](t), \\
\chi_2(t) &= [A_{1u}(b-c)](t), \\
\chi_3(t) &= [A_{1u}(b+c)+A_{1u}a](t),
\end{align*}
\]

The coefficients \( A_{1u} \) of the natural orbitals are given in Table I, however, for reasons of space, results are quoted only for selected values of \( Z \) and \( \theta \). The occupation numbers are given in Table II for all the \( Z: \theta \) values.

---


\* The letters \( a, b, \) and \( c \) represent the appropriate Slater-type orbital located on centers \( A, B, \) and \( C \), respectively; thus, the symmetry-adapted molecular orbitals \( \gamma_i(t) \) of Eq. (3) may be expressed in the abbreviated form used in Eq. (7).
Table II. Occupation numbers of the natural orbitals \( x_k \), \( \alpha \), and \( \beta \) for various \( Z/\theta \) values.

<table>
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<tr>
<th>( \theta )</th>
<th>1.0</th>
<th>1.4</th>
<th>1.8</th>
<th>2.2</th>
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<tr>
<td>30°</td>
<td>0.99000</td>
<td>0.98527</td>
<td>0.96482</td>
<td>0.93321</td>
</tr>
</tbody>
</table>
| &nbs
| 0.00731 | 0.00566 | 0.00307 | 0.00067 |
| &nbs
| 0.00787 | 0.001107 | 0.000111 | 0.00001 |
| 40° | 0.98845 | 0.99137 | 0.98838 | 0.98271 |
| &nbs
| 0.00437 | 0.00692 | 0.01138 | 0.01725 |
| &nbs
| 0.00508 | 0.00171 | 0.00024 | 0.00004 |
| 50° | 0.98609 | 0.98479 | 0.96653 | 0.96106 |
| &nbs
| 0.00321 | 0.01282 | 0.02294 | 0.03307 |
| &nbs
| 0.00239 | 0.00043 | 0.00024 | 0.00007 |
| 60° | 0.98546 | 0.97954 | 0.96050 | 0.94780 |
| &nbs
| 0.00727 | 0.01773 | 0.03888 | 0.06268 |
| &nbs
| 0.00273 | 0.00062 | 0.00011 | 0.00011 |
| 70° | 0.98378 | 0.97199 | 0.93792 | 0.85754 |
| &nbs
| 0.00956 | 0.02503 | 0.06130 | 0.14158 |
| &nbs
| 0.00666 | 0.00239 | 0.00087 | 0.00014 |
| 80° | 0.98208 | 0.96388 | 0.91129 | 0.81185 |
| &nbs
| 0.01194 | 0.03203 | 0.08724 | 0.18801 |
| &nbs
| 0.00598 | 0.00305 | 0.00087 | 0.00014 |
| 100° | 0.97874 | 0.94780 | 0.85754 | 0.71520 |
| &nbs
| 0.01657 | 0.04934 | 0.14158 | 0.24648 |
| &nbs
| 0.00409 | 0.00286 | 0.00088 | 0.00012 |
| 120° | 0.97589 | 0.93479 | 0.81721 | 0.61800 |
| &nbs
| 0.02465 | 0.06268 | 0.18198 | 0.3310 |
| &nbs
| 0.00666 | 0.00253 | 0.00080 | 0.00010 |
| 150° | 0.97345 | 0.92375 | 0.78601 | 0.52833 |
| &nbs
| 0.02394 | 0.07413 | 0.21327 | 0.37108 |
| &nbs
| 0.00621 | 0.00212 | 0.00080 | 0.00009 |
| 180° | 0.97294 | 0.92054 | 0.77759 | 0.62105 |
| &nbs
| 0.02483 | 0.07719 | 0.22172 | 0.37887 |
| &nbs
| 0.00223 | 0.00193 | 0.00069 | 0.00008 |

The definitions for overlap and atomic populations have been taken from Mulliken. Clearly, the usefulness of such quantities would be questionable unless they possessed the property of invariance with respect to any orthogonal transformation of the orbitals from which they arise. The natural orbitals discussed above possess such a property. Hence, by writing the wavefunction as a natural expansion, we can formulate a population analysis for the electron density.

