

CONFIGURATION INTERACTION STUDIES OF
SMALL MOLECULES

by

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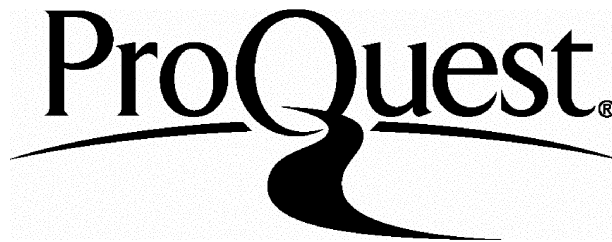
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ERRATA

The appropriate passage should read as follows:

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CHAPTER 4A.	Natural Spin-Orbital Analysis	23
APPENDIX IV	 FOR THE $D_{\infty h}$ 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	$\gamma(\bar{r}_1; \bar{r}_1') = 2 \sum_{ij} f_{ij} \sum_{lm} f_{lm} \varphi_i^*(\bar{r}_1) \varphi_l(\bar{r}_1) s_{jm}$	(4.2)
page 24 line 7	$\gamma(l i) = \sum_{jm} f_{ij} s_{jm} f_{ml}$	
page 24 line 8	 $f_{lm} = f_{ml}$. In	
page 27 line 11	 matrix, $\underline{X}^{-1} = \underline{X}^+$, thus	
page 27	$\underline{X}^{-1} \underline{W}^{-1} \underline{F} \triangleq \underline{F}^+ (\underline{W}^{-1})^+ (\underline{X}^{-1})^+$	(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	$\Lambda = \sum_1 m_1$	(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	$a_5 \quad 3.9409 \times 10^5 \quad -8.1705 \times 10^5 \quad -4.5959 \times 10^4$	

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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 ZHZ^{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 ZHZ 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⁽¹⁾ 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

$$\hat{h}\psi(\bar{x}_1, \bar{x}_2, \dots, \bar{x}_n) = E_E \psi(\bar{x}_1, \bar{x}_2, \dots, \bar{x}_n) \quad (1.1)$$

In (1.1) $\hat{h}$ is the Hamiltonian operator, E_E is an eigenvalue of $\hat{h}$, interpreted physically as the energy of the stationary state, and ψ is an eigenfunction of $\hat{h}$ 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 μ are denoted by $\bar{x}_\mu$. The Hamiltonian operator has the form

$$\hat{h} = \sum_{\mu} h_{\mu} + \sum_{\mu < \nu} g_{\mu\nu}, \quad (1.2)$$

where h_{μ} is the one-electron Hamiltonian operator for electron μ :

$$h_{\mu} = -1/2 \nabla_{\mu}^2 + V_{\mu} \quad (1.3a)$$

This operator, consisting of a sum of the kinetic and potential energy operators for electron μ , 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 μ , ν ,

$$g_{\mu\nu} = 1/r_{\mu\nu} \quad (1.3b)$$

and $r_{\mu\nu}$ is the distance between electron μ and electron ν . 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

$$E_E = \frac{\langle \Psi | \hat{h} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (1.4)$$

The operators $\hat{h}$, h_μ 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. Whenever 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_μ of electron μ will be denoted by $\varphi_i(\bar{r}_\mu)$, where $\bar{r}_\mu$ represents the spatial co-ordinates and i identifies the one-electron wave function or orbital. One-electron wave functions which are dependent on the spin co-ordinates are denoted by $\psi_i(\bar{x}_\mu)$, these are called spin-orbitals. The symbols $\varphi_i(\mu)$ and $\psi_i(\mu)$ 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 $\Theta_i(s_\mu)$. There are only two linearly independent spin functions which are designated α and β . Each orbital can be used to construct two spin-orbitals

$$\begin{aligned}\psi_{2i-1} &= \varphi_i \alpha, \\ \psi_{2i} &= \varphi_i \beta.\end{aligned}\tag{1.5}$$

Thus spin-orbitals with odd valued identifiers are associated with an α spin, and those with even valued identifiers with a β spin. It is well known ⁽²⁾ that if the set of orbitals $\{\varphi_i\}$ is subject to a unitary transformation, then the resulting set $\{\varphi'_i\}$ represents

the same physical situation. It is often convenient to choose the set

$$\{\varphi_i\} \quad \text{to be an orthonormal one,}$$

$$\int \varphi_i^*(\mu) \varphi_j(\mu) d\tau_\mu = \delta_{ij} \quad , \quad (1.6a)$$

hence

$$\int \psi_i^*(\mu) \psi_j(\mu) dx = \delta_{ij} \quad , \quad (1.6b)$$

where $d\tau_\mu$ is the one-electron volume element without spin, dx_μ the one-electron volume element with spin, and δ_{ij} is the Kronecker delta. The n -electron wave function Ψ 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_K , satisfies this principle. Thus

$$D_K = (n!)^{-1/2} \begin{vmatrix} \psi_{k1}(1) & \psi_{k2}(1) & \dots & \psi_{kn}(1) \\ \psi_{k1}(2) & \psi_{k2}(2) & \dots & \psi_{kn}(2) \\ \cdot & \cdot & \cdot & \cdot \\ \psi_{k1}(n) & \psi_{k2}(n) & \dots & \psi_{kn}(n) \end{vmatrix} \quad ,$$

and

$$\Psi = \sum_K D_K b_{KI} \quad . \quad (1.7)$$

The coefficients b_{KI} in (1.7) are determined by a variation method which minimizes E_E . 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:

$$\varphi_i = \sum_k \omega_k c_{ki} \quad , \quad (1.8)$$

where ω_k is a normalized atomic orbital. Hall (3) gives a list of the possible forms of ω_k . The coefficients c_{ki} are chosen so that the φ_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_{KI} 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):

$$\begin{aligned} S^2 \psi &= S(S + 1) \psi \\ S_z \psi &= S_z \psi \end{aligned} .$$

A single determinant is an eigenfunction of S_z with an eigenvalue of $S_z = 2^{-1}(n_\alpha - n_\beta)$, (4) where n_α is the number of spin-orbitals of α spin and n_β the number with β spin.

$$S_z D_K = 2^{-1}(n_\alpha - n_\beta) D_K . \quad (1.9)$$

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 $\hat{S}_z$. Thus, if

$$\psi_L = \sum_K D_K t_{KL} \quad , \quad (1.10)$$

and

$$\hat{S}^2 \psi_L = S(S + 1) \psi_L \quad ,$$

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

$$\Psi = \sum_L \psi_L a_{LI} \quad . \quad (1.11)$$

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

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 ψ_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 α spins are different from those associated with β spins. A determinant of such orbitals is no longer an eigenfunction of 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 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 'primitive function'. This is then multiplied by a total spin eigenfunction ⁽¹²⁾ 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

$$(\underline{H} - E\underline{S})\underline{A} = 0 \quad . \quad (1.12)$$

The elements of the real symmetric matrices $\underline{H}$ and $\underline{S}$ are

$$H_{IJ} = \langle \psi_I | \hat{H} | \psi_J \rangle , \quad (1.13a)$$

and

$$S_{IJ} = \langle \psi_I | \psi_J \rangle \quad . \quad (1.13b)$$

$\underline{A}$ is a column vector with elements $a_{\underline{L}\underline{I}}$. 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 $\underline{H}$ and its associated eigenvector $\underline{A}$. 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 $\underline{H}$, 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 $H_{\underline{I}\underline{J}}$ and $S_{\underline{I}\underline{J}}$ may be obtained by calculating $\langle D_{\underline{K}} | \hat{H} | D_{\underline{L}} \rangle$ and $\langle D_{\underline{K}} | D_{\underline{L}} \rangle$ first, and then transforming into $H_{\underline{I}\underline{J}}$ and $S_{\underline{I}\underline{J}}$ by use of (1.10). The calculation of $H_{\underline{I}\underline{J}}$ and $S_{\underline{I}\underline{J}}$ is simplified if the determinants are constructed from an orthonormal set of molecular orbitals, when the matrix $\underline{S}$ becomes the identity matrix:

$$S_{\underline{I}\underline{J}} = \delta_{\underline{I}\underline{J}}.$$

In this case it is also possible to obtain the $H_{\underline{I}\underline{J}}$'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

CHAPTER 2

INTRODUCTION - A THREE-CENTRE TWO-ELECTRON PROBLEM

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 H_2 molecule. The very detailed computational studies of Kolos⁽¹⁹⁾ are examples of the considerable attention that this molecule has received. The subsequent analysis of this type of calculation by Shull^(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⁽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 (H_3^+), consisting of three protons which are bound together by two electrons. A very detailed study of this system by Christoffersen⁽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 BBr_3 .

One of the smaller boron hydrides is diborane (B_2H_6). For many years the structure of diborane was thought to be the same as that of ethane (C_2H_6) shown in Fig. 1. The C-H bonds of this molecule have

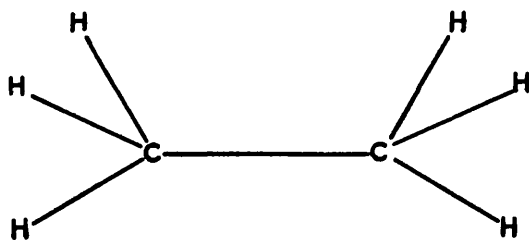


FIG. 1. ETHANE C_2H_6

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 B_2H_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

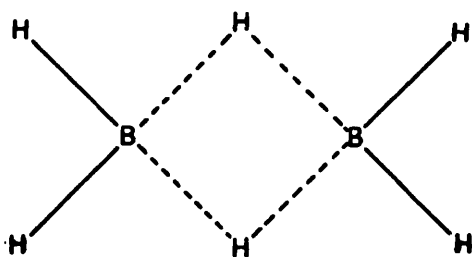


FIG. 2. DIBORANE B_2H_6

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

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_2H_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

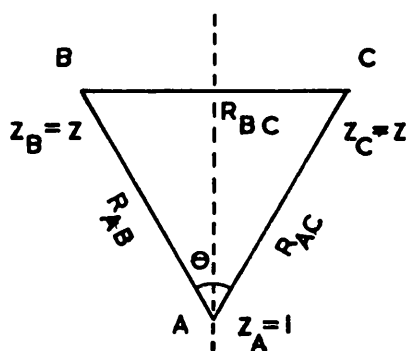


FIG. 3. THE PSEUDO MOLECULAR ION ZHZ^{2Z-1}

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 (θ in Fig. 3.), was studied for Z in the range $0.8 \leq Z \leq 2.2$ and θ 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° and it

might reasonably be expected that as the nuclear charge Z is increased in the ZHZ^{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 ZHZ^{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 ZHZ^{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⁽⁸⁾ provides an excellent means of examining these results, particularly as Shull⁽²⁶⁾ 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⁽²⁷⁾, 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 ZHZ^{2Z-1} ions⁽²⁵⁾. 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 ZHZ^{2Z-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 ZHZ^{2Z-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)

$$\begin{aligned} \hat{H} = & -\frac{1}{2} \sum_{t=1}^2 \nabla_t^2 - \sum_{t=1}^2 \left(\frac{1}{r_{At}} + \frac{Z}{r_{Bt}} + \frac{Z}{r_{Ct}} \right) + \frac{1}{r_{12}} \\ & + \frac{Z}{R_{AB}} + \frac{Z}{R_{AC}} + \frac{Z^2}{R_{BC}} . \end{aligned} \quad (3.1)$$

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

$$\Psi(\bar{x}_1, \bar{x}_2) = \sum_i c_i \Psi_i(\bar{x}_1, \bar{x}_2) , \quad (3.2)$$

where the $\{c_i\}$ are coefficients to be determined and the $\{\Psi_i\}$ are linearly independent determinantal wave functions. The energy E ,

of this state, is defined by

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (3.3)$$

Application of the variation method, which demands that

$$\frac{\partial E}{\partial c_i} = 0,$$

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

$$(\underline{H} - E\underline{S})\underline{C} = 0, \quad (3.4)$$

where $\underline{H}$ and $\underline{S}$ are matrices with elements:

$$H_{ij} = \langle \Psi_i | \hat{H} | \Psi_j \rangle$$

and

$$S_{ij} = \langle \Psi_i | \Psi_j \rangle$$

respectively, and $\underline{C}$ is a column vector with elements $\{c_i\}$. Once the forms of the two-electron configurations $\{\Psi_i\}$ 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 ZHZ^{2Z-1} , it is possible to factorize the configuration Ψ_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:

$$\Psi_i(\bar{x}_1, \bar{x}_2) = \frac{1}{\sqrt{2}}(\alpha(s_1)\beta(s_2) - \alpha(s_2)\beta(s_1))\phi_i(\bar{r}_1, \bar{r}_2),$$

so that we may write

$$\Phi(\bar{r}_1, \bar{r}_2) = \sum_i c_i \phi_i(\bar{r}_1, \bar{r}_2) \quad (3.5)$$

Ψ and Φ 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

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

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

In order to examine the ZHZ^{2Z-1} 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:

$$\begin{aligned} \phi_1(t) &= 1s_B(t) + 1s_C(t) & A_1 \\ \phi_2(t) &= 1s_A(t) & A_1 \\ \phi_3(t) &= 1s_B(t) - 1s_C(t) & B_1 \end{aligned} \quad (3.6)$$

where $t = \bar{r}_1$ or $\bar{r}_2$. 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 ZHZ^{2Z-1} . The fully symmetry-adapted space configurations are:

$$\phi_1(\bar{r}_1, \bar{r}_2) = 2\phi_1(\bar{r}_1)\phi_1(\bar{r}_2)$$

$$\phi_2(\bar{r}_1, \bar{r}_2) = 2\phi_2(\bar{r}_1)\phi_2(\bar{r}_2)$$

$$\phi_3(\bar{r}_1, \bar{r}_2) = 2\phi_3(\bar{r}_1)\phi_3(\bar{r}_2)$$

$$\phi_4(\bar{r}_1, \bar{r}_2) = \phi_1(\bar{r}_1)\phi_2(\bar{r}_2) + \phi_2(\bar{r}_1)\phi_1(\bar{r}_2) \quad .$$

Thus each of the calculations on the ZHZ^{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 ζ_B and ζ_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 θ , 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 θ 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 $Z=1.00A.U.$, $R=1.66BOHR$.

θ	C1	C2	C3	C4	ζ_A	ζ_B	ENERGY
30.00	0.06036	0.00119	-0.04919	0.16247	1.4190	1.5760	-1.13665
40.00	0.07624	0.00081	-0.04413	0.19661	1.4150	1.5070	-1.25386
50.00	0.07231	0.01689	-0.04280	0.21172	1.4090	1.4470	-1.29044
60.00	0.06334	0.02553	-0.04278	0.22223	1.4000	1.4000	-1.29786
70.00	0.06417	0.03499	-0.04317	0.23005	1.3870	1.3670	-1.29417
80.00	0.03394	0.04472	-0.04376	0.23761	1.3710	1.3430	-1.28670
100.00	0.05121	0.06496	-0.04439	0.24668	1.3370	1.3260	-1.27099
120.00	0.04436	0.08505	-0.04557	0.24998	1.3000	1.3205	-1.25927
150.00	0.03657	0.11363	-0.04579	0.24774	1.2560	1.3420	-1.24996
180.00	0.03371	0.12658	-0.04555	0.24485	1.2370	1.3590	-1.24746

TABLE 1.2. WAVE FUNCTION COEFFICIENTS, ORBITAL EXPONENTS, AND ENERGIES FOR $Z=1.40A.U.$, $R=1.66BOHR$.

θ	C1	C2	C3	C4	ζ_A	ζ_B	ENERGY
30.00	0.12612	-0.00602	-0.04750	0.09145	1.6680	1.9265	-1.53073
40.00	0.12510	-0.00421	-0.04339	0.11781	1.6370	1.8150	-1.67650
52.15	0.12167	0.00004	-0.05227	0.14604	1.6040	1.7130	-1.70761
60.00	0.11843	0.00416	-0.05509	0.16258	1.5800	1.6710	-1.70217
70.00	0.11372	0.01063	-0.05869	0.18079	1.5500	1.6360	-1.68797
80.00	0.10382	0.01766	-0.06213	0.19513	1.5220	1.6120	-1.67323
100.00	0.09939	0.03291	-0.06788	0.21525	1.4730	1.5970	-1.65113
120.00	0.09113	0.04755	-0.07165	0.22650	1.4300	1.6030	-1.63917
150.00	0.03233	0.06439	-0.07423	0.23357	1.3860	1.6230	-1.63239
180.00	0.07996	0.07099	-0.07481	0.23517	1.3700	1.6340	-1.63109

TABLE 1.3. WAVE FUNCTION COEFFICIENTS, ORBITAL EXPONENTS, AND ENERGIES FOR $Z=1.30A.U.$, $R=1.66BOHR$.

θ	C1	C2	C3	C4	ζ_A	ζ_B	ENERGY
30.00	0.14907	-0.00329	-0.04412	0.04021	1.9380	2.2850	-1.97917
40.00	0.15437	-0.00370	-0.05128	0.05976	1.8720	2.1230	-2.16339
50.50	0.15775	-0.00316	-0.06102	0.08136	1.8080	2.0120	-2.19412
60.00	0.15791	-0.00154	-0.07070	0.10155	1.7540	1.9530	-2.18557
70.00	0.15623	0.00119	-0.08101	0.11957	1.7030	1.9130	-2.17196
80.00	0.15333	0.00462	-0.09060	0.13403	1.6660	1.9020	-2.16270
100.00	0.14644	0.01174	-0.10553	0.15218	1.5930	1.8990	-2.15953
120.00	0.14015	0.01781	-0.11449	0.16134	1.5530	1.9080	-2.16668
150.00	0.13474	0.02311	-0.12052	0.16766	1.5250	1.9190	-2.17318
180.00	0.13313	0.02463	-0.12205	0.16909	1.5160	1.9220	-2.18253

TABLE 1.4. WAVE FUNCTION COEFFICIENTS, ORBITAL EXPONENTS, AND ENERGIES FOR $Z=2.20A.U.$, $R=1.66BOHR$.

θ	C1	C2	C3	C4	ζ_A	ζ_B	ENERGY
30.00	0.16201	-0.00144	-0.04223	0.01769	2.2300	2.6360	-2.39633
40.00	0.17235	-0.00201	-0.05450	0.02964	2.1040	2.4360	-2.66701
50.00	0.17941	-0.00217	-0.07033	0.04441	1.9390	2.3250	-2.73352
60.00	0.18253	-0.00169	-0.08352	0.05896	1.8960	2.2675	-2.76461
70.00	0.18205	-0.00057	-0.10666	0.07100	1.8220	2.2460	-2.78850
80.00	0.17993	0.00084	-0.12211	0.07901	1.7670	2.2410	-2.81345
100.00	0.17166	0.00330	-0.14159	0.03630	1.7080	2.2480	-2.88367
120.00	0.16657	0.00475	-0.15032	0.08873	1.6790	2.2540	-2.93646
150.00	-0.16304	-0.00572	0.15515	-0.09014	1.6650	2.2580	-2.98333
180.00	-0.16209	-0.00599	0.15624	-0.09058	1.6600	2.2590	-2.99775

TABLE 1.5. WAVE FUNCTION COEFFICIENTS, ORBITAL EXPONENTS, AND ENERGIES FOR $Z=1.80A.U.$, $R=1.50BOHR$.

θ	C1	C2	C3	C4	ζ_A	ζ_B	ENERGY
30.00	0.14344	-0.00417	-0.04174	0.04641	1.9575	2.3580	-1.75787
40.00	0.14750	-0.00468	-0.04694	0.06499	1.8970	2.1720	-2.03216
50.00	0.14896	-0.00408	-0.05363	0.08602	1.8410	2.0640	-2.10439
60.00	0.14816	-0.00229	-0.06112	0.10660	1.7880	1.9890	-2.11452
70.00	0.14530	0.00068	-0.06377	0.12532	1.7420	1.9440	-2.10797
80.00	0.14253	0.00437	-0.07616	0.14073	1.7030	1.9160	-2.09961
100.00	0.13437	0.01277	-0.08851	0.16246	1.6340	1.8950	-2.09189
120.00	0.12824	0.02046	-0.09700	0.17467	1.5900	1.9000	-2.09423
150.00	0.12203	0.02732	-0.10351	0.18242	1.5550	1.9080	-2.10221
180.00	-0.12012	-0.03019	0.10529	-0.18437	1.5440	1.9110	-2.10570

TABLE 1.6. WAVE FUNCTION COEFFICIENTS, ORBITAL EXPONENTS, AND ENERGIES FOR $Z=1.80A.U.$, $R=1.80BOHR$.

θ	C1	C2	C3	C4	ζ_A	ζ_B	ENERGY
30.00	0.15363	-0.00263	-0.04638	0.03572	1.9200	2.2340	-2.12196
40.00	0.16039	-0.00303	-0.05570	0.05491	1.8495	2.0790	-2.24476
50.00	0.16490	-0.00256	-0.06746	0.07593	1.7840	1.9840	-2.24912
60.00	0.16592	-0.00099	-0.08039	0.09599	1.7270	1.9310	-2.23061
70.00	0.16456	0.00148	-0.09317	0.11270	1.6780	1.9050	-2.21518
80.00	0.16161	0.00451	-0.10450	0.12546	1.6340	1.8975	-2.20783
100.00	0.15454	0.01046	-0.12051	0.14022	1.5700	1.9045	-2.21076
120.00	0.14903	0.01476	-0.12887	0.14674	1.5330	1.9150	-2.22194
150.00	0.14431	0.01354	-0.13335	0.15143	1.5040	1.9280	-2.23543
180.00	0.14249	0.01965	-0.13461	0.15237	1.4950	1.9030	-2.24018

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 (8,28) 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⁽²⁸⁾ and the spatial part may be written as

$$\phi(\bar{r}_1, \bar{r}_2) = \sum_{ij} f_{ij} \phi_i(\bar{r}_1) \phi_j(\bar{r}_2) \quad , \quad (4.1)$$

in matrix notation this is

$$\underline{\phi} = \underline{\phi} \underline{F} \underline{\phi}^+ \quad ,$$

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

$$\gamma(\bar{r}_1; \bar{r}_1') = 2 \int \phi^*(\bar{r}_1, \bar{r}_2) \phi(\bar{r}_1, \bar{r}_2) d\bar{r}_2 \quad .$$

After substitution for ϕ from (4.1) and integration over $\bar{r}_2$, this expression becomes

$$\gamma(\bar{r}_1; \bar{r}_1') = 2 \sum_{ij} f_{ij}^* \sum_{lm} f_{lm} \varphi_i(\bar{r}_1) \varphi_l(\bar{r}_1') s_{jm} , \quad (4.2)$$

where $s_{jm} = \langle \varphi_j | \varphi_m \rangle$, 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

$$\gamma(1|1) = \sum_{jm} f_{ij}^* s_{jm} f_{ml} ,$$

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

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

$\underline{\Delta}$ 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

$$\gamma(\bar{r}_1; \bar{r}_1') = 2 \underline{\phi} \underline{\gamma} \underline{\phi}^+ .$$

The natural orbitals are defined as that set of orthonormal orbitals which diagonalizes the (spinless) first order density matrix. Thus if

$\underline{\chi}$ represents the natural orbital basis, then since

$$\underline{\chi} = \underline{\phi} \underline{A} , \quad (4.4)$$

$$\gamma(\bar{r}_1; \bar{r}_1') = \underline{\chi} \underline{A}^{-1} \underline{\gamma} (\underline{A}^{-1})^+ \underline{\chi}^+ ,$$

and

$$\underline{A}^{-1} \underline{\gamma} (\underline{A}^{-1})^+ = \text{diag}(n_1, n_2, \dots) \quad . \quad (4.5)$$

Since the $\{\chi_i\}$ must be orthonormal then

$$\underline{A}^+ \underline{\Delta} \underline{A} = \underline{I} \quad (4.6)$$

($\underline{I}$ is the identity matrix). Equations (4.5) and (4.6) are the standard natural orbital equations, which define the matrix $\underline{A}$. (In the N- electron case these equations become the natural spin orbital equations, as both $\underline{\gamma}$ and $\underline{\Delta}$ are formed from the basis spin orbitals. This form of $\underline{\gamma}$ 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 $\underline{A}$ without constructing the first order density matrix; a tedious operation even for small basis sets. The procedure is as follows; let

$$\underline{\chi} = \underline{\phi} \underline{B} \quad , \quad (4.7)$$

such that

$$\underline{\phi} = \underline{\chi} \text{diag}(g_1, g_2, \dots) \underline{\chi}^+ \quad ,$$

and

$$\langle \chi_i | \chi_j \rangle = \delta_{ij} \quad .$$

It is easily seen that the transformation matrix $\underline{B}$ is defined by the conditions

$$\underline{B}^+ \underline{\Delta} \underline{B} = \underline{I} \quad , \quad (4.8)$$

and

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

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

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

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

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

Hence

$$\underline{W}^+ \underline{\Delta} \underline{W} = \underline{I} \quad . \quad (4.10)$$

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

$$\underline{B} = \underline{W} \underline{X} \quad \text{and} \quad \underline{B}^+ = \underline{X}^+ \underline{W}^+ \quad . \quad (4.11)$$

Substitution for $\underline{B}$ and $\underline{B}^+$ from (4.11) into (4.8) and use of (4.10) yields the result

$$\underline{X}^+ \underline{X} = \underline{I} \quad .$$

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

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

where

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

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

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

Therefore $\underline{W}$, $\underline{X}$, and hence the transformation matrix $\underline{B}$ may be determined.

Now consider the transformation

$$\underline{B}^{-1} \underline{\gamma} (\underline{B}^{-1})^+$$

Using (4.3) and (4.11) this becomes

$$\underline{X}^{-1} \underline{W} \underline{F} \underline{\Delta} \underline{F}^+ (\underline{W}^{-1})^+ (\underline{X}^{-1})^+ \quad (4.13)$$

This equation may be greatly simplified by using (4.8), (4.10), and the fact that $\underline{X}$ is unitary. The steps involved are not obvious and are shown in full, thus (4.13) is firstly rewritten as

$$\begin{aligned} \underline{X}^{-1} \underline{W}^{-1} \underline{F} (\underline{W}^{-1})^+ (\underline{W}^+ \underline{\Delta} \underline{W}) \underline{W}^{-1} \underline{F}^+ (\underline{W}^{-1})^+ (\underline{X}^{-1})^+ \\ = \underline{X}^{-1} \underline{M} \underline{I} \underline{M}^+ \underline{X} \\ = \underline{X}^+ \underline{M} \underline{M}^+ \underline{X} \end{aligned} \quad (4.14)$$

$$\begin{aligned} &= \underline{X}^+ \underline{M} \underline{X} \underline{X}^+ \underline{M}^+ \underline{X} \\ &= \text{diag}(g_1, g_2, \dots) \text{diag}(g_1, g_2, \dots) \\ &= \text{diag}(g_1^2, g_2^2, \dots) \end{aligned} \quad (4.15)$$

The conclusion is obvious; not only does the transformation matrix $\underline{B}$ 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, $\underline{B}$ is the transformation matrix $\underline{A}$ of (4.4), the diagonal elements of $\text{diag}(g_1, g_2, \dots)$ are the natural expansion coefficients, and the occupation numbers of the natural orbitals are the diagonal elements of $\text{diag}(g_1^2, g_2^2, \dots)$.

In summary, if

$$\underline{\chi} = \underline{\phi} \underline{B}$$

and B satisfies (4.8) and (4.9) then

$$\phi(\bar{r}_1, \bar{r}_2) = \sum_k g_k \chi_k(\bar{r}_1) \chi_k(\bar{r}_2) \quad , \quad (4.16)$$

$$\gamma(\bar{r}_1; \bar{r}_1') = 2 \sum_k n_k \chi_k(\bar{r}_1) \chi_k(\bar{r}_1') \quad , \quad (4.17)$$

and

$$n_k = g_k^2$$

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:

$$\Psi(\bar{x}_1, \bar{x}_2) = 2^{-1/2} [\alpha(s_1)\beta(s_2) - \beta(s_1)\alpha(s_2)] \sum_k g_k \chi_k(\bar{r}_1) \chi_k(\bar{r}_2) \quad . \quad (4.18)$$

It is possible to derive a form similar to (4.18) for the triplet state.

Integration of (4.17) over $\bar{r}_1$ gives the expected result,

$$\sum_k n_k = 1 \quad . \quad (4.19)$$

If the basis orbitals were orthonormal then

$$\underline{\Delta} = \underline{I}$$

and from (4.3)

$$\underline{\gamma} = \underline{F} \underline{F}^+$$

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⁽²⁹⁾, in this case the rank of the determinant with elements $\{f_{ij}\}$ (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 Ψ is an exact two-electron eigenfunction and Ψ_r an arbitrary two-electron wave function of rank r , then

$$\int |\Psi(\bar{x}_1, \bar{x}_2) - \Psi_r(\bar{x}_1, \bar{x}_2)|^2 dx_1 dx_2 =$$

$$2(1 - \int \Psi^*(\bar{x}_1, \bar{x}_2) \Psi_r(\bar{x}_1, \bar{x}_2) dx_1 dx_2)$$

has a minimum value if the function Ψ_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 $|g_1| > |g_2| > \dots > |g_r|$. The theorem is also true if Ψ is

not an exact eigenfunction but an approximation of rank greater than r .

Application of the natural orbital analysis to the ZHZ^{2Z-1} problem is straight forward. The elements $\{f_{ij}\}$ of the coefficient matrix $\underline{F}$ are simply

$$\begin{aligned} f_{11} &= 2C_1 \quad , \\ f_{22} &= 2C_2 \quad , \\ f_{33} &= 2C_3 \quad , \\ f_{12} &= f_{21} = C_4 \quad , \\ f_{13} &= f_{31} = f_{23} = f_{32} = 0 \quad . \end{aligned}$$

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

$$\begin{aligned} \Delta_{11} &= 2(1 + \langle 1s_B | 1s_C \rangle) \quad , \\ \Delta_{22} &= 1.0 \quad , \\ \Delta_{33} &= 2(1 - \langle 1s_B | 1s_C \rangle) \quad , \\ \Delta_{12} &= \Delta_{21} = 2\langle 1s_A | 1s_B \rangle \quad , \\ \Delta_{13} &= \Delta_{31} = \Delta_{23} = \Delta_{32} = 0 \quad . \end{aligned}$$

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 $Z=1.00A.U.$ AND $R=1.66BOHR.$

0.99499 -0.08870 -0.04613

0.42283 -0.44059 0.00000

0.33163 1.09361 0.00000

0.00000 0.00000 1.46034

$\theta = 30.00$

0.99421 -0.08988 -0.05895

0.41813 -0.48728 0.00000

0.36076 1.11519 0.00000

0.00000 0.00000 1.22370

$\theta = 40.00$

0.99347 -0.08831 -0.07220

0.41335 -0.53323 0.00000

0.38540 1.13510 0.00000

0.00000 0.00000 1.08886

$\theta = 50.00$

0.99270 -0.08529 -0.08529

0.40793 -0.57826 0.00000

0.40793 1.15652 0.00000

0.00000 0.00000 1.00158

$\theta = 60.00$

0.99187 -0.09773 -0.08151

0.40154 0.00000 -0.62243

0.42975 0.00000 1.17851

0.00000 0.93991 0.00000

$\theta = 70.00$

0.99100 -0.10925 -0.07731

0.39435 0.00000 -0.66539

0.45038 0.00000 1.20144

0.00000 0.39509 0.00000

$\theta = 80.00$

0.98929 -0.12380 -0.06866

0.37845 0.00000 -0.74456

0.48833 0.00000 1.24523

0.00000 0.33487 0.00000

$\theta = 100.00$

0.98787 -0.14300 -0.06051

0.36089 0.00000 -0.81242

0.52426 0.00000 1.28309

0.00000 0.79834 0.00000

$\theta = 120.00$

0.98664 -0.15473 -0.05105

0.33793 0.00000 -0.87994

0.56569 0.00000 1.31632

0.00000 0.76931 0.00000

$\theta = 150.00$

0.98633 -0.15759 -0.04719

0.32756 0.00000 -0.90220

0.58346 0.00000 1.32319

0.00000 0.76029 0.00000

$\theta = 180.00$

TABLE 2.2. NATURAL EXPANSION COEFFICIENTS (FIRST ROW) AND TRANSFORMATION MATRICES FOR $Z=1.40A.U.$ AND $R=1.66BCHR.$

0.99763 -0.06043 -0.03280

0.50584 0.00000 -0.30423

0.16004 0.00000 1.07071

0.00000 1.25334 0.00000

$\theta = 30.00$

0.99567 -0.03322 -0.04134

0.50671 0.00000 -0.36269

0.20124 0.00000 1.03573

0.00000 1.07833 0.00000

$\theta = 40.00$

0.99236 -0.11324 -0.04889

0.50430 0.00000 -0.43002

0.24540 0.00000 1.10494

0.00000 0.96079 0.00000

$\theta = 52.15$

0.93972 -0.13317 -0.05219

0.50105 0.00000 -0.47170

0.27240 0.00000 1.11697

0.00000 0.90959 0.00000

$\theta = 60.00$

0.93590 -0.15321 -0.05457

0.49572 0.00000 -0.52147

0.30403 0.00000 1.13159

0.00000 0.86135 0.00000

$\theta = 70.00$

0.93178 -0.18185 -0.05520

0.48963 0.00000 -0.56659

0.33136 0.00000 1.14595

0.00000 0.82694 0.00000

$\theta = 80.00$

0.97355 -0.22213 -0.05350

0.47623 0.00000 -0.64156

0.37773 0.00000 1.16339

0.00000 0.78176 0.00000

$\theta = 100.00$

0.96685 -0.25036 -0.05026

0.46242 0.00000 -0.69639

0.41337 0.00000 1.18447

0.00000 0.75654 0.00000

$\theta = 120.00$

0.96112 -0.27227 -0.04600

0.44597 0.00000 -0.74312

0.44970 0.00000 1.19401

0.00000 0.73367 0.00000

$\theta = 150.00$

0.95961 -0.27783 -0.04434

0.43948 0.00000 -0.75702

0.46254 0.00000 1.19503

0.00000 0.73334 0.00000

$\theta = 180.00$

TABLE 2.3. NATURAL EXPANSION COEFFICIENTS (FIRST ROW) AND
TRANSFORMATION MATRICES FOR $Z=1.80A.U.$ AND $R=1.66BOHR.$

0.99740 -0.07124 -0.01050

0.54714 0.00000 -0.20615

0.06955 0.00000 1.04242

0.00000 1.11300 0.00000

$\theta = 30.00$

0.99417 -0.10667 -0.01549

0.55913 0.00000 -0.26161

0.09961 0.00000 1.05735

0.00000 0.98057 0.00000

$\theta = 40.00$

0.98324 -0.15147 -0.02077

0.56693 0.00000 -0.31976

0.13340 0.00000 1.07236

0.00000 0.89762 0.00000

$\theta = 50.50$

0.98005 -0.19719 -0.02439

0.57073 0.00000 -0.37010

0.16363 0.00000 1.08571

0.00000 0.84631 0.00000

$\theta = 60.00$

0.96347 -0.24758 -0.02738

0.57249 0.00000 -0.41741

0.19263 0.00000 1.09714

0.00000 0.80894 0.00000

$\theta = 70.00$

0.95461 -0.29338 -0.02948

0.57249 0.00000 -0.45377

0.21795 0.00000 1.10681

0.00000 0.78191 0.00000

$\theta = 80.00$

0.92605 -0.37625 -0.02950

0.57001 0.00000 -0.52079

0.25568 0.00000 1.12094

0.00000 0.74398 0.00000

$\theta = 100.00$

0.90400 -0.42659 -0.02337

0.56556 0.00000 -0.55863

0.23160 0.00000 1.12742

0.00000 0.73263 0.00000

$\theta = 120.00$

0.88657 -0.46181 -0.02683

0.56067 0.00000 -0.53623

0.30143 0.00000 1.13163

0.00000 0.72245 0.00000

$\theta = 150.00$

0.88181 -0.47087 -0.02635

0.55900 0.00000 -0.59373

0.30709 0.00000 1.13264

0.00000 0.72000 0.00000

$\theta = 180.00$

TABLE 2.4. NATURAL EXPANSION COEFFICIENTS (FIRST ROW) AND TRANSFORMATION MATRICES FOR $Z=2.20A.U.$ AND $R=1.66BOHR.$

0.99665 -0.03166 -0.00362	0.99132 -0.13137 -0.00594
0.57025 0.00000 -0.14201	0.53936 0.00000 -0.19101
0.03020 0.00000 1.02302	0.04368 0.00000 1.03536
0.00000 1.01697 0.00000	0.00000 0.91087 0.00000
$\theta = 30.00$	$\theta = 40.00$
0.93033 -0.19716 -0.00848	0.96105 -0.27619 -0.01057
0.60542 0.00000 -0.24132	0.61715 0.00000 -0.28805
0.07120 0.00000 1.04813	0.09397 0.00000 1.05970
0.00000 0.84463 0.00000	0.00000 0.80064 0.00000
$\theta = 50.00$	$\theta = 60.00$
0.93317 -0.35925 -0.01171	0.90103 -0.43361 -0.01185
0.62573 0.00000 -0.32305	0.63173 0.00000 -0.35933
0.11457 0.00000 1.06904	0.13076 0.00000 1.07607
0.00000 0.77057 0.00000	0.00000 0.75050 0.00000
$\theta = 70.00$	$\theta = 80.00$
0.84570 -0.53355 -0.01083	0.81351 -0.58147 -0.00990
0.63373 0.00000 -0.39722	0.64158 0.00000 -0.41616
0.15113 0.00000 1.03362	0.16143 0.00000 1.08724
0.00000 0.72352 0.00000	0.00000 0.71904 0.00000
$\theta = 100.00$	$\theta = 120.00$
-0.79299 0.60916 0.00929	-0.78806 0.61552 0.00916
0.64293 0.00000 -0.42746	0.64306 0.00000 -0.43061
0.16832 0.00000 1.03895	0.17026 0.00000 1.08948
0.00000 0.71371 0.00000	0.00000 0.71250 0.00000
$\theta = 150.00$	$\theta = 180.00$

TABLE 2.5. NATURAL EXPANSION COEFFICIENTS (FIRST ROW) AND
TRANSFORMATION MATRICES FOR $Z=1.80A.U.$ AND $R=1.50BOHR.$

0.99303 -0.06130 -0.01320

0.53634 0.00000 -0.23367

0.03039 0.00000 1.05864

0.00000 1.16689 0.00000

$\theta = 30.00$

0.99584 -0.08931 -0.01820

0.54575 0.00000 -0.29605

0.10889 0.00000 1.07859

0.00000 1.02526 0.00000

$\theta = 40.00$

0.99225 -0.12209 -0.02314

0.55059 0.00000 -0.35346

0.14101 0.00000 1.09781

0.00000 0.93729 0.00000

$\theta = 50.00$

0.93699 -0.15846 -0.02731

0.55214 0.00000 -0.40895

0.17274 0.00000 1.11648

0.00000 0.87828 0.00000

$\theta = 60.00$

0.97999 -0.19675 -0.03028

0.55146 0.00000 -0.46021

0.20266 0.00000 1.13334

0.00000 0.83607 0.00000

$\theta = 70.00$

0.97156 -0.23463 -0.03196

0.54938 0.00000 -0.50578

0.22887 0.00000 1.14854

0.00000 0.80571 0.00000

$\theta = 80.00$

0.95309 -0.30094 -0.03243

0.54264 0.00000 -0.58008

0.27143 0.00000 1.17366

0.00000 0.76695 0.00000

$\theta = 100.00$

0.93666 -0.34884 -0.03133

0.53577 0.00000 -0.62848

0.30147 0.00000 1.18781

0.00000 0.74575 0.00000

$\theta = 120.00$

0.92179 -0.38657 -0.02955

0.52331 0.00000 -0.66620

0.32616 0.00000 1.19311

0.00000 0.73181 0.00000

$\theta = 150.00$

-0.91734 0.39705 0.02891

0.52567 0.00000 -0.67705

0.33353 0.00000 1.20096

0.00000 0.72827 0.00000

$\theta = 180.00$

TABLE 2.6. NATURAL EXPANSION COEFFICIENTS (FIRST ROW) AND
TRANSFORMATION MATRICES FOR $Z=1.80A.U.$ AND $R=1.80BOHR.$

0.99670 -0.03079 -0.00849

0.55543 0.00000 -0.13145

0.06165 0.00000 1.03186

0.00000 1.07155 0.00000

$\theta = 30.00$

0.99221 -0.12335 -0.01316

0.57012 0.00000 -0.23472

0.09136 0.00000 1.04382

0.00000 0.94341 0.00000

$\theta = 40.00$

0.93409 -0.17678 -0.01305

0.53022 0.00000 -0.23312

0.12337 0.00000 1.05524

0.00000 0.87360 0.00000

$\theta = 50.00$

0.97126 -0.23697 -0.02217

0.58674 0.00000 -0.33306

0.15444 0.00000 1.06513

0.00000 0.82370 0.00000

$\theta = 60.00$

0.95391 -0.29907 -0.02435

0.59062 0.00000 -0.33203

0.13195 0.00000 1.07327

0.00000 0.73935 0.00000

$\theta = 70.00$

0.93331 -0.35681 -0.02607

0.59249 0.00000 -0.41925

0.20543 0.00000 1.07967

0.00000 0.76535 0.00000

$\theta = 80.00$

0.89614 -0.44304 -0.02567

0.59263 0.00000 -0.47143

0.23923 0.00000 1.03751

0.00000 0.73756 0.00000

$\theta = 100.00$

0.87100 -0.49063 -0.02437

0.59095 0.00000 -0.50070

0.25922 0.00000 1.09105

0.00000 0.72477 0.00000

$\theta = 120.00$

0.85353 -0.52053 -0.02321

0.58782 0.00000 -0.52141

0.27548 0.00000 1.09236

0.00000 0.71715 0.00000

$\theta = 150.00$

0.85076 -0.52507 -0.02258

0.58522 0.00000 -0.53216

0.27955 0.00000 1.09742

0.00000 0.71607 0.00000

$\theta = 180.00$

TABLE 3. OCCUPATION NUMBERS.