Inspection of Mulliken's work revealed that the "local" and "shared" densities suggested in Part I could be likened to the total net atomic population and the total overlap population, respectively. For electron-deficient systems, information concerning the overlap between any pair of centers is also of obvious interest; hence, an examination was made of the sub-total overlap population. These quantities may be formulated as follows: from Eq. (5) the electron density \( \rho(x) \) can be written as

\[
\rho(x) = \gamma(f_1 | f_1) = 2 \sum_{i=1}^{3} n_k x_k^*(f_k),
\]

where

\[
x_1^* = A_{11}[\xi^2 + 2bc + c^2] + 2A_{11}A_{22}[ab + ac] + A_{12}[a^2],
\]

\[
x_2^* = A_{22}[\xi^2 + 2bc + c^2],
\]

and

\[
x_3^* = A_{13}[\xi^2 + 2bc + c^2] + 2A_{13}A_{23}[ab + ac] + A_{23}[a^2].
\]

Following Mulliken, we integrate Eq. (8) over the appropriate space coordinates and define the total net atomic population \( N(A) \), associated with center \( A \), to be

\[
N(A) = 2[n_1 A_1^2 + n_2 A_2^2];
\]

and similarly, we may write

\[
N(B) = 2[n_1 A_1^2 + n_2 A_2^2 + n_3 A_3^2].
\]

From considerations of geometrical symmetry we have \( N(B) = N(C) \). The sum of these three terms gives the total atomic population. The subtotal overlap popula-

\[ ^{10} \text{R. S. Mulliken, J. Chem. Phys. 23, 1833 (1955).} \]
\[ ^{11} \text{C. W. Scherr, J. Chem. Phys. 23, 569 (1955), see Appendix II.} \]
tion $S(BC)$ between the centers $B$ and $C$ is defined as

$$S(BC) = 4S_{ab}[n_1A_{11}^2 - n_2A_{22}^2 + n_3A_{33}^2];$$

similarly, we obtain

$$S(AB) = S(AC) = 4S_{ab}[n_1A_{11} + n_2A_{22}A_{23}];$$

where $S_{ab} = S_a$ and $S_b$ are overlap integrals. The total overlap population is obtained by the addition of these three components.

Variations of the total net atomic populations as a function of $\theta$ and $Z$ are shown in Figs. 1 and 2, respectively; similar graphs for the subtotal overlap populations are shown in Figs. 3 and 4. For $Z = 1.8$, optimized wavefunctions were available which allowed us to study changes in the overlap functions were available which allowed us to study changes in the $\mathrm{O}$ dependence of $N(A)$, $N(B)$, $S(AB)$, and $S(BC)$, with respect to variations of the bond length $R$. These results, although not illustrated graphically, will be discussed below.

C. Charge-Density Contours

From Eq. (8) the values of the density were obtained in the plane of the molecule for each set of $Z$:Contours of constant charge density were then determined, see Fig. 5. Each diagram is symmetric with respect to the line $XX'$ which bisects the bond angle $BAC$. For reasons of space, the contour maps are shown for only three groups of $Z$ values, namely $\theta = 60^\circ$, $120^\circ$, and $180^\circ$ for $Z = 1.0$, 1.8, and 2.2. Changes in the contours as $\theta$ or $Z$ vary are clearly illustrated. A general feature of all the contour diagrams is shown by tracing the density line of maximum charge, i.e., minimum slope, as we move between centers $B$ and $C$. This line is such that the density always decreases in magnitude when evaluated at adjacent positional coordinates along its normal. These curves, which are symmetric about $XX'$, are shown collectively in Fig. 6. They indicate, specifically, whether or not center $A$ is contained within the density contour of highest value which mutually embraces $B$ and $C$. In some instances, the line of minimum slope, as we move from $B$, is seen to divide such that $B$ is joined directly to both $A$ and $C$. The significance of this situation, indicated in Fig. 6 by dotted curves, will be discussed later.

D. Energy Analysis

In Part I, Fig. 8 showed the $\theta$ dependence of the total molecular energy for $Z = 0.8$ (0.2) 2.2. However, for convenience, our results for the energy analysis are presented only for $Z = 1.0$ (0.4) 2.2. In Fig. 7, the kinetic energy as a function of the bond angle $\theta$ is shown for different $Z$ values. Similarly, the $\theta$ dependence of the electron repulsion energy, the nuclear attraction, and nuclear repulsion energies for various $Z$ is shown in Figs. 8-10, respectively.