θ	Z=1.00 R=1.00	Z=1.40 R=1.66	Z=1.30 R=1.66	Z=2.20 R=1.66	Z=1.30 R=1.50	Z=1.80 R=1.80
30.00	0.99001 0.00787 0.00213	0.99527 0.00366 0.00103	0.99432 0.00507 0.00011	0.99332 0.00667 0.00001	0.99607 0.00376 0.00017	0.99340 0.00653 0.00007
40.00	0.93845 0.00803 0.00347	0.99137 0.00693 0.00171	0.93833 0.01133 0.00024	0.93271 0.01726 0.00004	0.99169 0.00793 0.00033	0.93449 0.01534 0.00017
50.00	0.93699 0.00780 0.00521	0.93479* 0.01282 0.00239	0.97663+ 0.02294 0.00043	0.96105 0.03837 0.00007	0.93456 0.01491 0.00054	0.93842 0.03125 0.00033
60.00	0.93545 0.00727 0.00727	0.97954 0.01773 0.00272	0.96050 0.03883 0.00062	0.92361 0.07628 0.00011	0.97414 0.02511 0.00075	0.94335 0.05615 0.00049
70.00	0.93331 0.00955 0.00664	0.97199 0.02503 0.00293	0.93793 0.06130 0.00073	0.87080 0.12906 0.00014	0.96037 0.03371 0.00092	0.90934 0.08944 0.00062
80.00	0.93209 0.01194 0.00593	0.96333 0.03307 0.00305	0.91129 0.03734 0.00037	0.81185 0.18801 0.00014	0.94393 0.05505 0.00102	0.87201 0.12731 0.00063
100.00	0.97370 0.01659 0.00471	0.94730 0.04934 0.00286	0.85757 0.14156 0.00087	0.71520 0.23463 0.00012	0.90333 0.09057 0.00105	0.80306 0.19623 0.00066
120.00	0.97539 0.02045 0.00363	0.93479 0.06263 0.00253	0.81721 0.13193 0.00031	0.66130 0.33311 0.00010	0.87733 0.12169 0.00093	0.75864 0.24077 0.00059
150.00	0.97345 0.02394 0.00261	0.92375 0.07413 0.00212	0.78601 0.21327 0.00072	0.62333 0.37103 0.00009	0.84969 0.14943 0.00037	0.72351 0.27095 0.00054
180.00	0.97294 0.02484 0.00223	0.92034 0.07719 0.00197	0.77759 0.22172 0.00069	0.62105 0.37837 0.00003	0.84151 0.15765 0.00084	0.72330 0.27569 0.00051

* Values for $\theta = 52.15$

+ Values for $\theta = 50.50$

The explicit forms and symmetries of the natural orbitals obtained in the ZHZ^{2Z-1} calculations are

$$\begin{aligned}\chi_1(t) &= [A_{11}(1s_B + 1s_C) + A_{21}1s_A(t)] , & A_1 \\ \chi_2(t) &= [A_{32}(1s_B - 1s_C)(t)] , & B_1 \\ \chi_3(t) &= [A_{13}(1s_B + 1s_C) + A_{23}1s_A(t)] , & A_1\end{aligned}\quad (4.20)$$

where t is $\bar{r}_1$ or $\bar{r}_2$. This order assumes that $n_1 > n_2 > n_3$, but in some cases χ_2 and χ_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

$$\gamma(\bar{x}_1 : \bar{x}_1') = N \int |\Psi(\bar{x}_1', \bar{x}_2, \dots, \bar{x}_N)|^2 dx_2 dx_3 \dots dx_N ,$$

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 $\gamma(\bar{r}_1 : \bar{r}_1')$ is obtained by integrating $\gamma(\bar{x}_1 : \bar{x}_1')$ over the remaining spin co-ordinate. The result may then be rearranged so that, for example, all of the terms containing the orbital product $\varphi_{iA}^*(\bar{r}_1) \varphi_{jB}(\bar{r}_1)$ are grouped together. $\varphi_{iA}(\bar{r}_1)$ and $\varphi_{jB}(\bar{r}_1)$ 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 $t_{ij} \varphi_{iA}^*(\bar{r}_1) \varphi_{jB}(\bar{r}_1)$, 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:

$$N(A) = \sum_{ij} t_{ij} \langle \varphi_{iA} | \varphi_{jA} \rangle,$$

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

$$S(AB) = \sum_{kl} t_{kl} \langle \varphi_{kA} | \varphi_{lB} \rangle, \quad (4.21)$$

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

Obviously

$$\int \gamma(\bar{x}_1 : \bar{x}_1) d\mathbf{x}_1 = \sum_A N(A) + \sum_{(AB)} S(AB).$$

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 ZHZ^{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,

$$\rho(r) = \gamma(\bar{r}_1; \bar{r}_1) = 2 \sum_k n_k \chi_k^*(\bar{r}_1) \chi_k(\bar{r}_1) \quad .$$

In general,

$$\chi_k(\bar{r}_1) = \sum_{Ai} \varphi_{iA}(\bar{r}_1) a_{iAk} \quad ,$$

where φ_{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 ;

$$N_k(A) = 2n_k \sum_{ij} \langle \varphi_{iA} | \varphi_{jA} \rangle a_{iAk}^* a_{jAk} \quad ,$$

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

$$N(A) = \sum_k N_k(A) \quad ,$$

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

$$S_k(AB) = 2n_k \sum_{ij} \langle \varphi_{iA} | \varphi_{jB} \rangle a_{iAk}^* a_{jBk} \quad ,$$

(iv) overlap population $S(AB)$ of the overlap region A-B;

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

(v) total atomic (or local) population N_L ;

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

(vi) total overlap (or shared) population S_S ;

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

and obviously

$$N_L + S_S = N \quad ,$$

the number of electrons.

The natural orbitals of the ZHZ^{2Z-1} ions are few in number, and of a relatively simple form. From (4.20) we have,

$$\begin{aligned} \chi_1^2 = & A_{11}^2(1s_B 1s_B + 2 \cdot 1s_B 1s_C + 1s_C 1s_C) + A_{21}^2(1s_A 1s_A) \\ & + 2A_{11}A_{21}(1s_B 1s_A + 1s_C 1s_A) \quad , \end{aligned}$$

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

$$\begin{aligned} \chi_3^2 = & A_{13}^2(1s_B 1s_B + 2 \cdot 1s_B 1s_C + 1s_C 1s_C) + A_{23}^2(1s_A 1s_A) \\ & + 2A_{13}A_{23}(1s_B 1s_A + 1s_C 1s_A) \quad . \end{aligned}$$

The atomic populations are:

$$N_1(A) = 2n_1 A_{21}^2 ; N_1(B) = N_1(C) = 2n_1 A_{11}^2 ;$$

$$N_2(A) = 0 ; N_2(B) = N_2(C) = 2n_2 A_{32}^2 ;$$

$$N_3(A) = 2n_3 A_{23}^2 ; N_3(B) = N_3(C) = 2n_3 A_{13}^2 ;$$

$$N(A) = 2(n_1 A_{21}^2 + n_3 A_{23}^2) ,$$

and

$$N(B) = N(C) = 2(n_1 A_{11}^2 + n_2 A_{32}^2 + n_3 A_{13}^2) .$$

The overlap populations are:

$$S_1(AB) = S_1(AC) = 4n_1 A_{11} A_{21} S_{AB} ; S_1(BC) = 4n_1 A_{11}^2 S_{BC} ;$$

$$S_2(AB) = S_2(AC) = 0 ; S_2(BC) = -4n_2 A_{32}^2 S_{BC} ;$$

$$S_3(AB) = S_3(AC) = 4n_3 A_{13} A_{23} S_{AB} ; S_3(BC) = 4n_3 A_{13}^2 S_{BC} ;$$

$$S(AB) = S(AC) = 4S_{AB}(n_1 A_{11} A_{21} + n_3 A_{13} A_{23}) ,$$

and

$$S(BC) = 4S_{BC}(n_1 A_{11}^2 - n_2 A_{32}^2 + n_3 A_{13}^2) .$$

S_{AB} and S_{BC} are the overlap integrals $\langle 1s_A | 1s_B \rangle$ and $\langle 1s_B | 1s_C \rangle$ respectively. A_{ij} are the elements of the transformation matrix.

Variations of the atomic and overlap populations as functions of Z and θ 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 θ (see Fig. 3.). Changes in the contours, as θ 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.

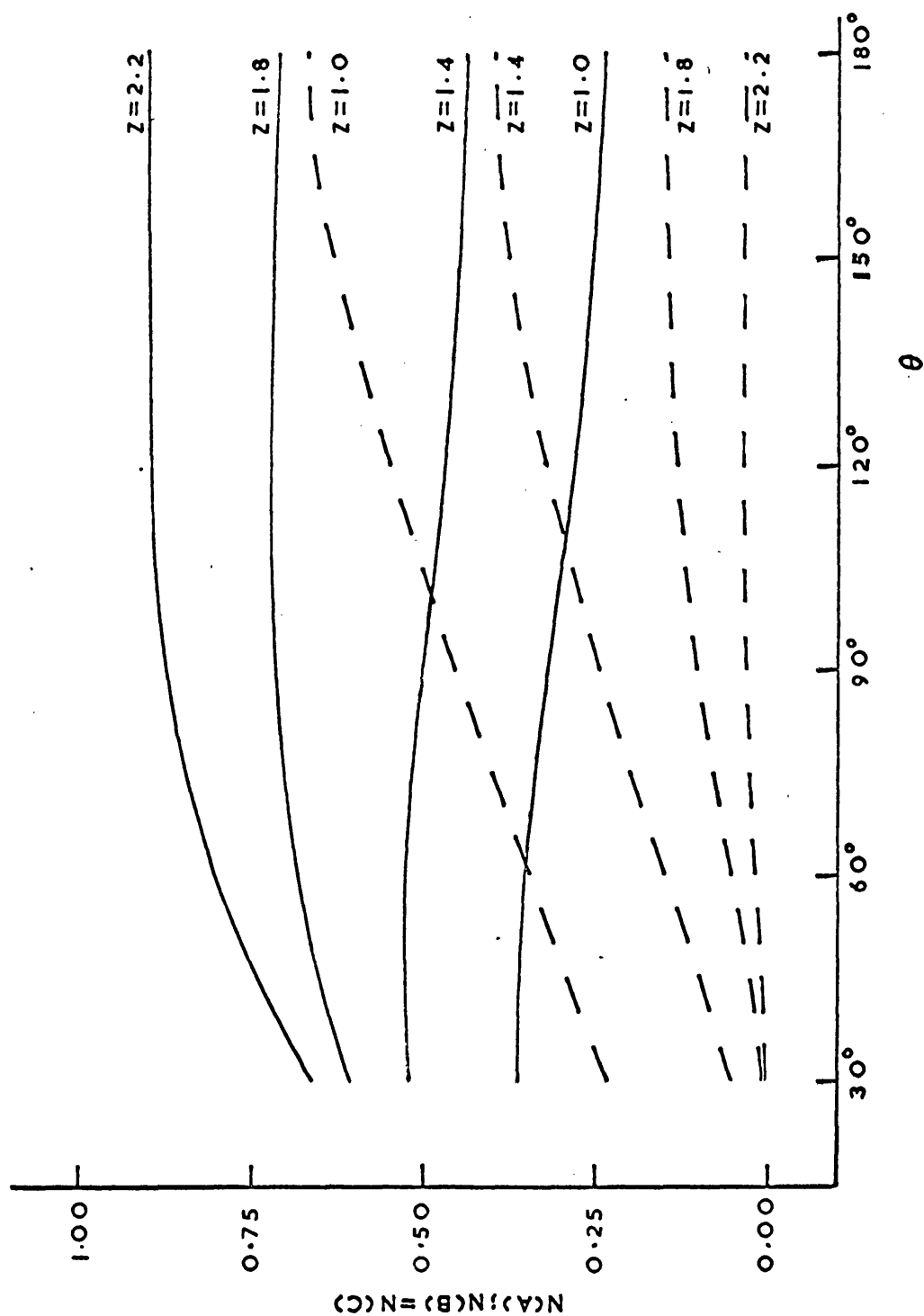


FIG. 4. The atomic population for centres A, B, and C as a function of the bond angle θ . The dotted lines are for centre A and the solid lines for centres B or C.

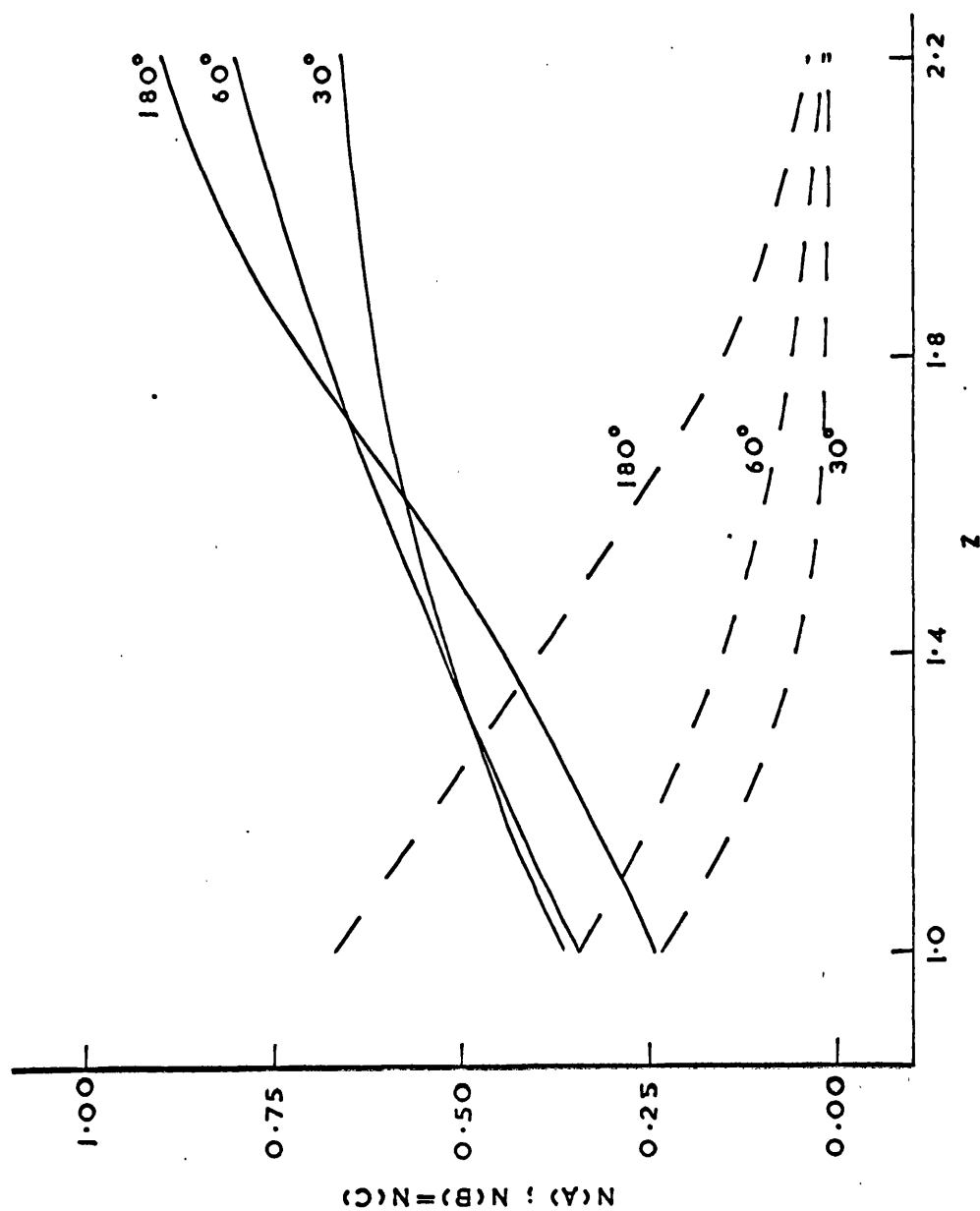


FIG. 5. The atomic population for centres A, B, and C as a function of Z . The dotted lines are for centre A and the solid lines for centres B or C.

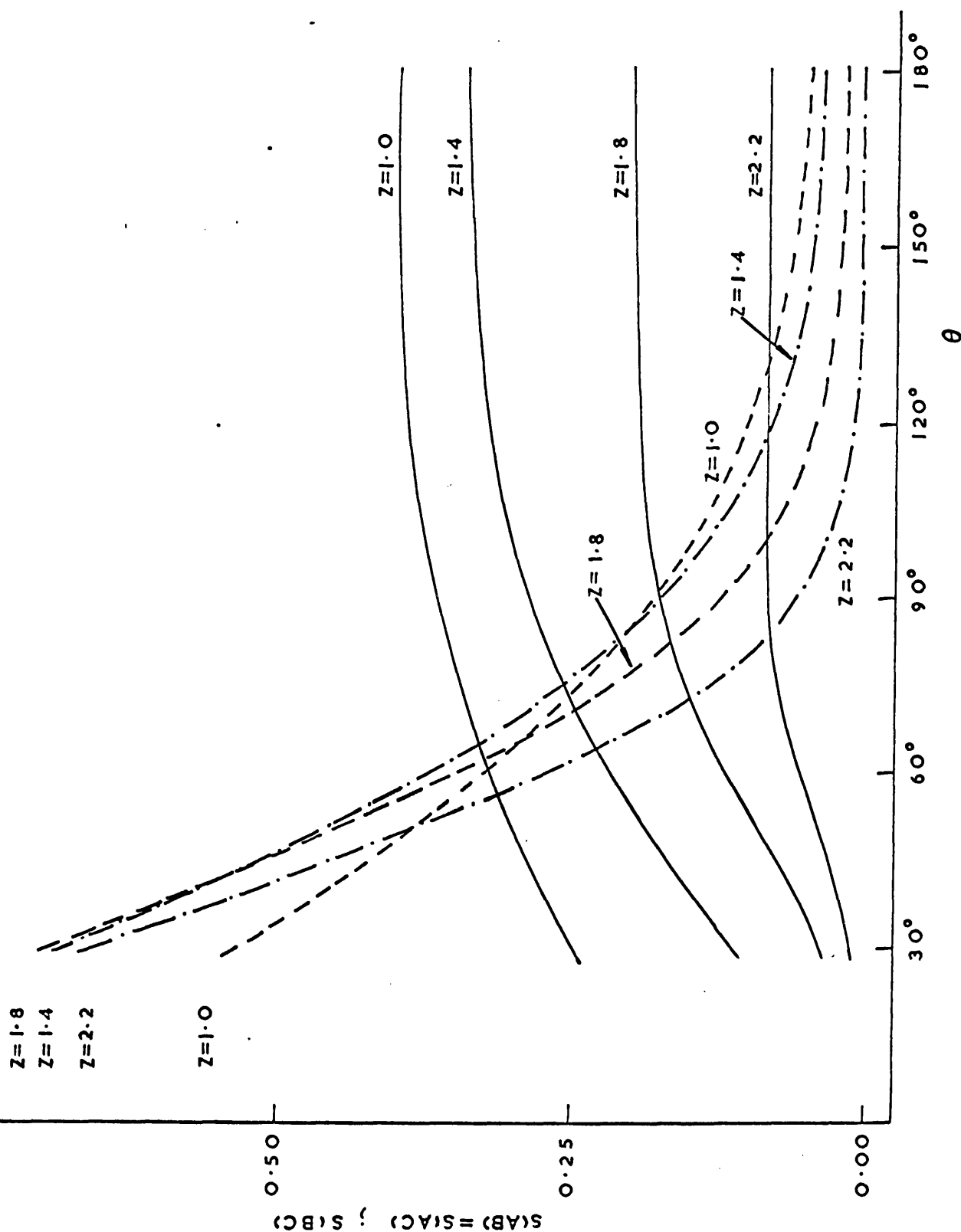


FIG.6. The overlap population for A-B, A-C, and B-C as a function of the bond angle θ . The dotted lines are for B-C and the solid lines for A-B or A-C.

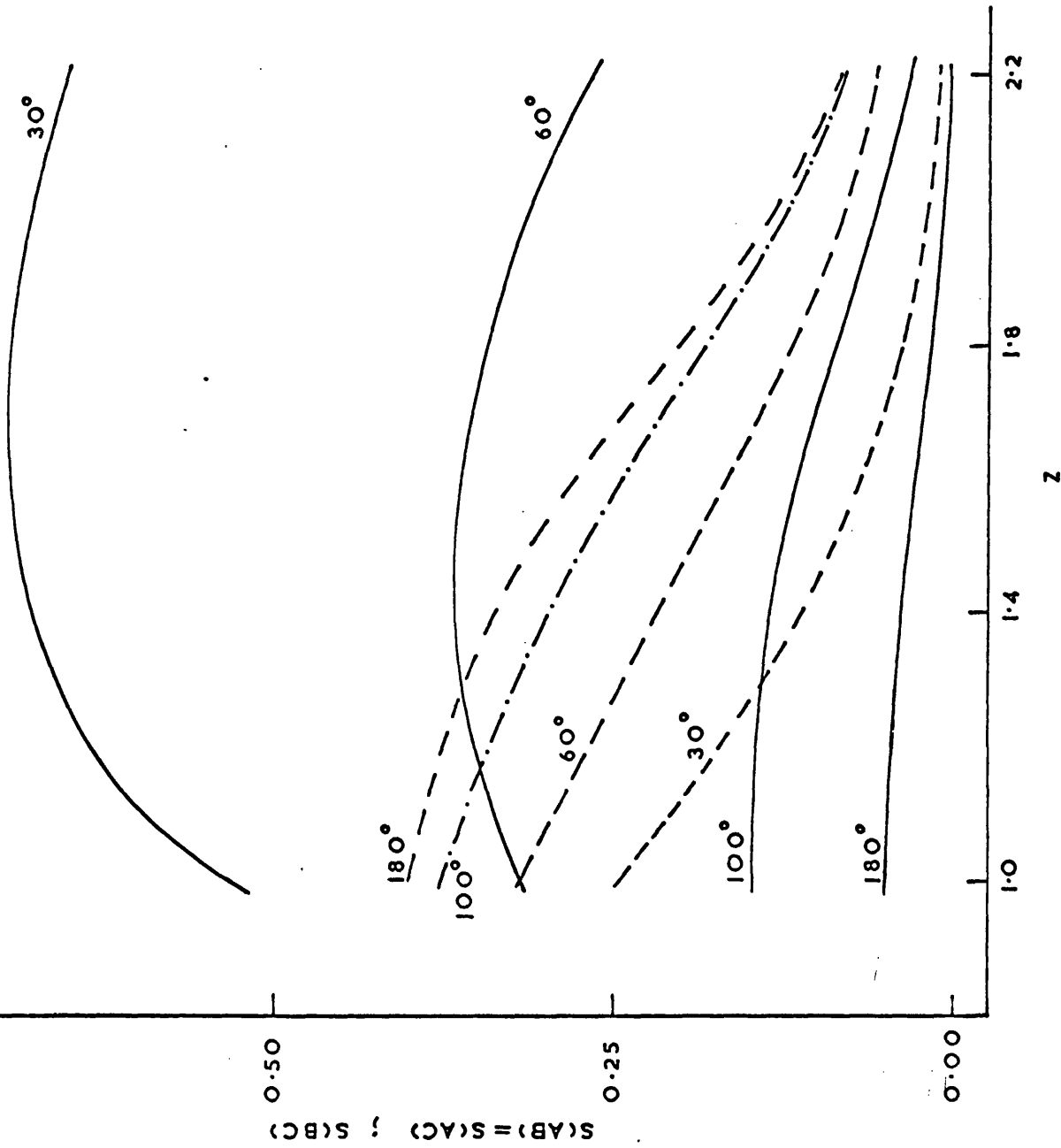


FIG. 7. The overlap population for A-B, A-C, and B-C as a function of Z . The dotted lines are for A-B or A-C and the solid lines for B-C.

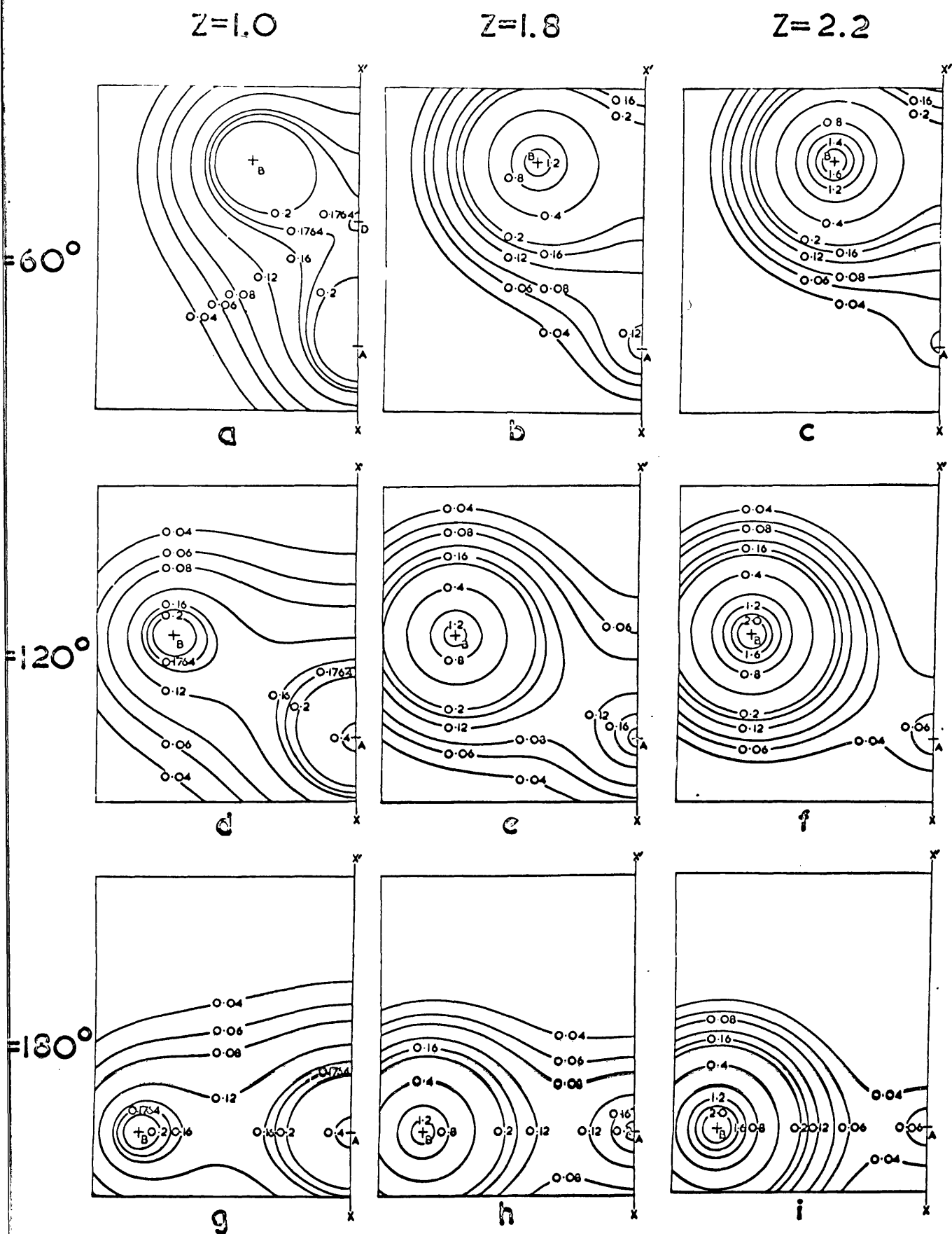


FIG. 8. Contour diagrams of the electron density in the plane of the molecule for selected values of Z and θ . The diagrams are symmetric about the line XX' which bisects the bond angle θ . In (a) the density at D is less than 0.1764.

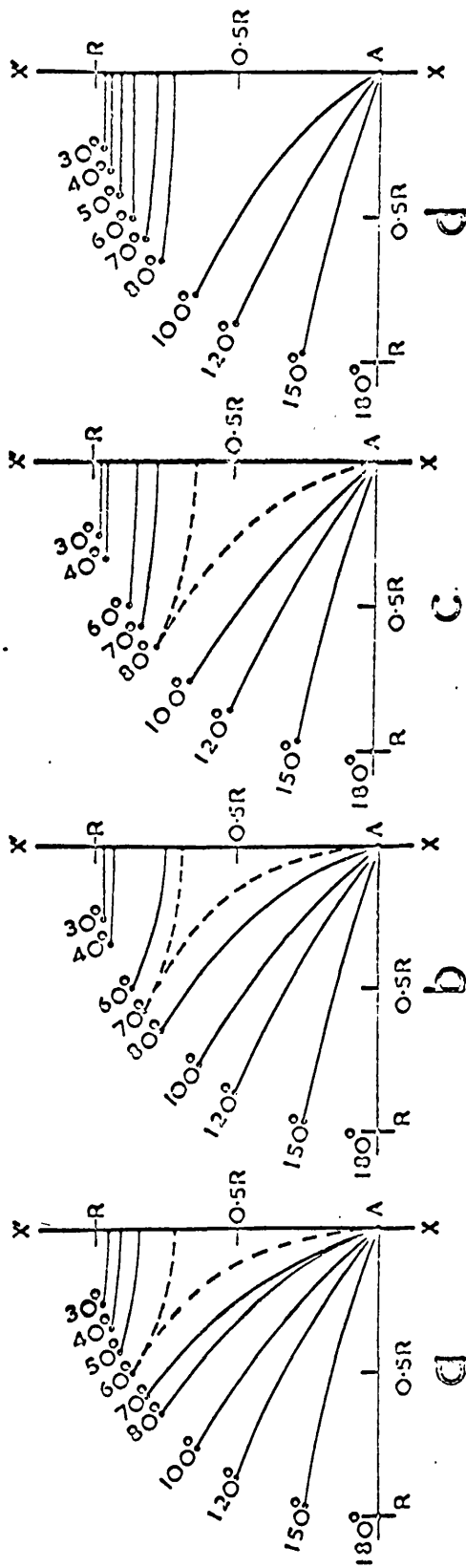


FIG. 9. The trace of points, between the centres B and C, with minimum slope in the electron-density surface when evaluated in the plane of the ZH_2^{2Z-1} ions for $Z = 1.0, 1.4, 1.8, \text{ and } 2.2$, see diagrams a, b, c, and d respectively. For each value of Z , the trace is shown for various values of the bond angle θ . The centre A is located at the origin and centre B is indicated by $\bullet$. Each set of diagrams is symmetric about XX' which bisects θ .

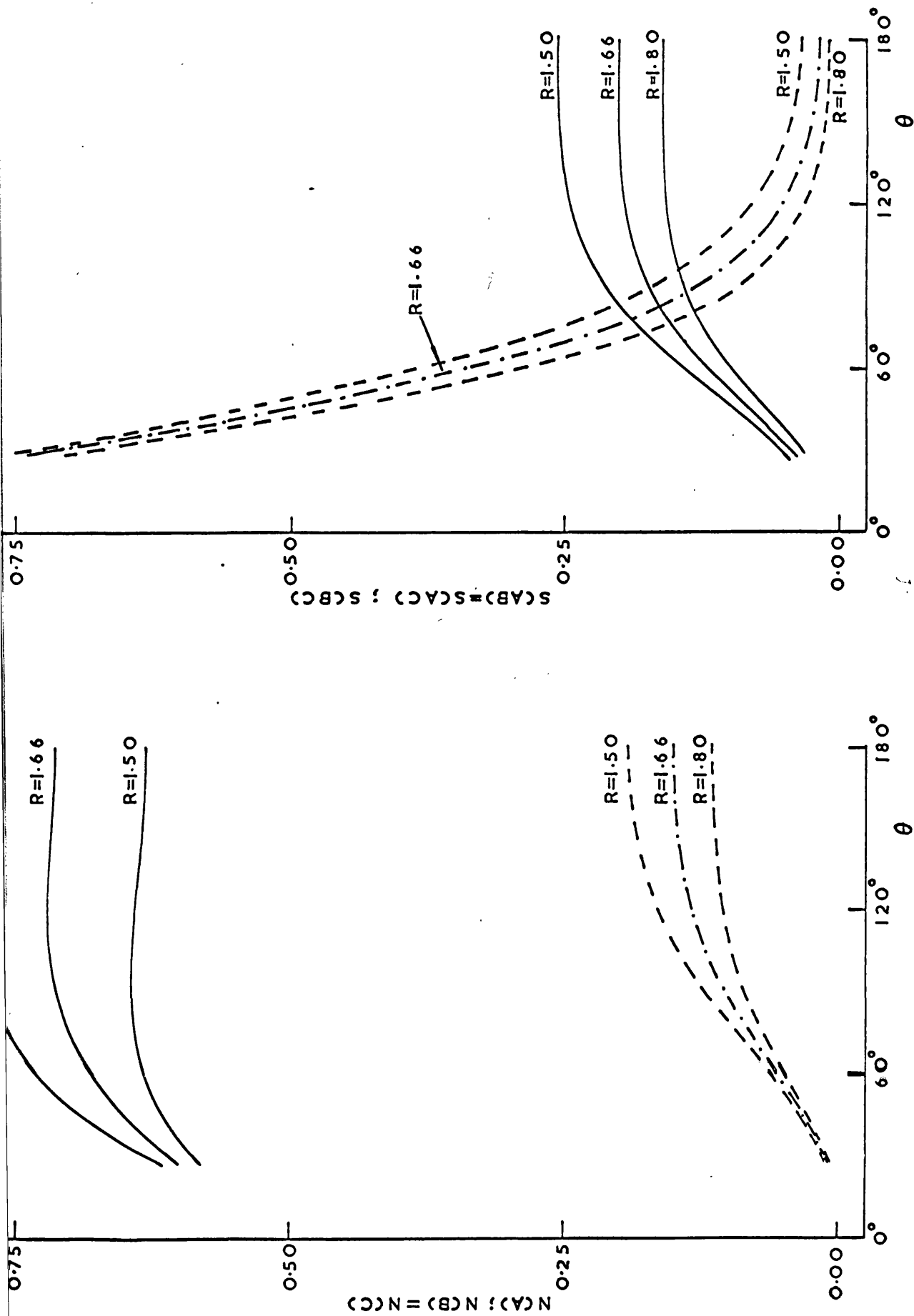


FIG. 10. The atomic and overlap populations for $Z = 1.8$ as a function of R . In the left-hand diagram the dotted lines are for A and in the right-hand diagram for B-C. The solid lines represent B or C in the left-hand diagram and A-B or A-C in the right-hand diagram.

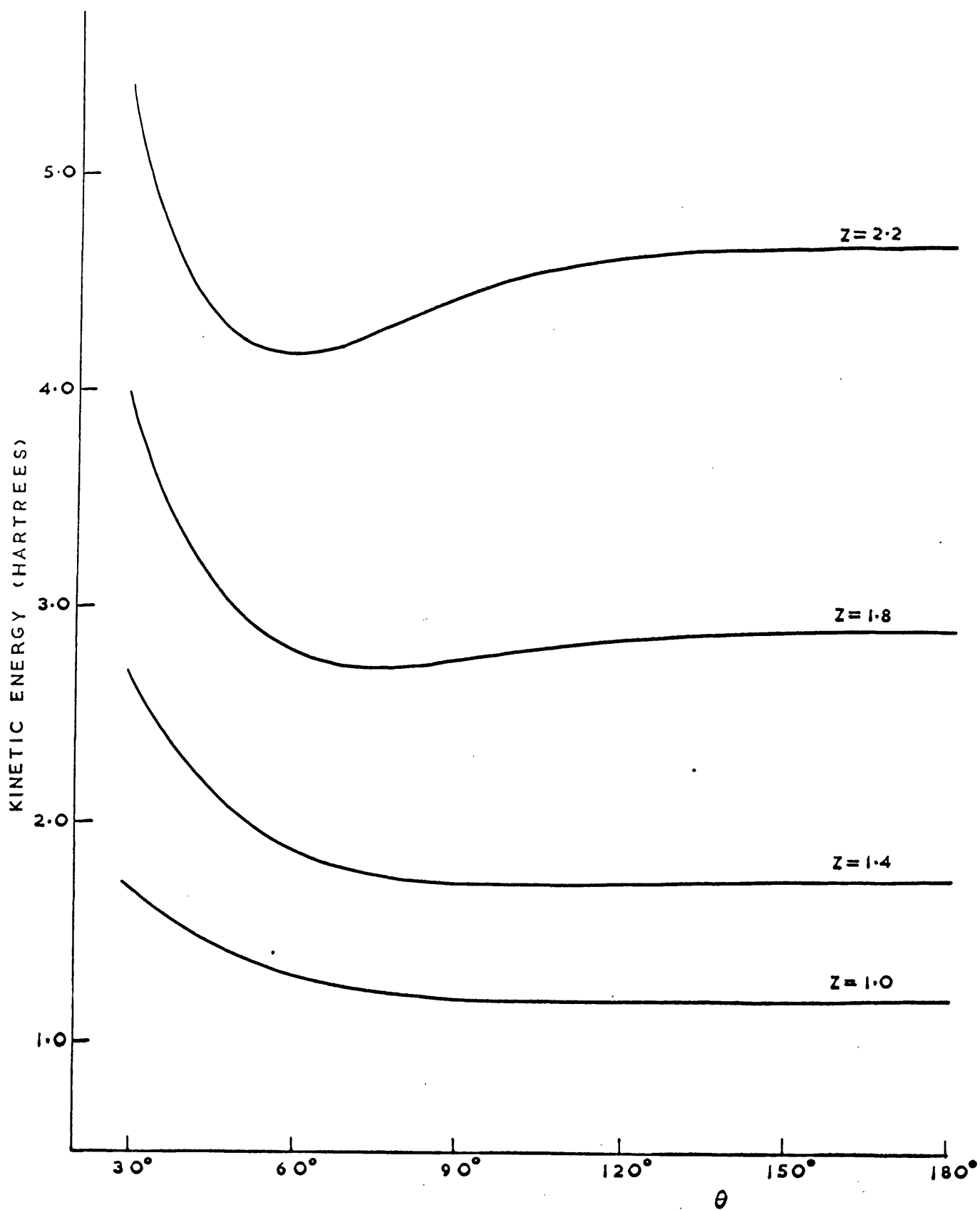


FIG. 11. The kinetic energy as a function of the bond angle θ .

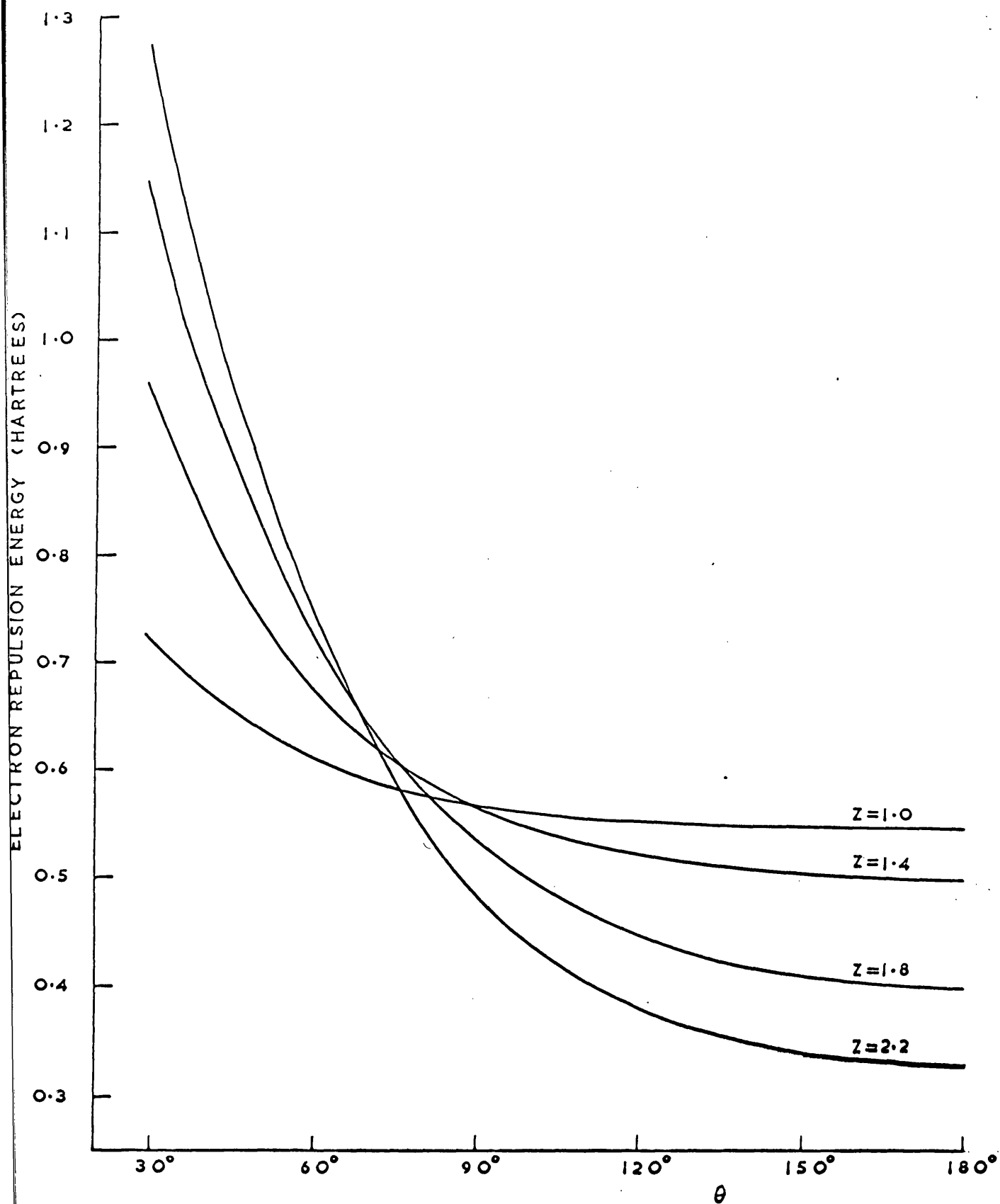


FIG. 12. The electron repulsion energy as a function of the bond angle θ .

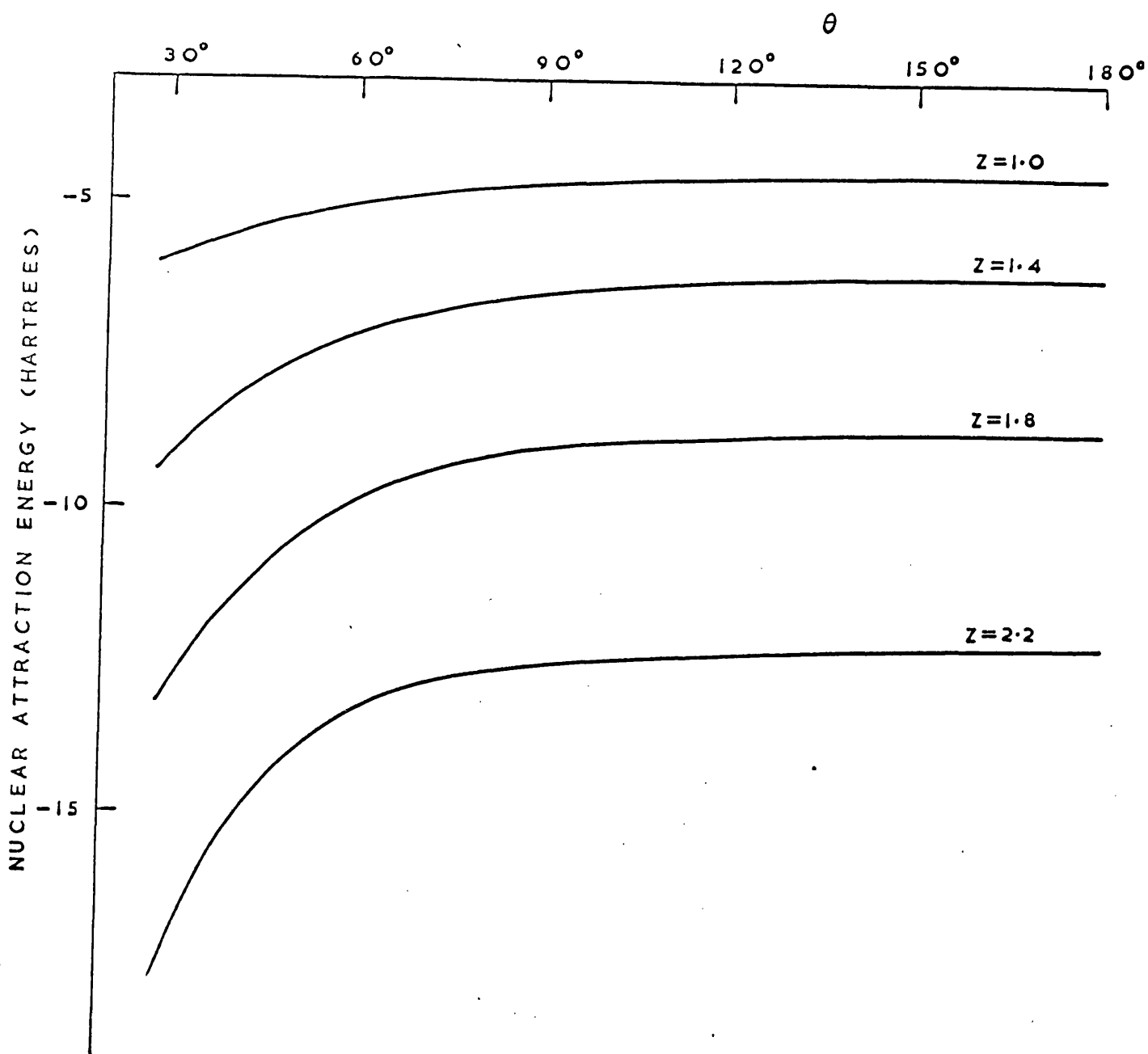


FIG. 13. The nuclear attraction energy as a function of the bond angle θ .

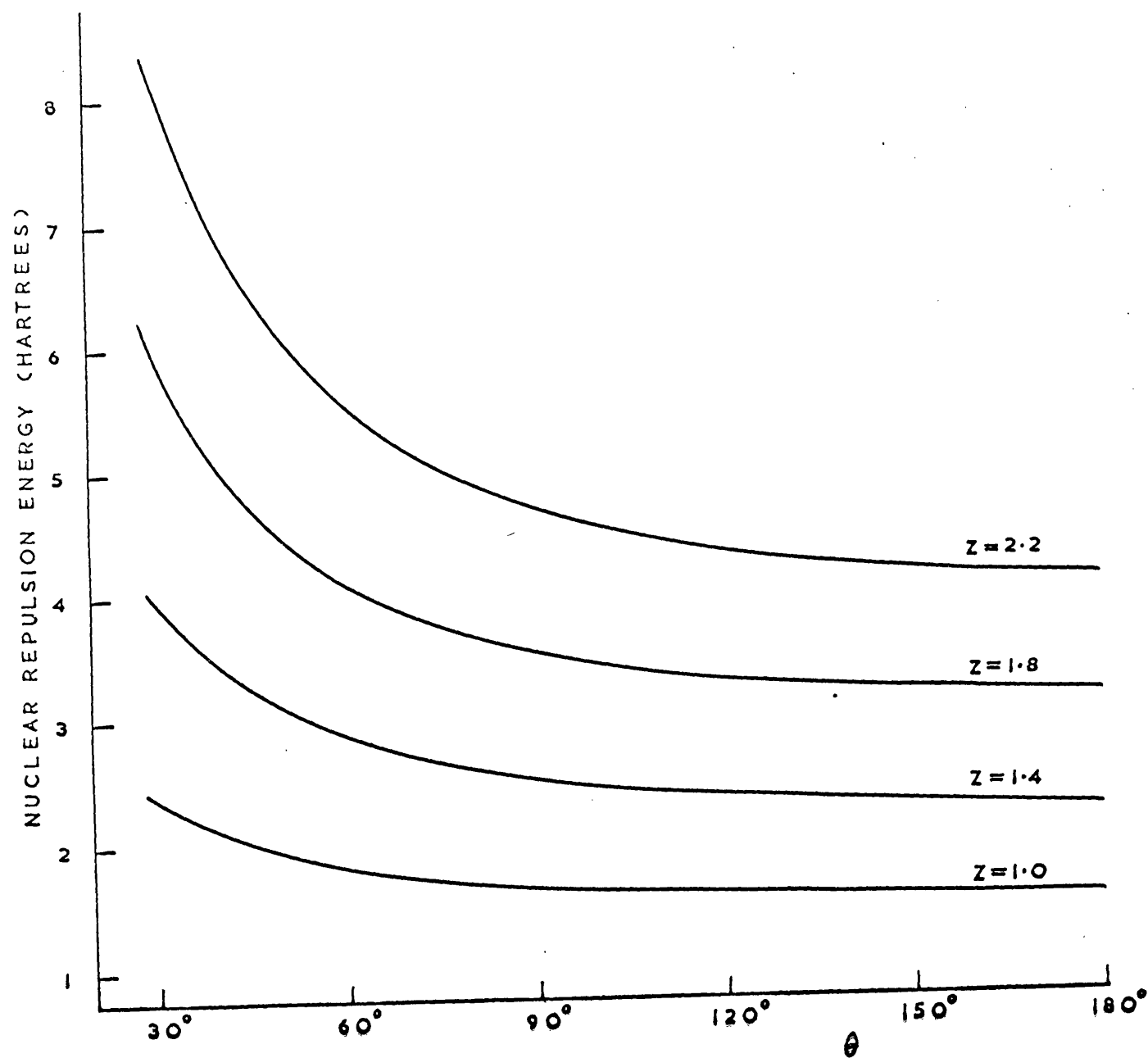


FIG. 14. The nuclear repulsion energy as a function of the bond angle θ .

D. Energy Analysis

As stated in Chapter 2, the behaviour of the electron energy of the $Z\text{H}Z^{2Z-1}$ 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 χ_1 and χ_3 are bonding-type orbitals whereas χ_2 is of an anti-bonding form. It is seen from the occupation numbers presented in Table 3 that for all values of θ , χ_1 predominates in the natural expansion of the wave function for $Z < 1.4$. Although a large occupation number for a bonding orbital does not necessarily guarantee the stability of the ZHZ^{2Z-1} ion for any choice of Z and θ , 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 ZHZ^{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° to 180° . 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 $\text{H} + \text{H} + \text{H}^+$. 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 θ . 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 θ increases, the occupation number associated with χ_2 increases greatly at the expense of n_1 . This would seem to indicate that, when Z and θ 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 θ increase, the occupation numbers for χ_1 and χ_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 ZHZ^{2Z-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 $S(AB) \simeq S(BC)$. 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 θ 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 θ increases, but the magnitude of $S(BC)$ is seen to decrease rapidly. Thus, as θ varies from 30° to 180° , 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 θ , 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⁽³¹⁾ of the configuration interaction wave function of Christoffersen⁽²²⁾ 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 χ_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 χ_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 χ_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 1s 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 ZHZ^{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 Φ (see (3.5)) are the valence bond (Φ_{VB}), the molecular orbital (Φ_{MO}), and three non-pairing of electrons forms (Φ_A , Φ_B , and Φ_C). Using the notation of the ZHZ^{2Z-1} work, these functions may be defined thus:

$$\begin{aligned}\Phi_{VB}(\bar{r}_1, \bar{r}_2) &= N_{VB} [(1s_B(\bar{r}_1) + k.1s_A(\bar{r}_1))(k.1s_B(\bar{r}_2) + 1s_A(\bar{r}_2)) \\ &\quad + (k.1s_B(\bar{r}_1) + 1s_A(\bar{r}_1))(1s_B(\bar{r}_2) + k.1s_A(\bar{r}_2)) \\ &\quad + (1s_C(\bar{r}_1) + k.1s_A(\bar{r}_1))(k.1s_C(\bar{r}_2) + 1s_A(\bar{r}_2)) \\ &\quad + (k.1s_C(\bar{r}_1) + 1s_A(\bar{r}_1))(1s_C(\bar{r}_2) + k.1s_A(\bar{r}_2))] \\ &= N_{VB} [0.5k\phi_1(\bar{r}_1, \bar{r}_2) + 2k\phi_2(\bar{r}_1, \bar{r}_2) + 0.5k\phi_3(\bar{r}_1, \bar{r}_2) \\ &\quad + (k^2 + 1)\phi_4(\bar{r}_1, \bar{r}_2)]\end{aligned}$$

$$\begin{aligned}\Phi_{MO}(\bar{r}_1, \bar{r}_2) &= N_{MO} [(1s_B(\bar{r}_1) + k.1s_A(\bar{r}_1) + 1s_C(\bar{r}_1)) \\ &\quad \cdot (1s_B(\bar{r}_2) + k.1s_A(\bar{r}_2) + 1s_C(\bar{r}_2))] \\ &= N_{MO} [0.5\phi_1(\bar{r}_1, \bar{r}_2) + 0.5k^2\phi_2(\bar{r}_1, \bar{r}_2) + k\phi_4(\bar{r}_1, \bar{r}_2)]\end{aligned}$$

$$\begin{aligned}\Phi_A(\bar{r}_1, \bar{r}_2) &= N_A [(1s_B(\bar{r}_1) + 1s_A(\bar{r}_1))(1s_C(\bar{r}_2) + 1s_A(\bar{r}_2)) \\ &\quad + (1s_C(\bar{r}_1) + 1s_A(\bar{r}_1))(1s_B(\bar{r}_2) + 1s_A(\bar{r}_2))]\end{aligned}$$

$$= N_A [0.25\phi_1(\bar{r}_1, \bar{r}_2) + \phi_2(\bar{r}_1, \bar{r}_2) - 0.25\phi_3(\bar{r}_1, \bar{r}_2) + \phi_4(\bar{r}_1, \bar{r}_2)] ,$$

$$\begin{aligned} \phi_B(\bar{r}_1, \bar{r}_2) &= N_B [(1s_B(\bar{r}_1) + k.1s_A(\bar{r}_1))(1s_C(\bar{r}_2) + k.1s_A(\bar{r}_2)) \\ &+ (1s_C(\bar{r}_1) + k.1s_A(\bar{r}_1))(1s_B(\bar{r}_2) + k.1s_A(\bar{r}_2))] \\ &= N_B [0.25\phi_1(\bar{r}_1, \bar{r}_2) + k^2\phi_2(\bar{r}_1, \bar{r}_2) - 0.25\phi_3(\bar{r}_1, \bar{r}_2) \\ &+ k\phi_4(\bar{r}_1, \bar{r}_2)] , \end{aligned}$$

$$\begin{aligned} \phi_C(\bar{r}_1, \bar{r}_2) &= N_C [(1s_B(\bar{r}_1) + k.1s_A(\bar{r}_1))(1s_A(\bar{r}_2) + k.1s_C(\bar{r}_2)) \\ &+ (1s_A(\bar{r}_1) + k.1s_C(\bar{r}_1))(1s_B(\bar{r}_2) + k.1s_A(\bar{r}_2)) \\ &+ (k.1s_B(\bar{r}_1) + 1s_A(\bar{r}_1))(k.1s_A(\bar{r}_2) + 1s_C(\bar{r}_2)) \\ &+ (k.1s_A(\bar{r}_1) + 1s_C(\bar{r}_1))(k.1s_B(\bar{r}_2) + 1s_A(\bar{r}_2))] \\ &= N_C [0.5k\phi_1(\bar{r}_1, \bar{r}_2) + 2k\phi_2(\bar{r}_1, \bar{r}_2) - 0.5k\phi_3(\bar{r}_1, \bar{r}_2) \\ &+ (k^2 + 1)\phi_4(\bar{r}_1, \bar{r}_2)] . \end{aligned}$$

The parameter k was chosen so as to maximise the overlap between each approximation ϕ_{APP} and ϕ . The general form of each approximation is the same as that of ϕ , i.e.

$$\phi_{APP}(\bar{r}_1, \bar{r}_2) = \sum_i c_i \phi_i(\bar{r}_1, \bar{r}_2) \quad (5.1)$$

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 ϕ_I and ϕ_{II} , namely

$$\begin{aligned} \phi_I(\bar{r}_1, \bar{r}_2) &= \chi_1(\bar{r}_1) \chi_1(\bar{r}_2) \\ &= 0.5 A_{11}^2 \phi_1(\bar{r}_1, \bar{r}_2) + 0.5 A_{21}^2 \phi_2(\bar{r}_1, \bar{r}_2) \\ &\quad + A_{11} A_{21} \phi_4(\bar{r}_1, \bar{r}_2) \quad , \end{aligned}$$

$$\begin{aligned} \phi_{II}(\bar{r}_1, \bar{r}_2) &= (n_1 + n_2)^{-1/2} [g_1 \chi_1(\bar{r}_1) \chi_1(\bar{r}_2) + g_2 \chi_2(\bar{r}_1) \chi_2(\bar{r}_2)] \\ &= (n_1 + n_2)^{-1/2} [0.5 g_1 A_{11}^2 \phi_1(\bar{r}_1, \bar{r}_2) + 0.5 g_1 A_{21}^2 \phi_2(\bar{r}_1, \bar{r}_2) \\ &\quad + 0.5 g_2 A_{32}^2 \phi_3(\bar{r}_1, \bar{r}_2) + g_1 A_{11} A_{21} \phi_4(\bar{r}_1, \bar{r}_2)] \quad . \end{aligned}$$

These are the natural expansions truncated after 1 and 2 terms and renormalized to unity. Since ϕ is of rank 3 it is the "best" rank 3 wave function. Obviously ϕ_I and ϕ_{II} are expressible in the form of (5.1). The overlap between each approximation and ϕ ,

TABLE 4. APPROXIMATIONS TO Φ EACH WAVEFUNCTION EXPRESSED AS $\Phi_{AP} = \sum c_i \phi_i$

	Φ	ϕ_I	ϕ_{II}	ϕ_{VB}	ϕ_{MO}	ϕ_A	ϕ_B	ϕ_C
RANK	3	1	2	3	1	2	2	3
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
$\langle \Phi \Phi_{AP} \rangle$	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

WITH 'BEST'

Φ OF SAME

RANK

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 ϕ than either ϕ_{VB} or ϕ_{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 ϕ (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 ϕ_{APP} . A comparison of greater validity than the straight forward comparison of values of this integral for different approximations is to determine the rank of ϕ_{APP} and then compare the overlap integrals between ϕ_{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 ϕ_I and ϕ_{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 ϕ_{MO} is the best approximation to ϕ .

As θ 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 $\theta \simeq 60^\circ$, 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 θ 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 θ 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 θ , 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 θ . However, a continued increase of θ 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 interpretation 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

θ -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 θ 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 , 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 ZHZ^{2Z-1} system.

The comparison of the results of the analysis for the ZHZ^{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 ZHZ^{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 $\text{ZHZH}^{2(Z-1)}$ shows that this behaviour is not confined to the ZHZ^{2Z-1} pseudomolecular ions. In the $\text{ZHZH}^{2(Z-1)}$ 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° 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.

CHAPTER 6

CONCLUSION

The wave functions of a series of pseudomolecular ions of the form ZHZ^{2Z-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 ZHZ ($= \theta$), 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 θ 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 θ . 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⁽²⁵⁾ that the ions are energetically stable for $Z < 1.3$.

The occupation numbers of the natural orbitals for H_3^+ 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 reveals that H_3^+ possesses a strong united atom character. The contour diagrams also showed that, when $\theta = 60^\circ$, the "bonds" in H_3^+ were directed towards the centroid of the positive charges. The elaborate wave function of Christoffersen⁽²²⁾, analysed by Christoffersen and Shull⁽³¹⁾, also revealed this "bonding" arrangement. For fixed bond lengths BA and CA (Fig. 3), as θ was increased, the charge moved from the centres B and C towards A, indicating that the proton dominates the linear H_3^+ system. These results do not support the conclusion that a

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 θ 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 θ decreases, the ZHZ^{2Z-1} 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 ZHZ^{2Z-1} ions, the θ 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 ZHZ^{2Z-1} 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 $ZHZH^{2(Z-1)}$ (37) indicate that its behaviour is somewhat similar to that of ZHZ^{2Z-1} 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 θ vary within the simply ZHZ^{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 $\hat{S}_z$ operator.

(ii) DETOR: A determinant constructed from a set of orthonormal spin-orbitals⁽³⁸⁾.

(iii) CONFIGURATION: A linear combination of determinants which is an eigenfunction of the total spin operator $\hat{S}^2$; it is also a basis for an irreducible representation of the molecular symmetry group.

(iv) CODETOR: A configuration in which the determinants are detors⁽³⁸⁾.

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.

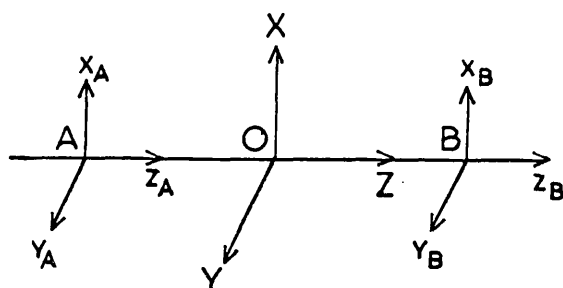


FIG. 15. The co-ordinate systems for a homonuclear diatomic molecule, OX, OY and OZ define the global co-ordinate system.

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, θ, ϕ) 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

$$P(\mu) = \frac{n_\mu}{g} \sum_R \chi^{(\mu)*}(R) \hat{O}_R \quad (7.2)$$

In (7.2) the superscript μ refers to a particular irreducible representation. $\chi^{(\mu)*}(R)$ is the character of the element R in the μ irreducible representation, and $\hat{O}_R$ is the operator corresponding to the element R . n_μ 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_η about the axis of symmetry by an angle η ,
- (ii) the inversion i in the centre of symmetry,
- (iii) a reflection σ 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 2π , the integrand being η . The projection operator for the group $D_{\infty h}$ has the form

$$P^{(\mu)} = \frac{r}{8\pi} \left[\int_0^{2\pi} \chi^{(\mu)*}(C_\eta) \hat{O}_{C_\eta} d\eta + \int_0^{2\pi} \chi^{(\mu)*}(iC_\eta) \hat{O}_{iC_\eta} d\eta + \int_0^{2\pi} \chi^{(\mu)*}(\sigma C_\eta) \hat{O}_{\sigma C_\eta} d\eta + \int_0^{2\pi} \chi^{(\mu)*}(i\sigma C_\eta) \hat{O}_{i\sigma C_\eta} d\eta \right] \quad (7.3)$$

TABLE 5. THE CHARACTER TABLE OF $D_{\infty h}$.

μ	E	C_η	iC_η	σC_η	$i\sigma C_\eta$
Σ_g^+	1	1	1	1	1
Σ_u^+	1	1	-1	1	-1
Σ_g^-	1	1	1	-1	-1
Σ_u^-	1	1	-1	-1	1
Π_g	2	$2\cos\eta$	$2\cos\eta$	0	0
Π_u	2	$2\cos\eta$	$-2\cos\eta$	0	0
Δ_g	2	$2\cos 2\eta$	$2\cos 2\eta$	0	0
Δ_u	2	$2\cos 2\eta$	$-2\cos 2\eta$	0	0
Γ_g	2	$2\cos 4\eta$	$2\cos 4\eta$	0	0

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-orthogonal SAMOs. Let this matrix be $\underline{S}$. The elements of $\underline{S}$ are

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

φ_i and φ_j are members of the set of non-orthogonal SAMOs. $\underline{S}$ 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 $\underline{L}$ and its transpose $\underline{L}^T$:

$$\underline{S} = \underline{L} \underline{L}^T, \quad (7.5)$$

and

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

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

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

$$\therefore \underline{U}^T = \underline{L}^{-1}$$

(7.6a) may be written

$$\underline{U}^T \underline{S} \underline{U} = \underline{I} \quad (7.6b)$$

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

$$\varphi_i = \sum_{j=1}^i \varphi_j' u_{ji} \quad , \quad (7.7)$$

where u_{ji} is an element of $\underline{U}$. It is immediately obvious from (7.7) that the orbital φ_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 $\underline{S}$ 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 $\hat{A}$ ⁽¹²⁾ is a permutation operator which commutes with the Hamiltonian $\hat{H}$, $\hat{S}^2$, $\hat{S}_z$, 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

$\psi_{k1}, \psi_{k2}, \dots, \psi_{kn}$ are members of the chosen set of molecular spin-orbitals, then

$$P_K = \psi_{k1}(1) \psi_{k2}(2) \dots \psi_{kn}(n) \quad ,$$

where the spin-orbital identifiers $k_1, k_2, \dots, k_n$ satisfy the condition

$$k_1 < k_2 < k_3 < \dots < k_n \quad . \quad (7.8)$$

The corresponding detor D_K is then given by

$$D_K = \Delta P_K$$

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

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⁾, Kotari 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_K 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 ψ_6 for a four electron system with two frozen orbitals; six P_K are generated,

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

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⁽¹¹⁾. Because of its computational simplicity, the method selected in the present work is based on the diagonalization of the operator $\mathcal{S}^2$ over the chosen set of detors. The matrix involved has $\langle D_K | \mathcal{S}^2 | D_L \rangle$ as its elements and as the antisymmetrizer commutes with $\mathcal{S}^2$, these elements may be calculated as $\langle P_K | \mathcal{S}^2 | P_L \rangle$.

The total spin operator may be written

$$\mathcal{S}^2 = \mathcal{S}_+ \mathcal{S}_- + \mathcal{S}_z^2 - \mathcal{S}_z, \quad (7.10)$$

where $\mathcal{S}_+$ and $\mathcal{S}_-$ are the 'step-up' and 'step-down' operators⁽¹¹⁾. The effect of $\mathcal{S}_z$ and hence $\mathcal{S}_z^2$ on a product of spin-orbitals is given by (1.9). $\mathcal{S}_+$ and $\mathcal{S}_-$ must be expanded as

$$\mathcal{S}_+ = \sum_{i=1}^n s_{i+} \quad (7.11a)$$

and

$$\mathcal{S}_- = \sum_{i=1}^n s_{i-} \quad (7.11b)$$

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)

$$\begin{aligned} s_+ \psi_{2i-1} &= s_+ \varphi_i \alpha = 0 \\ s_- \psi_{2i-1} &= s_- \varphi_i \alpha = \varphi_i \beta = \psi_{2i} \\ s_+ \psi_{2i} &= s_+ \varphi_i \beta = \varphi_i \alpha = \psi_{2i-1} \\ s_- \psi_{2i} &= s_- \varphi_i \beta = 0 \end{aligned} \quad (7.12)$$

Applying S^2 to P_3 :

$$\begin{aligned}
 S^2 P_3 &= S^2(\psi_1 \psi_2 \psi_3 \psi_6) \\
 &= S_+ S_- (\psi_1 \psi_2 \psi_3 \psi_6) + 0 \cdot P_3 \\
 &= S_+ ((\psi_2 \psi_2 \psi_3 \psi_6) + (\psi_1 \psi_2 \psi_4 \psi_6)) \\
 &= (\psi_1 \psi_2 \psi_3 \psi_6) + (\psi_2 \psi_1 \psi_3 \psi_6) + (\psi_2 \psi_2 \psi_3 \psi_5) \\
 &\quad + (\psi_1 \psi_1 \psi_4 \psi_6) + (\psi_1 \psi_2 \psi_3 \psi_6) + (\psi_1 \psi_2 \psi_4 \psi_5) \quad . \quad (7.13)
 \end{aligned}$$

There are six terms in (7.13); the first is P_3 , the second- P_3 since ψ_1 and ψ_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,

$$S^2 P_3 = P_3 + P_4 \quad . \quad (7.14)$$

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 ψ_3 and ψ_6 . This is because the frozen core is an eigenfunction of S^2 with $S = 0$. The final step of evaluating $\langle P_K | S^2 | P_L \rangle$ is achieved using the knowledge that

$$\langle P_K | P_L \rangle = \delta_{KL},$$

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

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

and

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

$$\left[\frac{d}{d \cos \theta} \right]^{l+|m|} \sin^{2l} \theta \exp(jm\phi) \quad . \quad (7.15c)$$

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⁽⁴⁾ 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 Λ 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.

$$\Lambda = \sum_{i=1} m_i \quad . \quad (7.16)$$

The corresponding irreducible representation is partly determined by the value of Λ ; $\Lambda = 0, 1, 2, \dots$ gives rise to the Σ , Π , Δ , ... 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 Λ_i , where i is replaced by g for gerade detors and u for ungerade detors. The Σ detors are also characterized by their behaviour under the reflection σ in the plane containing the inter-nuclear axis. The operation σ 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, 46)). 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).

$$\sigma P_L = \pm P_L \quad , \quad (7.17a)$$

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

If the wave function changes sign the superscript - is added to Σ 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

$$\Psi_{S\sigma} = \underline{DT}_{S\sigma} \quad . \quad (7.18)$$

$\underline{\Psi}_{S\sigma}$ is a row vector with elements that are simultaneously eigenfunctions of S^2 and σ . $\underline{D}$ is a row vector of detors, each corresponding to the same values of S_z and Λ_i . The matrix $\underline{T}_{S\sigma}$ can be regarded as a projection matrix which projects $\underline{\Psi}_{S\sigma}$ from $\underline{D}$. The elements of $\underline{T}_{S\sigma}$ 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:

$$H_{IJ} = \langle \Psi_I | \hat{h} | \Psi_J \rangle \quad (1.13a)$$

and

$$S_{IJ} = \langle \Psi_I | \Psi_J \rangle \quad (1.13b)$$

From (7.18)

$$\Psi_I = \sum_K D_K t_{KI} \quad (7.19)$$

Substitution of (7.19) into (1.13) gives

$$H_{IJ} = \sum_K \sum_L t_{IK} t_{LJ} \langle D_K | \hat{h} | D_L \rangle \quad (7.20a)$$

and

$$S_{IJ} = \sum_K \sum_L t_{IK} t_{LJ} \langle D_K | D_L \rangle \quad (7.20b)$$

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 $\underline{H}_D$ and $\underline{S}_D$. In matrix notation (7.20) becomes

$$\underline{H} = \underline{T}_{S\sigma}^T \underline{H}_D \underline{T}_{S\sigma} \quad (7.21a)$$

and

$$\underline{S} = \underline{T}_{S\sigma}^T \underline{S}_D \underline{T}_{S\sigma} \quad (7.21b)$$

($\underline{T}_{S\sigma}^T$ is the transpose of $\underline{T}_{S\sigma}$). Löwdin⁽⁸⁾ has given general formulae for evaluating the elements of $\underline{H}_D$ and $\underline{S}_D$ 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 $\underline{H}_D$ and $\underline{S}_D$ 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

$$\langle D_K | D_L \rangle = \delta_{KL} \quad . \quad (7.22)$$

The evaluation of $\langle D_K | \mathbf{h} | D_L \rangle$ is split into two parts as shown in (7.23)

$$\begin{aligned} \langle D_K | \mathbf{h} | D_L \rangle &= \langle D_K | \sum_{\mu=1}^n h_{\mu} | D_L \rangle \\ &+ \langle D_K | \sum_{\mu < \nu} g_{\mu\nu} | D_L \rangle \quad . \quad (7.23) \end{aligned}$$

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, ψ_m entering D_K where ψ_p enters D_L ;
- (iii) D_K and D_L differ by two spin-orbitals, ψ_m and ψ_n entering D_K where ψ_p and ψ_q enter D_L , and
- (iv) D_K and D_L differ by more than two spin-orbitals

The following notation will be used:

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

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

$$J_{ij} = [ii|jj] \quad , \quad (7.26)$$

$$K_{ij} = [ij|ji] \quad . \quad (7.27)$$

Thus,

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

and

$$\langle D_K | \sum_{\mu < \nu} g_{\mu\nu} | D_L \rangle \begin{cases} = \sum_i \sum_j (J_{ij} - K_{ij}) \text{ for case (i)} \\ = \sum_{i \neq m} ([ii|mp] - [ip|mi]) \text{ for case (ii)} \\ = [mp|nq] - [mq|np] \text{ for case (iii)} \\ = 0 \text{ for case (iv)} \end{cases} \quad . \quad (7.29)$$

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 ψ_m in D_K and ψ_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:

$$\varphi_i' = \sum_j \omega_j c_{ji}' \quad , \quad (7.30a)$$

or in matrix form

$$\underline{\varphi}' = \underline{\omega} \underline{C}' \quad . \quad (7.30b)$$

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

$$\varphi_k = \sum_i \varphi_i' u_{ik} \quad , \quad (7.31a)$$

or in matrix form

$$\underline{\varphi} = \underline{\varphi}' \underline{U} \quad (7.31b)$$

Combining (7.30) with (7.31) gives

$$\underline{\varphi} = \underline{\omega} \underline{C}' \underline{U} = \underline{\omega} \underline{C} \quad . \quad (7.32)$$

The integrals h_{ij} are the elements of the one-electron Hamiltonian matrix $\underline{h}$, hence the transformation to integrals over the set $\{\varphi_i\}$ takes the form of a matrix product

$$\underline{h} = \underline{C}^T \underline{h}_\omega \underline{C} \quad , \quad (7.33)$$

where the elements of $\underline{h}_\omega$ are the integrals $\int \omega_i^*(1) h_1 \omega_j(1) dr_1$. 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

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

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

$$m_j - m_i = m_k - m_l \quad . \quad (7.35)$$

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

$$n_r = 1/2(\max(i,j)(\max(i,j) - 1)) + \min(i,j) ,$$

$$n_e = 1/2(\max(k,l)(\max(k,l) - 1)) + \min(k,l) \quad . \quad (7.36)$$

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

$$[\omega_\mu \omega_\nu | \varphi_k \varphi_l] = \sum_\lambda \sum_\sigma c_{\lambda k} c_{\sigma l} [\omega_\mu \omega_\nu | \omega_\lambda \omega_\sigma] , \quad (7.37a)$$

where μ , ν , k , and l take all possible values, whilst λ and σ are subject to the condition $\lambda \geq \sigma$. The second stage is

$$[\varphi_i \varphi_j | \varphi_k \varphi_l] = \sum_\mu \sum_\nu c_{\mu i} c_{\nu j} [\omega_\mu \omega_\nu | \varphi_k \varphi_l] , \quad (7.37b)$$

Once the matrix elements between the detors have been computed, the transformation of (7.21a) is performed to obtain the matrix elements H_{ij} , (1.13a). As a consequence of (7.22), the matrix $\underline{S}$ of (7.21b) is the identity matrix, since the columns of $\underline{T}_{S\sigma}$ 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 Ψ (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 Λ_i 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 $\underline{T}_{S\sigma}$. 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

$$(\underline{H} - E_I \underline{I}) \underline{A} = 0 \quad . \quad (7.38)$$

The energies E_I are the eigenvalues of $\underline{H}$, $\underline{A}$ is a column vector, an eigenvector of $\underline{H}$ corresponding to a particular E_I . Two possible methods of solving (7.38) are the method of Jacobi and the QR-Algorithm, both described by Wilkinson^(13, 47, 48). 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 Ψ is

$$\Psi = \sum_L \Psi_L a_{LI} \quad (1.11)$$

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

$$\Psi = \sum_K D_K \sum_L t_{KL} a_{LI} \quad . \quad (7.39)$$

The coefficient of D_K may be simply written as b_{KI} ,

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

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

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

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 ψ_k and that over L is over those determinants D_L which contain ψ_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 $D_{KK}(k|l) = \delta_{kl}$. The second is when D_K and D_L differ by one spin-orbital, ψ_k appears in the i -th column of D_K and ψ_l appears in the j -th column of D_L , in this case

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

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 $\{\chi_k\}$ (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 Λ , and are of either gerade or ungerade symmetry. The required values of S_Z and Λ 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,

$$P_1 = 1, 2, 3, \dots, n-1, n$$

$$\equiv \psi_1 \psi_2 \psi_3 \dots \psi_{n-1} \psi_n ,$$

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

$$P_{\text{LAST}} = N - n, N - n + 1, \dots, N - 1, N$$

$$\equiv \psi_{N-n} \psi_{N-n+1} \dots \psi_{N-1} \psi_N$$

On encountering the final ordered product $C\text{OMBIN}$ 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 , Λ , 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 $\langle P_L | g^2 | P_K \rangle$. For $\Lambda = 0$, i.e. Σ 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 $\hat{O}$ which may be either σ , g^2 , or i , then

$$\hat{O} P_K = \sum_L P_L^\dagger C_{LK} \quad (8.1)$$

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 $C\text{PLATE}$. If P_L cannot be found in $IS\phi$ an error message is printed and

execution ceases. The evaluation of $\langle P_L | \mathcal{G}^2 | P_K \rangle$ begins with the application of the $\mathcal{G}_-$ 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 α , if the entry in the row of $IS\phi$ corresponding to P_K is odd, and β 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 $ISM\phi P$. The $\mathcal{G}_+$ operator is then applied to the entries in $ISM\phi P$ and the resulting spin-orbital products are held as rows in the array $ISP\phi P$. By use of the subroutines PERMUT and C\phi LATE the values of C_{LK} in (8.1) are determined. For each P_K the values of L for which C_{LK} is non-zero after the operation $(\mathcal{G}_z^2 - \mathcal{G}_z)$ are stored in the array $IC\phi L$, and the non-zero value of C_{LK} is stored in the array C\phi E, since $\langle P_L | \mathcal{G}^2 | P_K \rangle = \langle D_L | \mathcal{G}^2 | D_K \rangle = C_{LK}$. As each P_K is processed the results are written onto a disc or tape file. The rows of $IS\phi$ 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 $IS\phi$. $\mathcal{G}^2$ is applied to P_1 first, and the next product examined is the first one in (8.1), for which C_L^r 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 $\mathcal{G}^2$ 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 $\mathcal{G}^2$ operator is block diagonal, and makes interpretation of the results easier. The P_K are numbered according to the order in which $\mathcal{G}^2$ is applied. The output from GENDET comprises:

- (i) P_K on cards,

- (ii) K , iP_K , σP_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 SECSØL (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 SECSØL. This program called ØNECEN is listed in Appendix V, and the non-zero Clebsch-Gordon coefficients⁽⁴¹⁾ $C_{L_1 m_1 L_2 m_2}^{M m}$ used in the expansion of a product of spherical harmonics are also given. The method of indexing $C_{L_1 m_1 L_2 m_2}^{M m}$ is easily determined by examination of the sub-program INDEX 1 and the coefficients are limited to the range $0 \leq l_1 \leq 3$

with $i = 1$ or 2 .

ØNECEN uses the function subprogram IPAR listed in Appendix III. The parameter list of IPAR consists of a single integer variable name. On being called 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. 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 IPAR is the use of the intrinsic function MOD ⁽⁴⁹⁾. A call of $\text{MOD}(N, 2)$ has the same effect as $\text{IPAR}(N)$, 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 ØNECEN. 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. ØNECEN computes all the integrals arising from a basis set of 1s, 2s, $2p_0$, $2p_-$, and $2p_+$ 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 ØNECEN. 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 $\underline{U}$ 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 ØNECEN (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 $\underline{I}$ with elements $I_{n_r n_e}$, where n_r and n_e are defined by (7.36). Only the lower triangle of $\underline{I}$ 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 $\underline{I}$ 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 $\underline{I}$ 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 $\underline{J}$ has a lower triangle equal to that of $\underline{I}$ and an upper triangle of zeros. The matrix $\underline{J}$ is then transposed by the subroutine BIGTRA. The lower triangle of $\underline{J}$ is then merged with the transpose of $\underline{J}$ to give the complete matrix $\underline{I}$.

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 be $NR\emptyset W$. The process in the N th pass over the matrix to be transposed consists of the following sequence of operations: read first $NR\emptyset W$ records into a two-dimensional array A, transpose the $NR\emptyset W * NR\emptyset W$ square matrix beginning at column $(NR\emptyset W * (N-1) + 1)$ of A, and enter this into the first $NR\emptyset W * NR\emptyset W$ block of the two-dimensional array B. The next $NR\emptyset W$ records are read into A, transposed as before and entered into the second $NR\emptyset W * NR\emptyset W$ 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 $(NR\emptyset W * (N-1) + 1)$ to $NR\emptyset W * N$ 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 $NR\emptyset W$. 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 $\emptyset RTH\emptyset N$ and TRANSH. Firstly the matrix $\underline{C}'$ 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 $\underline{C}'$ is the identity matrix. The resulting overlap matrix $\underline{S}$ overwrites the original one. The subroutine ORTHO obtains the matrix $\underline{U}$ of (7.7) by Choleski decomposition of $\underline{S}$. The matrix $\underline{L}^T$ of (7.5) is held in the array QU, which is then inverted to give the matrix $\underline{U}$ which is stored in the array QC. The one-electron Hamiltonian matrix $\underline{h}_\omega$ is transformed by the matrix product

$$\underline{h} = \underline{C}^T \underline{h}_\omega \underline{C} \quad (8.2)$$

where $\underline{C} = \underline{C}'\underline{U}$. The transformed overlap matrix (i.e. $\underline{U}^T \underline{S} \underline{U}$) 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 TWOTRA and its control routine 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 $[\omega_\mu \omega_\nu | \varphi_k \varphi_l]$ according to (7.37a) and it is seen from (7.36) that for a given set of μ and ν all the integrals over the atomic orbitals appear in the same record. The partially transformed integrals are obtained for all possible values of μ , ν , k , and l . Partially transformed integrals for which

$$m_{\mu} - m_{\nu} = m_k - m_l^* \quad (8.3)$$

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

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

and the position of the element in the record by

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

(Obviously $\mu_{\max} = k_{\max} = \text{number of basis orbitals}$). Inspection of (7.37b) shows that the $[\omega_{\mu}\omega_{\nu}|\varphi_k\varphi_l]$ 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 $[\varphi_i\varphi_j|\varphi_k\varphi_l]$ written in records with

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

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 SECSØL 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 SECSØL in terms of the functions of the following three groups of subprograms,

(i) computation of the matrix elements $\langle D_L | h | D_K \rangle$

between detors,

(ii) construction and solution of $(\underline{H} - E\underline{I}) \underline{A} = 0$,

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

Computation of the $\langle D_L | h | D_K \rangle$ 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 $\langle D_L | h | D_K \rangle$ is symmetric only the lower triangle is evaluated and stored in a one-dimensional array G, where

$$G(KL) = \langle D_L | h | D_K \rangle, \quad (K \leq L) \quad (8.5)$$

and

$$KL = (L*(L - 1))/2 + K \quad . \quad (8.6)$$

Before evaluating $G(KL)$ it is necessary to bring D_L and D_K into the condition of maximum coincidence. The subroutine MAXCØN 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 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 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 $\langle D_K | h | D_K \rangle$. This constant is computed in the subprogram PASØNE. The remaining interaction for the diagonal elements, and the values of the off-diagonal elements are computed in the subroutine PASTWØ.

In PASTWØ the two electron integrals $[\varphi_i \varphi_j | \varphi_k \varphi_l]$ 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 (± 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 $\underline{T}_{S\sigma}$ can be obtained by inspection of the output from GENDET. The evaluation of (7.21a) is the basis of the subroutine SECSØL (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⁽¹³⁾. The eigenvalues are the energies of the state projected by $\underline{T}_{S\sigma}$ and each eigenvector defines a wave function for this state.

Finally the program SECSØL will perform a natural spin orbital analysis on the i -th level of the state given by $\underline{T}_{S\sigma}$. 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_{KI} 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 NATØRB and FØDMA4 constitute this section of SECSØL.

By use of the projection matrix $\underline{T}_{S\sigma}$ 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 SECSØL 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 SECSØL (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 accidentally corrupt or overwrite the master results tape or the master transformed integrals tape; the program SECSØL 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 SECSØL both the specification of the detors and $\underline{T}_{S\sigma}$ may be read in the first set of data and used in subsequent runs. This substantially reduces the number

of data cards required. SECSØL 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 $9 \text{ } ^3\Sigma_g^-$ codetors and $12 \text{ } ^1\Sigma_g^+$ codetors; the corresponding projection matrices $\underline{T}_{1-}$ and $\underline{T}_{0+}$ 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 $\underline{T}_{1-}$ that they used for their $^3\Sigma_g^-$ wave function. The detors have $S_z = 1$. This particular paper also contains the elements of the matrix $\underline{U}$ ((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 3P , 1D , and 1S states of the oxygen atom. Test runs for the $^3\Sigma_g^-$ and $^1\Sigma_g^+$ 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 ØNECEN. 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 O_2 are given in Chapter 10, together with the spectroscopic constants and molecular properties computed using the methods described in Chapter 9.