III. DISCUSSION OF RESULTS

Inspection of the natural orbitals given in Eq. (7) indicates that $\psi_1$ and $\psi_2$ are bonding-type orbitals, whereas $\psi_3$ possesses a form which is antibonding. Reference to the occupation numbers given in Table II reveals that, for all values of $\theta$, $\psi_1$ predominates in the natural expansion of the wavefunction when $Z \leq 1.4$. Although a large occupation number for a bonding orbital does not necessarily guarantee the molecular stability of $Z^2H^2$ for any choice of $Z$ and $\theta$, it is of interest to note, from Part I, that for $Z \leq 1.3$ the ions are stable with respect to dissociation.

For $Z = 1.0$, i.e., $\text{H}_2^+$, we observe from Table II that $n_1$ and $n_2$ decrease and $n_3$ becomes larger as the bond angle changes from $30^\circ$ to $180^\circ$. To place these results in perspective we refer to the occupation numbers of the natural orbitals of $\psi_3$ and $\psi_4$ symmetry determined by Christoffersen and Shull for the united atom $\text{Li}^+$. 12

12 R. E. Christoffersen and H. Shull, J. Chem. Phys. 48, 1790 (1968). We are very grateful to these authors for the opportunity of reading a preprint of their work.
Fig. 5. Contour diagrams of the electron density in the plane of the molecule for selected values of $Z: \theta$. The diagrams are symmetric about the line $XX'$ which bisects the bond angle $\theta$. In (a) the density at $D$ is less than 0.1764.
and the dissociation products $\text{H}^+\text{H}^+\text{H}^+$. For $\text{Li}^+$, they quote total occupation numbers of 0.998121 and 0.001223 for the $a_1'$- and $e'$-type natural orbitals, respectively. For the dissociation products of $\text{H}_3^+$, the total occupation numbers for orbitals of $a_1'$ and $e'$ symmetry are 0.666667 and 0.333333, respectively. When $Z$ is large, the dissociation products of minimum energy will have corresponding natural orbitals with occupation numbers of 0.5. Thus, the united atom character is seen to feature strongly in the description of $\text{H}_3^+$ for all values of $\theta$. Table II shows that such a conclusion is valid as far as $Z \approx 1.4$. When $Z \geq 1.8$ it is seen that, as $\theta$ increases, the occupation number associated with $X_2$ increases greatly at the expense of $n_1$. This would seem to indicate that, when $Z$ and $\theta$ are large, the charge density begins to concentrate predominantly around the "outer" nuclei $B$ and $C$ at the expense of the proton and the internuclear regions. This conclusion is supported by noting that, as $Z$ and $\theta$ increase, the occupation numbers for $X_1$ and $X_2$ are each approaching 0.5. Further support is obtained by inspection of the electron-population analysis, see Figs. 1-4, and the contour diagrams shown in Fig. 5.

The results of the electron-population analysis illustrated in Figs. 1-4 indicate that when the subtotal overlap population between centers $B$ and $C$ is greater than that for $A-B$, the $\text{ZH}_2^+\text{e}^{-}$ ions may be regarded, essentially, as a two-center system plus a strongly perturbing proton. However, when $S(BC) < S(AB)$ the ion is more ideally regarded as forming a three-center system. Such an interpretation is strongly supported by the evidence shown in the diagrams of Fig. 6. It is of interest to observe that a "divided" trace of points possessing minimum slope in the density surface as we pass from $B$ to $C$ (see the dashed curves of Fig. 6) occurs only when the bond angle is such that $S(AB) < S(BC)$. Concomitant with this condition is a small depression in the electron-density surface located in the central region of the molecular plane: see, for example, diagram (a) of Fig. 5. The results of Christoffersen and Shull[12] for $\text{H}_3^+$ did not reveal a similar depression in the density surface[12]; hence, the effect may be due to our minimal basis set.