CHAPTER 9

SPECTROSCOPIC CONSTANTS OF

DIATOMIC MOLECULES

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 preceeding 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⁽⁵⁵⁾, who expanded the potential function about the equilibrium nuclear separation R_e in a power series:

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

where

$$\xi = (R - R_e)/R_e \quad ,$$

$$a_0 = \omega_e^2 / 4B_e \quad ,$$

and

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

In (9.2) ω_e is the classical frequency of small oscillations, assuming the system is a harmonic oscillator, and μ is the reduced mass of the

diatomic molecule. Using the Wentzel-Kramers-Brillouin method Dunham obtained the equation

$$E_{vJ} = \sum_{l,j} Y_{lj} (v + 1/2)^l J^j (J + 1)^j \quad (9.3)$$

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 ω_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

$$E_{v0} = Y_{00} + Y_{10}(v + 1/2) + Y_{20}(v + 1/2)^2 + Y_{30}(v + 1/2)^3 + Y_{40}(v + 1/2)^4 + \dots \quad (9.4)$$

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

$$\begin{aligned} E_{10} - E_{00} &= Y_{10} - 2Y_{20} + 13Y_{30}/4 + 5Y_{40} + \dots, \\ E_{20} - E_{10} &= Y_{10} - 4Y_{20} + 49Y_{30}/4 + 34Y_{40} + \dots \end{aligned} \quad (9.5)$$

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

$$\begin{aligned} E_{v0} &= \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 \\ &+ \omega_e y_e(v + 1/2)^3 + \omega_e z_e(v + 1/2)^4 + \dots \end{aligned} \quad (9.6)$$

(9.6) is obtained ⁽⁵⁶⁾ by solving the appropriate Schrödinger equation using a potential function of the form

$$V(R) = V(R_e) + f\xi^2 - g\xi^3 \quad ,$$

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

$$E_{10} - E_{00} = \omega_e - 2\omega_e x_e + 13\omega_e y_e/4 + 5\omega_e z_e + \dots \quad ,$$

$$E_{20} - E_{10} = \omega_e - 4\omega_e x_e + 49\omega_e y_e/4 + 34\omega_e z_e + \dots \quad . \quad (9.7)$$

Comparison of (9.5) and (9.7) gives

$$\begin{aligned} Y_{10} &\approx \omega_e \quad , \\ Y_{20} &\approx -\omega_e x_e \quad , \\ Y_{30} &\approx \omega_e y_e \quad , \\ Y_{40} &\approx \omega_e z_e \quad , \end{aligned} \quad (9.8)$$

Y_{10} is not exactly equal to ω_e because it contains terms in B_e^2/ω_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⁾

$$E_{vJ} - E_{v0} = B_v J(J+1) - D_v J^2(J+1)^2 + H_v J^3(J+1)^3 + \dots \quad . \quad (9.9)$$

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

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

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

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

Expansion of (9.3) gives

$$\begin{aligned} E_{vJ} - E_{v0} = & (Y_{01} + Y_{11}(v + 1/2) + Y_{21}(v + 1/2)^2 + \dots)J(J + 1) \\ & + (Y_{02} + Y_{12}(v + 1/2) + Y_{22}(v + 1/2)^2 + \dots)J^2(J + 1)^2 \\ & + (Y_{03} + Y_{13}(v + 1/2) + \dots)J^3(J + 1)^3 \\ & + (Y_{04} + \dots)J^4(J + 1)^4 . \end{aligned} \quad (9.11)$$

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

$$\begin{aligned} Y_{01} &\approx B_e , \\ Y_{11} &\approx -\alpha_e , \\ Y_{21} &\approx \gamma_e , \\ Y_{31} &\approx \delta_e , \\ Y_{02} &\approx D_e , \\ Y_{03} &\approx H_e . \end{aligned} \quad (9.12)$$

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

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

$$B_e = 60.2014/(\mu R_e^2) \quad . \quad (9.13)$$

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

$$\underline{A} \underline{p} = \underline{V} \quad . \quad (9.14b)$$

In (9.14b) the elements of the matrix $\underline{A}$ are $A_{ij} = R_i^{j-1}$, $\underline{p}$ is a column vector of the unknown coefficients, $\underline{V}$ 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 $\underline{V} - \underline{A} \underline{p}$, only exists when the columns of $\underline{A}$ are linearly independent⁽⁶⁰⁾. By taking powers of R_i

accuracy is reduced and the columns of $\underline{A}$ may be nearly linearly dependent⁽⁶¹⁾.

These difficulties can be avoided if R_i , the independent variable, is transformed into the normalized independent variable X_i where

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

and

$$|X_i| \leq 1.$$

In (9.15) R_1 is the minimum value of R_i and R_{n+1} the maximum value. A_{ij} is now X_i^{j-1} and the solution of the least squares problem results in the coefficients q_j of the polynomial

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

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 ξ where $X = a\xi + b$. In the present case $a = (R_1 + R_{n+1}) / (R_1 - R_{n+1})$ 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 SPECTRØ 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 ØRLIN2 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

	McLean	Spectro	Experimental
ω_e	4399.33	4399.45	4395.2
k_e	574563.	574613.	
B_e	60.841	60.843	60.800
D_e	0.0465	0.0465	
Y_{00}	10.75	10.75	
Y_{10}	4393.8	4394.0	4400.39
Y_{20}	-104.34	-104.34	-120.82
Y_{30}	-5.42	-5.42	-0.724
Y_{40}	0.056	0.056	
Y_{01}	60.798	60.800	60.864
Y_{11}	-2.834	-2.834	-3.076
Y_{21}	-0.032	-0.032	0.0601
Y_{31}	-0.031	-0.031	
Y_{02}	-0.0466	-0.0466	-0.0466
Y_{12}	0.0022	0.0022	0.0016
a_0	7.9528×10^4	7.9529×10^4	7.9566×10^4
a_1	-1.565	-1.565	-1.598
a_2	1.900	1.900	1.868
a_3	-2.478	-2.478	-2.072
a_4	2.391	2.391	2.261
a_5	-0.959	-0.959	
a_6			
a_7			
$E_{\min}$	-1.174442 a.u.	-1.174442	
$R_{\min}$	1.40127 a.u.	1.40127	

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 $V(R_i)$ are converted in the program from hartrees to cm^{-1} using the conversion factor given in Appendix I. The value of $V(R_e)$ in both cm^{-1} and hartrees is given in the program output.

McLean⁽⁶³⁾ published a comprehensive set of results for the Dunham analysis of a wave function for H_2 obtained by Kolos and Roothaan⁽¹⁹⁾. McLean's results, the experimental values^(56,64) and those obtained by SPECTRØ are given in Table 6. As far as the a_i s of (9.1) are concerned the results given by SPECTRØ 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⁽⁶³⁾.

CHAPTER 10

RESULTS AND DISCUSSION

The diatomic oxygen molecule has been thoroughly studied by spectroscopists^(56, 65) and the extensive theoretical study of Schaefer and Harris⁽⁴⁵⁾ 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⁽⁶⁶⁾, 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⁽⁶⁷⁾. 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⁽⁴⁵⁾, 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^(49,50) 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 Λ 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^(42, 43), also confirms the number of configurations given in Table I of Schaefer and Harris⁽⁴⁵⁾.

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⁽¹⁰⁾.

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 ⁽⁶⁸⁾.

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

(i) 3P , 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 detectors, 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 detectors it is possible to obtain one 3P codetector, one 1D codetector, and two 1S codetectors. The wave functions for the 3P 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 7. ATOMIC DETORS AND CODETORS

P-type detors :

$$D_1 = (1)(2)(3)(6)(7)(8)$$

$$D_2 = (1)(2)(4)(5)(7)(8)$$

D-type detor :

$$D_3 = (1)(2)(3)(4)(7)(8)$$

S-type detors :

$$D_4 = (1)(2)(3)(4)(5)(8)$$

$$D_5 = (1)(2)(3)(4)(6)(7)$$

$$D_6 = (1)(2)(5)(6)(7)(8)$$

$$D_7 = (3)(4)(5)(6)(7)(8)$$

3P codetor :

$$\Psi_1 = 2^{-\frac{1}{2}} (D_1 + D_2)$$

1D codetor :

$$\Psi_2 = D_3$$

1S codetors :

$$\Psi_3 = 3^{-\frac{1}{2}} (D_4 - D_5 + D_6)$$

$$\Psi_4 = D_7$$

TABLE 8. ORBITAL EXPONENTS

orbital	oxygen	sulphur
1s	7.6568	15.5409
2s	2.2472	5.3144
2p	2.2262	5.9885
3s	-	2.1223
3p	-	1.8273

TABLE 9. ELECTRONIC ENERGIES OF
ATOMIC STATES (HARTREES)

State	Oxygen		Sulphur	
	Present work	Ref. 45	Present work	Ref. 73
3P	-74.5404	-74.5406	-396.5936	-396.6276
1D	-74.4464	-74.4469	-396.5341	-
1S	-74.3663	-74.3665	-396.5287	-

TABLE 10. DISSOCIATION ENERGIES CALCULATED FROM
ENERGIES OF ATOMIC STATES (HARTREES)

Atomic States	Oxygen	Sulphur
$^3P + ^3P$	-149.0808	-793.1872
$^3P + ^1D$	-148.9868	-793.1277
$^3P + ^1S$	-148.9067	-793.1223
$^1D + ^1D$	-148.8928	-793.0682
$^1D + ^1S$	-148.8127	-793.0628
$^1S + ^1S$	-148.7326	-793.0574

"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 detectors are specified in Table 7 where only the identifiers of the valence shell spin-orbitals are given, these conform to the rule:

$$\begin{aligned} ns \ \alpha &= 1, \quad ns \ \beta = 2, \\ np_0 \ \alpha &= 3, \quad np_0 \ \beta = 4, \\ np_- \ \alpha &= 5, \quad np_- \ \beta = 6, \\ np_+ \ \alpha &= 7, \quad np_+ \ \beta = 8. \end{aligned}$$

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

oxygen the molecular orbitals are

$$(1s\sigma_g)(1s\sigma_u)(2s\sigma_g)(2s\sigma_u)(2p\sigma_g)(2p\sigma_u)(2p\pi_g)(2p\pi_u) \quad .$$

The π_g and π_u orbitals may contain up to four electrons, and each σ -orbital a maximum of two. The molecular orbitals for sulphur include the orbitals

$$(3s\sigma_g)(3s\sigma_u)(3p\sigma_g)(3p\sigma_u)(3p\pi_g)(3p\pi_u) \quad ,$$

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 Σ_g 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 Σ_g 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 Δ_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 "primitive 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

TABLE 11. ENERGIES OF ${}^3\Sigma_g^-$ STATES OF O_2 (HARTREES)

R (Bohrs)	$X^3\Sigma_g^- I$	${}^3\Sigma_g^- II$	${}^3\Sigma_g^- III$	${}^3\Sigma_g^- IV$	${}^3\Sigma_g^- V$
2.0	-149.0731	-148.1717	-147.7918	-147.7264	-147.6618
2.1	-149.1407	-148.3509	-148.0268	-147.9082	-147.8404
2.2	-149.1807	-148.4932	-148.2185	-148.0506	-147.9693
2.3	-149.2031	-148.6059	-148.3743	-148.1626	-148.0672
2.4	-149.2134	-148.6941	-148.4985	-148.2511	-148.1428
2.5	-149.2151	-148.7645	-148.6002	-148.3212	-148.2177
2.6	-149.2103	-148.8205	-148.6814	-148.3762	-148.3386
2.7	-149.1996	-148.8640	-148.7476	-148.4459	-148.4184
2.8	-149.1882	-148.8980	-148.8006	-148.5324	-148.4531
2.9	-149.1741	-148.9244	-148.8431	-148.6039	-148.4798
3.0	-149.1597	-148.9455	-148.8769	-148.6630	-148.5014
3.1	-149.1465	-148.9600	-148.9043	-148.7105	-148.5180
3.3	-149.1210	-148.9807	-148.9398	-148.7818	-148.5421
3.5	-149.1018	-148.9910	-148.9607	-148.8286	-148.5572
4.0	-149.0838	-148.9923	-148.9772	-148.8846	-148.5698
∞	-149.0808	-148.9868	-148.9868	-	-

TABLE 12. ENERGIES OF ${}^1\Sigma_g^+$ STATES OF O_2 (HARTREES)

R (Bohrs)	$b\,{}^1\Sigma_g^+I$	${}^1\Sigma_g^+II$	${}^1\Sigma_g^+III$	${}^1\Sigma_g^+IV$	${}^1\Sigma_g^+V$
2.0	-149.0014	-148.2544	-148.0743	-147.7025	-147.6210
2.1	-149.0712	-148.3808	-148.2502	-147.9200	-147.8762
2.2	-149.1178	-148.4799	-148.3869	-148.1113	-148.0804
2.3	-149.1480	-148.5608	-148.4905	-148.2723	-148.2422
2.4	-149.1626	-148.6296	-148.5700	-148.4068	-148.3717
2.5	-149.1680	-148.6890	-148.6240	-148.5182	-148.4771
2.6	-149.1667	-148.7368	-148.6681	-148.6103	-148.5596
2.7	-148.1637	-148.7744	-148.7011	-148.6901	-148.6268
2.8	-149.1562	-148.8055	-148.7551	-148.7275	-148.6775
2.9	-149.1487	-148.8283	-148.8116	-148.7545	-148.7150
3.0	-149.1391	-148.8581	-148.8455	-148.7823	-148.7378
3.1	-149.1307	-148.8987	-148.8594	-148.8039	-148.7531
3.3	-149.1156	-148.9584	-148.8747	-148.8407	-148.7692
3.5	-149.1032	-149.0011	-148.8827	-148.8629	-148.8131
4.0	-149.0883	-149.0569	-148.8891	-148.8824	-148.8675
∞	-149.0808	-149.0808	-148.8928	-148.8928	-148.8928

TABLE 13. ENERGIES OF $^3\Sigma_g^-$ STATES OF S_2 (HARTREES)

R (Bohrs)	$X^3\Sigma_g^-I$	$^3\Sigma_g^-II$	$^3\Sigma_g^-III$	$^3\Sigma_g^-IV$	$^3\Sigma_g^-V$
2.9	-792.9403	-792.3457	-792.1966	-792.1669	-792.1100
3.0	-793.0255	-792.4779	-792.3281	-792.2864	-792.2322
3.1	-793.0938	-792.5903	-792.4413	-792.3853	-792.3313
3.2	-793.1473	-792.6842	-792.5397	-792.4686	-792.4131
3.3	-793.1891	-792.7632	-792.6246	-792.5394	-792.4797
3.4	-793.2303	-792.8402	-792.6913	-792.5958	-792.5321
3.5	-793.2408	-792.8856	-792.7608	-792.6501	-792.5805
3.6	-793.2563	-792.9322	-792.8151	-792.6931	-792.6184
3.7	-793.2671	-792.9717	-792.8640	-792.7286	-792.6550
3.8	-793.2732	-793.0031	-792.9019	-792.7593	-792.6860
3.9	-793.2752	-792.0296	-792.9361	-792.7847	-792.7353
4.0	-793.2756	-793.0525	-792.9666	-792.8066	-792.7809
4.1	-793.2731	-793.0708	-792.9920	-792.8268	-792.8189
4.2	-793.2698	-793.0856	-793.0144	-792.8571	-792.8383
4.4	-793.2585	-793.1079	-793.0490	-792.9134	-792.8624
4.6	-793.2458	-793.1223	-793.0749	-792.9568	-792.8790
4.8	-793.2341	-793.1315	-793.0936	-792.9894	-792.8913
∞	-793.1872	-793.1277	-793.1223	-	-

TABLE 14. ENERGIES OF $1\Sigma^+$ STATES OF S_2 (HARTREES)

R (Bohrs)	$b\ 1\Sigma_g^+$	$1\Sigma_g^+ II$	$1\Sigma_g^+ III$	$1\Sigma_g^+ IV$	$1\Sigma_g^+ V$
2.9	-792.8896	-792.4562	-792.2849	-792.1671	-792.1059
3.0	-792.9770	-792.5538	-792.4155	-792.2993	-792.2397
3.1	-793.0460	-792.6357	-792.5248	-792.4101	-792.3532
3.2	-793.1004	-792.7025	-792.6186	-792.5065	-792.4524
3.3	-793.1437	-792.7572	-792.6959	-792.5904	-792.5380
3.4	-793.1894	-792.8062	-792.7689	-792.6494	-792.6056
3.5	-793.2009	-792.8455	-792.8109	-792.7257	-792.6766
3.6	-793.2193	-792.8827	-792.8500	-792.7813	-792.7326
3.7	-793.2311	-792.9236	-792.8763	-792.8285	-792.7809
3.8	-793.2394	-792.9454	-792.9040	-792.8712	-792.8209
3.9	-793.2449	-792.9706	-792.9235	-792.9087	-792.8568
4.0	-793.2472	-792.9913	-792.9412	-792.9399	-792.8872
4.1	-793.2469	-793.0092	-792.9708	-792.9538	-792.9125
4.2	-793.2456	-793.0226	-792.9963	-792.9668	-792.9335
4.4	-793.2397	-793.0422	-793.0391	-792.9896	-792.9636
4.6	-793.2326	-793.0748	-793.0549	-793.0113	-792.9803
4.8	-793.2250	-793.1022	-793.0626	-793.0292	-792.9908
∞	-793.1872	-793.1223	-793.0628	-793.0574	-

TABLE 15. ENERGIES OF ${}^1\Delta_g$ STATES OF S_2 (HARTREES)

R (Bohrs)	${}^1\Delta_g I$	${}^1\Delta_g II$	${}^1\Delta_g III$	${}^1\Delta_g IV$	${}^1\Delta_g V$
2.9	-792.9085	-792.3002	-792.1257	-792.0438	-791.8553
3.0	-792.9948	-792.4323	-792.2521	-792.1729	-791.9940
3.1	-793.0638	-792.5445	-792.3617	-792.2768	-792.1097
3.2	-793.1178	-792.6392	-792.4582	-792.3618	-792.2089
3.3	-793.1596	-792.7185	-792.5430	-792.4316	-792.2944
3.4	-793.2035	-792.7954	-792.6103	-792.4858	-792.3564
3.5	-793.2151	-792.8413	-792.6807	-792.5382	-792.4308
3.6	-793.2322	-792.8880	-792.7356	-792.5797	-792.4910
3.7	-793.2436	-792.9257	-792.7914	-792.6160	-792.5511
3.8	-793.2512	-792.9581	-792.8250	-792.6510	-792.6123
3.9	-793.2556	-792.9846	-792.8604	-792.6887	-792.6545
4.0	-793.2565	-793.0068	-792.8915	-792.7294	-792.6848
4.1	-793.2563	-793.0248	-792.9183	-792.7679	-792.7091
4.2	-793.2542	-793.0389	-792.9412	-792.8019	-792.7297
4.4	-793.2466	-793.0597	-792.9780	-792.8584	-792.7635
4.6	-793.2370	-793.0728	-793.0047	-792.9016	-792.7894
4.8	-793.2277	-793.0804	-793.0245	-792.9344	-792.8086
∞	-793.1872	-793.1223	-	-	-

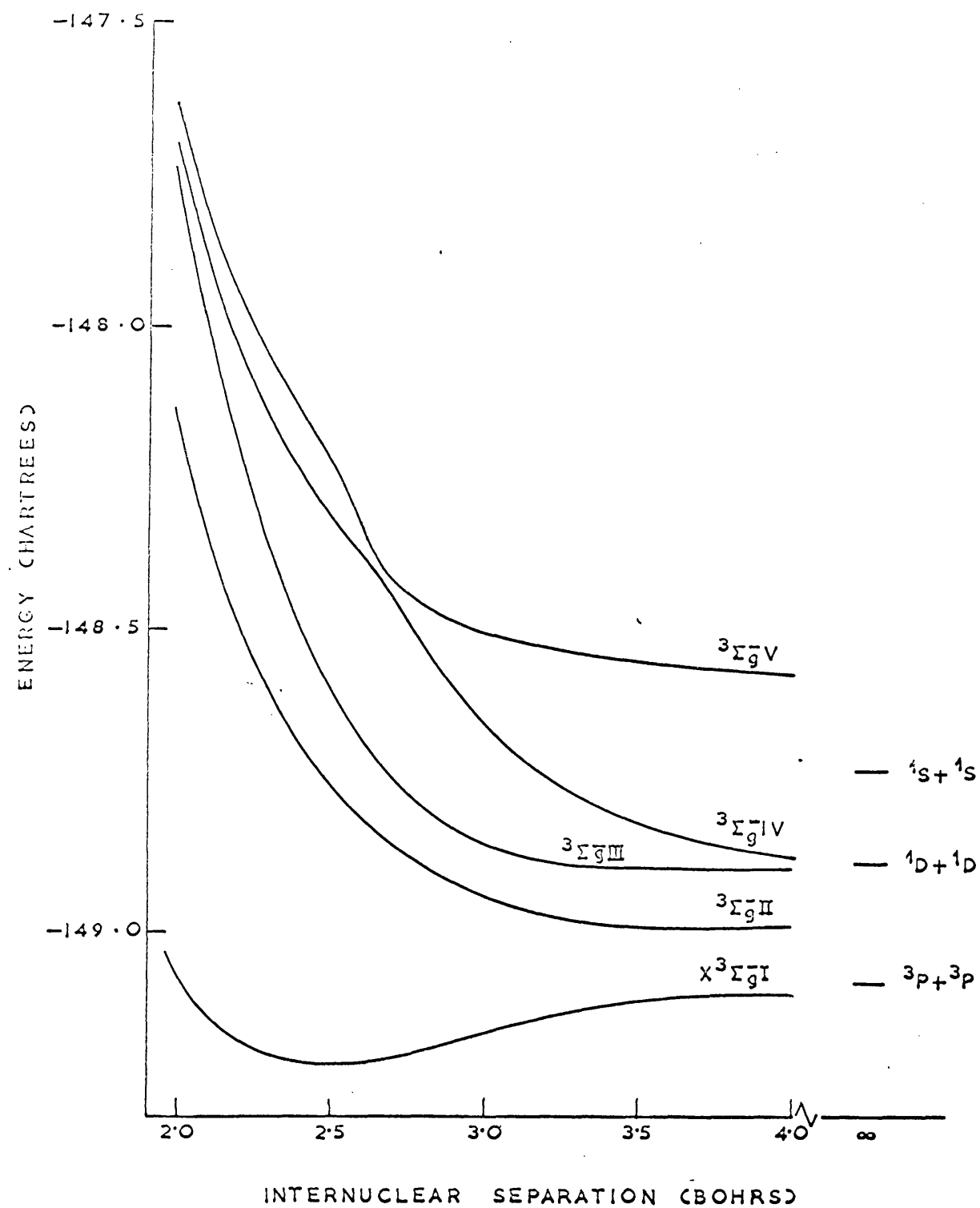


FIG. 16. Potential curves for the five lowest $3\Sigma_g^-$ levels of O_2 .

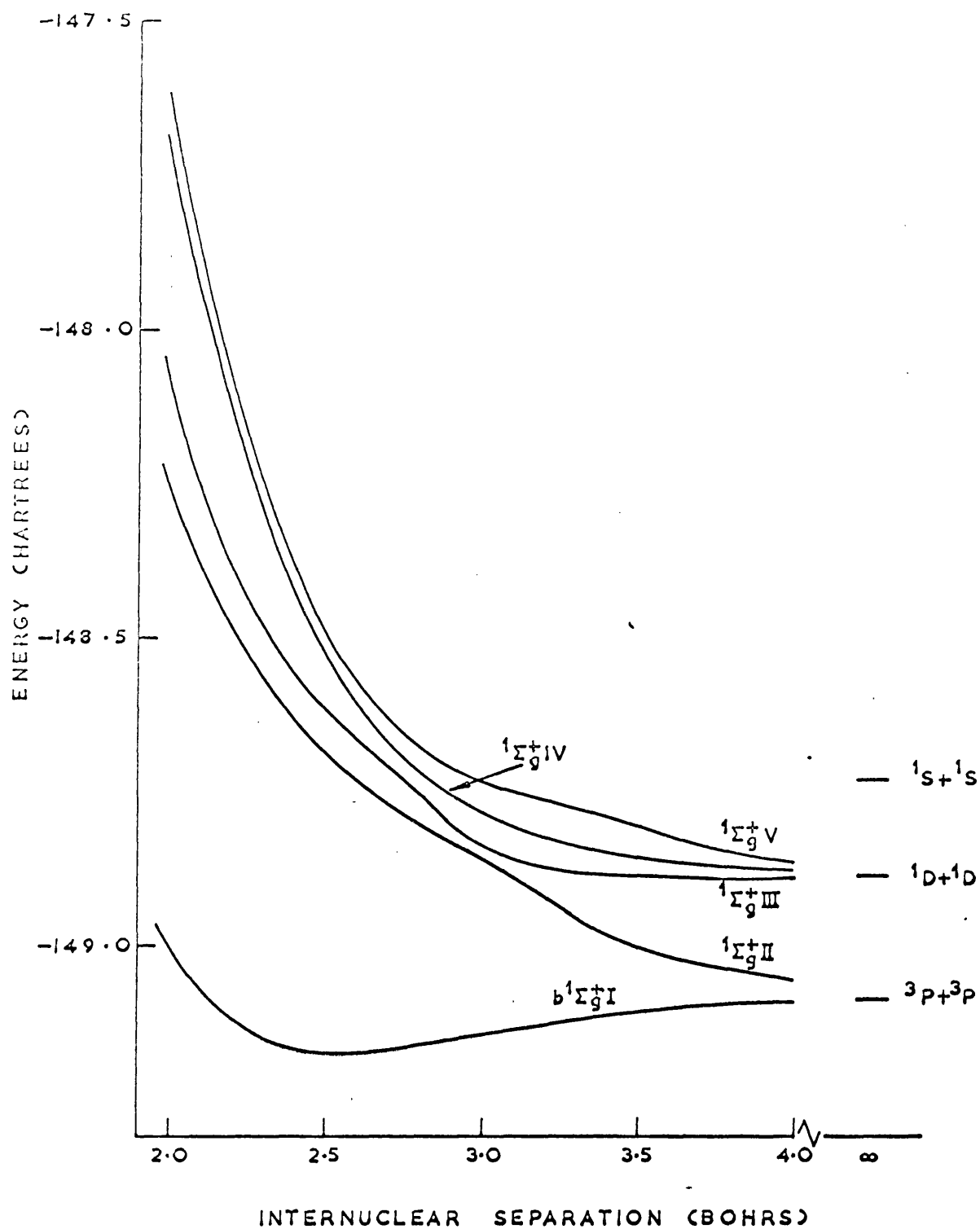


FIG. 17. Potential curves for the five lowest $1\Sigma_g^+$ levels of O_2 .

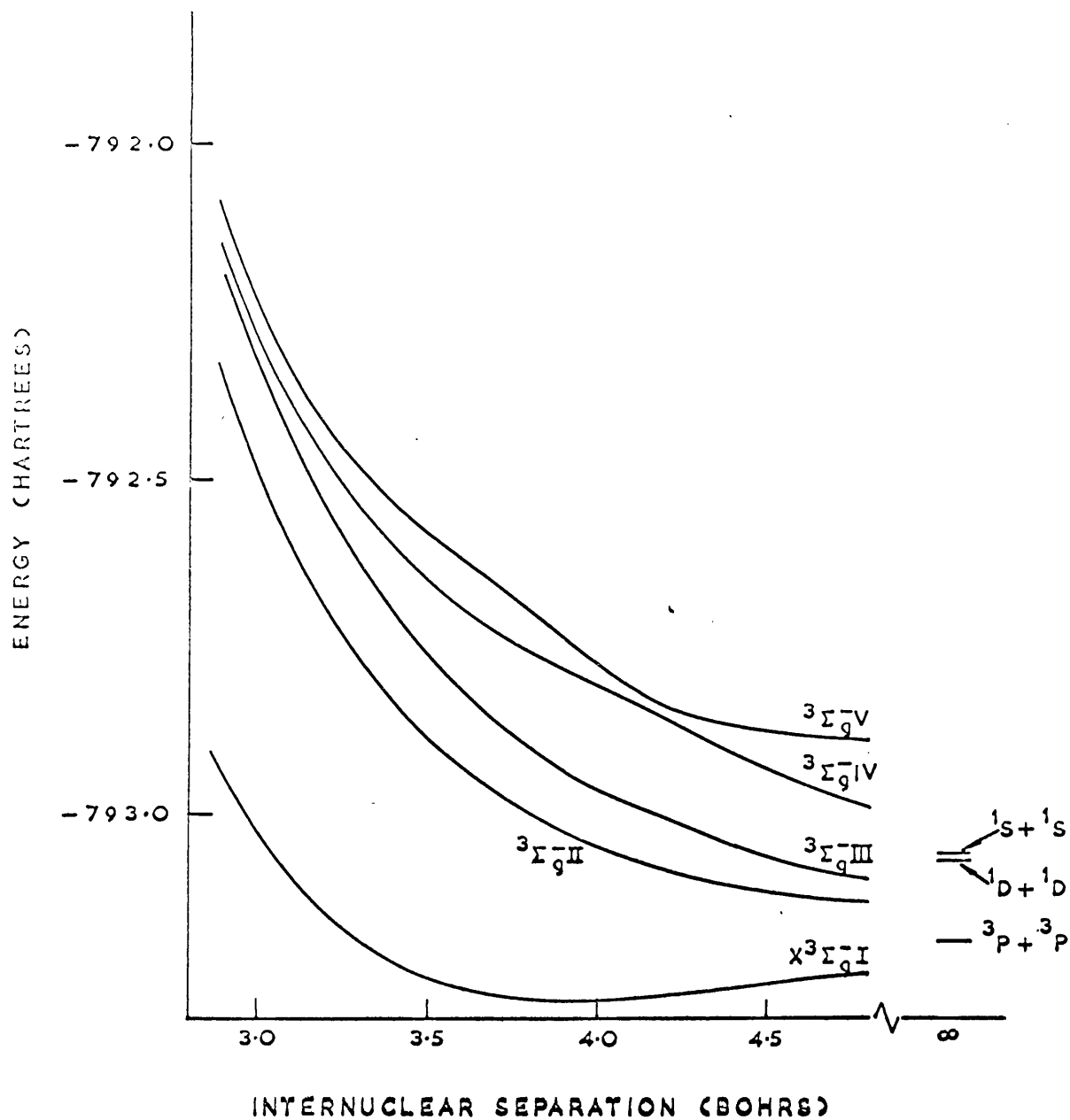


FIG. 18. Potential curves for the five lowest $3\Sigma_g^-$ levels of S_2

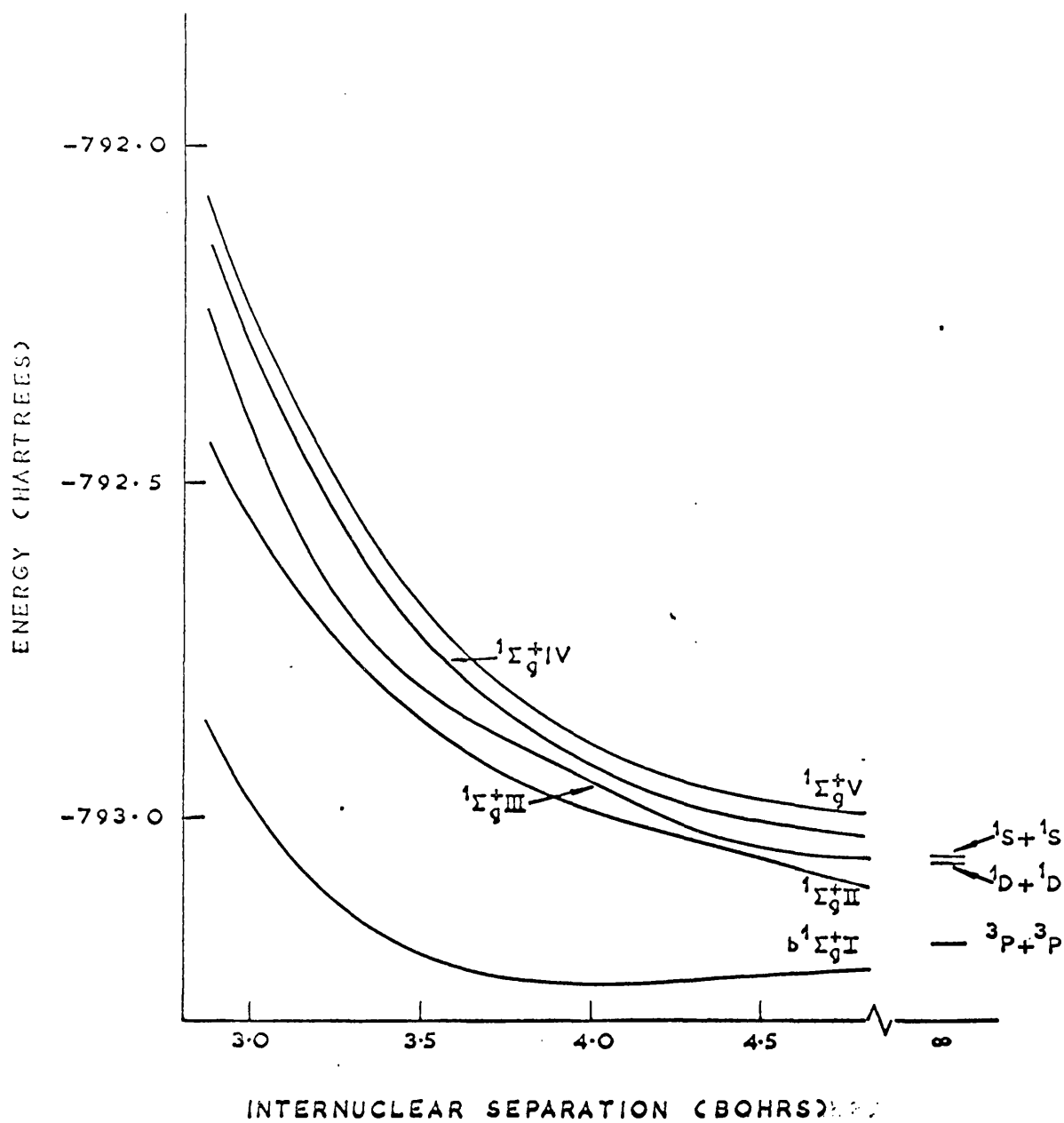


FIG. 19. Potential curves for the five lowest $1\Sigma_g^+$ levels of S_2 .

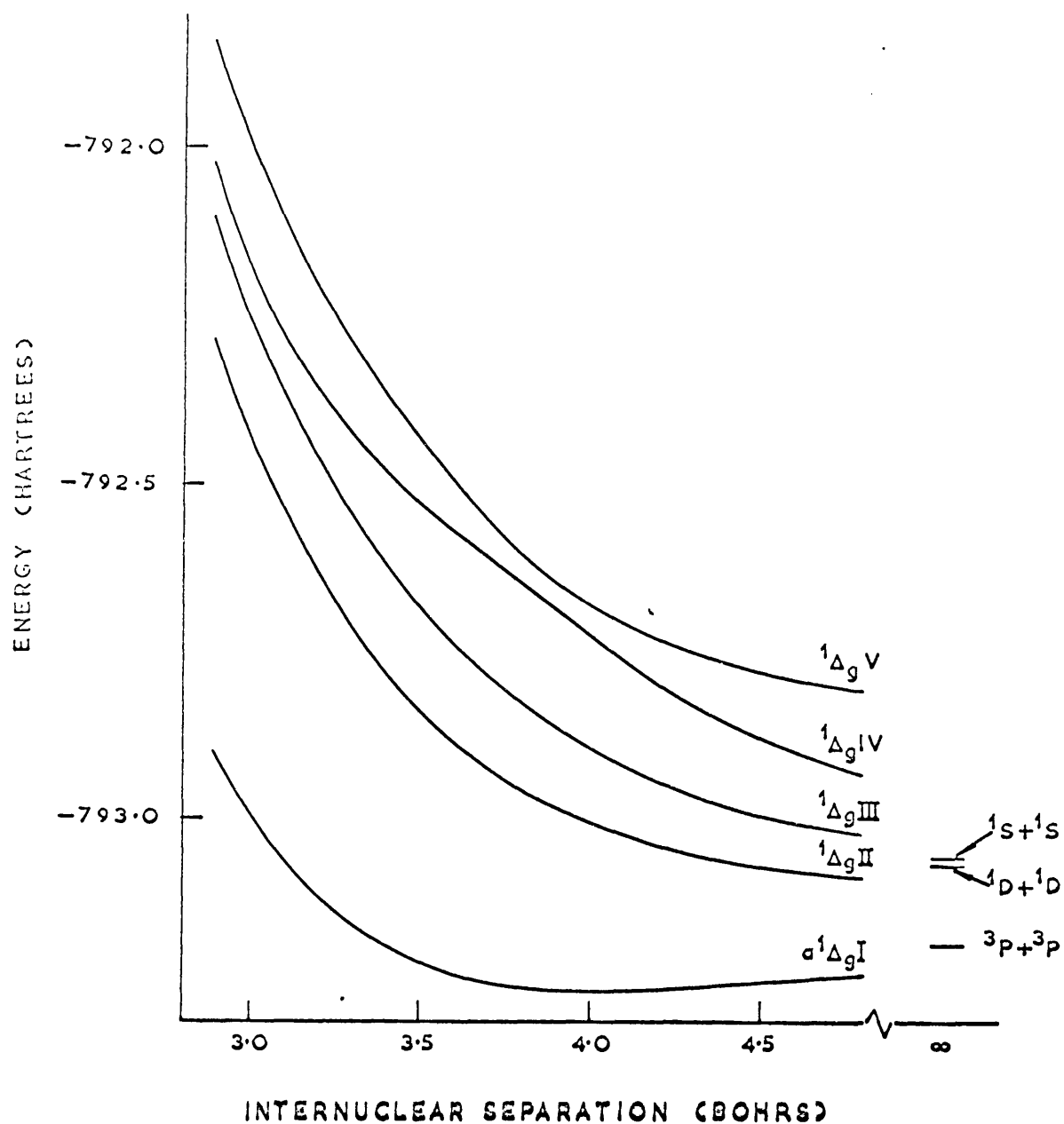


FIG. 20. Potential curves for the five lowest $1\Delta_g$ levels of S_2 .

TABLE 16 Spectroscopic Constants

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

	$\text{O}_2\text{X}^3 \Sigma_g^-$		$\text{O}_2\text{b}^1 \Sigma_g^+$	
	calc	Expr ⁺	calc	Expr ⁺
R_e bohrs	2.4618	2.2817	2.5435	2.3183
$V(R_e)$ hartrees	-149.2156		-149.1685	
$V'(R_e)$	0.0		10^{-8}	
D_E hartrees	0.1348		0.0877	
D_0 hartrees	0.1312	0.1867	0.0849	0.1506
$G(0)$ hartrees	0.0036	0.0036	0.0028	0.0033
Y_{00}	-1.4979		1.6769	
Y_{10}	1607.56	1580.36	1251.04	1432.69
Y_{20}	-19.1019	-12.0730	-6.8935	-13.9500
Y_{30}	0.1539	0.0546	-0.2558	-0.0108
Y_{40}	0.0066		-0.0031	
Y_{01}	1.2422	1.4457	1.1636	1.4004
Y_{11}	-0.0129	-0.0158	-0.0016	-0.0182
Y_{21}	-7.9×10^{-5}		0.0003	
Y_{31}	9.3×10^{-6}		-6.5×10^{-5}	
Y_{02}	-3.0×10^{-6}		-4.0×10^{-6}	
Y_{12}	-1.1×10^{-7}		1.3×10^{-7}	
Y_{22}	$<10^{-8}$ *		-2.3×10^{-8}	
Y_{03}	$<10^{-9}$ *		$<10^{-8}$ *	
Y_{13}	$<10^{-8}$ *		$<10^{-8}$ *	
Y_{04}	$<10^{-8}$ *		$<10^{-8}$ *	
a_0	5.2006×10^5		3.3651×10^5	
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)

	$S_2X^3\Sigma_g^-I$		$S_2a^1\Delta_gI$		$S_2b^1\Sigma_g^+I$	
	calc	Expr +	calc	Expr +	calc	Expr +
R_e bohrs	3.9761	3.5754	3.9962	3.5905	4.0243	
$V(R_e)$ hartrees	-793.2757		-793.2565		-793.2472	
$V'(R_e)$	2×10^{-7}		3×10^{-7}		3.2×10^{-6}	
D_e hartrees	0.0885		0.0693		0.0600	
D_0 hartrees	0.0869	0.1610	0.0147		0.0588	
$G(0)$ hartrees	0.0016	0.0016	0.0546		0.0012	
Y_{00}	-10.0430		-44.5515		-36.3408	
Y_{10}	703.4343	714.29	584.1429	689.87	591.0864	693 ?
Y_{20}	-61.1350	2.844	3581.93	3.02	123.0598	3.4 ?
Y_{30}	117.2205		-387.0931		-164.2823	
Y_{40}	110.0685		1667.08		1.5303	
Y_{01}	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}	-6.9×10^{-8}		-7.7×10^{-7}		-2.4×10^{-7}	
Y_{12}	-2.2×10^{-7}		-1.9×10^{-6}		-4.4×10^{-7}	
Y_{22}	2.7×10^{-7}		-1.0×10^{-5}		-1.3×10^{-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	4.0375×10^5		2.0498×10^5		3.7238×10^5	
a_1	18.1835		-34.6309		-22.2509	
a_2	80.4469		195.7953		-127.9481	
a_3	-6369.01		1.0117×10^4		6036.38	
a_4	5.2347×10^4		4.2089×10^4		8.2559×10^4	
a_5	3.9409×10^5		-8.1705×10^5		-4.5959×10^4	
a_6	5.5152×10^6		-7.4275×10^6		-6.6482×10^6	

* 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; namely $X^3 \Sigma_g^- I < a^1 \Delta_g I < b^1 \Sigma_g^+ I$. 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 $2S+1 \Lambda_i(\sigma)$ 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, $^3 \Sigma_g^- I$ is energetically lower than $^3 \Sigma_g^- II$. Spectroscopic constants for the $X^3 \Sigma_g^- I$ (i.e. ground state) and $b^1 \Sigma_g^+ I$ states of diatomic oxygen were calculated using the program listed in Appendix VIII. Similar calculations were performed for the $X^3 \Sigma_g^- I$, $a^1 \Delta_g I$, and $b^1 \Sigma_g^+ I$ 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

$$\left| R - R_e \right| \leq \left| t/3A_{n-1} \right|^{1/n+1} .$$

All values of R_i must lie in the range prescribed, t is the estimated machine error in each $V(R_i)$ and n is the degree of the fitted polynomial. $V(R)$ is expressed as a power series in $(R-R_e)$ rather than ξ (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 $X^3 \Sigma_g^-$ 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 SPECTRØ by setting the variable $NØ$ 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 $\omega_e X_e$, $\omega_e Y_e$, and $\omega_e Z_e$ 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 $X^3 \Sigma_g^-$ ground state of O_2 dissociates into the $^3P + ^3P$ states of the atoms as does the $b^1 \Sigma_g^+$ state. The problem of the dissociation of 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 $X^3 \Sigma_g^-$ state. The accepted value is 0.161 hartree^(65, 69) and the dissociation products are atoms in the 3P 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_E measured from the minimum of the potential curve differs from D_0 by the zero-point energy $G(0)$.

$$\begin{aligned} D_E &= V(R_e) - V(\infty) \\ &= D_0 + G(0) \end{aligned}$$

D_E and $G(0)$ are given by the program SPECTRØ (In the computer output the symbol ZO 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, π -ORBITAL VCI, AND SCF ENERGIES
FOR THE LOWEST STATES OF O₂ (HARTREES)

R Bohrs	$X^3\Sigma_g^- I$			$b^1\Sigma_g^- I$	
	30 TERM	9 TERM	SCF*	37 TERM	12 TERM
2.1	-149.1407	-149.0598	-149.0521	-149.0712	-148.9792
2.3	-149.2031	-149.1411	-149.0912	-149.1480	-149.0797
2.5	-149.2151	-149.1702	-149.0743	-149.1680	-149.1188
2.7	-149.1996	-149.1674	-149.0281	-149.1637	-149.1295
2.9	-149.1741	-149.1514	-149.9679	-149.1487	-149.1261
3.1	-149.1465	-149.1311	-149.9024	-149.1307	-149.1166
3.3	-149.1210	-149.1112	-148.8372	-149.1156	-149.1073
3.5	-149.1018	-149.0961	-148.7744	-149.1032	-149.0986
4.0	-149.0838	-149.0826	-148.6413	-149.0883	-149.0873

* Reference 71 . The author is grateful to Dr M. Dixon for permission to include these results.