![Fig. 6. The trace of points, between the centers $B$ and $C$, with minimum slope in the electron-density surface when evaluated in the plane of the $\text{ZH}_2^+\text{e}^{-}$ ions for $Z=1.0, 1.4, 1.8$, and 2.2, see diagrams a, b, c, and d, respectively. For each value of $Z$, the trace is shown for various values of the bond angle $\theta$. The center $A$ is located at the origin and center $B$ is indicated by . Each set of diagrams is symmetric about $XX'$ which bisects $\theta$.](image1)

![Fig. 7. The kinetic energy expressed as a function of the bond angle $\theta$ for various values of $Z$.](image2)

![Fig. 8. The electron repulsion energy expressed as a function of the bond angle $\theta$ for various values of $Z$.](image3)
For $Z=1.0$, we see from Fig. 1 that, as $\theta$ becomes larger, $N(A)$ increases fairly sharply but $N(B)=N(C)$ becomes smaller; correspondingly, the overlap $S(AB)=S(AC)$ shown in Fig. 3 increases but the value of $S(BC)$ falls considerably. This behavior is illustrated in part by the contour diagrams (a), (d), and (g) of Fig. 5. Similar comments hold for $Z=1.4$. However, for $Z=1.8$, we see from Fig. 1 that the total net atomic population increases for each nuclear center as the bond angle is enlarged. The overlap also increases with increasing $\theta$, but the magnitude of $S(BC)$ is seen to fall off rapidly. Thus, as $\theta$ varies from $30^\circ$ to $180^\circ$, a value of $Z > 1.8$ is capable of causing charge to move from the internuclear region $B-C$ towards the centers $B$ and $C$, whereas when $Z=1.0$, charge is moved from $B$ and $C$ towards center $A$.

Figure 4 reveals that, for any fixed bond angle, $S(AB)$ decreases in value as $Z$ is increased, this indicates the diminishing influence of the proton on the system. This conclusion is substantiated by the fact that $N(A)$ tends to zero for all angles as $Z$ becomes large. Figure 4 also shows that when $\theta < 100^\circ$, then $S(BC)$ increases initially and then decreases as $Z$ becomes larger. This effect is greatest for small angles. For $\theta \geq 100^\circ$, $S(BC)$ shows no initial increase as a function of $Z$. Hence, as $Z$ is increased for a fixed bond angle, charge is initially drawn away from $A$ into the regions associated with $B$, $C$, and $B-C$. A further increase in $Z$ removes charge from the internuclear region $B-C$ and localizes it about $B$ and $C$ as mentioned previously.

For $Z=1.8$, the electron-population analysis was performed for wavefunctions corresponding to $R=1.5$, 1.66, and 1.8 a.u. For constant $\theta$, as expected, $N(A)$ decreases in value and $N(B)$ increases as $R$ becomes larger, whereas $S(AB)$ and $S(BC)$ each become smaller.

Changes in the above results caused by extending the basis set may be examined most readily by studying $H_3^+$, this is made possible by the recent analysis of the configuration-interaction wavefunction of Christoffersen which involved a basis set of 12 STO's. The occupation number of 0.98487 which Christoffersen and Shull obtained for the first natural orbital $\chi_1$ differs from our result, see Table II when $Z=1.0$ and $\theta=60^\circ$, by only 0.00059. The virtual independence of the occupation numbers in the natural expansion, with respect to the size and nature of the basis set, has been commented on by Shull. Due to the large occupation number, the form of $\chi_1$ for $H_3^+$ will govern the essential features of the population analysis. Thus, the evaluation of $N(A)$ and $S(AB)$ derived from $\chi_1$ taken, firstly, from the work of Christoffersen and Shull and, secondly, from Table I for $H_3^+$ ($\theta=60^\circ$) should indicate the general effect of an extended basis set. In both cases the occupation numbers for $\chi_1$ were renormalized to unity, i.e., each natural expansion was truncated after one term. For the minimal basis set, $N(A)$ and $S(AB)$ were found to be 0.33281 and 0.33386, respectively, while the extended basis set gave values of 0.30113 and 0.36554. Thus, extending the basis set causes a lowering of the total net atomic population on each center with a corresponding increase of the subtotal overlap populations. Such changes in the electron population analysis are not too surprising since the 15 minimal basis set could only be extended by the inclusion of higher orbitals which, by their more diffuse nature, provide greater overlap. It is anticipated that an extension of the basis set for the remaining $ZHZ^{+}\text{II}$ ions will have a similar effect, although this should become less marked as $Z$ is increased.