TABLE 18. VCI , π -ORBITAL VCI , AND SCF ENERGIES
FOR LOW-LYING STATES OF S_2 (HARTREES)

R Bohrs	$X^3\Sigma_g^-I$			$b^1\Sigma_g^+I$	
	30 TERM	9 TERM	SCF*	37 TERM	12 TERM
3.0	-793.0255	-792.9955	-793.0624	-792.9770	-792.9401
3.2	-793.1473	-793.1176	-793.1798	-793.1004	-793.0645
3.4	-793.2303	-793.2024	-793.2646	-793.1894	-793.1562
3.6	-793.2563	-793.2303	-793.2760	-793.2193	-793.1889
3.8	-793.2732	-793.2499	-793.2830	-793.2394	-793.2127
4.0	-793.2756	-793.2550	-793.2750	-793.2472	-793.2244
4.2	-793.2698	-793.2520	-793.2573	-793.2456	-793.2266
4.4	-793.2585	-793.2435	-793.2336	-793.2397	-793.2245
4.6	-793.2458	-793.2334	-793.2073	-793.2326	-793.2208
4.8	-793.2341	-793.2242	-793.1802	-793.2250	-793.2161

* See footnote to Table 17 .

The greatest contributory factor to the discrepancy between theory and experiment for S_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_2 will lower the energy by almost twice this amount. A VCI calculation in which the $ns\sigma_g$ and $ns\sigma_u$ valence shell molecular orbitals are full is conveniently called a π -orbital VCI and in the present work is easily obtained. In Appendix IX it is seen that the first 31 detors of Σ_g symmetry have the valence shell $ns\sigma_g$ and $ns\sigma_u$ orbitals doubly occupied. The $^3\Sigma_g^-$ and $^1\Sigma_g^+$ codetors arising from these detors are components of the π -orbital VCI wave functions (see Chapters 7 and 8, also Meckler⁽⁴²⁾) for these states. There are $9^3\Sigma_g^-$ codetors and $12^1\Sigma_g^+$ codetors in the π -orbital VCI. The results of these investigations are summarized in Tables 17 and 18, where the 9-term VCI represents the π -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 π -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 π -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_2 , which includes detors corresponding to excitations from the inner shell π -orbitals. The present result for $R = 2.3$ in the ground state of O_2 is in good agreement with that of Kotani et alia⁽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 $^{2S+1}\Lambda_i^{(\sigma)}I$ and $^{2S+1}\Lambda_i^{(\sigma)}II$ may be written

$$\Psi_I = \sum_i \psi_i c_{iI} \quad , \quad (10.1a)$$

and

$$\Psi_{II} = \sum_k \psi_k c_{kII} \quad , \quad (10.1b)$$

respectively. In (10.1) ψ_i and ψ_k are codetors of $^{2S+1}\Lambda_i^{(\sigma)}$ symmetry. Let

$$V_{ik} = \langle \psi_i | \hat{H} | \psi_k \rangle \quad ,$$

V_{ii} is the total energy of the codetors ψ_i and the off-diagonal elements V_{ik} are very small. The energies corresponding to Ψ_I and Ψ_{II} are

$$V_I = \sum_{ik} c_{iI} c_{kI} V_{ik} \quad ,$$

and

$$V_{II} = \sum_{ik} c_{iII} c_{kII} V_{ik} \quad .$$

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 Ψ_I and Ψ_{II} . As the inter-nuclear 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 19 Part I $^3\Sigma_g^-$ IV eigenvectors

$R \backslash \psi_i$	2.1	2.3	2.5	2.7	2.9	3.1	4.0
1	0.00620	-0.01029	-0.04302	0.96567*	0.98217*	0.98062*	0.93762*
2	0.01694	0.01725	0.01794	-0.01679	-0.01454	-0.01397	-0.01158
3	-0.00590	0.02600	0.02367	0.05256	0.07454	0.09302	0.16493
4	0.12081	0.08073	0.05455	0.01031	0.02281	0.03404	0.12546
5	0.17624	0.10293	0.06357	0.00725	0.02052	0.02656	0.03267
6	0.38746	0.51682	0.62340*	-0.11398	-0.01272	0.00603	0.10165
7	0.20499	0.31317	0.35884	-0.09148	-0.04043	-0.04820	-0.16944
8	0.03023	0.02835	0.03840	-0.03908	-0.03906	-0.03932	0.01834
9	-0.05263	-0.01761	0.03098	-0.00245	0.01802	0.03070	0.11285
10	-0.02417	0.02290	0.07268	-0.00158	0.01134	0.00953	0.00315
11	0.06835	0.09198	0.10552	-0.05251	-0.02904	-0.02117	-0.00665
12	0.80838*	0.65843*	0.51481	-0.04700	-0.00439	-0.00459	-0.00657
13	0.13037	0.24529	0.25133	-0.07919	-0.02513	-0.01326	0.00032
14	-0.00829	0.00274	0.00635	0.00716	0.00592	0.00465	0.00216
15	-0.13560	-0.16379	-0.17224	0.04747	0.02205	0.01841	0.01091
16	-0.05875	-0.07683	-0.08561	-0.00802	-0.01920	-0.01868	-0.01135
17	0.01873	0.01539	0.01298	-0.07651	-0.07443	-0.07268	-0.07105
18	-0.07670	-0.01986	-0.00119	-0.02956	-0.02339	-0.02191	-0.02849
19	-0.01132	0.02101	0.03127	-0.02345	-0.01452	-0.01114	-0.00395
20	-0.19044	-0.21266	-0.21795	0.00252	-0.02024	-0.01815	-0.00935
21	-0.10738	-0.16293	-0.17633	0.08308	0.04329	0.03154	0.01114
22	0.04098	0.05292	0.06053	-0.02103	-0.01235	-0.01044	-0.00405
23	0.01696	0.02785	0.03503	0.00699	0.01306	0.01255	0.00597
24	-0.03655	-0.01154	0.01425	-0.00376	0.00223	0.00277	0.00297
25	0.04104	0.04570	0.04916	-0.00473	0.00096	0.00156	0.00170
26	-0.01685	-0.00470	0.00174	-0.01129	-0.00889	-0.00737	-0.00330
27	-0.03192	-0.03354	-0.03191	-0.05155	-0.05706	-0.05826	-0.06634
28	0.00201	-0.01307	-0.01717	0.09162	0.08865	0.08812	0.09599
29	-0.00585	-0.00524	-0.00411	-0.04242	-0.04646	-0.04928	-0.06142
30	-0.00533	-0.01089	-0.01366	-0.00950	-0.01376	-0.01578	-0.02646

* Absolutely largest value

TABLE 19 Part II $^3\Sigma_g^-$ V eigenvectors

ψ_i^R	2.1	2.3	2.5	2.7	2.9	3.1	4.0
1	-0.06121	-0.11033	0.82322*	0.17734	0.03692	0.02279	0.01154
2	-0.01842	-0.03088	0.01227	0.01311	0.01166	0.00382	0.00048
3	0.14482	0.12900	-0.01417	0.00561	-0.05414	-0.12597	-0.35295
4	-0.12672	-0.11699	0.05829	0.03289	0.00198	-0.03576	-0.26789
5	0.20405	0.09113	-0.01841	0.04288	0.02746	0.01769	-0.00119
6	0.13786	0.13443	-0.02577	-0.69700*	0.75736*	0.77633*	0.61308*
7	0.34260	0.29359	-0.12350	0.35463	0.34743	0.31466	0.23417
8	-0.06850	-0.10226	0.05114	0.05363	0.09526	0.15001	0.40174
9	0.08865	0.15059	-0.09927	0.10051	0.18437	0.27387	0.43057
10	0.09020	0.15635	-0.08002	0.11812	0.14507	0.15416	0.07244
11	0.02507	-0.00180	-0.01395	0.09484	0.08976	0.07215	0.02514
12	-0.30428	-0.52333	0.35901	0.39495	0.29767	0.22071	0.07335
13	0.72745*	0.62575*	-0.29901	0.21027	0.18704	0.15178	0.03512
14	-0.03350	-0.03305	0.03140	0.00814	0.00447	0.00155	0.00235
15	-0.05902	-0.01801	0.00030	-0.16376	-0.16133	-0.14993	-0.08220
16	-0.02897	-0.02715	-0.01376	-0.09007	-0.07881	-0.06137	0.00974
17	-0.00996	-0.01587	-0.05324	-0.00908	-0.00123	-0.00191	-0.00206
18	0.24979	0.22469	-0.11858	0.00591	-0.00398	-0.00805	-0.00762
19	0.00411	0.04020	-0.04532	0.02680	0.02762	0.02452	0.00482
20	-0.01918	0.01374	0.06452	-0.21772	-0.19843	-0.17152	-0.04519
21	-0.23702	-0.20634	0.13189	-0.15120	-0.14343	-0.12094	-0.05003
22	-0.00147	-0.02314	0.01961	0.05961	0.05911	0.05271	0.02081
23	0.03561	0.04558	-0.01554	0.04198	0.04145	0.03782	0.00359
24	0.05486	0.09636	-0.06036	0.03743	0.05510	0.06363	0.02557
25	-0.05371	-0.07264	0.05191	0.04849	0.04235	0.03286	0.00551
26	0.00815	0.02062	-0.02145	0.00187	0.00441	0.00430	0.00091
27	0.00605	0.01397	-0.05607	-0.04388	-0.03483	-0.03264	-0.01908
28	-0.07603	-0.07477	0.10560	0.08730	0.00241	0.00833	0.01357
29	0.00491	0.00982	-0.03924	-0.01427	-0.00858	-0.00859	-0.01028
30	-0.01409	-0.01433	-0.00196	-0.01885	-0.02025	-0.02277	-0.01603

* Absolutely largest value

the dominant codetor in Ψ_I 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 $^3 \Sigma_g^- IV$ and $^3 \Sigma_g^- V$ 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 SECSØL (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 $X^3 \Sigma_g^- I$ 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 π -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 $X^3\Sigma_g^-$ 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 π -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 π -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 detectors than the present limit of 120.

CHAPTER 11

CONCLUSION

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 detors 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 detors which correspond to excitations from the inner shell π -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 π -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 SECSØL (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 rewritting 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 $\langle \hat{O} \rangle = \text{Tr}(\underline{\gamma} \underline{P})$, where $\hat{O}$ is a one-electron operator, $\underline{\gamma}$, the first order density matrix and $\underline{P}$ the matrix of integrals of the one-electron property over the same orbital basis as $\underline{\gamma}$.

The ease with which the matrix elements between detors 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, SECSØL 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 Π_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.

APPENDICES

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⁽⁷²⁾, 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

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

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

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

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 2π , 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:

$$1 \text{ bohr} = \frac{\hbar^2}{m_e e^2} \quad .$$

Rewriting (I.1) in these units gives

$$\left(\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + (E_E + \sum_{K=1}^M \sum_{i=1}^N \frac{Z_K}{r_{iK}} - \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{1}{r_{ij}}) \right) \psi = 0 \quad .$$

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⁽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⁽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).

TABLE I-1. FUNDAMENTAL PHYSICAL CONSTANTS

Constant	Symbol	Value	SI unit
Speed of light in a vacuum	c	2.997925	$\times 10^8 \text{ ms}^{-1}$
Elementary charge	e	1.60210	$\times 10^{-19} \text{ C}$
Avagadro constant	N_A	6.02252	$\times 10^{26} \text{ Kmole}^{-1}$
Mass unit	u	1.66043	$\times 10^{-27} \text{ kg}$
Electron rest mass	m_e	9.10908	$\times 10^{-31} \text{ kg}$
Planck constant	h	6.62559	$\times 10^{-34} \text{ Js}$
$h/2\pi$	$\hbar$	1.054494	$\times 10^{-34} \text{ Js}$
Fine structure constant	α	7.29720	$\times 10^{-3}$
Rydberg constant	R_∞	1.0973731	$\times 10^7 \text{ m}^{-1}$
Bohr radius	a_0	5.29167	$\times 10^{-11} \text{ m}$

TABLE 1-2 Conversion Factors for Energy units

	Hartrees	Joules	Electron Volts	cm^{-1}
1 Hartree	= 1	4.35942×10^{-18}	2.721070×10^4	2.1947462×10^5
1 Joule	= 2.29388×10^{17}	1	6.24181×10^{18}	5.03447×10^{22}
1 Electron Volt	= 3.675025×10^{-2}	1.60210×10^{-19}	1	8.06573×10^3
1 cm^{-1}	= 4.556335×10^{-6}	1.98631×10^{-23}	1.23981×10^{-4}	1
1 $^{\circ}\text{K}$	= 3.16678×10^{-6}	1.38054×10^{-23}	8.61705×10^{-5}	6.95028×10^{-1}
1 kcal	= 9.6017×10^{20}	4.1858×10^3	2.6127×10^{22}	2.1073×10^{26}
1 kcal mole $^{-1}$	= 1.5936×10^{-3}	6.9473×10^{-21}	4.3363×10^{-2}	3.4976×10^2
1 kg.	= 2.06164×10^{34}	8.98755×10^{16}	5.60985×10^{35}	4.52477×10^{39}

/continued

TABLE I-2 Conversion Factors for Energy units

	$^{\circ}\text{K}$	kcal	kcal mole $^{-1}$	kg.
1 Hartree	=	3.15778×10^5	1.0415×10^{-21}	6.2751×10^2
1 Joule	=	7.24356×10^{22}	2.3890×10^{-4}	4.85052×10^{-35}
1 Electron volt	=	1.16049×10^4	3.8275×10^{-23}	1.11265×10^{-17}
1 cm $^{-1}$	=	1.43879×10^0	4.7454×10^{-27}	1.78258×10^{-36}
1 $^{\circ}\text{K}$	=	1	3.2982×10^{-27}	2.21006×10^{-40}
1 kcal	=	3.0320×10^{26}	1	1.53605×10^{-40}
1 kcal mole $^{-1}$	=	5.0323×10^2	1.6597×10^{-24}	4.6573×10^{-14}
1 kg.	=	6.51019×10^{39}	2.1472×10^{13}	7.7299×10^{-38}
			1.2937×10^{37}	1

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 $\exp(jm\phi)$ is an eigenfunction of the rotation operator of the group⁽³⁹⁾. For the purposes of this appendix the notation $\varphi_C(n, l, m, \zeta)$ 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

$$\sigma_{C_\eta} \varphi_A(n, l, m, \zeta) = \varphi_A(n, l, m, \zeta) \exp(jm\eta) ,$$

$$\sigma_{iC_\eta} \varphi_A(n, l, m, \zeta) = (-1)^l \varphi_B(n, l, m, \zeta) \exp(jm\eta) ,$$

$$\sigma_{\sigma C_\eta} \varphi_A(n, l, m, \zeta) = \varphi_A(n, l, m, \zeta) \exp(-jm\eta) ,$$

$$\text{and } \sigma_{i\sigma C_\eta} \varphi_A(n, l, m, \zeta) = (-1)^l \varphi_B(n, l, m, \zeta) \exp(-jm\eta) .$$

A similar set of results is obtained for $\varphi_B(n, l, m, \zeta)$.

Using these relations and the projection operator defined in (7.4) the following SAMOs are obtained:

$$\sigma_g : \varphi_A(n, l, 0, \zeta) + (-1)^l \varphi_B(n, l, 0, \zeta) ,$$

$$\sigma_u : \varphi_A(n, l, 0, \zeta) - (-1)^l \varphi_B(n, l, 0, \zeta) ,$$

$$\pi_g^+ : \varphi_A(n, l, \pm 1, \zeta) + (-1)^l \varphi_B(n, l, \pm 1, \zeta) ,$$

$$\pi_u^+ : \varphi_A(n, l, \pm 1, \zeta) - (-1)^l \varphi_B(n, l, \pm 1, \zeta) ,$$

$$\delta_g^+ : \varphi_A(n, l, \pm 2, \zeta) + (-1)^l \varphi_B(n, l, \pm 2, \zeta) ,$$

$$\delta_{\text{u}}^{\pm} : \varphi_{\text{A}}(n, l, \pm 2, f) - (-1)^l \varphi_{\text{B}}(n, l, \pm 2, f) \quad ,$$

$$\gamma_{\text{g}}^{\pm} : \varphi_{\text{A}}(n, l, \pm 3, f) + (-1)^l \varphi_{\text{B}}(n, l, \pm 3, f) \quad ,$$

$$\gamma_{\text{u}}^{\pm} : \varphi_{\text{A}}(n, l, \pm 3, f) - (-1)^l \varphi_{\text{B}}(n, l, \pm 3, f) \quad .$$

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 σ , π , δ , γ , ... and each orbital transforms according to the Σ_{g}^{+} , Σ_{u}^{+} , Π_{g} , Π_{u} , 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:

$$1s\sigma_{\text{g}} = \varphi_{\text{A}}(1, 0, 0, f) + \varphi_{\text{B}}(1, 0, 0, f) \quad ,$$

$$1s\sigma_{\text{u}} = \varphi_{\text{A}}(1, 0, 0, f) - \varphi_{\text{B}}(1, 0, 0, f) \quad ,$$

$$2p_0\sigma_{\text{g}} = \varphi_{\text{A}}(2, 1, 0, f) - \varphi_{\text{B}}(2, 1, 0, f) \quad ,$$

$$2p_{+}\pi_{\text{g}} = \varphi_{\text{A}}(2, 1, 1, f) - \varphi_{\text{B}}(2, 1, 1, f) \quad ,$$

$$2p_{-}\pi_{\text{u}} = \varphi_{\text{A}}(2, 1, -1, f) + \varphi_{\text{B}}(2, 1, -1, f) \quad .$$

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 detors which are eigenfunctions of the reflection operator (σ_{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

$$\sigma_{xz} \pi_g^+ = \pi_g^-$$

and

$$\sigma_{xz} \pi_u^+ = \pi_u^-$$

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

$$\varphi = c_1(1s\sigma_g) + c_2(2s\sigma_g) + c_3(2p\sigma_g) \quad ,$$

reflection in the xz-plane leaves this orbital unchanged as each of the σ -molecular orbitals is invariant under σ_{xz} however the orbital

$$\varphi_+ = c_1(2p_+\pi_g) + c_2(3d_+\pi_g)$$

is carried into

$$\varphi_- = c_1(2p_{-}\pi_g) + c_2(3d_{-}\pi_g) \quad ,$$

since the sign of m is changed by σ_{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 FØRTRAN V versions of routines written, in FØRTRAN 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(PNAME,NO)
C.....VERSION 3.
      TEXT PNAME
      DATA LP/0/
      IF(NO) 1,3,1
1 CALL CNTR(I)
      WRITE(LP,2) PNAME,I
2 FORMAT(' NUMBER OF INSTRUCTIONS USED ON ENTRY TO SUBPROGRAM ',A6,
1' = ',I5)
3 RETURN
      END
```

```
*FORTRAN LIB
      SUBROUTINE ERROR(A)
      DATA LDNO2/0/
      TEXT A
      WRITE(LDNO2,1) A
1 FORMAT(IHO,15A8)
      CALL BEXIT
      RETURN
      END
```

```
*FORTRAN LIB
      INTEGER FUNCTION IPAR(N)
C.....IF N IS EVEN THEN IPAR = 0,
C.....IF N IS ODD THEN IPAR = 1.
C.....*** ATLAS BASIC LANGUAGE ***
      101,81, 1,-0.4
      101,81,81,0.4
      121,82,0,1
      127,82,81, 0
      113,82,0,IPAR+0.4
      121,82,0,*03000000
      113,82,0,IPAR
      RETURN
      END
```

```
*FORTRAN LIB
      SUBROUTINE QUIT(PNAME,NO)
C.....VERSION 2.
      TEXT PNAME
      DATA LP/0/
      IF(NO) 1,3,1
1 CALL CNTR(I)
      WRITE(LP,2) PNAME,I
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)
```

```

CLEAR F,B,E(N)
DO 20 L = 1,N
CLEAR J
H=EPS*(ABS(D(L))+ABS(E(L)))
IF ( B .GE. H ) GOTO 2
B = H
2 DO 30 M = L,N
30 IF ( ABS(E(M)) .LE. B ) GOTO 3
3 IF ( M .EQ. L ) GOTO 4
5 IF ( J .EQ. 30 ) GOTO 6
J = J+1
P = (D(L+1) - D(L))/2*E(L)
R = SQRT(P**2 + 1)
IF ( P .LT. 0 ) GOTO 7
H = D(L) - E(L)/(P+R)
GOTO 111
7 H = P(L) - E(L)/(P-R)
111 DO 40 I = L,N
40 E(I) = D(I) - H
F = F+H
P = F(M)
C = 1
CLEAR S
IF ( M .EQ. L ) GOTO 3
KK = -(M-1)
KKK = -L
DO 50 II = KK,KKK
I = -II
G = C*E(I)
H = C*P
IF ( ABS(P) .LT. ABS(E(I))) GOTO 9
C = E(I)/P
R = SQRT(C**2+1)
E(I+1) = S*P*R
S = C/R
C = 1/R
GOTO 110
9 C = P/E(I)
R = SQRT(C**2+1)
E(I+1) = S*E(I)*R
S = 1/R
C = C/R
110 P = C*D(I) - S*G
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 E(L) = S*P
D(L) = C*P
IF ( ABS(E(L)) .GT. B ) GOTO 5
4 D(L) = D(L) + F
20 CONTINUE
DO 70 I = 1,N
K = I
P = D(I)
IF ( I .EQ. N ) GOTO 11
II = I+1
DO 80 J = II,N

```

```

      IF ( D(J) .GE. P ) GOTO 80
      K = J
      P = D(J)
80  CONTINUE
11  IF ( K .EQ. I ) GOTO 13
      D(K) = D(I)
      D(I) = P
      DO 90 J = 1,N
      P = Z(J,I)
      Z(J,I) = Z(J,K)
90  Z(J,K) = P
13  CONTINUE
70  CONTINUE
600 RETURN
      1 D(1)=Z(1,1)
      Z(1,1)=1.0
      GO TO 600
      6 NN=1
      RETURN
      END

```

*FORTRAN LIB

SUBROUTINE TREED2(N,TOL,NA,A,Z,D,E)

C THIS SUBROUTINE TRIDIAGONALISES A SYMETRIC 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

NN = -2

DO 30 II = M ,NN

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 .GT. TOL) GOTO 3

E(I) = F

CLEAR H

GOTO 111

3 L = L+1

IF (F .GE. 0) GOTO 4

E(I) = SQRT(H)

G = E(I)

GOTO 7

4 E(I) = -SQRT(H)

G = E(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 G = G + Z(J,K) * Z(I,K)
   IF ( J .EQ. L ) GOTO 5
   JJ = J+1
   DO 70 K = JJ,L
70 G = G + Z(K,J) * Z(I,K)
   E(J) = G/H
50 F = F + G * Z(J,I)
   HH = F/(H-HI)
   DO 80 J = 1,L
   F = Z(I,J)
   E(J) = E(J) - HH*F
   G = E(J)
   DO 140 K = 1,J
   Z(J,K) = Z(J,K) - F*E(K)-G*Z(I,K)
140 CONTINUE
30 CONTINUE
111 D(I) = H
30 CONTINUE
   CLEAR D(1),E(1)
   DO 100 I = 1,N
   L = I-1
   IF ( D(I) .EQ. 0 ) GOTO 6
   IF ( I .EQ. 1 ) GOTO 6
   DO 110 J = 1,L
   CLEAR G
   DO 120 K = 1,L
120 G = G + Z(I,K) * Z(K,J)
   DO 150 K = 1,L
   Z(K,J) = Z(K,J) - G*Z(K,I)
150 CONTINUE
110 CONTINUE
6 D(I) = Z(I,I)
  Z(I,I) = 1
  IF ( I .EQ. 1 ) GOTO 100
  DO 130 J = 1,L
  CLEAR Z(J,I),Z(I,J)
130 CONTINUE
100 CONTINUE
1 RETURN
END

```

*FORTRAN LIB

```

SUBROUTINE WRITMX(A,NROW,NCOL,MROW,MCOL,LP)
C.....CUTPUT OF REAL MATRIX TO DEVICE NUMBER LP.
  DIMENSION A(NROW,NCOL)
  DO 4 I=1,MCOL,5
  J=I+4
  IF(J-MCOL) 2,2,1
1 J=MCOL
2 WRITE(LP,3) I,J
3 FORMAT('0',52K,'COLUMNS',I3,' TO ',I3/)
  DO 4 K=1,MROW
  WRITE(LP,5) (A(K,L),L=I,J)
4 CONTINUE
5 FORMAT(' ',1P5E24,10)
  RETURN
END

```

APPENDIX IV

GENDET. A PROGRAM FOR GENERATING DETORS

OF A GIVEN ANGULAR MOMENTUM AND ELECTRON

SPIN FOR THE $D_{\infty h}$ SYMMETRY GROUP

GENDET is described in Chapters 7 and 8 and, although specifically designed for the $D_{\infty h}$ symmetry group, can be easily adapted to work for both $D_{\infty h}$ and $C_{\infty v}$. As stated in Chapter 7 each detor is characterized by its axial angular momentum Λ 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 Σ detors the effect of a reflection in the xz-plane. The matrix elements $\langle D_i | g^2 | D_j \rangle$ are computed (D_i and D_j are detors) and the corresponding matrix is diagonalized to provide eigenfunctions of g^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 NKEEP, 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. NKEEP, NFULL, MKEEP, INVERS, MREQ, SREQ

FORMAT (5I5, F10.5)

NKEEP	{	= 0 to stop execution,
	{	= number of spin-orbitals

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, Λ

SREQ = required value of z-component of
 electron spin, S_z .

Card 2 (I) IREF(I), INVR(I), MØM(I)

FØRMAT (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 ≤ I ≤ NKEEP)

Card 3 F

FØRMAT (9A8)

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

(('b', I3, 1X, mI3, nX, I4, 6X, I4))

or ((1Hb, I3, 1X, 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 Λ 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, LP, M, MKEEP, MB1, MREQ, NC, NFULL, NKEEP, NP, SREQ,
1 ISO(200, 30), IFU(30), IGU(30), IREF(30), INVR(30), MOM(30), F(9), LI(30)
TEXT F
DIMENSION ICLEAR(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.....MREQ=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 GRADE AND 1 IF ORBITAL I IS UNGRADE.
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.....INVERS=0 FOR GRADE DETERMINANTS AND 1 FOR UNGRADE DETERMINANTS.
1000 CLEAR ICLEAR
READ(ICR,1) NKEEP,NFULL,MKEEP,INVERS,MREQ,SREQ
1 FORMAT(5I5,F10.5)
IF(NKEEP.EQ.0) GO TO 109
READ(ICR,2) (IREF(I),INVR(I),MOM(I),I=1,NKEEP)
2 FORMAT(3I5)
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)) 998,997,997
998 IGU(I)=1
997 CONTINUE
IF(INVERS) 3,4,3
3 TEMP=' UNGRADE'
GO TO 5
4 TEMP=' GRADE'
5 WRITE(LP,6) MKEEP,NKEEP,NFULL,TEMP,MREQ,SREQ
6 FORMAT('1'//',27X,12,'-ELECTRON DETERMINANTS FROM',13,' SPIN-ORBI
1TALS(FIRST',13,' ARE FROZEN)//',10X,' DETERMINANTS ARE ',A3,' WIT
2H ',12,' UNITS OF AXIAL ANGULAR MOMENTUM AND ',F4.1,' UNITS OF SPI
3N IN Z-DIRECTION//')
WRITE(LP,7)
7 FORMAT('0',34X,' ORBITALS HAVE FOLLOWING PROPERTIES'//',4X,' ORBITA
1L',10X,' INVERSION',10X,' REFLECTION',10X,' INVERSION SYMMETRY',10X,
2' SPIN',10X,' AXIAL MOMENTUM')
DO 15 I=1,NKEEP
IF(IGU(I)) 9,8,9
8 TEMP=' GRADE'
GO TO 10
9 TEMP=' UNGRADE'

```

```

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(' ',I8,13X,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
   MM1=M-1
   NP=NFULL+1
X   DISPLAY(LP,13) /N,M,NP
   FIRST=.TRUE.
   CLEAR IC
17 CALL COMBIN(IFU,N,M,FIRST)
   IF(FIRST) GO TO 18
   CALL SETUP
   GO TO 17
18 CALL SPINIR
   WRITE(LP,108) NC,MKEEP,NFULL,IC
108 FORMAT('0', 4X,2I4,'-ELECTRON DETERMINANTS WITH FIRST ',I4,' SPIN
1ORBITALS FROZEN-',I4,' HAVE REQUIRED SYMMETRY AND SPIN VALUES')
   GO TO 1000
109 STOP
   END

```

*FORTRAN LIB

```

SUBROUTINE COLATE(IMAST,IQ,M,MAX1,MAX2,IC,ID)
C.....IMAST CONTAINS ORDERED SETS OF CONFIGURATIONS, IQ IS AN ORDERED
C.....CONFIGURATION TO BE IDENTIFIED WITH ONE OF THE IMAST.
COMMON KC,INVERS,LP
DIMENSION IMAST(MAX1,MAX2),IQ(MAX2)
DO 4 I1=1,IC
  I4=0
  DO 2 I2=1,M
    IF(IMAST(I1,I2)-IABS(IQ(I2))) 1,2,1
1  I4=I4+1
2  CONTINUE
  IF(I4) 4,3,4
3  ID=I1
  GO TO 7
4  CONTINUE
  IF(I4) 5,7,5
5  WRITE(LP,6)
6  FORMAT(1H0,9X,100H****COLLATION HAS NOT IDENTIFIED RESULT OF A REF
1LECTION OR INVERSION AS AN ORDERED CONFIGURATION****/)
  STOP
7  RETURN
END

```

*FORTRAN LIB

```

SUBROUTINE COMBIN(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  M=J(I)
      DO 3 L=I,K
      M=M+1
      J(L)=M
3  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),WK(20)
      DATA ICP,IDISC,JDISC,LP/5,58,59,0/
      TEXT F(9)
      TEXT TEMP/'SINGLET'/
      WRITE(ICP,14) IC
14  FORMAT(' ',I4)
      CLEAR NBLOCK
      TOL=2**(-347)
X  WRITE(LP,141) (I,INDEX(I),I=1,IC)
X 141  FORMAT(( ' ',2I5))
      EPS=2.0**(-35)
      DO 21 NLM=1,IC
      READ(IDISC) I,(ID(J),J=1,MKEEP),IRE,IVR,K,IALPHA,(ICOL(J),COE(J),
1J=1,IALPHA)
      IF(IRE) 12,13,12
12  IRE=ISIGN(INDEX(IABS(IRE)),IRE)
13  IVR=ISIGN(INDEX(IABS(IVR)),IVR)*(-1)**INVERS
X  DISPLAY(LP,5) /I,INDEX(I),IALPHA,K,ICOL(1)
      I=INDEX(I)
      WRITE(LP,F) I,(ID(J),J=1,MKEEP),IRE,IVR
      IF(K) 3,1,3
1  WRITE(LP,2) TEMP
2  FORMAT(' ',99X,A3)
      GO TO 9
3  DO 4 J=1,IALPHA
      ICOL(J)=INDEX(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
5  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(' ',90X,I10,4X,F7.3))
9 WRITE(ICP,10) (ID(J),J=1,MKEEP)
10 FORMAT(' ',32I2)
TRACE 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 NBLOCK=NBLOCK+1
LIMSET(NBLOCK,1)=MIN
LIMSET(NBLOCK,2)=MAX
GO TO 21
19 IF(MIN-LIMSET(NBLOCK,2)) 20,20,18
20 LIMSET(NBLOCK,1)=MINO(MIN,LIMSET(NBLOCK,1))
LIMSET(NBLOCK,2)=MAXO(MAX,LIMSET(NBLOCK,2))
21 CONTINUE
REWIND IDISC
REWIND JDISC
C.....DIAGONALIZATION OF SPIN OPERATOR MATRIX.
WRITE(LP,22) NBLOCK
22 FORMAT('0',36X,'SPIN OPERATOR MATRIX HAS',I4,' BLOCKS ON DIAGONAL'
1)
X WRITE(LP,220)
X 220 FORMAT('0',51X,'CONTENTS OF LIMSET'/ ' ')
X WRITE(LP,221) ((I,J,LIMSET(I,J),J=1,2),I=1,NBLOCK)
X 221 FORMAT(((' ',40X,2('LIMSET(' ,I3,' ',I1,' ')=' ',I4,4X)))
DO 36 NLM=1,NBLOCK
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
KVAL=ICOL(JVAL)-IVR
OP(JMIN,KVAL)=COE(JVAL)
23 CONTINUE
X CALL WRITMX(OP,20,20,IRE,IRE,LP)
CALL TRED2(IRE,TOL,20,OP,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',I4,' TO ',I4,' FORM TOTAL SPIN E

```

```

1EIGENFUNCTIONS AS FOLLOWS')
  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,'MULTIPLICITIES (=2*S+1) FOR EIGENFUNCTIONS',I4,' T
10 ',I4/(' ',1P5E24.10))
    WRITE(LP,27) IVAL,JVAL
27 FORMAT('0',43X,'EIGENVECTORS',I4,' TO ',I4/' ')
    DO 29 KVAL=1,IRE
      WRITE(LP,28) (OP(KVAL,JMIN),JMIN=IVAL,JVAL)
28 FORMAT(' ',1P5E24.10)
29 CONTINUE
36 CONTINUE
  REWIND IDISC
  REWIND JDISC
  RETURN
  END

```

*FORTRAN LIB

```

  SUBROUTINE PERMUT(IOTA,IE,M,MM1,MAX)
C.....PERMUTES ELEMENTS (KI) OF IOTA SO THAT RESULT IS AN ORDERED
C.....CONFIGURATION WITH K1.LE.K2.LE.K3...LE.KM.
C.....IE=PARITY OF PERMUTATION.
  DIMENSION IOTA(MAX)
  IE=0
  DO 3 I1=1,MM1
    K1=I1+1
    DO 2 J1=K1,M
      IF(ABS(IOTA(J1))-ABS(IOTA(I1))) 1,2,2
1 I2=IOTA(I1)
      IOTA(I1)=IOTA(J1)
      IOTA(J1)=I2
      IE=IE+1
2 CONTINUE
3 CCNTINUE
  IE=(-1)**IE
  RETURN
  END

```

*FORTRAN LIB

```

  SUBROUTINE SETUP
C.....COMPUTES MZ AND SZ FOR DETERMINANT NC+1 AND DETERMINES SYMMETRY.
  COMMON IC,INVERS,LP,M,MKEEP,MM1,MREQ,NC,NFULL,NKEEP,NP,SREQ,
1 ISO(200,30),IFU(30),IGU(30),IREF(30),INVR(30),MEM(30),F(9)
  TEXT F
  NC=NC+1
  IC=IC+1
  CLEAR ISZ,MZ,INVERT
  DO 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

```

```

2 ISZ=ISZ-1
3 MZ=MZ+MCM(J)
  INVERT=INVERT+IGU(J)
4 CONTINUE
X   WRITE(LP,100) (IFU(I),I=1,M),ISZ,MZ,INVERT
X 100 FORMAT(' ',20X,12I3,4X,'ISZ=',I2,' MZ=',I2,' INVERT=',I2)
      IF(MREQ-MZ) 7,5,7
      5 IF(MOD(INVERT,2)-INVERS) 7,6,7
      6 IF(SREQ-0.5*ISZ) 7,8,7
      7 IC=IC-1
      RETURN
      8 IF(IC-200) 11,11,9
C.....TOO MANY DETERMINANTS.
      9 WRITE(LP,10) (IFU(I),I=1,M)
     10 FORMAT('0',37X,'TOO MANY DETERMINANTS - LAST ONE GENERATED WAS'//
     1' ',15X,30I3)
      CALL EXIT
     11 RETURN
      END

```

*FORTRAN LIB

```

      SUBROUTINE SPINIR
C.....DETERMINES RESULT OF INVERSION, REFLECTION AND TOTAL SPIN
C.....(S**2) OPERATIONS.
      COMMON IC,INVERS,LP,M,MKEEP,MM1,MREQ,NC,NFULL,NKEEP,NP,SREQ,
     1ISO(200,30),IFU(30),IGU(30),IREF(30),INVR(30),MCM(30),F(9)
      TEXT F
      TEXT TEMP/' SINGLET'/
      DIMENSION IUO(10,2),ISMOP(10,10),ISPOP(252,10),ICOEF(252),ID(30),
     1ICOL(252),ISOR(30),ISOI(30),COE(252)
      EQUIVALENCE (IFU,ID),(ICOEF,COE)
      DIMENSION INDEX(200)
      DATA IDISC/58/
      CLEAR INDEX,NCOUNT,IRE
      IF(IC) 39,39,990
990 DO 33 NLM=1,IC
      I=NLM
      42 IF(INDEX(I)) 33,43,33
      43 NCCUNT=NCOUNT+1
      INDEX(I)=NCOUNT
      CLEAR ICOEF,COE
      DO 1 J=1,M
      K=ISO(I,J)
      ISOR(J)=IREF(K)
      ISOI(J)=INVR(K)
      1 CONTINUE
C.....PERMUTE ELEMENTS (KI) OF RESULTING DETERMINANTS SO THAT THEY FORM
C.....ORDERED DETERMINANTS WITH K1.LT.K2.LT.....LT.KM. DETERMINE WHICH
C.....ORDERED DETERMINANTS THESE ARE.
      IF(MREQ) 102,101,102
     101 CALL PERMUT(ISOR,IR,M,MM1,30)
      CALL COLATE(ISO,ISOR,M,200,30,IC,IRE)
      IRE=ISIGN(IRE,IR)
     102 CALL PERMUT(ISOI,IV,M,MM1,30)
      CALL COLATE(ISO,ISOI,M,200,30,IC,IVR)
      IVR=ISIGN(IVR,IV)
      CLEAR ISMOP,ISPOP,IUO,K
C.....START OF TOTAL SPIN OPERATOR SECTION.
C.....DETERMINE WHICH SPATIAL ORBITALS ARE SINGLY OCCUPIED - ONLY

```

```

C.....THESE CONTRIBUTE TO S**2.
  IF((ISO(I,1)+1)/2-(ISO(I,2)+1)/2) 2,3,2
2 K=K+1
  IUO(K,1)=ISO(I,1)
  IUO(K,2)=1
3 DO 6 J=2,MM1
  JORB=(ISO(I,J)+1)/2
  IF((ISO(I,J-1)+1)/2-JORB) 4,6,4
4 IF((ISO(I,J+1)+1)/2-JORB) 5,6,5
5 K=K+1
  IUO(K,1)=ISO(I,J)
  IUO(K,2)=J
6 CONTINUE
  IF(JORB-(ISO(I,M)+1)/2) 7,8,7
7 K=K+1
  IUO(K,1)=ISO(I,M)
  IUO(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 IALPHA=1,K
  IF(IPAR(IUO(IALPHA,1))) 10,15,10
C.....OPERATE ON ALPHA SPIN WITH S-.
10 LSM=LSM+1
DO 11 J=1,K
  ISMOP(LSM,J)=IUO(J,1)
11 CONTINUE
  ISMOP(LSM,IALPHA)=IUO(IALPHA,1)+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.
DO 16 IALPHA=1,LSP
  ICCEF(IALPHA)=1
16 CONTINUE
  LSM=LSP-1
  IF(LSM) 211,211,161
161 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
19 ICOEF(INNER)=ICCEF(INNER)+ICOEF(IOUTER)
  CLEAR ICOEF(IOUTER)
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)=ISO(I,J)
23 CONTINUE
    DO 24 J=1,K
    INLIM=IUO(J,2)
    ID(INLIM)=ISPOP(IALPHA,J)
24 CONTINUE
C.....RE-ORDER ID AND COLLATE WITH ISO.
    CALL PERMUT(ID,IE,M,MM1,30)
    CALL COLATE(ISO,ID,M,200,30,IC,ICO)
    ICCL(IALPHA)=ICO
    COE(IALPHA)=ICOEF(IALPHA)
C.....OPERATE ON I-TH. DETERMINANT WITH SZ*(SZ-1).
    IF(I-ICO) 26,25,26
25 COE(IALPHA)=FLOAT(ICOE(IALPHA))+SREQ*(SREQ-1.0)
26 COE(IALPHA)=SIGN(COE(IALPHA),IE)
23 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=NP,MKEEP
    ID(J)=ISO(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
32 CLEAR COE(1)
    IALPHA=1
    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,MKEEP),IRE,IVR,K,IALPHA,(ICOL(J),COE(J),
    1J=1,IALPHA)
X    DISPLAY(LP,10) /K,IALPHA
X    WRITE(LP,95) (J,ICOL(J),J,COE(J),J=1,IALPHA)
X 95 FORMAT(' ',4('ICOL(',I3,')=',I3, ' COE(',I3,')=',F7.3))
    IF(K) 361,371,361
361 DO 37 J=1,IALPHA
    IF(COE(J)) 362,37,362
362 IF(INDEX(ICCL(J))) 37,363,37
363 I=ICOL(J)
    GO TO 43
37 CONTINUE
371 IF(MREQ) 33,372,33
372 IF(INDEX(IABS(IRE))) 33,373,33
373 I=IABS(IRE)
    GO TO 43

```

```
33  CONTINUE
    ENDFILE IDISC
    REWIND IDISC
42  FORMAT(' ',32I2)
    CALL OUTDET(INDEX,COE,ICOL,ID,F,IC,MKEEP)
39  RETURN
    END
*ENDLIB
```


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

ORBITALS HAVE FOLLOWING PROPERTIES		INVERSION SYMMETRY		SPIN	AXIAL MOMENTUM
ORBITAL	INVERSION	REFLECTION	GERADE		
1	1	1	GERADE	ALPHA	0
2	2	2	GERADE	BETA	0
3	3	3	UNGERADE	ALPHA	0
4	4	4	UNGERADE	BETA	0
5	5	5	GERADE	ALPHA	0
6	6	6	GERADE	BETA	0
7	7	7	UNGERADE	ALPHA	0
8	8	8	UNGERADE	BETA	0
9	9	9	GERADE	ALPHA	0
10	10	10	GERADE	BETA	0
11	11	11	UNGERADE	ALPHA	0
12	12	12	UNGERADE	BETA	0
13	13	13	GERADE	ALPHA	0
14	14	14	GERADE	BETA	0
15	15	15	UNGERADE	ALPHA	0
16	16	16	UNGERADE	BETA	0
17	17	17	GERADE	ALPHA	1
18	18	18	GERADE	BETA	1
19	19	19	UNGERADE	ALPHA	1
20	20	20	UNGERADE	BETA	1

NO.	DETERMINANT																REFLECTION INVERSION		S**2
	1	2	3	4	5	6	7	8	9	10	11	16	17	18	19	20	0	1	
1	1	2	3	4	5	6	7	8	9	10	11	16	17	18	19	20	0	1	1.0
2	1	2	3	4	5	6	7	8	9	10	12	15	17	18	19	20	0	2	1.0
3	1	2	3	4	5	6	7	8	9	11	12	14	17	18	19	20	0	3	1.0
4	1	2	3	4	5	6	7	8	10	11	12	13	17	18	19	20	0	4	1.0
5	1	2	3	4	5	6	7	9	10	11	12	16	17	18	19	20	0	5	1.0
6	1	2	3	4	5	6	8	9	10	11	12	15	17	18	19	20	0	6	1.0 ¹⁸⁰
7	1	2	3	4	5	7	8	9	10	11	12	14	17	18	19	20	0	7	1.0
8	1	2	3	4	6	7	8	9	10	11	12	13	17	18	19	20	0	8	1.0

SPIN OPERATOR MATRIX HAS 4 BLOCKS ON DIAGONAL

DETERMINANTS 1 TO 2 FORM TOTAL SPIN EIGENFUNCTIONS AS FOLLOWS

MULTIPLICITIES ($2S+1$) FOR EIGENFUNCTIONS 1 TO 2
 1.0000000000E+00 3.0000000000E+00

EIGENVECTORS 1 TO 2

7.0710678119E-01 7.0710678119E-01
 -57.0710678119E-01 7.0710678119E-01

DETERMINANTS 3 TO 4 FORM TOTAL SPIN EIGENFUNCTIONS AS FOLLOWS

MULTIPLICITIES (2*S*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

DETERMINANTS 5 TO 6 FORM TOTAL SPIN EIGENFUNCTIONS AS FOLLOWS

MULTIPLICITIES (E2*S*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

DETERMINANTS 7 TO 8 FORM TOTAL SPIN EIGENFUNCTIONS AS FOLLOWS

MULTIPLICITIES (2*S*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

320 16-ELECTRON DETERMINANTS WITH FIRST 4 SPIN ORBITALS FROZEN 8 HAVE REQUIRED SYMMETRY AND SPIN VALUES

APPENDIX V

~~ONECEN.~~ A PROGRAM FOR COMPUTING ONE-CENTRE

ONE- AND TWO-ELECTRON INTEGRALS OVER COMPLEX

SLATER-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.

$\emptyset$ NECEN 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 $\emptyset$ NECEN 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 ONECEN

```
Card 1      I
            FØRMAT (I5)
            I { = 0 to stop execution
                = 1 to continue execution
```

[illegible]

Card 3, 4. TITLE

~~F~~ORMAT (9A8/6A8)

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

Card 5 NBASIS, CH

~~F~~ORMAT (I5, F10.5)

NBASIS = number of basis orbitals

CH = nuclear charge (a.u.)

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

~~F~~ORMAT (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-GORDON COEFFICIENTS $C_{L_1 m_1 L_2 m_2}^{M m_1 m_2}$

NUMBER OF NON-ZERO COEFFICIENTS = 152.

CG(1)= 0.2820947918 CG(9)= 0.2820947918 CG(17)= 0.2820947918
CG(18)= 0.2523132522 CG(25)= 0.2820947918 CG(34)= 0.2185096861
CG(42)= 0.3090193616 CG(45)= 0.2820947918 CG(46)= -0.1261566261
CG(50)= 0.2820947918 CG(57)= 0.2523132522 CG(58)= 0.2477666951
CG(65)= -0.1261566261 CG(66)= 0.2023006594 CG(73)= 0.2820947918
CG(74)= 0.1802237516 CG(75)= 0.2417955358 CG(82)= 0.2820947918
CG(89)= 0.2185096861 CG(90)= 0.2335966803 CG(98)= 0.2611690283
CG(101)= 0.2185096861 CG(102)= -0.1430481681 CG(106)= 0.0901118758
CG(107)= 0.2207281154 CG(114)= 0.2207281154 CG(115)= 0.2548748737
CG(117)= 0.2820947918 CG(118)= 0.0901118758 CG(119)= -0.1611970239
CG(122)= 0.2820947918 CG(130)= 0.1846743909 CG(138)= 0.3198654279
CG(141)= 0.3090193616 CG(142)= -0.0825888984 CG(146)= -0.1802237516
CG(147)= 0.1560783472 CG(155)= 0.2384136135 CG(158)= 0.2207281154
CG(159)= -0.0901118758 CG(163)= 0.3371677657 CG(165)= 0.2820947918
CG(166)= -0.1802237516 CG(167)= 0.0402992560 CG(170)= 0.2820947918
CG(178)= 0.2477666951 CG(179)= 0.2462325212 CG(186)= -0.1430481681
CG(187)= 0.1946639003 CG(193)= 0.2477666951 CG(194)= 0.1682088348
CG(195)= 0.2396146972 CG(201)= -0.1430481681 CG(202)= 0.0594708039
CG(203)= 0.2143179006 CG(210)= -0.1880631945 CG(211)= 0.1417579666
CG(217)= 0.2820947918 CG(218)= 0.1682088348 CG(219)= 0.1538698864
CG(220)= 0.2370879339 CG(226)= 0.2820947918 CG(234)= 0.2335966803
CG(235)= 0.2384136135 CG(242)= -0.0825888984 CG(243)= 0.2384136135
CG(246)= 0.2023006594 CG(247)= -0.1507860088 CG(249)= 0.2023006594
CG(250)= 0.1261566261 CG(251)= 0.2273184612 CG(258)= 0.1628675040
CG(259)= 0.2455320005 CG(261)= 0.2335966803 CG(262)= 0.0594708039
CG(263)= -0.1694331773 CG(266)= -0.1329807601 CG(267)= 0.2004760390
CG(269)= -0.0825888984 CG(270)= 0.2060129077 CG(271)= -0.0928023732
CG(274)= 0.0594708039 CG(275)= 0.0993225846 CG(276)= 0.2217754548
CG(282)= 0.2060129077 CG(283)= 0.1621931015 CG(284)= 0.2429428385
CG(285)= 0.2820947918 CG(286)= 0.1261566261 CG(287)= 0.0256449811
CG(288)= -0.1778159504 CG(290)= 0.2820947918 CG(298)= 0.1846743909
CG(299)= 0.2132436186 CG(307)= 0.2820947918 CG(310)= 0.2611690283
CG(311)= -0.1066218093 CG(314)= -0.0000000000 CG(315)= 0.1901882698
CG(322)= 0.2102610435 CG(323)= 0.2535843598 CG(325)= 0.2611690283
CG(326)= 0.1628675040 CG(327)= -0.1173867486 CG(331)= 0.2689668306
CG(333)= 0.1846743909 CG(334)= -0.1880631945 CG(335)= 0.0535794751
CG(338)= -0.1880631945 CG(339)= -0.0444184102 CG(340)= 0.1774203638
CG(347)= 0.0959547329 CG(348)= 0.2304758133 CG(350)= 0.1628675040
CG(351)= 0.1450699201 CG(352)= -0.1214714193 CG(355)= 0.2145613054
CG(356)= 0.2661305457 CG(357)= 0.2820947918 CG(358)= -0.0000000000
CG(359)= -0.1795148675 CG(360)= 0.0711263802 CG(362)= 0.2820947918
CG(371)= 0.1628675040 CG(379)= 0.3257350079 CG(382)= 0.3198654279
CG(383)= -0.0615581303 CG(386)= -0.2102610435 CG(387)= 0.1267921799
CG(395)= 0.2196104975 CG(398)= 0.2102610435 CG(399)= -0.0633960899
CG(403)= 0.3472346852 CG(405)= 0.3198654279 CG(406)= -0.1329807601
CG(407)= 0.0239614697 CG(411)= -0.2035507269 CG(412)= 0.1086473403
CG(419)= -0.1661984725 CG(420)= 0.1717865286 CG(422)= -0.1329807601
CG(423)= 0.1884513543 CG(424)= -0.0627275712 CG(428)= 0.2548005987
CG(430)= 0.2102610435 CG(431)= -0.1404633462 CG(432)= 0.0313637856
CG(436)= 0.3603424623 CG(437)= 0.2820947918 CG(438)= -0.2102610435
CG(439)= 0.0769349432 CG(440)= -0.0118543967 CG(0)= 0.0000000000

```

*FORTRAN LIB 3,1,0
C.....MAIN PROGRAM FOR SINGLE CENTRE INTEGRAL PROGRAM.
C.....VERSION 2. 12/05/71.
      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(465,2),L(30),M(30),N(30),S(30,30),TITLE(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) I,K
      READ(ID) (CG(I),I=1,440)
      UNLOAD ID
      FCTRL(1)=1.0
      DO 1 I=2,25
      K=I-1
      FCTRL(I)=K*FCTRL(K)
1 CONTINUE
2 READ(ICR,3) I
  IF(I.EQ.0) STOP
3 FORMAT(15)
  CALL OUTBRK(LP)
  CALL ALLONE
  GO TO 2
END

*FORTRAN LIB
      SUBROUTINE ALLONE
C.....ONE-CENTRE ONE- AND TWO- ELECTRON INTEGRALS.
      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(465,2),L(30),M(30),N(30),S(30,30),TITLE(15),Z(30)
      READ(ICR,36) NXBLOC
      CALL SEARCH(MTD25,NXBLOC,0)
      READ(ICR,1) TITLE
      READ(ICR,2) NBASIS,CH,(N(I),L(I),M(I),Z(I),I=1,NBASIS)
      WRITE(LP,3) TITLE
      WRITE(LP,35) CH
      WRITE(LP,4) (N(I),L(I),M(I),Z(I),I=1,NBASIS)
1 FORMAT(9A3/6A3)
2 FORMAT(15,F10.5/(3I5,F10.5))
3 FORMAT(1H1/1H ,15A3)
4 FORMAT(1H ,40X,23HN      L      M      EXPONENT/((1H ,44X,3I5,F12.5)))
      NB=(NBASIS*(NBASIS+1))/2
      NI=(NB*(NB+1))/2
      WRITE(LP,33) NI
      WRITE(LP,37) NXBLOC
      DO 16 I=1,NBASIS
      NI=2*N(I)+1
      ANORM(I)=SQRT((2.0*Z(I))**NI/FCTRL(NI))
      DO 16 K=1,I
      S(I,K)=0.0
      H(I,K)=0.0
      IF(L(I)-L(K)) 15,11,15
11 IF(M(I)-M(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))
IF(N(K)-L(K)-1) 14,14,13
13 N2=N(I)+N(K)-1
NP=2*N(K)-3
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)*DIV**N2*SQRT(ZK**NP/FCTRL(NP))
N2=N2+1
S(I,K)=ANORM(I)*ANORM(K)*DIV**N2*FCTRL(N2)
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(1H1/1H ,43X,34H)OVERLAP 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
DO 21 J=1,NBASIS
WRITE(LP,20) (S(J,KK),KK=I,K)
20 FORMAT((1H ,1P5E24.10))
21 CONTINUE
WRITE(LP,22)
22 FORMAT(1H0,34X,51H)ONE-ELECTRON HAMILTONIAN MATRIX FOR ATOMIC ORBIT
1ALS/)
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
I=100000
WRITE(MTD25) I
WRITE(MTD25) TITLE,J
DO 26 I=1,NBASIS
WRITE(MTD25) (S(I,J),J=1,NBASIS)
WRITE(MTD25) (H(I,J),J=1,NBASIS)
26 CONTINUE
WRITE(LP,34)
IF(NBASIS.GT.5) WRITE(LP,38)
DO 27 I=1,NBASIS
J=(I*(I-1))/2
DO 27 K=1,I
KK=K+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
      WRITE(MTD25) (ERI(J),J=1,I)
      IF(NBASIS.GT.5) GO TO 31
      WRITE(LP,30) I
30  FORMAT(1H0,49X,19HCONTENTS OF RECORD ,I2/)
      WRITE(LP,20) (ERI(J),J=1,I)
31  CONTINUE
32  FORMAT(1H0,52X,8HCOLUMNS ,I2,4H TO ,I2/)
33  FORMAT(1H0,32X,51HNUMBER OF TWO-ELECTRON INTEGRALS TO BE CALCULATE
      ID =,I7/)
34  FORMAT(1H0,49X,22HTWO-ELECTRON INTEGRALS)
35  FORMAT(1H0,45X,17HNUCLEAR CHARGE = ,F10.5/)
      CALL WHITPS
      REWIND MTD25
36  FORMAT(I5)
37  FORMAT('0',38X,'INTEGRALS BEGIN AT BLOCK',I4,' OF MASTER FILE')
38  FORMAT('0',37X,'PRINTING OF TWO-ELECTRON INTEGRALS SUPPRESSED')
      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*MIN0(I1,I2)+LL/2
      IF(IABS(MM)-IM1-IM2) 2,1,2
1  I=7
      GO TO 3
2  I=3
3  INDEX1=IZ-I
      RETURN
      END

```

*FORTRAN LIB

```

      FUNCTION SC(IA,IC,IB,ID)
      COMMON /TOALL/ KEEP(22),ANORM(30),CG(440),ERI(465),FCTRL(25),
      1H(30,30),IN(465,2),L(30),M(30),N(30),S(30,30),TITLE(15),Z(30)
      CLEAR SC
      LOWAC=IABS(L(IA)-L(IC))
      LOWBD=IABS(L(IB)-L(ID))
      IF(IPAR(LOWAC)-IPAR(LOWBD)) 4,1,4
1  FOURPI=1.2566370614E+01
      LOW=MAX0(LOWAC,LOWBD)+1
      IGH=MIN0(L(IA)+L(IC),L(IB)+L(ID))+1
      IF(IGH-LOW) 4,2,2
2  MM=M(IC)-M(IA)
      Z1=Z(IA)+Z(IC)
      Z2=Z(IB)+Z(ID)
      N1=N(IA)+N(IC)
      N2=N(IB)+N(ID)
      DO 3 MUP=LOW,IGH,2
      MU=MUP-1

```



```
JA=INDEX1( MM,-M(IA),M(IC),MU,L(IA),L(IC))
JB=INDEX1(-MM,-M(IB),M(ID),MU,L(IB),L(ID))
SC=SC+FOURPI/FLOAT(2*MU+1)*CG(JA)*CG(JD)*W(MU,N1,N2,Z1,Z2)
3 CONTINUE
SC=ANORM(IA)*ANORM(IB)*ANORM(IC)*ANORM(ID)*SC
4 RETURN
END
```

*FORTRAN LIB

```
FUNCTION W(IMU,N1,N2,Z1,Z2)
COMMON /TOALL/ KEEP(22),ANORM(30),CG(440),ERI(465),FCTRL(25),
1H(30,30),IN(465,2),L(30),K(30),N(30),S(30,30),TITLE(15),Z(30)
X1=Z1
X2=Z2
NU=N2-IMU-1
MU=N1+N2
IP=-MU-1
CLEAR JUMP
1 A=1.0+X1/X2
MIN=MU-NU
X1=FCTRL(MIN)/A**MIN
MIN=MIN+1
CLEAR M
DO 2 I=MIN,MU
M=M+1
X1=M*X1+FCTRL(I)/A**I
2 CONTINUE
IF(JUMP) 4,3,4
3 JUMP=1
W=X2**IP*X1
NU=N1-IMU-1
X1=Z2
X2=Z1
GO TO 1
4 W=W+X2**IP*X1
RETURN
END
```


ONECEN TEST DATA - INTEGRALS FOR ATOMIC OXYGEN (SCHAEFER AND HARRIS'S EXPONENTS),

NUCLEAR CHARGE = 8.00000		
V	L	M
1	0	0
2	0	0
2	1	0
2	1	-1
2	1	1

NUMBER OF TWO-ELECTRON INTEGRALS TO BE CALCULATED = 120

INTEGRALS BEGIN AT BLOCK 50 OF MASTER FILE

OVERLAP MATRIX FOR ATOMIC ORBI

		COLUMNS 1 TO 5
1.0000000000E+00	2.3092477658E-01	0.0000000000E+00
2.3092477658E-01	9.9999999995E-01	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00	1.0000000000E+00
0.0000000000E+00	0.0000000000E+00	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00	0.0000000000E+00

ONE-ELECTRON HAMILTONIAN MATRIX FOR ATC

		COLUMNS 1 TO 5
-3.1941106880E+01	-7.0326342795E+00	0.0000000000E+00
-7.0326342795E+00	-8.1471486930E+00	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00	-6.4268167801E+00
0.0000000000E+00	0.0000000000E+00	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00	0.0000000000E+00

TWO-ELECTRON INTEGRALS

4.7855000002E+00

CONTENTS OF RECORD 1:

6.7428461270E-01

.1,2109572047E-01

CONTENTS OF RECORD 2:

1.1160172066E+00

2.4866514181E-01

CONTENTS OF RECORD 3:
8.1636582501E-01

0.0000000000E+00

0.0000000000E+00

CONTENTS OF RECORD 4:
0.0000000000E+00

0.0000000000E+00

0.0000000000E+00

CONTENTS OF RECORD 5:
0.0000000000E+00

1.1057938455E+00

2.4658162661E-01

CONTENTS OF RECORD 6:
8.1252421597E-01

8.7134859387E-01

CONTENTS OF RECORD 7:
0.0000000000E+00

0.0000000000E+00

0.0000000000E+00

0.0000000000E+00

2.4875854665E-02

CONTENTS OF RECORD 8:
0.0000000000E+00
1.7957634874E-01

0.0000000000E+00

0.0000000000E+00

0.0000000000E+00

3.8251260845E-02

CONTENTS OF RECORD 9:
0.0000000000E+00
0.0000000000E+00

0.0000000000E+00

0.0000000000E+00

0.0000000000E+00

0.0000000000E+00

CONTENTS OF RECORD 10:
8.1252421597E-01
0.0000000000E+00

1.1057938455E+00

2.4658162661E-01

7.7743078136E-01

0.0000000000E+00

CONTENTS OF RECORD 11:
0.0000000000E+00
3.8251260845E-02

0.0000000000E+00

0.0000000000E+00

0.0000000000E+00

2.4875854665E-02

2.4875854665E-02

0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
1.0000000000E+00
0.0000000000E+00

0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
1.0000000000E+00

11C ORBITALS

0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
-6.4268167801E+00
0.0000000000E+00

0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
-6.4268167801E+00

2.4875854665E-02

3.8251260845E-02

1.7957634274E-01

0.0000000000E+00

0.0000000000E+00

0.0000000000E+00

0.0000000000E+00

0.0000000000E+00

0.0000000000E+00

0.0000000000E+00
4.6958906255E-02

0.0000000000E+00

0.0000000000E+00
0.0000000000E+00

0.0000000000E+00
8.2438968761E-01

0.0000000000E+00
0.0000000000E+00

0.0000000000E+00
0.0000000000E+00

0.0000000000E+00
0.0000000000E+00
3.8251260845E-02

0.0000000000E+00
3.8251260845E-02
1.7957634874E-01

CONTENTS OF RECORD 12

0.0000000000E+00
1.7957634874E-01

0.0000000000E+00
0.0000000000E+00
0.0000000000E+00

0.0000000000E+00
0.0000000000E+00
0.0000000000E+00

CONTENTS OF RECORD 13

0.0000000000E+00
0.0000000000E+00
4.6958906255E-02

0.0000000000E+00
0.0000000000E+00
0.0000000000E+00

0.0000000000E+00
0.0000000000E+00
0.0000000000E+00

CONTENTS OF RECORD 14

0.0000000000E+00
0.0000000000E+00
0.0000000000E+00

1.1057938455E+00
7.7743078136E-01
0.0000000000E+00

2.4658162661E-01
0.0000000000E+00
0.0000000000E+00

CONTENTS OF RECORD 15

8.1252421597E-01
0.0000000000E+00
0.0000000000E+00

TAPE POSITIONED AT
NUMBER BLOCK WORD
1 50 214

TAPE POSITIONED AT
NUMBER BLOCK WORD
3 6 0

0.0000000000E+00
0.0000000000E+00

0.0000000000E+00
0.0000000000E+00

0.0000000000E+00
4.6958906255E-02

0.0000000000E+00
0.0000000000E+00

0.0000000000E+00
0.0000000000E+00
9.3917812509E-02

0.0000000000E+00
0.0000000000E+00

0.0000000000E+00
0.0000000000E+00
0.0000000000E+00

0.0000000000E+00
8.2438968761E-01
8.2438968761E-01

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, ERRØR, 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:

VARIABLE NAME	VALUE = DEVICE No.
------------------	-----------------------

LDNØ3	3	A common disc area of 710 blocks.
-------	---	-----------------------------------

LDNØ8	4	A common disc area of 555 blocks.
-------	---	-----------------------------------

LDNØ9	5	A common disc area of 555 blocks
-------	---	----------------------------------

LDN10	6	A private magnetic tape containing the file of untransformed integrals, produced in the same order as those of ØNECEN
-------	---	---

LDN11	Defined in	Master transformed integral tape which will data contain the file of transformed integrals.
-------	------------	--

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 (I5)

NBASIS = number of basis orbitals

Card 2 IWHERE, ISTART (15)

FORMAT (2I5)

IWHERE = 1

ISTART(15) $\left\{ \begin{array}{l} = 0 \text{ to suppress timing information} \\ = 1 \text{ to obtain timing information} \end{array} \right.$

Card 3 NEXTBL

FORMAT (I5)

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 (2I5)

IWHERE = 2

ISTART(15) : see section 1 card 2

Card 2 JSER, ISTOP

FORMAT (2I5)

JSER = serial number given to the untransformed
integral file by the integral generation
program. If the program ~~ONECEN~~ was used
then JSER = 100000

ISTOP = 1

Card 3

(M(I), I = 1, NBASIS)

FORMAT (30I2)

	{	= 0 if the magnetic quantum number of the I-th atomic orbital and the I-th transformed orbital are different.
M(I)		= magnetic quantum number of the I-th atomic orbital if the magnetic quantum number of the I-th transformed orbital is the same.

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

Card 1

IWHERE, ISTART(15)

FORMAT (2I5)

IWHERE = 3

	{	= 0 to suppress timing information and printing of one-electron integrals (untransformed)
ISTART(15)		= 1 to obtain timing information and printing of untransformed one-electron integrals

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

Card 1

IWHERE, ISTART(15)

FORMAT (2I5)

IWHERE = 4

ISTART(15) = see section 1 card 2

Card 2 ~~N~~ØNO

~~F~~ØRMAT (I5)

~~N~~ØNO = 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)

~~F~~ØRMAT (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~~ØNO)

Card 4 NIR

~~F~~ØRMAT (I5)

NIR = number of different irreducible representations
to which the transformed orbitals belong;
subspecies are counted as different.

Card 5 (IRI(I), I = 1, NBASIS)

~~F~~ØRMAT (16I5)

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 ≤ IRI(I) ≤ 10000
(continue onto successive cards if
NBASIS > 16)

Section 5 : Transformation of two-electron integrals

Card 1 IWHERE, ISTART(15)

FØRMAT (2I5)

IWHERE = 5

ISTART(15) $\left\{ \begin{array}{l} = 0 \text{ to suppress timing information and} \\ \text{the printing of the transformed two-} \\ \text{electron integrals} \\ = 1 \text{ to obtain timing information and the} \\ \text{printing of the transformed two-electron} \\ \text{integrals} \end{array} \right.$

Card 2 ISER

FØRMAT (I10)

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

Card 3 (ISTART(I), I = 5, 12)

FØRMAT (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)

 FØRMAT(2I5)

 IWHERE = 6

 ISTART(15) : see section 1 card 2

Card 2, 3 TITLE

 FØRMAT (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

 FØRMAT (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)

 FØRMAT (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)
 FØRMAT (2I5)
 IWHERE = 8
 ISTART(15) = 0

Restrictions

1 ≤ NBASIS ≤ 30


```

*FORTRAN LIB 8,5,325
C.....MAIN ROUTINE FOR INTEGRAL TRANSFORMATION PROGRAM.
      COMMON /TOALL/ NBASIS,NB,ISTOP,ISTART(20),M(30),LDN01,LDN02,LDN03,
      1LDN08,LDN09,LDN10,LDN11
      COMMON /TOSUM/ AREA1(3469)
      COMMON AREA2(13530)
C.....DEFINE DEVICE NUMBERS,
C.....LDN01=CARD READER,
C.....LDN02=LINE PRINTER,
C.....LDN03=INTEGRAL FILE,
C.....LDN08=WORK FILE 1,
C.....LDN09=WORK FILE 2,
C.....LDN10=MASTER INTEGRAL FILE.
      CLEAR LDN01,LDN02
      LDN03=3
      LDN08=4
      LDN09=5
      LDN10=6
11 CLEAR ISTART,M,AREA1,AREA2
      CALL CUTBRK(LDN02)
      REWIND LDN03
      REWIND LDN08
      REWIND LDN09
      READ(LDN01,1) NBASIS
      NB=(NBASIS*(NBASIS+1))/2
1  FORMAT(2I5)
2  READ(LDN01,1) IWHERE,ISTART(15)
      GO TO (3,4,5,6,7,8,9,11),IWHERE
C.....TRANSFER INTEGRALS FROM LDN10 TO LDN03 IF NECESSARY.
3  CALL MFILE2
      GO TO 2
C.....READ DATA AND CHECK INTEGRAL FILE SERIAL NUMBER.
4  CALL RESSET
      GO TO 2
C.....SET UP COMPLETE MATRIX OF DISTINCT TWO-ELECTRON INTEGRALS.
5  CALL SETERI
      GO TO 2
C.....DIAGONALIZE OVERLAP MATRIX AND TRANSFORM H-MATRIX.
6  CALL TRANSH
      GO TO 2
C.....TRANSFORM TWO-ELECTRON INTEGRALS.
7  CALL CONTRA
      GO TO 2
C.....TRANSFER TRANSFORMED INTEGRALS FROM LDN03 TO LDN10 IF NECESSARY.
8  CALL MFILE3
      GO TO 2
C.....JOB COMPLETE.
9  CALL CNTR(NB)
      WRITE(LDN02,10) NB
10 FORMAT('D',36X,'**** JOB COMPLETE -',I5,' INSTRUCTIONS USED ****')
      STOP
      END

```

```

*FORTRAN LIB
      SUBROUTINE BIGTRA(A,B,MTD01,MTD02,NCOL,NROW,NPASS)
C.....TRANSPOSE OF A LARGE MATRIX.
      DIMENSION A(NROW,NCOL),B(NRCW,NCOL)
      REWIND MTD01
      REWIND MTD02
      NCCW=NCOL-NRCW

```

```

DO 8 IPASS=1,NPASS
READ (MTD01) ISER
JK=(IPASS-1)*NRCW
JR=NRCW
IF(JK-NCON) 2,2,1
1 JR=NCOL-JK
2 DO 6 IPART=1,NPASS
IK=(IPART-1)*NRCW
IR=NRCW
IF(IK-NCON) 4,4,3
3 IR=NCOL-IK
4 DO 5 I=1,IR
READ(MTD01) (A(I,J),J=1,NCOL)
5 CONTINUE
DO 6 I=1,JR
JC=I+JK
DO 6 J=1,IR
IC=J+IK
B(I,IC)=A(J,JC)
6 CONTINUE
DO 7 I=1,JR
WRITE(MTD02) (B(I,J),J=1,NCOL)
7 CONTINUE
REWIND MTD01
8 CONTINUE
ENDFILE MTD02
REWIND MTD02
WRITE (MTD01) ISER
DO 9 I=1,NCOL
READ (MTD02) (A(I,J),J=1,NCOL)
WRITE(MTD01) (A(I,J),J=1,NCOL)
9 CONTINUE
ENDFILE MTD01
REWIND MTD01
REWIND MTD02
RETURN
END

```

*FORTRAN LIB

SUBROUTINE CONTRA

C.....CONTROL ROUTINE FOR TWO-ELECTRON INTEGRAL TRANSFORMATION.

TEXT DUMM

```

COMMON /TCALL/ NBASIS,NB,ISTOP,ISTART(20),M(30),LDN01,LDN02,LDN03,
1LDN08,LDN09,LDN10,LDN11
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),I1),(IDUM(28),I2)
EQUIVALENCE (DUMY(3),DUMM),(DUMY(4),SMAT),(DUMY(5),IMAT),(DUMY(6),
1ERIMAT)

```

CALL ENTR(GHCONTRA,ISTART(15))

C.....SKIP TITLE AND SERIAL NUMBER OF TAPE ON UNIT 03. SKIP UNTRANS-

C.....FORMED S AND H MATRICES.

```

READ(LDN03) ISER
READ(LDN03) DUMM
DO 1 I=1,NBASIS
READ(LDN03) SMAT
READ(LDN03) IMAT
1 CONTINUE

```

C.....TAPE ON UNIT 03 CORRECTLY POSITIONED - SERIALIZE TAPE ON UNIT 04.

READ(LDN01,3) ISER

```

3 FORMAT(I10)
WRITE(LDNO2,301) ISER
301 FORMAT(1H0,37X,3CHSERIAL NUMBER OF TAPE ON UNIT 04 IS ,I10/)
REWIND LDNO2
WRITE(LDNO2) ISER
C.....SET UP ISTART
READ(LDNO1,4) (ISTART(I),I=5,12)
4 FORMAT(J15)
C.....CHECK DATA. ISTOP=50 IF ISTART(L).NE.NBASIS.NE.ISTART(S).
J=1
DO 7 I=5,11,2
IP=I-1
IF(ISTART(I)-ISTART(IP)) 7,7,5
5 WRITE(LDNO2,6) I,IP
6 FORMAT(3H ISTART(,I3,14H) .GT. ISTART(,I3,1H))
J=0
7 CONTINUE
IF(J) 9,8,9
8 CALL EXIT
9 J=1
DO 13 I=6,8,2
IF(ISTART(I)-NBASIS) 10,13,11
10 ISTOP=50
GO TO 13
11 WRITE(LDNO2,12) I
12 FORMAT(3H ISTART(,I3,13H) .GT. NBASIS)
J=0
13 CONTINUE
IF(J) 15,8,15
15 J=1
DO 17 I=10,12,2
IF(ISTART(I)-NBASIS) 17,17,16
16 WRITE(LDNO2,12) I
J=0
17 CONTINUE
IF(J) 18,8,18
18 CALL TWOTRA
C.....CHECK IF RESTART NECESSARY.
I1=5
I2=7
19 IF(ISTART(I2+1)-NBASIS) 20,21,21
20 ISTART(I2)=ISTART(I2+1)+1
GO TO 27
21 IF(ISTART(I1+1)-NBASIS) 22,23,23
22 ISTART(I1)=ISTART(I1+1)+1
ISTART(I2)=1
GO TO 27
23 IF(I1-9) 24,29,24
24 I1=9
I2=11
GO TO 19
27 WRITE(LDNO2,28) (I,ISTART(I),I=5,11,2)
28 FORMAT(1H0,23X,74HA RESTART IS NECESSARY IN THE TWO-ELECTRON INTEG
1RAL TRANSFORMATION ROUTINE/1H ,22X,20HRESTART VALUES ARE -,4(3H IS
2TART(,I2,2H)=,I2))
GO TO 33
29 WRITE(LDNO2,30)
30 FORMAT(1H0,35X,49HTRANSFORMATION OF TWO-ELECTRON INTEGRALS COMPLET
1E/)
C.....CHECK FOR HALT AT THIS POINT.

```

```

      IF(ISTOP-5) 34,31,34
31 WRITE(LDNO2,32)
32 FORMAT(1H0,21X,77HUSER REQUEST - PROGRAM TO STOP AT END OF TWO-ELE
      1CTRON INTEGRAL TRANSFORMATION/)
33 REWIND LDNO3
      REWIND LDNO9
      STOP
34 CALL QUIT(6HCONTRA,ISTART(15))
      RETURN
      END

```

*FORTRAN LIB

```

      SUBROUTINE DUMPSH(S,H,NBASIS,NO)
C.....OPTIONAL OUTPUT OF OVERLAP AND ONE-ELECTRON HAMILTONIAN MATRICES.
      COMMON /TOALL/ NBASIS,NB,ISTOP,ISTART(20),M(30),LDNO1,LDNO2,LDNO3,
      1LDNO8,LDNO9,LDNO10,LDNO11
      DIMENSION S(30,30),H(30,30)
      IF(NO) 1,4,1
1 WRITE(LDNO2,2)
2 FORMAT('1/'0',53X,'OVERLAP MATRIX')
      CALL WRITMX(S,30,30,NBASIS,NBASIS,LDNO2)
      WRITE(LDNO2,3)
3 FORMAT('0',44X,'ONE-ELECTRON HAMILTONIAN MATRIX')
      CALL WRITMX(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 /TOALL/ NBASIS,NB,ISTOP,ISTART(20),M(30),LDNO1,LDNO2,LDNO3,
      1LDNO8,LDNO9,LDNO10,LDNO11
      COMMON S(30,30),H(30,30),ERI(900)
      TEXT TITLE(15)
      EQUIVALENCE (LDNO2,NEXTBL),(ERI,TITLE)
      CALL ENTR('MFILE2',ISTART(15))
      READ(LDNO1,1) NEXTBL
1 FORMAT(I5)
C.....POSITION MASTER INTEGRAL FILE AT NEXTBL.
      MTDRE=LDNO10
      MTDWR=LDNO3
      CALL SEARCH(LDNO10,NEXTBL,0)
      WRITE(LDNO2,2) NEXTBL
2 FORMAT('1/'0',21X,'INTEGRALS FOR THIS RUN ARE IN THE MASTER INTEG
      1RAL FILE STARTING AT BLOCK',I5)
      READ (MTDRE) ISEB
      WRITE(MTDWR) ISEB
      READ (MTDRE) TITLE,IRUN
      WRITE(MTDWR) TITLE,IRUN
      DISPLAY /TITLE
      DO 3 I=1,NBASIS
      READ (MTDRE) (S(J,I),J=1,NBASIS)
      WRITE(MTDWR) (S(J,I),J=1,NBASIS)
      READ (MTDRE) (H(J,I),J=1,NBASIS)
      WRITE(MTDWR) (H(J,I),J=1,NBASIS)
3 CONTINUE
      DO 4 I=1,NB
      READ (MTDRE) (ERI(J),J=1,I)
      WRITE(MTDWR) (ERI(J),J=1,I)
4 CONTINUE

```

```
C.....DETERMINE POSITIONS OF ALL MAGNETIC DEVICES.
WRITE(LDNO2,5)
5 FORMAT('C',20X,'POSITIONS OF MAGNETIC DEVICES')
CALL WHTPS
ENDFILE MTDWR
REWIND MTDWR
CALL SEARCH(LDNO10,NEXTBL,0)
CALL QUIT('MFILE2',ISTART(15))
RETURN
END
```

*FORTRAN LIB

```
SUBROUTINE MFILE3
C.....TRANSFERS TRANSFORMED INTEGRALS FROM DISC (LDNO3) TO MASTER
C.....(TRANSFORMED) INTEGRAL FILE (LDN11).
COMMON /TOALL/ NBASIS,NB,ISTOP,ISTART(20),M(30),LDNO1,LDNO2,LDNO3,
1LDNO3,LDNO3,LDNO1,LDN11
COMMON ERI(900),H(30,30)
TEXT TITLE(15)
EQUIVALENCE (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) LDN11,NEXTBL
12 FORMAT(2I5)
13 WRITE(LDNO2,2) TITLE,NEXTBL
2 FORMAT('0',15A3/' ',21X,'WILL BE FOUND IN THE MASTER (TRANSFORMED)
1 INTEGRAL FILE STARTING AT BLOCK',I5)
CALL SEARCH(LDN11,NEXTBL,0)
MTDRE=LDNO3
MTDWR=LDN11
CLEAR ERI
NSQRD=NBASIS*NBASIS
DO 3 I=1,NSQRD
READ (MTDRE) (ERI(J),J=1,NSQRD)
WRITE(MTDWR) (ERI(J),J=1,NSQRD)
3 CONTINUE
READ (MTDRE) ((H(I,J),I=1,NBASIS),J=1,NBASIS)
WRITE(MTDWR) ((H(I,J),I=1,NBASIS),J=1,NBASIS)
ENDFILE MTDWR
C.....DETERMINE POSITIONS OF ALL MAGNETIC DEVICES.
WRITE(LDNO2,5)
5 FORMAT('C',20X,'POSITIONS OF MAGNETIC DEVICES')
CALL WHTPS
REWIND MTDWR
REWIND MTDRE
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
DO 1 K=1,IB
C(I,J)=C(I,J)+A(I,K)*B(K,J)
1 CONTINUE
```

RETURN
END

*FORTRAN LIB

SUBROUTINE MXTAN(A,B,IA,IB)

C.....TRANSPOSE OF REAL SQUARE MATRIX A STORED IN B.

DIMENSION A(IA,IA),B(IA,IA)

DO 1 I=1,IB

DO 1 J=1,IB

B(J,I)=A(I,J)

1 CONTINUE

RETURN

END

*FORTRAN LIB

SUBROUTINE ORTHON

C.....ORTHONORMALIZATION OF BASIS ORBITALS.

COMMON /TOALL/ N,NB,ISTOP,ISTART(20),M(30),LDN01,LDN02,LDN03,

1LDN08,LDN09,LDN10,LDN11

COMMON C(30,30),H(30,30),S(30,30)

DIMENSION QC(30,30),QS(30,30),QU(30,30),QV(30,30),QW(30,30),QX(30)

QSQR(Q)=SQRT(Q)

CALL ENTR(GHORTHEN,ISTART(15))

C.....SET UP WORKSPACE.

DO 2 I=1,N

DO 1 J=1,N

CLEAR QC(I,J),QU(I,J),QV(I,J),QW(I,J)

QS(I,J)=S(I,J)

1 CONTINUE

2 CONTINUE

C.....CHOLESKY DECOMPOSITION OF QS.

DO 11 I=1,N

QA=QS(I,I)

IM1=I-1

IF(IM1) 5,5,3

3 DO 4 J=1,IM1

QA=QA-QV(I,J)*QV(I,J)

4 CONTINUE

5 QV(I,I)=QSQR(QA)

QU(I,I)=QV(I,I)

IF(N-I) 11,11,6

6 IP1=I+1

DO 10 J=IP1,N

QV(J,I)=QS(J,I)

IF(IM1) 9,9,7

7 DO 8 K=1,IM1

QV(J,I)=QV(J,I)-QV(J,K)*QV(I,K)

8 CONTINUE

9 QV(J,I)=QV(J,I)/QV(I,I)

QU(I,J)=QV(J,I)

10 CONTINUE

11 CONTINUE

C.....QC = INVERSE OF QU.

DO 12 IM1=2,N

L=N-IM1+2

QX(L)=1.0/QU(L,L)

QC(L,L)=QX(L)

LM1=L-1

DO 12 LL=1,LM1

I=LM1-LL+1

```

      IP1=I+1
      CLEAR QA
      DO 111 J=IP1,L
      QA=QA-QU(I,J)*QX(J)
111  CONTINUE
      K(I)=QA/QU(I,I)
      QC(I,L)=QX(I)
12  CONTINUE
      QC(1,1)=1.0/QU(1,1)
C.....COMPUTE TRANSFORMED OVERLAP MATRIX.
      CALL MTRAN(QC,QV,30,N)
      CALL MKPROD(QV,QS,QW,30,N)
      CALL MKPROD(QW,QC,QS,30,N)
      WRITE(LDNO2,20)
      CALL WRITMX(QS,30,30,N,N,LDNO2)
      DO 14 I=1,N
      DO 14 J=1,N
      C(I,J)=QC(I,J)
14  CONTINUE
20  FORMAT(1H0,55X,10HCT*S*C = 1/1H )
      CALL QUIT(6HORTHON,ISTART(15))
      RETURN
      END