The kinetic energy undergoes an initial decrease for all values of $Z$, see Fig. 7. The decrease becomes greater as $Z$ is increased. When $Z=1.0$, the kinetic energy becomes constant for $\theta > 90^\circ$, however, the curve for

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Footnotes:
15 Throughout this work, this is the only instance when natural expansions have been truncated.
16 For $H_3^+$, with $\theta=60^\circ$, we have $N(A)=N(B)=N(C)$ and $S(AB)=S(AC)=S(BC)$. 
$Z = 2.2$ shows a pronounced minimum when $\theta \sim 60^\circ$ and a constant value is attained only when $\theta > 140^\circ$. Figures 8–10 show that, for $Z = 1.0$, the other energy contributions are virtually constant when $\theta > 90^\circ$. This lack of angular dependence indicates that, when $\theta > 90^\circ$, the proton at center $A$ tends to dominate the $H_2^+$ system.

As pointed out by Ruedenberg, a lowering of the kinetic energy may be associated with an increased “smoothness” of the electron-density surface throughout the molecule. It is related in character to the lowering of the kinetic energy of potential-free electrons when the volume containing them is increased. Thus, the kinetic-energy curves shown in Fig. 7 may be interpreted as a measure of the relative freedom of movement of electrons within the ions as $\theta$ is increased. For example, when $Z = 2.2$ and $\theta = 30^\circ$, we have seen that the charge density is localized essentially about the $B$–$C$ region of the ion, hence, the value of the kinetic energy is high. As $\theta$ is increased to a value of about $60^\circ$, the kinetic energy suffers a decrease, suggesting that the larger value for the $B$–$C$ separation allows the charge density to become more diffuse. However, for a further increase in $\theta$, the kinetic energy is now seen to increase: this is in keeping with our observations that, for $Z = 2.2$, the charge cloud will divide and become more localized about the separate centers $B$ and $C$ as $\theta$ approaches $180^\circ$. For $Z = 1.0$, a similar situation will occur, namely, as $B$ and $C$ separate, the charge cloud will become more diffuse throughout space and the value of the kinetic energy will therefore decrease for an initial increase of $\theta$. However, a continued increase of $\theta$ causes the electronic charge to flow towards center $A$ instead of dividing and localizing the charge about each center $B$ and $C$, as was the case for $Z = 2.2$. Thus, for $H_2^+$, it is not surprising that the kinetic energy remains virtually constant for $\theta > 90^\circ$.

The curves for $Z = 1.4$ and $1.8$ shown in Fig. 7 are clearly states of transition between the two cases already discussed. Additional support for the above interpretation is gained by noting that, for each value of $Z$, the $\theta$ dependence of the electron density evaluated at center $B$ (or $C$) has the same form as the corresponding curve for the kinetic energy shown in Fig. 7.

From Figs. 8–10, we see that the electron repulsion energy, the nuclear attraction, and nuclear repulsion energies each become slightly more $\theta$ dependent as $Z$ becomes larger. This is quite reasonable since our previous analysis has shown that, as $Z$ increases, the tendency for the charge to cluster around centers $B$ and $C$ will also increase as $\theta$ approaches $180^\circ$. Hence, when the division of the charge cloud becomes more effective, the drop in the electron repulsion energy will become greater: see the curves in Fig. 8. For a fixed value of $Z$, Fig. 9 shows that the nuclear attraction energy will increase for an increase in $\theta$, presumably related to the fact that the charge cloud will be influenced less by the combined effect of the nuclei at $B$ and $C$. The nuclear repulsion curves shown in Fig. 10 are simply dependent on $Z$ and the geometry of the $ZH_{2+}^Z$ system.