*FORTRAN LIB
      SUBROUTINE RESSET
C.....RESTART AT BEGINNING OF TRANSFORMATION SECTION.
      COMMON /PCALL/ NBASIS,NB,ISTOP,ISTART(20),M(30),LDNO1,LDNO2,LDNO3,
1LDNO8,LDNO9,LDNO10,LDNO11
      TEXT TITLE(15)
      CALL ENTR(6HRESSET,ISTART(15))
      READ(LDNO1,1) JSER,ISTOP
      READ(LDNO3) ISER
1  FORMAT(110,15)
   IF(JSER-ISER) 2,3,2
2  CALL WRONTP(JSER,ISER,3)
3  READ(LDNO3) TITLE,IRUN
   WRITE(LDNO2,4) TITLE
4  FORMAT(1H1/1H0,39X,42HDIATOMIC CONFIGURATION INTERACTION PROGRAM/
11H0,44X,31HHEMONUCLEAR VERSION 1. 1/09/69./1H0,56X,8HA.D.TAIT/1H0,
244X,32HQUANTUM MOLECULAR PHYSICS GROUP,/1H0,49X,22HDEPARTMENT OF P
3HYSICS,/1H0,48X,24HUNIVERSITY OF LEICESTER,/1H0,46X,28HLEICESTER,
4HENGLAND. LD1 7RH./1H0,15A3/)
C.....READ AND CHECK DATA.
      READ(LDNO1,5) (M(I),I=1,NBASIS)
5  FORMAT(30I2)
C.....CHECK M-VALUES.
      WRITE(LDNO2,6) (I,M(I),I=1,NBASIS)
6  FORMAT('0',46X,'MAGNETIC QUANTUM NUMBERS'//( ' ',56X,'M(' ,I2,' )=' ,
1I2))
      CLEAR J
      DO 9 I=1,NBASIS
      IF(IABS(M(I))-3) 9,9,7
7  WRITE(LDNO2,3) I
3  FORMAT(' ',45X,'M-VALUE TOO BIG IN ORBITAL ',I2)
      J=1
9  CONTINUE
   IF(J) 10,11,10
10 CALL REXIT
11 CALL QUIT('RESSET',ISTART(15))

```

RETURN
END

*FORTRAN LIB

SUBROUTINE SETERI

C.....SETS UP COMPLETE MATRIX OF DISTINCT TWO-ELECTRON INTEGRALS FROM
C.....LOWER TRIANGLE. VERSION 3. 06/09/71.

COMMON /TOALL/ NBASIS,NB,ISTOP,ISTART(20),M(30),LDNO1,LDNO2,LDNO3,
1LDNO8,LDNO9,LDNO10,LDNO11

COMMON A(5000),B(5000)

DIMENSION C(66,66),ERI(900),H(30,30),S(30,30)

EQUIVALENCE (A,ERI),(A(901),H),(A(1801),S),(B,C)

ON ERROR KB,KW,NB,I,J

CALL ENTR('SETERI',ISTART(15))

C.....SKIP OVER SERIAL NUMBER, TITLE, AND ONE-ELECTRON INTEGRALS.

REWIND LDNO3

READ(LDNO3) I

READ(LDNO3) I

X CALL TPPOSN(LDNO3,KB,KW)

X 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

X CALL TPPOSN(LDNO3,KB,KW)

X DISPLAY(LP,5) /I,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)

DO 4 I=1,NB

WRITE(LDNO3) (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(LDNO9) (ERI(J),J=1,NB)

7 CONTINUE

REWIND LDNO9

NRCW=5000/NB

NPASS=1

IF(MOD(NB,NRCW)) 9,8,9

8 CLEAR NPASS

9 NPASS=NPASS+NB/NRCW

CALL BIGTRA(A,B,LDNO9,LDNO8,NB,NRCW,NPASS)

CALL SEARCH(LDNO3,KB,KW)

DO 10 I=1,NB

READ (LDNO9) (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 LDNO8


```

DO 11 I=1,NB
  READ (LDN03) (ERI(J),J=1,NB)
  WRITE(LDN03) (ERI(J),J=1,NB)
11 CONTINUE
12 REWIND LDN03
  REWIND LDN02
  REWIND LDN09
C.....READ OVERLAP AND ONE-HAMILTONIAN MATRICES.
  READ(LDN03) I
  READ(LDN03) I
  DO 13 I=1,NBASIS
    READ(LDN03) (S(J,I),J=1,NBASIS)
    READ(LDN03) (H(J,I),J=1,NBASIS)
13 CONTINUE
  CALL SEARCH(LDN03,KB,KW)
C.....PRINT S AND H IF REQUIRED.
  CALL DUMPSH(S,H,NBASIS,ISTART(15))
  CALL QUIT('SETERI',ISTART(15))
  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 ORTHONORMAL 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.
  COMMON /TCALL/ NBASIS,NB,ISTOP,ISTART(20),M(30),LDN01,LDN02,LDN03,
1LDN03,LDN09,LDN10,LDN11
  COMMON C(30,30),H(30,30),S(30,30),IRI(30),WSP1(30,30),WSP2(30,30),
1WSP3(30,30)
  CALL ENTR('TRANSH',ISTART(15))
  WRITE(LDN02,1)
1  FORMAT(1H1/1H0,40X,40HTRANSFORMATION OF ONE-ELECTRON INTEGRALS/)
C.....TAPE 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 WSP2
  READ(LDN01,30) NONO
30  FORMAT(1G15)
  DO 32 K=1,NONO
    READ(LDN01,31) I,J,WSP2(I,J)
31  FORMAT(2I3,F4.1)
32  CONTINUE
  WRITE(LDN02,40)
40  FORMAT('0',45X,'SYMMETRY TRANSFORMATION MATRIX'/)
  CALL WRITMX(WSP2,30,30,NBASIS,NBASIS,LDN02)
C.....TRANSFORM OVERLAP MATRIX.
33  CALL MXTRAN(WSP2,WSP1,30,NBASIS)
  CALL MXPROD(WSP1,S,C,30,NBASIS)
  CALL MXPROD(C,WSP2,S,30,NBASIS)
X  WRITE(LDN02,46)
X  CALL WRITMX(S,30,30,NBASIS,NBASIS,LDN02)
43  FORMAT(' ',1P5E24.10)
  CALL ORTHON
X  WRITE(LDN02,43)
X  CALL WRITMX(C,30,30,NBASIS,NBASIS,LDN02)
X 46  FORMAT('0',40X,'OVERLAP MATRIX FOR NON-ORTHOGONAL M.O.S')
X 43  FORMAT('0',43X,'MATRIX WHICH ORTHOGONALIZES M.O.S')
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```

49 FORMAT('0',40X,'TRANSFORMED ONE-ELECTRON INTEGRAL MATRIX')
READ(LDN01,30) NIR
READ(LDN01,30) (IRI(I),I=1,NBASIS)
WRITE(LDN02,50) NIR,(I,IRI(I),I=1,NBASIS)
50 FORMAT('0',24X,'TRANSFORMED ORBITALS BELONG TO',I3,' DIFFERENT IRR
REDUCIBLE REPRESENTATIONS'/'',40X,'(SUBSPECIES COUNTED AS DIFFEREN
2T)'/'',36X,'TRANSFORMED ORBITALS ARE ASSIGNED AS FOLLOWS'/'('',
34GX,'ORBITAL',I3,' BELONGS TO IR',I3))
8 CALL MXPROD(WSP2,C,WSP1,30,NBASIS)
DO 9 I=1,NBASIS
DO 9 J=1,NBASIS
C(I,J)=WSP1(I,J)
9 CONTINUE
C.....OUTPUT TRANSFORMATION MATRIX.
WRITE(LDN02,90)
90 FORMAT('0',50X,'TRANSFORMATION MATRIX'//)
CALL WRITMX(C,30,30,NBASIS,NBASIS,LDN02)
C.....WRITE TRANSFORMATION MATRIX ONTO UNIT 03.
10 WRITE(LDN03) ((C(I,J),I=1,NBASIS),J=1,NBASIS)
C.....TRANSFORM H-MATRIX.
CALL MXTRAN(C,WSP1,30,NBASIS)
CALL MXPROD(WSP1,H,S,30,NBASIS)
CALL MXPROD(S,C,H,30,NBASIS)
C.....IF ORBITAL I AND ORBITAL J BELONG TO DIFFERENT IRREDUCIBLE
C.....REPRESENTATIONS THEN H(I,J)=H(J,I)=0. IN GENERAL H(I,J)=H(J,I).
NCON=NBASIS-1
DO 15 I=1,NCON
K=I+1
DO 14 J=K,NBASIS
IF(IRI(I)-IRI(J)) 11,12,11
11 CLEAR H(I,J),H(J,I)
GO TO 14
12 IF(1.0E-09-ABS(H(I,J)-H(J,I))) 13,14,14
13 WRITE(LDN02,16) I,J,J,I
14 CONTINUE
15 CONTINUE
16 FORMAT(' ',50X,'H(',I2,',',',I2,')=NE.H(',I2,',',',I2,')')
WRITE(LDN02,49)
CALL WRITMX(H,30,30,NBASIS,NBASIS,LDN02)
WRITE(LDN03) ((H(I,J),I=1,NBASIS),J=1,NBASIS)
C.....TAPE ON UNIT 03 CONTAINS - UNTRANSFORMED S AND H MATRICES WRITTEN
C.....ALTERNATELY BY COLUMNS, COMPLETE MATRIX OF DISTINCT ERI,
C.....TRANSFORMATION AND TRANSFORMED H MATRICES BY COLUMNS.
REWIND LDN03
CALL QUIT('TRANSH',ISTART(15))
RETURN
END

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*FORTRAN LIB

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SUBROUTINE TWOEPI
C.....TRANSFORMS TWO-ELECTRON INTEGRALS (ERI).
C.....TAPE 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 ICD
COMMON /TCALL/ NBASIS,NB,ISTOP,IST(4),ISTARS,ISTARS,ISTARW,ISTARS,
1ISTAR9,ISTAR0,ISTAR1,ISTAR2,IS(5),IUMP,I10,I20,H(30),LDN01,LDN02,
2LDN03,LDN08,LDN09,LDN10,LDN11
DIMENSION C(30,30),DUMA(5000),DUMB(5000)
DIMENSION WSP1(900),WSP2(900),H(30,30),A(64,64)

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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('0INTEGRAL(',4I3,') IS COMPOSED OF -')
X 105 FORMAT('C(',2I3,')*INTEGRAL(',4I3,'). INTEGRAL INDEX IS ',I4)
X 106 FORMAT('OPARTIALLY TRANSFORMED INTEGRALS'/((' ',4(3X,'ERI(',I4,')='
X 1,1PE17.10)))
X 107 FORMAT('0**** TRANSFORMED INTEGRALS ****'/((' ',4(3X,'ERI(',I4,')='
X 1,1PE17.10)))
      ON ERROR/NSQRD,IJUMP,ISTAGE,NGOT,NWANT,/MU,NU,MAX,MIN,NMOVE,/KK,LL
      CALL ENTR(6HTWOTRA,I5(3))
      CALL WHTPS
      NSQRD=NBASIS*NBASIS
C.....TEST FOR RESTART AT THE END OF THIS STAGE.
      IF(IJUMP) 29,1,29
      1 ISTAGE=1
      CLEAR NGOT
C.....COMMENCE TRANSFORMATION OF CHARGE DISTRIBUTION 2.
      DO 22 MU=ISTAR5,ISTAR6
      DO 21 NU=ISTAR7,ISTAR8
C.....PICK UP REQUIRED BLOCK OF DISTINCT ERI.
      MAX=MAXO(MU,NU)
      NWANT=(MAX*(MAX-1))/2+MINO(MU,NU)
X      WRITE(LDNO2,103) MU,NU,NGOT,NWANT
      NMOVE=NWANT-NGOT
      IF(NMOVE) 2,2,4
      2 NMOVE=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 WSP1
      DO 13 LAMBDA=1,NBASIS
      KI=NBASIS*(LAMBDA-1)
      DO 12 LL=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=KI+LL
X      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)
X      WRITE(LDNO2,105) IS,LL,MU,NU,LAMBDA,IS,J
      WSP1(K2)=WSP1(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
      KI=NBASIS*(KK-1)
      DO 18 LL=1,NBASIS
C.....CHECK 1.

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```

      IF(IM-M(KK)+M(LL)) 18,15,18
15 K2=K1+LL
X   WRITE(LDNO2,104) 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
X   WRITE(LDNO2,105) LAMBDA,KK,MU,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(LDNO9) (WSP2(K),K=1,NSQRD)
X   WRITE(LDNO2,106) (K,WSP2(K),K=1,NSQRD)
21 CONTINUE
22 CONTINUE
      ENDFILE LDNO9
C.....THIS STAGE IS COMPLETE IF ISTAR6=ISTAR8=NBASIS.
      IF(ISTAR6+ISTAR8-NBASIS-NBASIS) 23,25,23
23 ICD=4H2ND.
      WRITE(LDNO2,24) ICD
24 FORMAT(1H0,31X,18HTRANSFORMATION OF ,A4,35HCHARGE DISTRIBUTION IS
1NOT COMPLETE/)
      REWIND LDNO3
      REWIND LDNO9
      GO TO 27
25 WRITE(LDNO2,26)
26 FORMAT(1H0,34X,51HTRANSFORMATION OF 2ND. CHARGE DISTRIBUTION COMPL
1ETE/)
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(LDNO3) CMAT
      READ(LDNO3) HMAT
29 Istage=2
C.....TRANSPOSE PARTIAL 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
X   WRITE(LDNO2,293) NSQRD,NSQRD,LDNO9,LDNO8,NROW,NPASS,LDNO9
X 293 FORMAT(' ',15X,I4,'*',I4,'-MATRIX ON DEVICE',I3,' TO BE TRANSPOSED
X 1, DEVICE',I3,' IS USED AS TEMPORARY STORAGE',I3,' 23X,I5,' RECORDS
X 2RE READ EACH TIME AND',I5,' PASSES ARE MADE OVER DEVICE',I5/)
X   CALL CNTR(INSTR)
      CALL BIGTRA(DUMA,DUMB,LDNO9,LDNO8,NSQRD,NROW,NPASS)
X   CALL CNTR(JNSTR)
X   SEC=(JNSTR-INSTR)/160.0
X   WRITE(LDNO2,294) SEC
X 294 FORMAT(' ',43X,'TRANSPOSE TIME =',F10.2,' SECONDS')
      GO TO 303

```

```

300 READ(LDNO9) ISER
DO 301 I=1,NSQRD
READ(LDNO9) (A(I,J),J=1,NSQRD)
301 CONTINUE
REWIND LDNO9
WRITE(LDNO9) ISER
DO 302 I=1,NSQRD
WRITE(LDNO9) (A(J,I),J=1,NSQRD)
302 CONTINUE
REWIND LDNO9
303 READ(LDNO9) ISER
C.....COMMENCE TRANSFORMATION OF 1ST.CHARGE DISTRIBUTION.
DO 44 KK=ISTAR9,ISTAR0
K1=NBASIS*(KK-1)
DO 43 LL=ISTAR1,ISTAR2
NCOI=K1+LL
IM=M(LL)-M(KK)
READ(LDNO9) (WSP1(NROW),NROW=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
X WRITE(LDNO2,104) MU,J,KK,LL
DO 33 NU=1,NBASIS
C.....CHECK 2.
IF(C(NU,J)) 32,33,32
32 I=K1+NU
X 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
X WRITE(LDNO2,104) I,J,KK,LL
DO 39 MU=1,NBASIS
C.....CHECK 2.
IF(C(MU,I)) 38,39,38
38 II=NBASIS*(MU-1)+J
X 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) (WSP1(K),K=1,NSQRD)
X WRITE(LDNO2,107) (K,WSP1(K),K=1,NSQRD)
43 CONTINUE
44 CONTINUE
ENDFILE LDNO3
C.....TAPE ON UNIT 03 CONTAINS UNTRANSFORMED S AND H MATRICES, LOWER

```

```

C.....TRANSFORMED H MATRICES AND ALL OR PART OF THE TRANSFORMED ERI.
C.....THIS STAGE IS COMPLETE IF ISTAR0=ISTAR2=NBASIS.
      IF(ISTAR0+ISTAR2-NBASIS-NBASIS) 45,451,45
45  ICD='1ST,'
      WRITE(LDNO2,24) ICD
      REWIND LDNO3
      REWIND LDNO9
      GO TO 46
C.....OVER WRITE INTEGRALS ON DEVICE LDNO3 WITH TRANSFORMED ERI AND
C.....TRANSFORMED H-MATRIX.
451  REWIND LDNO3
      REWIND LDNO9
      READ(LDNO3) ISER
      READ(LDNO3) ICD
      DO 452 I=1,NBASIS
        READ(LDNO3) SMAT
        READ(LDNO3) IMAT
452  CONTINUE
      DO 453 I=1,NB
        READ(LDNO3) ERIMAT
453  CONTINUE
      READ(LDNO3) ((C(I,J),I=1,NBASIS),J=1,NBASIS)
      CLEAR H
      READ(LDNO3) ((H(I,J),I=1,NBASIS),J=1,NBASIS)
      CLEAR NROW
      MTDRE=LDNO3
      MTDWR=LDNO9
454  DO 455 I=1,NSQRD
        READ(MTDRE) (WSP1(J),J=1,NSQRD)
        WRITE(MTDWR) (WSP1(J),J=1,NSQRD)
455  CONTINUE
      IF(NROW) 457,456,457
456  NROW=1
      NPASS=MTDRE
      MTDRE=MTDWR
      MTDWR=NPASS
      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)) 458,4585,458
458  CALL OUTBRK(LDNO2)
      WRITE(LDNO2,4586)
      DO 4581 I=1,NSQRD
        WRITE(LDNO2,4582) I
        READ(MTDWR) (WSP1(J),J=1,NSQRD)
        WRITE(LDNO2,4583) (WSP1(J),J=1,NSQRD)
4581 CONTINUE
4582 FORMAT('0',49X,'CONTENTS OF RECORD',I4/)
4583 FORMAT((',1P5E24.10))
      READ(MTDWR) ((H(I,J),I=1,NBASIS),J=1,NBASIS)
      WRITE(LDNO2,4584)
4584 FORMAT('0',38X,'TRANSFORMED ONE-ELECTRON HAMILTONIAN MATRIX'//)
      CALL WRITMK(H,30,30,NBASIS,NBASIS,LDNO2)
4585 CALL WHTPS
      REWIND MTDWR
4586 FORMAT('1'/'0',43X,'TRANSFORMED TWO-ELECTRON INTEGRALS'//)
46  CALL QUIT('TWOTRA',I5(3))

```

RETURN
END

*FORTRAN LIB

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(40H0THE WRONG TAPE HAS BEEN MOUNTED ON UNIT ,12/

128H THE TAPE REQUIRED IS NUMBER,110/28H THE TAPE MOUNTED IS NUMBE

2R,110/29H CONTINUATION IS NOT POSSIBLE/////)

CALL EEXIT

RETURN

END

55

1972

Programmer

21. 3. 72.

[illegible]

Date 21.3.72

Date 21.3.72

Date 21.3.72

Date 21.3.72

Date 21.3.72

IDENTIFICATION
AND
SEQUENCE ANALYSIS

2101011211314151617181920212223242526272829303132333435363738394041424344454647484950515253545556575859606162636465666768697071727374757677787980

-

INTRA TEST DATA - INTEGRALS FOR ATOMIC OXYGEN (SCHAE

FER AND HARRIS' S EXPONENTS)

1

- 221

1

INTEGRALS FOR THIS RUN ARE IN THE MASTER INTEGRAL FILE STARTING AT BLOCK 50
ONECEN TEST DATA - INTEGRALS FOR ATOMIC OXYGEN (SCHAEFER AND HARRIS'S EXPONENTS).

POSITIONS OF MAGNETIC DEVICES

TAPE
NUMBER 3
POSITIONED AT
BLOCK 1
WORD 214

TAPE
NUMBER 4
POSITIONED AT
BLOCK 1
WORD 0

TAPE
NUMBER 5
POSITIONED AT
BLOCK 1
WORD 0

TAPE
NUMBER 6
POSITIONED AT
BLOCK 50
WORD 214

TAPE
NUMBER 7
POSITIONED AT
BLOCK 1
WORD 0

TAPE
NUMBER 8
POSITIONED AT
BLOCK 20
WORD 0

NUMBER OF INSTRUCTIONS USED ON EXIT FROM SUBPRCGRAM MFILE2 = 331
NUMBER OF INSTRUCTIONS USED ON ENTRY TO SUBPRCGRAM RESET = 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.

ONECEN 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 SUBPRCGRAM RESET = 346
NUMBER OF INSTRUCTIONS USED ON ENTRY TO SUBPRCGRAM SETERI = 348

OVERLAP MATRIX

COLUMNS 1 TO 5

1.0000000000E+00	2.3098477658E-01	0.0000000000E+00	0.0000000000E+00	0.0000000000E+00
2.3098477658E-01	9.9999999995E-01	0.0000000000E+00	0.0000000000E+00	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00	1.0000000000E+00	0.0000000000E+00	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00	0.0000000000E+00	1.0000000000E+00	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00	0.0000000000E+00	0.0000000000E+00	1.0000000000E+00

ONE-ELECTRON HAMILTONIAN MATRIX

COLUMNS 1 TO 5

-3.1941106880E+01	-7.0326342795E+00	0.0000000000E+00	0.0000000000E+00	0.0000000000E+00
-7.0326342795E+00	-8.1471486930E+00	0.0000000000E+00	0.0000000000E+00	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00	-6.4268167801E+00	0.0000000000E+00	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00	0.0000000000E+00	-6.4268167801E+00	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00	0.0000000000E+00	0.0000000000E+00	-6.4268167801E+00

TRANSFORMATION OF ONE-ELECTRON INTEGRALS

SYMMETRY TRANSFORMATION MATRIX

	COLUMNS 1 TO 5
1.0000000000E+00	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00
0.0000000000E+00	1.0000000000E+00
0.0000000000E+00	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00
OF INSTRUCTIONS USED ON ENTRY TO SUBPRCGRAM ORTHON = 457	

CT*SC = 1

	COLUMNS 1 TO 5
1.0000000000E+00	0.0000000000E+00
-3.6379788070E-12	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00
0.0000000000E+00	1.0000000000E+00
0.0000000000E+00	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00
OF INSTRUCTIONS USED ON EXIT FROM SUBPRCGRAM ORTHON = 470	

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

TRANSFORMED ORBITALS ARE ASSIGNED AS FOLLOWS

CRBITAL 1	BELONGS TO IR 1
CRBITAL 2	BELONGS TO IR 1
CRBITAL 3	BELONGS TO IR 2
CRBITAL 4	BELONGS TO IR 3
CRBITAL 5	BELONGS TO IR 4

TRANSFORMATION MATRIX

0.0000000000E+00	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00
0.0000000000E+00	1.0000000000E+00
0.0000000000E+00	0.0000000000E+00
1.0000000000E+00	0.0000000000E+00

0.0000000000E+00	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00
0.0000000000E+00	1.0000000000E+00
0.0000000000E+00	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00

TRANSFORMATION MATRIX

	COLUMNS 1 TO 5	
1.0000000000E+00	0.0000000000E+00	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00	0.0000000000E+00
0.0000000000E+00	1.0000000000E+00	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00	1.0000000000E+00
0.0000000000E+00	0.0000000000E+00	0.0000000000E+00

TRANSFORMED ONE-ELECTRON INTEGRAL MATRIX

	COLUMNS 1 TO 5	
-3.1941106880E+01	0.0000000000E+00	0.0000000000E+00
3.5487182665E-01	0.0000000000E+00	0.0000000000E+00
0.0000000000E+00	-6.4268167801E+00	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00	-6.4268167801E+00
0.0000000000E+00	0.0000000000E+00	0.0000000000E+00

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

NUMBER OF INSTRUCTIONS USED ON ENTRY TO SUBPRCGRAM TWOTRA = 512
 SERIAL NUMBER OF TAPE ON UNIT 04 IS 200000

TAPE POSITIONED AT
 NUMBER 3 BLOCK 1 WORD 79

TAPE POSITIONED AT
 NUMBER 4 BLOCK 1 WORD 0

TAPE POSITIONED AT
 NUMBER 5 BLOCK 1 WORD 2

TAPE POSITIONED AT
 NUMBER 6 BLOCK 50 WORD 0

TAPE POSITIONED AT
 NUMBER 7 BLOCK 1 WORD 0

TAPE POSITIONED AT
 NUMBER 8 BLOCK 20 WORD 0

END OUTPUT 3 BLOCKS

TRANSFORMATION OF 2ND. CHARGE DISTRIBUTION COMPLETE

CONTENTS OF RECORD 1

0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
1.1057938455E+00
0.0000000000E+00
1.1057938455E+00
0.0000000000E+00

0.4307495009E-01
1.1195775587E+00
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00

0.7855000002E+00
0.4307495009E-01
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00

CONTENTS OF RECORD 2

0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
-9.0856167517E-03
0.0000000000E+00
-9.0856167517E-03
0.0000000000E+00

6.8581250140E-02
-1.7490310809E-02
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00

0.4307495009E-01
6.8581250140E-02
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00

CONTENTS OF RECORD 3

0.0000000000E+00
2.4875854665E-02
3.3408778537E-02
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00

0.0000000000E+00
0.0000000000E+00
3.3408778537E-02
0.0000000000E+00
0.0000000000E+00

0.0000000000E+00
0.0000000000E+00
0.4875854665E-02
0.0000000000E+00
0.0000000000E+00

CONTENTS OF RECORD 4

0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00

0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
3.3408778537E-02
0.0000000000E+00

0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
0.4875854665E-02
0.0000000000E+00

CONTENTS OF RECORD 5

0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00

0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
3.3408778537E-02

0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
0.4875854665E-02

CONTENTS OF RECORD 6

0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
-9.0856167517E-03
0.0000000000E+00
-9.0856167517E-03
0.0000000000E+00

6.8581250140E-02
-1.7490310809E-02
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00

0.4307495009E-01
6.8581250140E-02
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00

[illegible]

[illegible]

CONTENTS OF RECORD 19

-9.0856167517E-03
8.0030916955E-01
0.000000000E+00
0.000000000E+00
0.000000000E+00

1.1057938455E+00
=9.0856167517E-03
0.000000000E+00
0.000000000E+00
0.000000000E+00

CONTENTS OF RECORD 20

[illegible]
$$\begin{array}{r} 0.000000E+00 \\ 0.000000E+00 \\ 0.000000E+00 \\ 0.000000E+00 \\ 0.000000E+00 \end{array}$$

CONTENTS OF RECORD 21

0,00000000E+00
0,00000000E+00
0,00000000E+00
3,34877853E-02
0,00000000E+00

0.000000000E+00
0.000000000E+00
0.000000000E+00
2.487585465E-02
0.000000000E+00

CONTENTS OF RECORD 22

0,00000000E+00
0,00000000E+00
0,00000000E+00
0,00000000E+00
I,7243262076F-01
0,00000000E+00

0.000000000E+00
0.000000000E+00
0.000000000E+00
3.3408778537E-02
0.000000000E+00

CONTENTS OF RECORD 23

[illegible][illegible]

CONTENTS OF RECORD 24

[illegible]

3.00000000E+00
3.00000000E+00
3.00000000E+00
3.00000000E+00
3.00000000E+00

0.00000000E+00
0.00000000E+00
0.00000000E+00
8.2433968761E+01
0.00000000E+00

0.000 00000E+00
0.000 00000E+00
0.000 00000E+00
0.000 00000E+00
8.2438968761E-01

0.00000000E+00
0.00000000E+00
0.00000000E+00
0.00000000E+00
9.3917812509E-02

00+2101000	000.0
00+3101000	900.0
00+3101000	000.0
00+3101000	000.0
00+3101000	000.0
00+3101000	000.0

[illegible]

2. 4375554665E+02
3. 3408773537E+02
0.000 000000E+00
0.000 000000E+00
0.000 000000E+00

[illegible]

3.3408778537E+02
1.7243262176E+01
0.090 000100E+00
0.000 000100E+00
0.000 000100E+00

[illegible]

0.000 07010JE+00
0.000 00010JE+00
4.6958916255E+02
0.000 00000JE+00
0.000 00010JE+00

[illegible]

0.000 0000JE+00
0.000 0000JE+00
0.000 0000JE+00
9.3917812509E+02
0.000 0000JE+00

1057938455E+00	-9.0856167517E-03	0.0000000000E+00	0.0000000000E+00	0.0000000000E+00
0856167517E-03	8.0030916955E-01	0.0000000000E+00	0.0000000000E+00	0.0000000000E+00
0000000000E+00	0.0000000000E+00	7.7743078136E-01	0.0000000000E+00	0.0000000000E+00
0000000000E+00	0.0000000000E+00	0.0000000000E+00	8.2438968761E-01	0.0000000000E+00
0000000000E+00	0.0000000000E+00	0.0000000000E+00	0.0000000000E+00	8.2433968761E-01

TRANSFORMED ONE-ELECTRON HAMILTONIAN MATRIX

1941106890E+01	3.5487182665E-01	0.0000000000E+00	0.0000000000E+00	0.0000000000E+00
5487182665E-01	-6.9745927313E+00	0.0000000000E+00	0.0000000000E+00	0.0000000000E+00
0000000000E+00	0.0000000000E+00	-6.4268167801E+00	0.0000000000E+00	0.0000000000E+00
0000000000E+00	0.0000000000E+00	0.0000000000E+00	-6.4268167801E+00	0.0000000000E+00
0000000000E+00	0.0000000000E+00	0.0000000000E+00	0.0000000000E+00	-6.4268167801E+00

TAPE POSITIONED AT
NUMBER 3 BLOCK 2 WORD 164

TAPE POSITIONED AT
NUMBER 4 BLOCK 1 WORD 0

TAPE POSITIONED AT
NUMBER 5 BLOCK 2 WORD 138

TAPE POSITIONED AT
NUMBER 6 BLOCK 50 WORD 0

TAPE POSITIONED AT
NUMBER 7 BLOCK 1 WORD 0

TAPE POSITIONED AT
NUMBER 8 BLOCK 20 WORD 0

NUMBER OF INSTRUCTIONS USED ON EXIT FROM SUBPROGRAM THOTRA = 972

TRANSFORMATION OF TWO-ELECTRON INTEGRALS COMPLETE

NUMBER OF INSTRUCTIONS USED ON EXIT FROM SUBPROGRAM CONTRA = 974

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

POSITIONS OF MAGNETIC DEVICES:

TAPE
NUMBER 3
POSITIONED AT
BLOCK 2
WORD 164

TAPE
NUMBER 4
POSITIONED AT
BLOCK 1
WORD 0

TAPE
NUMBER 5
POSITIONED AT
BLOCK 2
WORD 138

TAPE
NUMBER 6
POSITIONED AT
BLOCK 50
WORD 0

TAPE
NUMBER 7
POSITIONED AT
BLOCK 53
WORD 0

TAPE
NUMBER 8
POSITIONED AT
BLOCK 20
WORD 0

*** JOB COMPLETE - 1007 INSTRUCTIONS USED ***

APPENDIX VII

SECSØL. 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 FØRTRAN 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 SECSØL requires the routines ENTR, ERRØR, IPAR, QUIT, and WRITMX from Appendix III.

SECSØL uses two magnetic tapes and three disc areas which are assigned as follows:

VARIABLE NAME	VALUE = DEVICE No.	
MTD01	Defined in	Private disc area of > 150 blocks.
	data	Contains results of current run.
MTD02	Defined in	Master results tape.
	data	
MTD	3	Private disc area of 30 blocks. Contains specification of detors and projection matrix $T_{-S\sigma}$.
IDISC	4	Private disc area of 3 blocks. Contains contents tables of MTD01, MTD02.

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 detectors 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 SECSØL

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

Card 1 IWHERE, NØ
 FØRMAT (2I5)
 IWHERE = 1
 NØ { = 0 to suppress timing information
 = 1 to obtain timing information

Card 2, 3 TITLE
 FØRMAT (9A8/6A8)
 TITLE is an array of 15 elements (120 characters)
 used to identify the run.

Card 4 MTDO1, MTDO2, NBASIS, NDET, NELEC, NFULL
 FØRMAT (6I5)
 MTDO1 = Device number of private disc area
 MTDO2 = Device number of master results tape
 NBASIS = Number of basis orbitals
 NDET = Number of detectors
 NELEC = Number of electrons
 NFULL = Number of spin-orbitals frozen.

Card 5 $N\emptyset NO$

$F\emptyset R\emptyset MAT (I5)$

$N\emptyset NO$ $\left\{ \begin{array}{l} = 0 \text{ If the detors have to be specified} \\ = 1 \text{ If the detors were specified in the} \\ \text{previous run} \end{array} \right.$

Card 6 F

(omitted if $F\emptyset R\emptyset MAT (9A8)$

$N\emptyset NO = 1)$

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

$((\text{'b'}, I8, mX, nI3))$

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) $(IDET(I, J,), J = 1, NELEC)$

(Omitted if $F\emptyset R\emptyset MAT (1X, 32I2)$

$N\emptyset NO = 1)$

$IDET(I, J)$ specifies the Jth spin-orbital of the Ith
deter. These cards, of which there are NDET,
will normally be these output by the program
GENDET.

$(1 \leq I \leq NDET).$

Section 2 : Computation of $G(k) = \langle D_{\mu} | h | D_{\nu} \rangle$, where

$k = (\mu(\mu - 1))/2 + \nu$ and $\mu \geq \nu$. The

transformed integrals must be on MTDO1 at word 0, block 1.

Card 1 IWHERE, NØ

FORMAT (2I5)

IWHERE = 2

NØ : see section 1 card 1

Section 3 : Compute H and solve $(\underline{H}-E\underline{I}) \underline{C} = 0$

Card 1 IWHERE, NØ

FORMAT (2I5)

IWHERE = 3

NØ : see section 1 card 1

Card 2 NCØNF, NØNO

FORMAT (2I5)

NCØNF = number of codetors

NØNO = number of non-zero elements in the
 projection matrix $\underline{T}_{S\sigma}$

Card 3 IFILE

FORMAT (I5)

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

Card 4(K) I, J, T(I, J)

(Omitted if FORMAT (2I5, F10.2)

IFILE = 1)

T(I, J) is the I, J-th element of the projection
matrix $\underline{T}_{S\sigma}$. It should be non-zero and
written as an integer in real form, e.g.
1.000000. The program normalizes the columns
of $\underline{T}_{S\sigma}$

(1 ≤ K ≤ NØNO)

Card 5 NCEN
 FØRMAT (I5)
 NCEN = number of nuclei

Card 6(I) CH(I), X(I), Y(I), Z(I)

(Omitted if FØRMAT (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 ≤ I ≤ NCEN)

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

Card 1 IWHERE, NØ
 FØRMAT (2I5)
 IWHERE = 4
 NO : see section 1 card 1

Card 2 ICØL
 FØRMAT (I5)
 ICØL defines the energy level for which the
 analysis is required
 (1 ≤ ICØL ≤ NCØNF)

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

Card 4 (DN(NENTRY, J), J = 1, 4)
 FØRMAT (4A8)

This card contains 32 characters used to
 identify the NSØ analysis, NENTRY is known
 to the program.

Section 5 Entries to the subprogram TDFILE: the data is divided into
five sections.

Card 1 IWHERE, NØ
FØRMAT (2I5)
IWHERE = 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
FØRMAT (2I5)
IFILE = 1
JFILE = 1

Card 3A IENTRY, NXBLØC
FØRMAT (2I5)
IENTRY = 2
NXBLØC = number of block at which transformed integral
file will begin on MTD02

Card 4A INTRA, IGØ, NBLØC
FØRMAT (3I5)
INTRA = device number for Master transformed integral
tape.
IGØ { = 0 To initialize the contents tables of MTD01
 and MTD02
 = 1 If the contents table of MTD02 contains
 entries
NBLØC = number of block at which transformed integral
file begins on INTRA.

Card 5A (DN(1, K), K = 1, 4)
 FØRMAT (4A8)

This card contains 32 characters used to
identify the integrals.

B : Copy selected entries from MTD02 onto MTD01

Card 2B IFILE, JFILE
 FØRMAT (2I5)

IFILE = 1

JFILE = 0

Card 3B IENTRY, NXBLØC
 FØRMAT (2I5)

IENTRY = number of entries to be copied from MTD02
 onto MTD01 and must always include the
 last entry on MTD02.

NXBLØC = 0

Card 4B (LD(I), I = 1, IENTRY)
 FØRMAT (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 IFILE, JFILE
 FØRMAT (2I5)

IFILE = 2

JFILE = 0

Card 3C IENTRY
 FØRMAT (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

JFILE	{	= 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

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 ≤ NBASIS ≤ 30

1 ≤ NDET ≤ 120

1 < NELEC ≤ 32

0 ≤ NFULL ≤ 8

1 ≤ NC~~Ø~~NF ≤ 78

1 ≤ NCEN ≤ 20

The number of entries in the contents table of MTDO2 must not exceed 158, and the number in that of MTDO1 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~~Ø~~R n, where n is a number in the list below:

ERR Ø R n	CAUSE
1	NBASIS > 30
2	NELEC > 32
3	NDET > 120
4	NFULL > 8
5	NC Ø NF > 78

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 MTDO2 than are actually present.

*FORTRAN LIB 6,19,302

C.....MAIN PROGRAM FOR SECSOL - CONSTRUCTION AND SOLUTION OF THE SECULAR
C.....EQUATION WITH AN OPTIONAL NATURAL SPIN-ORBITAL ANALYSIS.

COMMON /SECEQN/ AA(33767),ICR,LP,MTD,NO,ANYO,ANY1,ANY2,ANY3,ANY4,
1GF,ICOL,IDISC,IFILE,JFILE,LINK,MTD01,MTD02,NBASIS,NCONF,NDET,NELC
2,NF,NFULL,NSQRD,NXBLOC
EQUIVALENCE (NXBLOC,IWHERE)

C.....DEFINE DEVICE NUMBERS,

C.....LP = LINE PRINTER,

C.....ICR = CARD READER,

C.....MTD = WORKFILE.

C.....IDISC=CONTENTS TABLES FILE.

CLEAR ICR,LP

MTD=3

IDISC=4

1 READ(ICR,2) IWHERE,NO

2 FORMAT(2I5)

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 MAXCON

CALL PASTWO

CALL HPASS

MTD=3

GO TO 1

C.....COMPUTE H-MATRIX AND SOLVE $(H-E*I)*C=0$.

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('0',33X,'**** 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(I5)

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(1P4E20.10)

WRITE(LP,5) NCEN,(I,CH(I),X(I),Y(I),Z(I),I=1,NCEN)

5 FORMAT('0',30X,'GEOMETRY OF MOLECULE.',I3,' NUCLEI AS FOLLOWS'/)


```

1,24X,'NUCLEUS   NUCLEAR CHARGE   X CO-ORDINATE   Y CO-ORDINATE   Z
2 CO-ORDINATE'/(',27X,I2,1PE19.7,1P3E16.6))
  CLEAR ERN
  MCEN=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 FORMAT('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=' ,I5,'. NCEN MUST NOT EXCEED 20')
  CALL LEXIT
  STOP
  END

```

*FORTRAN LIB

```

  SUBROUTINE EAO3A(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
X  DISPLAY(LP,20)/EPS,TOL
  CALL TRED2(N,TOL,ND,A,B,D,E)
  CALL TQL2(N,EPS,ND,B,D,E,NN)
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
1E',48X,'*/'*,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 FODMA4
C.....COMPUTES FIRST ORDER DENSITY MATRIX. VERSION 4. 03/05/71.
C.....ASSUMES BASIS SPIN ORBITALS ARE ORTHONORMAL.
  COMMON/SECEQN/T(120,73),AA(60,60),C(120),JD(1182,2),O,GAMMA(60,60)
1,IDET(120,32),ID(843),KDET(32),EV(78,78),SP(3923),ICR,LF,MTD,NO,
2ANYO,ANY1,ANY2,ANY3,ANY4,GF,ICCL,IDISC,IFILE,JFILE,LINK,MTD01,
3MTD02,NBASIS,NCONF,NDET,NELEC,NF,NFULL,NSQRD,NXBLOC
  EQUIVALENCE (SP,FACTOR),(SP(2),I),(SP(3),ICRB),(SP(4),IR),(SP(5),
1IS),(SP(6),I1),(SP(7),I2),(SP(8),J),(SP(9),JORB),(SP(10),K),
2(SP(11),L)
  CALL ENTR('FODMA4',NO)
X  WRITE(LP,28) ((IDET(I,J),J=1,NELEC),I=1,NDET)
X  DISPLAY(LP,4) /NF,NFULL,NELEC,NDET
  CLEAR LINK
  NBASIS=NBASIS+NBASIS

```

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 8 I=NF,NELEC
        IF(IDET(K,I)-KDET(I)) 6,8,6
6 I2=I2+1
        IF(I2-1) 7,7,11
7 IORB=I
        JORB=KDET(I)
8 CONTINUE
        DO 9 I=NF,NELEC
          J=I
          IF(IDET(L,I)-JORB) 9,10,9
9 CONTINUE
10 LINK=LINK+1
    ID(LINK)=IS
    JD(LINK,1)=IORB
    JD(LINK,2)=J
11 CONTINUE
12 CONTINUE
X   WRITE(LP,13) (ID(I),I=1,LINK)
X 13 FORMAT('0',51X,'DIFFERENCE TABLES'/'(',12I10))
X   WRITE(LP,14) ((JD(I,J),J=1,2),I=1,LINK)
X 14 FORMAT(' ' / (' ',12(' (',I2,',',I2,',') ')))
    CLEAR GAMMA
C.....CCOMPUTE 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)) 141,23,141
141 DO 22 L=1,NDET
      IF(C(L)) 142,22,142
142 I2=K-L
      IF(I2) 17,15,17
C.....DETORS K AND L ARE IDENTICAL.
15 FACTOR=C(K)*C(K)
    DO 16 I=1,NELEC
      I1=IDET(K,I)
      GAMMA(I1,I1)=GAMMA(I1,I1)+FACTOR
16 CONTINUE

```

```

      GO TO 22
C.....DETORS 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 18 I=1, LINK
            J=I
            IF(IS-ID(I)) 18,19,18
      18 CONTINUE
         GO TO 22
      19 IORB=JD(J,1)
         JCRB=JD(J,2)
         IF(I2) 20,21,21
      20 I1=IORB
         IORB=JORB
         JORB=I1
      21 I=IDET(K, IORB)
         J=IDET(L, JORB)
         GAMMA(J, I)=GAMMA(J, I)+C(K)*C(L)*(-1.0)**(IORB+JORB)
      22 CONTINUE
      23 CONTINUE
C.....CHECK SYMMETRY OF GAMMA
      DO 27 I=1, NBASIS
         I1=I+1
         DO 26 J=I1, NBASIS
            FACTOR=ABS(GAMMA(I, J)-GAMMA(J, I))
            IF(1.0E-10-FACTOR) 24,26,26
      24 WRITE(LP,25) I,J,J,I,FACTOR
      25 FORMAT(' ',35X, 'GAMMA(',I2,',',',I2,',') .NE. GAMMA(',I2,',',',I2,',') . DIFF
         REFERENCE=' ',1PE9.2)
      26 CONTINUE
      27 CONTINUE
X 23 FORMAT((',',12X,32I3))
      CALL QUIT('FODMA4',NO)
      RETURN
      END