### IV. Conclusion

The wavefunctions for a series of pseudomolecular ions of the form $ZH_{2+}^Z$, where $Z = 1.0$ (0.4) 2.2, have been reformulated in terms of natural orbitals. Consequently, changes in the one-particle electron density, due to variations of $Z$ and the bond angle $ZH$, were able to be investigated by means of the population analysis suggested by Mulliken. Contour diagrams were constructed for the charge density when evaluated in the plane of the molecule. In addition, the kinetic energy, the nuclear attraction energy, the electron and nuclear repulsion energies are presented graphically as a function of the bond angle $\theta$ for each value of $Z$.

For $Z \leq 1.4$, the first natural orbital in the natural expansion of the wavefunction was found to have a large occupation number for all values of $\theta$. Such a feature is essential, although no guarantee, for obtaining molecular stability with respect to dissociation; nevertheless, the present results are in accord with the observation made in Part I that the ions are energetically stable for $Z \leq 1.3$.

The occupation numbers of the natural orbitals for $H_2^+$ were placed in perspective by making a comparison with similar quantities for the united atom $Li^+$ and the dissociation products $H+H+H^+$. Such a comparison clearly revealed the united atom character of $H_2^+$. The contour diagrams also showed that, when $\theta = 60^\circ$, the “bonds” in $H_2^+$ were directed from the nuclei towards the centroid of the positive charges. The elaborate wavefunction of Christoffersen and Shull, also revealed this “bonding” arrangement. For fixed bond lengths $BA$ and $CA$, as $\theta$ was increased, we found that charge moved from the centers $B$ and $C$ towards $A$, indicating that the proton at $A$ begins to dominate the $H_2^+$ system.

When $Z$ is large, the dissociation products of minimum energy have natural orbitals with occupation numbers of 0.5. This situation is most closely represented when $Z = 2.2$ and $\theta$ approaches $180^\circ$. The contour diagrams and the electron-population analysis show that, at large values of $Z$, the electron density in the region of center $A$ is small and, as $\theta$ increases, charge flows from the internuclear region $B$–$C$ towards the “outer,” $A$, nuclei. The diagrams and analysis also show that, as $Z$ increases and $\theta$ decreases, the $ZH_{2+}^Z$ ions change from a three-center system to what is essentially a two-center system plus a strongly perturbing proton.

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17 K. Ruedenberg, Rev. Mod. Phys. 34, 326 (1962).
Of the various components of the energy of the $ZH_2Z^{12-1}$ ions, the $\theta$ dependence of the kinetic energy is perhaps most striking. As emphasized by Ruedenberg, a decrease in magnitude of the kinetic energy may be associated with an increase in the spatial freedom of the electrons. Such an interpretation assisted not only with our understanding of the kinetic-energy curves but also permitted variations in the remaining energy components to be understood.

The present examination has allowed us to observe, in detail, the changes which occur in the electron density throughout a series of three-center two-electron systems $ZH_2Z^{12-1}$ as the bond angle $Z\hat{\mathbf{Z}}$ and the nuclear charges $Z$ are allowed to vary.

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ABSTRACT

The method of Configuration Interaction (CI) has been used in a number of studies of small atomic and molecular systems. In Part I, CI wave functions for a series of pseudomolecular ions \( Z^2_{\aleph} \) are reformulated in terms of natural orbitals. Changes in the electron density as a function of the nuclear charge \( Z \) and bond angle \( \angle \) are investigated by means of an electron population analysis based on the natural orbitals. Contour diagrams of the electron density in the plane of the molecule are obtained. The total energy for each system is analysed in terms of the kinetic energy, nuclear attraction energy, and the electron and nuclear repulsion energies.

In Part II, the CI method is examined in detail. Techniques for obtaining CI wave functions of atoms and molecules are discussed in detail. Computer programs based on these techniques are described, and listed in the Appendices. The Valence Configuration Interaction (VCI) method is also examined as a means of reducing the size of the secular equation, and results of VCI calculations are given for various states of atomic and diatomic oxygen and sulphur. Spectroscopic constants for the \( X^3\Sigma_g^- \) and \( b^1\Sigma_u^+ \) states of \( O_2 \) and for the \( X^3\Sigma_g^- \), \( a^1\Delta_g \) and \( b^1\Sigma_u^+ \) states of \( S_2 \) are given. The methods by which these results can be obtained are also discussed. Finally the results of the VCI calculations are compared with some recent SCF calculations on \( O_2 \) and \( S_2 \).