```

*FORTRAN LIB

```

      SUBROUTINE HPASS
C.....COMPUTES ONE-ELECTRON CONTRIBUTION TO MATRIX ELEMENTS.
C.....READ ONE-ELECTRON HAMILTONIAN MATRIX.
      COMMON /SECEQN/ G(7260), ERI(900), IDET(120,32), IDIFF(3073,7),
      1 IDUM(261), ANY1, ANY2, ANY3, ANY4, GF, ICOL, IDISC, IFILE, JFILE, LINK, MTD01
      2, MTD02, NBASIS, NCONF, NDET, NELEC, NF, NFULL, NSQRD, NXBLOC
      EQUIVALENCE (IDUM(149), I), (IDUM(150), J), (IDUM(151), FSUM),
      1 (IDUM(152), L), (IDUM(153), KL), (IDUM(154), LI), (IDUM(155), LL1),
      2 (IDUM(156), LM), (IDUM(157), KP), (ANY3, LNO), (ANY4, LU), (IDUM(259), MTD)
      DIMENSION H(30,30)
      EQUIVALENCE (ERI, H)
      CALL ENTR(' HPASS', IDUM(260))
      READ(MTD01) ((H(I, J), J=1, NBASIS), I=1, NBASIS)
      CLEAR FSUM
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)
         FSUM=FSUM+H(I, I)
      2 CONTINUE

```

```

      FSUM=2.0*FSUM
      3 NF=NFULL+1
C.....CCOMPUTE DIAGONAL ELEMENTS.
      DO 5 L=1,NDET
      KL=(L*(L+1))/2
      DO 4 LI=NF,NLEEC
      LL1=(IDET(L,LI)+1)/2
      G(KL)=G(KL)+H(LL1,LL1)
      4 CONTINUE
      G(KL)=G(KL)+FSUM+GF
      5 CONTINUE
C.....CCOMPUTE OFF-DIAGONAL ELEMENTS - IF DETORS L AND K DIFFER BY
C.....MORE THAN ONE SPIN ORBITAL THE ONE ELECTRON CONTRIBUTION IS ZERO.
      LNO=3073
      DO 13 LU=1,ICOL
      IF(ICOL-1) 51,53,51
      51 READ(MTD) IDIFF
      IF(LU-ICOL) 54,52,54
      52 IF(LINK) 53,13,53
      53 LNO=LINK
      54 DO 9 L=1,LNO
      KL=IDIFF(L,7)
      IF(IDIFF(L,1)-1) 6,6,8
C.....DETORS L AND K DIFFER BY LM 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(IDUM(258),12)/FSUM
X      WRITE(IDUM(258),10) (KL,G(KL),KL=1,(NDET*(NDET+1))/2)
X 10 FORMAT(' G(',I4,')=',1PE17.10)
X 11 FORMAT('0',50X,'CONTRIBUTIONS TO FSUM'//)
X 12 FORMAT(' ',47X,'H(',I2,',',I2,')=',1PE17.10)
      13 CONTINUE
      REWIND MTD
      CALL QUIT('HPASS',IDUM(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 /SECEQN/ G(7260),ERI(900),IDET(120,32),IDIFF(3073,7),
      1IDUM(261),ANY1,ANY2,ANY3,ANY4,GF,ICOL,IDISC,IFILE,JFILE,LINK,MTD01
      2,MTD02,NBASIS,NCCNF,NDET,NLEEC,NF,NFULL,NSQRD,HEKBLOC
      DIMENSION KDET(32)
      EQUIVALENCE (IDUM(109),KDET),(IDUM(142),L),(IDUM(143),LM1),
      1(IDUM(144),K),(IDUM(145),IPERM),(IDUM(146),I),(IDUM(147),ITEMP),
      2(IDUM(148),IDC),(IDUM(175),LIN),(IDUM(176),J),(IDUM(259),MTD)
      IF(NDET.EQ.1) RETURN
      CALL ENTR('MAXCON',IDUM(260))
      CLEAR IDIFF,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,NELESC
      KDET(I)=IDET(K,I)
1 CONTINUE
      DO 5 I=NF,NELESC
      IF(IDET(L,I)-KDET(I)) 2,5,2
2 DO 3 J=NF,NELESC
      IF(IDET(L,I)-KDET(J)) 3,4,3
3 CONTINUE
      GO TO 5
4 ITEMP=KDET(I)
      KDET(I)=KDET(J)
      KDET(J)=ITEMP
      IPERM=IPERM+1
5 CONTINUE
      J=2
      LIN=LIN+1
      DO 3 I=NF,NELESC
      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
      IDIFF(LIN,J)=KDET(I)
8 CONTINUE
      IDIFF(LIN,2)=(-1)**IPERM
      IDIFF(LIN,1)=IDC
      IDIFF(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(253),15) (I,(IDIFF(I,J),J=1,7),I=1,LINK)
X 15 FORMAT(' ',51X,'CONTENTS OF IDIFF'/( ' ',45X,'I= ',I4,3X,7I3))
      I=3073*(ICOL-1)+LIN
      WRITE(LP,16) I
16 FORMAT(' ',26X,'NUMBER OF NON-ZERO OFF-DIAGONAL MATRIX ELEMENTS BE
      TWEEN DETORS= ',I5)
      CALL QUIT('MAXCON',IDUM(260))
      RETURN
      END

```

*FORTRAN LIB

SUBROUTINE MMULT(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

```

*FORTRAN LIB

```

SUBROUTINE NATORB
C.....CONTROL ROUTINE FOR NATURAL SPIN ORBITAL ANALYSIS.
COMMON/SECERN/T(120,78),AA(60,60),C(120),JD(1182,2),O,GAMMA(60,60)
1,IDET(120,32),ID(343),KDET(32),EV(78,78),SP(3923),ICR,LP,MTD,NO,
2,ANYO,ANY1,ANY2,ANY3,ANY4,GF,ICOL,IDISC,IFILE,JFILE,LINK,MTD01,
3,MTD02,NBASIS,NCONF,NDET,NLEEC,NF,NFULL,NSQRD,NXBLOC
EQUIVALENCE (SP(1),I),(SP(2),J),(SP(3),K),(SP(4),L)
CALL ENTR('NATORB',NO)
C.....READ DATA FROM DEVICE MTD.
READ(MTD) ((IDET(I,J),J=1,NLEEC),I=1,NDET)
READ(MTD) ((T(I,J),J=1,NCONF),I=1,NDET)
REWIND MTD
C.....COMPUTE COEFFICIENTS OF INDIVIDUAL DETERMINANTS FOR LEVEL ICOL OF
C.....THIS STATE.
CLEAR C
READ(ICR,12) ICOL
WRITE(LP,13) ICOL
DO 11 I=1,NDET
DO 1 J=1,NCONF
X DISPLAY(LP,10) /I,J,T(I,J),ICOL,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,NDET)
CLEAR GAMMA
CALL FODMA4
C.....WRITE FIRST ORDER DENSITY MATRIX ONTO MTD01.
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 DAO3A(GAMMA,AA,NBASIS,60,GF)
C.....THE OCCUPATION NUMBERS ARE THE DIAGONAL ELEMENTS OF GAMMA, A IS
C.....THE TRANSFORMATION MATRIX.
WRITE(LP,2)
2 FORMAT('0',40X,'RESULTS OF NATURAL SPIN ORBITAL ANALYSIS')
CLEAR GF
DO 5 I=1,NBASIS,5
J=I+4
IF(J-NBASIS) 4,4,3
3 J=NBASIS
4 WRITE(LP,6) I,J
WRITE(LP,7) (GAMMA(K,K),K=I,J)
WRITE(LP,8) I,J
DO 5 K=1,NBASIS
WRITE(LP,7) (AA(K,L),L=I,J)
5 CONTINUE

```

```

6 FORMAT('0',40X,'OCCUPATION NUMBERS OF ORBITALS',I3,' TO ',I2/' ')
7 FORMAT(' ',1P5E24.10)
8 FORMAT('0',41X,'TRANSFORMATION MATRIX COLUMNS',I3,' TO ',I2/' ')
DO 9 I=1,NBASIS
  GF=GF+GAMMA(I,I)
9 CONTINUE
  WRITE(LP,10) GF,NELEC
10 FORMAT('B',33X,'SUM OF OCCUPATION NUMBERS =',1PE17.10/' ',44X,'NUM
  1BER OF ELECTRONS =',I3)
12 FORMAT(I5)
13 FORMAT('1'/'0',39X,'NATURAL SPIN ORBITAL ANALYSIS OF LEVEL',I3)
14 FORMAT(' ',40X,'COEFFICIENTS OF INDIVIDUAL DETERMINANTS'/' ')
15 FORMAT(' ',4(6X,'C(',I3,')=' ,1PE17.10)))
  CALL QUIT('NATORB',NC)
  RETURN
END

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SUBROUTINE PASONE
C.....COMPUTES ELECTRON-ELECTRON INTERACTION BETWEEN FROZEN CORE
C.....ELECTRONS. THIS IS ZERO IF NFULL IS ZERO.
COMMON /SECEQN/ G(7260),ERI(900),IDET(120,32),IDIFF(3073,7),
1IDUM(261),ANY1,ANY2,ANY3,ANY4,GF,ICOL,IDISC,IFILE,JFILE,LINK,MTD01
2,MTD02,NBASIS,NCONF,NDET,NELEC,NF,NFULL,NSQRD,NXBLOC
DIMENSION KEEP(40,3)
EQUIVALENCE (IDUM,KEEP),(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),L1),
3(IDUM(132),ICC),(IDUM(250),MTD)
CALL ENTR('PASONE',IDUM(260))
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)=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 IREC=2,IC
    K2=MAX0(K2,KEEP(IREC,3))
3 CONTINUE
X   DISPLAY /K2
  DO 10 IREC=1,K2
    READ(MTD01) (ERI(J),J=1,NSQRD)
X   WRITE(IDUM(258),14) IREC
X   WRITE(IDUM(258),15) (ERI(J),J=1,NSQRD)

```

```

DO 9 ICC=1,IC
  IF(IREC-KEEP(ICC,3)) 9,4,9
4 IF(KEEP(ICC,1)-KEEP(ICC,2)) 7,5,7
5 LIM1=KEEP(ICC,1)-1
X WRITE(IDUM(258),16)
  DO 6 K=1,LIM1
    KI=(K+1)/2
    GF=GF+ERI(NBASIS*(KI-1)+KI)
X WRITE(IDUM(258),17) NBASIS*(KI-1)+KI,ERI(NBASIS*(KI-1)+KI)
6 CONTINUE
  GO TO 9
7 IF(IPAR(KEEP(ICC,1))-IPAR(KEEP(ICC,2))) 9,8,9
8 LI=(KEEP(ICC,1)+1)/2
X WRITE(IDUM(258),16)
  KI=(KEEP(ICC,2)+1)/2
  GF=GF-ERI(NBASIS*(KI-1)+LI)
X WRITE(IDUM(258),17) NBASIS*(KI-1)+LI,ERI(NBASIS*(KI-1)+LI)
9 CONTINUE
10 CONTINUE
  REWIND MTD01
11 CALL QUIT('PASONE',IDUM(260))
X 12 FORMAT('O',44X,'CONTENTS OF KEEP FOR L =',I2,',K =',I2/)
X 13 FORMAT('O',45X,3I10))
X 14 FORMAT('O',49X,'CONTENTS OF RECORD',I4/)
X 15 FORMAT('O',1P5E24.10))
X 16 FORMAT('O',56X,'CONTRIBUTIONS TO GF'/)
X 17 FORMAT('O',47X,'ERI(',I3,')=',1PE17.10)
  RETURN
END

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SUBROUTINE PASTWO
C.....COMPUTES CORE-VALENCE AND VALENCE-VALENCE ELECTRON INTERACTION
C.....CONTRIBUTIONS TO MATRIX ELEMENTS.
  COMMON /SECBQN/ G(7260),ERI(900),IDET(120,32),IDIFF(3073,7),
1 IDUM(261),ANY1,ANY2,ANY3,ANY4,GF,ICOL,IDISC,IFILE,JFILE,LINK,MTD01
2,MTD02,NBASIS,NCONF,NDET,NELEC,NF,NFULL,NSQRD,NKBLOC
  EQUIVALENCE (IDUM(1),I),(IDUM(2),J),(IDUM(3),L),(IDUM(4),KI),
1 (IDUM(5),LI),(IDUM(6),LIM1),(IDUM(7),L2),(IDUM(8),LL2),
2 (IDUM(9),LVAL),(IDUM(10),LM),(IDUM(11),KP),(IDUM(12),LN),
3 (IDUM(13),KQ),(IDUM(179),LI),(ANY3,LNO),(ANY4,LU),(IDUM(259),MTD)
X EQUIVALENCE (IDUM(258),LP)
  CALL ENTR('PASTWO',IDUM(260))
  IF(NELEC.EQ.NFULL) GO TO 331
  CLEAR G
  NKBLOC=NF
  IF(NF.EQ.1) NKBLOC=2
  DO 37 I=1,NBASIS
  DO 37 J=1,NBASIS
X WRITE(LP,30) I,J
  READ(MTD01) (ERI(L),L=1,NSQRD)
X WRITE(LP,40) (ERI(L),L=1,NSQRD)
C.....DIAGONAL ELEMENTS.
  IF(I-J) 6,1,6
C.....(II/ ) TYPE INTEGRALS.
1 DO 5 L=1,NDET
  KI=(L*(L+1))/2
C.....SUM OVER VALENCE ELECTRONS.
  DO 4 LI=NKBLOC,NELEC
  IF(I-(IDET(L,LI)+1)/2) 4,2,4

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```

2 LIM1=L1-1
C.....SUM OVER CORE AND VALENCE ELECTRONS.
DO 3 L2=1,LIM1
  LL2=(IDET(L,L2)+1)/2
  G(KL)=G(KL)+ERI(NBASIS*(LL2-1)+LL2)
X  WRITE(LP,42) NBASIS*(LL2-1)+LL2,ERI(NBASIS*(LL2-1)+LL2)
3 CONTINUE
X  WRITE(LP,43) KL,G(KL)
4 CONTINUE
5 CONTINUE
GO TO 13
C.....(I / I) TYPE INTEGRALS.
6 DO 12 L=1,NDET
  KL=(L*(L+1))/2
C.....SUM OVER VALENCE ELECTRONS.
DO 11 L1=NXBLOC,NBLOC
  IF(I-(IDET(L,L1)+1)/2) 11,7,11
7 LIM1=L1-1
C.....SUM OVER CORE AND VALENCE ELECTRONS.
DO 10 L2=1,LIM1
  LL2=(IDET(L,L2)+1)/2
  IF(J-LL2) 10,8,10
8 IF(IPAR(IDET(L,L1))-IPAR(IDET(L,L2))) 10,9,10
C.....SPINS ARE THE SAME FOR ORBITALS IDET(L,L1) AND IDET(L,L2).
9 G(KL)=G(KL)-ERI(NBASIS*(LL2-1)+I)
X  WRITE(LP,42) NBASIS*(LL2-1)+I , -ERI(NBASIS*(LL2-1)+I )
10 CONTINUE
X  WRITE(LP,43) KL,G(KL)
11 CONTINUE
12 CONTINUE
C.....OFF-DIAGONAL ELEMENTS'
13 IF(NDET.NQ.1) GO TO 361
  LVAL=1
  LNO=3073
  DO 361 LU=1,ICOL
    IF(ICOL-1) 131,133,131
131 READ(MTD) IDIFF
    IF(LU-ICOL) 134,132,134
132 IF(LINK) 133,361,133
133 LNC=LINK
134 DO 36 L=1,LNO
C.....PICK UP INDEX OF NEXT PAIR OF DETORS THAT DIFFER BY NO MORE
C.....THAN TWO SPIN ORBITALS.
  KL=IDIFF(L,7)
  IF(2-IDIFF(L,1)) 27,27,14
C.....DETORS L AND K DIFFER BY ONE SPIN-ORBITAL - LM IN L AND KP
C.....IN K. KL=(L*(L-1))/2+K - THE VALUE OF L IS REQUIRED.
14 L1=(LVAL*(LVAL+1))/2
  IF(L1-KL) 15,15,16
15 LVAL=LVAL+1
  GO TO 14
16 IF(I-J) 21,17,21
C.....(II/MP) TYPE INTEGRALS.
17 LM=IDIFF(L,3)
  KP=IDIFF(L,4)
C.....CHECK THAT SPINS DO NOT CAUSE THE INTEGRAL TO BE ZERO.
  IF(IPAR(LM)-IPAR(KP)) 36,13,36
18 DO 20 L1=1,NBLOC
  IF(I-(IDET(LVAL,L1)+1)/2) 20,19,20
19 G(KL)=G(KL)+ERI(NBASIS*((LM+1)/2-1)+(KP+1)/2)

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X      IWSP=NBASIS*((LM+1)/2-1)+(KP+1)/2
X      WRITE(LP,42) IWSP,ERI(IWSP)
20 CONTINUE
X      WRITE(LP,43) KL,G(KL)
      GO TO 36
C.....(IP/MI) TYPE INTEGRALS.
21 KP=IDIFF(L,4)
      IF(J-(KP+1)/2) 36,22,36
22 DO 26 LI=1,NSELEC
      LI=IDET(LVAL,LI)
      IF(I-(LI+1)/2) 26,23,26
23 IF(IPAR(KP)-IPAR(LI)) 26,24,26
C.....SPINS OF SPIN ORBITALS LI AND KP ARE THE SAME.
24 LM=IDIFF(L,3)
      IF(IPAR(LM)-IPAR(LI)) 26,25,26
C.....SPINS OF SPIN ORBITALS LI AND LM ARE THE SAME.
25 G(KL)=G(KL)-ERI(NBASIS*((LM+1)/2-1)+(LI+1)/2)
X      IWSP=NBASIS*((LM+1)/2-1)+(LI+1)/2
X      WRITE(LP,42) IWSP,-ERI(IWSP)
26 CONTINUE
X      WRITE(LP,43) KL,G(KL)
      GO TO 36
C.....DETORS L AND K DIFFER BY TWO SPIN-ORBITALS - LM,KN IN L AND
C.....KP,KQ IN K.
27 LM=IDIFF(L,3)
      IF(I-(LM+1)/2) 36,28,36
28 KP=IDIFF(L,4)
      IF(J-(KP+1)/2) 32,29,32
C.....(MP/NQ) TYPE INTEGRALS.
29 IF(IPAR(LM)-IPAR(KP)) 36,30,36
C.....SPINS OF SPIN ORBITALS LM AND KP ARE THE SAME.
30 LN=IDIFF(L,5)
      KQ=IDIFF(L,6)
      IF(IPAR(LN)-IPAR(KQ)) 36,31,36
C.....SPINS OF SPIN ORBITALS LN AND KQ ARE THE SAME.
31 G(KL)=G(KL)+ERI(NBASIS*((LN+1)/2-1)+(KQ+1)/2)
X      IWSP=NBASIS*((LN+1)/2-1)+(KQ+1)/2
X      WRITE(LP,42) IWSP,ERI(IWSP)
X      WRITE(LP,43) KL,G(KL)
      GO TO 36
C.....(MQ/NP) TYPE INTEGRALS.
32 KQ=IDIFF(L,6)
      IF(J-(KQ+1)/2) 36,33,36
33 IF(IPAR(LM)-IPAR(KQ)) 36,34,36
C.....SPINS OF SPIN ORBITALS LM AND KQ ARE THE SAME.
34 LN=IDIFF(L,5)
      KP=IDIFF(L,4)
      IF(IPAR(LN)-IPAR(KP)) 36,35,36
C.....SPINS OF SPIN ORBITALS LN AND KP ARE THE SAME.
35 G(KL)=G(KL)-ERI(NBASIS*((LN+1)/2-1)+(KP+1)/2)
X      IWSP=NBASIS*((LN+1)/2-1)+(KP+1)/2
X      WRITE(LP,42) IWSP,-ERI(IWSP)
X      WRITE(LP,43) KL,G(KL)
36 CONTINUE
361 CONTINUE
      REWIND MTD
37 CONTINUE
X      WRITE(IDUM(253),36) (KL,G(KL),KL=1,(IDET*(NDET+1))/2)
X 38 FORMAT(( ' G( ',I4, ' )= ',1PE17.10))
381 CALL QUIT('PASTWO',IDUM(260))

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X 39 FORMAT('0',40X,'CONTENTS OF ERI RECORD FOR I =',I3,',J =',I3)
X 40 FORMAT(' ',1P5E24.10))
X 42 FORMAT(' ',47X,'ERI(',I3,')=',1PE17.10)
X 43 FORMAT(' ',43X,'G(',I4,')=',1PE17.10)
      RETURN
      END

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      SUBROUTINE SECDDAT(JUMP)
C.....READS AND CHECKS DATA.
      COMMON /SECEQN/ TT(78,120),H(120,120),T(120,78),IDUM(652),ANY1,
1ANY2,ANY3,ANY4,GF,ICOL,IDISC,IFILE,JFILE,LINK,MTD01,MTD02,NBASIS,
2NCONF,NDET,NELEC,NF,NFULL,NSQRD,NBLOC
      TEXT TITLE
      TEXT LINE(9,5)/ *****
1 *****
2** * * * * *
3* * * * *
4 *****
5* * * * *
6 ** * * * *
7* *****
      DIMENSION G(7260),ERI(900),IDET(120,32),IDIFF(3000,7),TITLE(15),
1F(9)
      EQUIVALENCE (TT,G,TITLE),(TT(6,94),ERI,F),(TT(49,105),IDET),
1(H(1,23),IDIFF)
      EQUIVALENCE (IDUM(520),I),(IDUM(521),J),(IDUM(522),NCON),
1(IDUM(523),K),(IDUM(524),L),(IDUM(648),ICR),(IDUM(649),LP),
1(IDUM(650),MTD)
      CALL ENTR('SECDDAT',IDUM(651))
      GO TO (1,12),JUMP
C.....READ DATA FOR MATRIX ELEMENTS BETWEEN DETORS.
1 READ(ICR,2) TITLE,MTD01,MTD02,NBASIS,NDET,NELEC,NFULL
  NSQRD=NBASIS*NBASIS
  NF=NFULL+1
2 FORMAT(9A3/6A3/6I5)
  CALL CUTBRK(LP)
  WRITE(LP,60)
  WRITE(LP,77) LINE
66 FORMAT('F')
77 FORMAT(' ',27X,9A3,21X))
  WRITE(LP,3) TITLE,NDET,NELEC,NBASIS,NFULL,MTD01,MTD02
3 FORMAT('1/'0',39X,' GENERAL CONFIGURATION INTERACTION PROGRAM/'
1'0',35X,' CONSTRUCTION AND SOLUTION OF THE SECULAR EQUATION/'0',
256X,' A.P.TAIT/'0',44X,' QUANTUM MOLECULAR PHYSICS GROUP/'0',40X,
3'DEPARTMENT OF PHYSICS/'0',43X,' UNIVERSITY OF LEICESTER/'0',
446X,' LEICESTER, ENGLAND. LE1 7RH.'//0',15A3/0',33X,' WAVE FUNCTION
5N CONSTRUCTED FROM ',2I3,'-ELECTRON DETORS/'0',20X,' DETORS CONSTR
6UCTED FROM ',I3,' SPATIAL ORBITALS WITH FIRST ',I3,' SPIN-ORBITALS
7 FROZEN/'0',40X,' PRIVATE WORKFILE IS DEVICE NUMBER ',I7/'0',40X,' H
8ASTER RESULTS FILE IS DEVICE NUMBER ',I4)
  IF(NBASIS-30) 4,4,21
4 IF( NELEC-32) 5,5,22
5 IF( NDET-120) 6,6,23
6 IF( NFULL-3) 7,7,24
7 DO 71 I=1,NDET
  DO 71 J=1,NELEC
    CLEAR IDET(I,J)
71 CONTINUE
  READ(ICR,13) NCON

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      IF(NCNO) 72,74,72
72  REWIND MTD
      READ(MTD) ((IDET(I,J),J=1,NELEC),I=1,NDET)
      WRITE(LP,73)
73  FORMAT('0',39X,'**** DETORS SPECIFIED IN A PREVIOUS RUN ****'/0)
      GO TO 201
74  WRITE(LP,8)
      READ(ICR,11) F
      8  FORMAT('1'/0,48X,'SPECIFICATION OF DETORS'/0      NUMBER',55X,'DE
1TOR')
      DO 10 I=1,NDET
      READ(ICR,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(9A3)
      WRITE(MTD) ((IDET(I,J),J=1,NELEC),I=1,NDET)
      GO TO 201
C.....READ PROJECTION MATRIX FOR WAVE FUNCTION.
12  READ(ICR,13) NCONF,NONO
      READ(ICR,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 *
1***'/0)
      REWIND MTD
      GO TO 201
13  FORMAT(2I5)
130  CLEAR T
      IF(NCONF-78) 131,131,25
131  READ(ICR,14) (I,J,T(I,J),K=1,NONO)
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
C.....CHECK ORTHONORMALITY OF CO-DETORS.
      CLEAR IFILE
      NCNO=NCONF-1
      DO 145 I=1,NCNO
      J=I+1
      DO 147 K=J,NCONF
      CLEAR ANY2
      DO 144 L=1,NDET
      ANY2=ANY2+T(L,I)*T(L,K)
144  CONTINUE
      IF(ABS(ANY2)-1.0E-10) 147,147,145
145  WRITE(LP,146) I,K
146  FORMAT(' ',40X,'CO-DETORS',I4,' AND ',I4,' ARE NOT ORTHOGONAL')
      IFILE=1
147  CONTINUE
148  CONTINUE
      IF(IFILE.EQ.0) GO TO 149

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CALL EXIT
149 WRITE(MTD) ((T(I,J),J=1,NCONF),I=1,NDET)
ENDDFILE MTD
REWIND MTD
WRITE(LP,15) NCONF
15 FORMAT('1/'0',34X,12,' CO-DETERS OF CORRECT SYMMETRY AND SPIN ARE
1 FORMED')
DO 20 K=1,NCONF
WRITE(LP,16) K
16 FORMAT('0',45X,'CO-DETOR('I4,') =')
DO 19 L=1,NDET
IF(T(L,K)) 17,19,17
17 WRITE(LP,13) T(L,K),L
18 FORMAT(' ',45X,S+,-,1PE17.10,'*DETOR('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

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SUBROUTINE SECSOL
C.....FORMS H-MATRIX AND SOLVES SECULAR EQUATION FOR THIS CASE.
COMMON /SECEQN/ TT(78,120),H(120,120),T(120,78),IDUM(652),ANY1,
1ANY2,ANY3,ANY4,GF,ICOL,IDISC,IFILE,JFILE,LINK,MTD01,MTD02,NBASIS,
2NCONF,NDET,NELEC,NF,NFULL,NSQRD,NXBLOC
DIMENSION G(7260),W(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),K),(IDUM(528),
1KL),(IDUM(529),NML),(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,NDET,LP)
CALL SECDAT(2)
X WRITE(LP,12)
X CALL WRITMX(T,120,78,NDET,NCONF,LP)
CALL MXMULT(H,T,W,NDET,NDET,NCONF,120,120,120)
DO 2 L=1,NDET
DO 2 K=1,NCONF
H(L,K)=W(L,K)
2 CONTINUE
X WRITE(LP,13)
X CALL WRITMX(H,120,120,NDET,NCONF,LP)
CALL TRANS(T,TT,NDET,NCONF,120,78)
X WRITE(LP,14)
X CALL WRITMX(TT,78,120,NCONF,NDET,LP)

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```

DO 3 L=1,NDET
DO 3 K=1,NCONF
T(L,K)=H(L,K)
3 CONTINUE
CALL MMULT(TT,T,HM,NCONF,NDET,NCONF,78,120,78)
X WRITE(LP,10)
X CALL WRITEX(HM,78,78,NCONF,NCONF,LP)
C..... ENERGIES ARE THE EIGENVALUES OF HM.
CALL EAO3A(HM,EV,NCONF,78,AMIN)
C..... ADD NUCLEAR REPULSION ENERGY TO EIGENVALUES IF SYSTEM IS NOT
C..... SINGLE CENTRE.
CALL ADDNRE(HM,78,NCONF,IDUM(648),LP)
C..... OUTPUT SOLUTION OF SECULAR EQUATION.
WRITE(LP,4)
4 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
6 WRITE(LP,7) I,J,(HM(K,K),K=I,J)
7 FORMAT('0',46X,'ENERGIES OF STATES',I3,' TO ',I3/'0',1P5E24.10)
WRITE(LP,8) I,J
8 FORMAT('0',43X,'EIGENVECTORS FOR STATES',I3,' TO ',I3/' ')
DO 9 K=1,NCONF
WRITE(LP,91) (EV(K,L),L=I,J)
9 CONTINUE
91 FORMAT(' ',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',51X,'EIGENVALUES OF HM'/' )
CALL QUIT('SECSOL',IDUM(651))
RETURN
END

*FORTRAN LIB
SUBROUTINE TDFILE
C..... CONTROLS ALL TRANSFERS FROM CORE TO PERIPHERALS AND VICE VERSA.
COMMON /SECEQN/ AA(33767),ICR,LP,MTD,NO,ANYO,ANY1,ANY2,ANY3,ANY4,
1GF,ICOL,IDISC,IFILE,JFILE,LINK,MTD01,MTD02,NBASIS,NCONF,NDET,NELC
2,NF,NFULL,NSQD,NXBLOC
DIMENSION HM(73,78),EV(73,78),GA(60,60),A(60,60),ERI(900)
1KT(153,4),LT(153),KD(10,4),LD(10)
EQUIVALENCE (AA(7261),ERI),(AA(9361),HM,A),(AA(15446),GA),(AA(2376
11),EV)
TEXT TN(153,4),DN(10,4)
TEXT W(4)/'****','NEXT NEW','RECORD','****'/'
CALL ENTR('TDFILE',NO)
READ(ICR,2) IFILE,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)
REWIND MTD01
REWIND MTD02
IF(NXBLOC) 2001,204,2001
C..... COPY TRANSFORMED INTEGRALS INTO DISC AND MASTER RESULTS FILES.

```

```

2001 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
    IF(IGO) 2002,2004,2002
C.....MASTER RESULTS FILE TABLE CONTAINS ENTRIES.
2002 READ(IDISC) MENTRY,IENTRY,((TN(K,L),L=1,4),(KT(K,L),L=1,4),LT(K),
    IK=1,MENTRY)
    REWIND IDISC
    I=MENTRY
    J=I+1
    LD(1)=LT(I)
    LD(2),LT(J)=LT(I)+1
    IF(NXBLOC-KT(I,1)) 2003,2003,2004
2003 NXBLOC=KT(I,1)+1
2004 CALL SEARCH(MTD02,NXBLOC,0)
    KT(I,1)=NXBLOC
    KD(1,1),KT(I,4),KD(1,4)=1
    KT(I,3),KD(1,3)=NSQRD
    KT(J,4),KD(2,4)=5
    CLEAR KD(1,2),KT(I,2),KD(2,3),KT(J,3)
    READ(ICR,26) (DN(1,K),K=1,4)
    DO 2005 K=1,4
    TN(I,K)=DN(1,K)
    TN(J,K),LN(2,K)=W(K)
2005 CONTINUE
    I=NSQRD+1
    DO 2006 J=1,I
    READ(INTRA) (ERI(K),K=1,NSQRD)
    WRITE(MTD01) (ERI(K),K=1,NSQRD)
    WRITE(MTD02) (ERI(K),K=1,NSQRD)
2006 CONTINUE
    MENTRY=MENTRY+1
    CALL TPPOSN(MTD01,KD(2,1),KD(2,2),MTD02,KT(MENTRY,1),KT(MENTRY,2))
    GO TO 17
C.....MASTER CONTENTS TABLE PRESENT.
204 READ (IDISC) MENTRY,NENTRY,((TN(I,J),J=1,4),(KT(I,J),J=1,4),LT(I),
    II=1,MENTRY)
    REWIND IDISC
    IF(MENTRY-IENTRY) 3,5,5
3 WRITE(LP,4) IENTRY,MENTRY
4 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 EEXIT
5 READ(ICR,2) (LD(I),I=1,IENTRY)
C.....CHECK ENTRIES IN-ASCENDING ORDER.
    DO 8 I=2,IENTRY
    IF(LD(I)-LD(I-1)) 6,6,8
6 WRITE(LP,7)
7 FORMAT('0',37X,'DISC TABLE ENTRIES MUST BE IN ASCENDING ORDER')
    CALL EEXIT
8 CONTINUE
    DO 16 I=1,IENTRY
    DO 9 J=1,4
    DN(I,J)=TN(LD(I),J)
9 CONTINUE
    KD(I,3)=KT(LD(I),3)
    KD(I,4)=KT(LD(I),4)
    CALL SEARCH(MTD02,KT(LD(I),1),KT(LD(I),2))
    GO TO (10,12,13,14,15),KD(I,4)

```

C.....INTEGRALS.

```
10 L=KD(I,3)+1
   DO 11 K=1,L
     READ (MTDO2) (ERI(M),M=1,KD(I,3))
     WRITE(MTDO1) (ERI(M),M=1,KD(I,3))
11 CONTINUE
   GO TO 15
```

C.....G-VECTOR (MATRIX ELEMENTS BETWEEN DETERMINANTS).

```
12 READ (MTDO2) (AA(K),K=1,KD(I,3))
   WRITE(MTDO1) (AA(K),K=1,KD(I,3))
   GO TO 15
```

C.....ENERGIES AND EIGENVECTORS.

```
13 READ (MTDO2) (HM(K,K), (EV(L,K), L=1, KD(I,3)), K=1, KD(I,3))
   WRITE(MTDO1) (HM(K,K), (EV(L,K), L=1, KD(I,3)), K=1, KD(I,3))
   GO TO 15
```

C.....FIRST ORDER DENSITY MATRIX.

```
14 READ (MTDO2) ((GA(K,L), L=1, KD(I,3)), K=1, KD(I,3))
   WRITE(MTDO1) ((GA(K,L), L=1, KD(I,3)), K=1, KD(I,3))
15 CALL TPPOSN(MTDO1, KD(I+1,1), KD(I+1,2))
16 CONTINUE
   KD(1,1)=1
   CLEAR KD(1,2)
   NENTRY=IENTRY
17 WRITE(IDISC) MENTRY, NENTRY, ((TN(I,J), J=1, 4), (KT(I,J), J=1, 4), LT(I),
1I=1, MENTRY), ((DN(I,J), J=1, 4), (KD(I,J), J=1, 4), LD(I), I=1, NENTRY)
   REWIND IDISC
   REWIND MTDO1
   REWIND MTDO2
   CLEAR JUMP
   GO TO 45
```

C.....DATA TO BE READ INTO CORE FROM DISC.

```
18 READ (IDISC) MENTRY, NENTRY, ((TN(I,J), J=1, 4), (KT(I,J), J=1, 4), LT(I),
1I=1, MENTRY), ((DN(I,J), J=1, 4), (KD(I,J), J=1, 4), LD(I), I=1, NENTRY)
   REWIND IDISC
   JUMP=1
   GO TO 45
```

C.....READ SUBSCRIPT VALUE FOR ENTRY TO DISC CONTENTS TABLE.

```
19 READ(ICR,2) IENTRY
   WRITE(LP,20)
20 FORMAT('0',43X,'THE FOLLOWING IS REQUIRED IN CORE'/)
   WRITE(LP,47) (DN(IENTRY,J), J=1, 4), (KD(IENTRY,J), J=1, 4), LD(IENTRY)
   CALL SEARCH(MTDO1, KD(IENTRY,1), KD(IENTRY,2))
   GO TO (21,23,24,21,21), KD(IENTRY,4)
```

C.....IMPROPER REQUEST.

```
21 WRITE(LP,22)
22 FORMAT('0',33X,'IMPROPER REQUEST - CONTINUATION NOT POSSIBLE')
   CALL EXIT
```

C.....G-VECTOR.

```
23 READ(MTDO1) (AA(I), I=1, KD(IENTRY,3))
   GO TO 49
```

C.....ENERGIES AND EIGENVECTORS.

```
24 READ(MTDO1) (HM(K,K), (EV(L,K), L=1, KD(IENTRY,3)), K=1, KD(IENTRY,3))
   GO TO 49
```

C.....RESULTS TO BE ADDED TO DISC AND DISC CONTENTS TABLE UPDATED.

```
25 READ (IDISC) MENTRY, NENTRY, ((TN(I,J), J=1, 4), (KT(I,J), J=1, 4), LT(I),
1I=1, MENTRY), ((DN(I,J), J=1, 4), (KD(I,J), J=1, 4), LD(I), I=1, NENTRY)
   REWIND IDISC
   READ(ICR,26) (DN(NENTRY,J), J=1, 4)
26 FORMAT(4A3)
   IENTRY=NENTRY-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)=MAXO(LD(NENTRY),LT(NENTRY))
    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 KD(NENTRY,3)=NCONF
    KD(NENTRY,4)=3
    WRITE(MTD01) (HM(K,K),(EV(L,K),L=1,NCONF),K=1,NCONF)
    GO TO 30
C.....FIRST ORDER DENSITY MATRIX.
29 KD(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)=W(I)
31 CONTINUE
    WRITE(IDISC) MENTRY,NENTRY,((TN(I,J),J=1,4),(KT(I,J),J=1,4),LT(I),
1 I=1,MENTRY),((DN(I,J),J=1,4),(KD(I,J),J=1,4),LD(I),I=1,NENTRY)
    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),
1 I=1,MENTRY),((DN(I,J),J=1,4),(KD(I,J),J=1,4),LD(I),I=1,NENTRY)
    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,NENTRY
X   DISPLAY(LP,5)/I/
    DO 33 J=1,M
        IF(LD(I)-LT(J)) 33,42,33
33 CCNTINUE
X   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)

```

```

KT(IENTRY,4)=KD(I,4)
CALL SEARCH(MTDO1,KD(I,1),KD(I,2))
GO TO (35,37,38,39,43),KD(I,4)
C.....TRANSFORMED INTEGRALS.
35 IGO=NSQRD+1
DO 36 K=1,IGO
READ (MTDO1) (ERI(L),L=1,NSQRD)
WRITE(MTDO2) (ERI(L),L=1,NSQRD)
36 CONTINUE
GO TO 40
C.....G-VECTOR.
37 READ (MTDO1) (AA(K),K=1,KD(I,3))
WRITE(MTDO2) (AA(K),K=1,KD(I,3))
GO TO 40
C.....ENERGIES AND EIGENVECTORS.
38 READ (MTDO1) (EM(K,K),(EV(L,K),L=1,KD(I,3)),K=1,KD(I,3))
WRITE(MTDO2) (EM(K,K),(EV(L,K),L=1,KD(I,3)),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(MTDO2) ((GA(K,L),L=1,KD(I,3)),K=1,KD(I,3))
40 IENTRY=IENTRY+1
CALL TPPOSN(MTDO2,KT(IENTRY,1),KT(IENTRY,2))
42 CONTINUE
43 MENTRY=IENTRY
WRITE(IDISC) MENTRY,NENTRY,((TN(I,J),J=1,4),(KT(I,J),J=1,4),LT(I),
1I=1,MENTRY),((DN(I,J),J=1,4),(KD(I,J),J=1,4),LD(I),I=1,NENTRY)
REWIND IDISC
CLEAR JUMP
C.....PRINT CONTENTS TABLES.
44 FORMAT('D',33X,'TDFILE PARAMETER VALUES,IFILE =',I2,' JFILE =',I2)
45 WRITE(LP,46) KT(1,1)
WRITE(LP,47) ((TN(I,J),J=1,4),(KT(I,J),J=1,4),LT(I),I=1,MENTRY)
451 WRITE(LP,48) KD(1,1)
WRITE(LP,47) ((DN(I,J),J=1,4),(KD(I,J),J=1,4),LD(I),I=1,NENTRY)
46 FORMAT('B',40X,'CONTENTS OF MASTER FILE FROM BLOCK',I5//)
47 FORMAT(' ',4A3,' FROM BLOCK',I5,' WORD',I4,' . LOOP PARAMETER =',I5
1,' . RECORD TYPE =',I2,' . SEQUENCE NUMBER =',I3)
48 FORMAT('B',40X,'CONTENTS OF PRIVATE FILE FROM BLOCK',I5//)
IF(JUMP) 50,49,19
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

```

16F2

A. D. TAIT

21. 3. 72.

FORM 1/542(9.68)

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,

SEC SOL 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

SPECIFICATION

NUMBER

1
21 2
1 2

NUMBER OF INSTRUCTIONS USED ON EXIT FROM SUBPROGRAM SEC DAT =
 NUMBER OF INSTRUCTIONS USED ON ENTRY TO SUBPROGRAM TDFILE =

TDFILE PARAMETER VALUE

CONTENTS OF MASTER F

OXYGEN ATOM INTEGRALS. FROM BLOCK 100 WORD 0. L
 **** NEXT NEW RECORD **** FROM BLOCK 101 WORD 164. L

CONTENTS OF PRIVATE

OXYGEN ATOM INTEGRALS. FROM BLOCK 1 WORD 0. L
 **** NEXT NEW RECORD **** 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 MA
 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 HPASS =
 NUMBER OF INSTRUCTIONS USED ON EXIT FROM SUBPROGRAM HPASS =
 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 168. L
 NUMBER OF INSTRUCTIONS USED ON EXIT FROM SUBPROGRAM TDFILE =
 NUMBER OF INSTRUCTIONS USED ON ENTRY TO SUBPROGRAM SEC SOL =
 NUMBER OF INSTRUCTIONS USED ON ENTRY TO SUBPROGRAM SEC DAT =

N OF DETORS

DETOR
3 4 5 8 9 10
3 4 6 7 9 10
4287
4289

S, IFILE = 1 JFILE = 1

FILE FROM BLOCK 100

OOP PARAMETER = 25. RECORD TYPE = 1. SEQUENCE NUMBER = 1
OOP PARAMETER = 0. RECORD TYPE = 5. SEQUENCE NUMBER = 2

FILE FROM BLOCK 1

OOP PARAMETER = 25. RECORD TYPE = 1. SEQUENCE NUMBER = 1
OOP PARAMETER = 0. RECORD TYPE = 5. SEQUENCE NUMBER = 2

4338
4340
4342
4343

TRIX ELEMENTS BETWEEN DETORS= 1

4367
4368
4400
4401
4404
4406

S, IFILE = 3 JFILE = 2

FILE FROM BLOCK 1

OOP PARAMETER = 25. RECORD TYPE = 1. SEQUENCE NUMBER = 1
OOP PARAMETER = 3. RECORD TYPE = 2. SEQUENCE NUMBER = 2
OOP PARAMETER = 0. RECORD TYPE = 5. SEQUENCE NUMBER = 3

4425
4428
4429

1 CO-DETECTORS OF CORRECT SYMMETRY AND SPIN ARE FORMED

```
CO-DETOR( 1) =  
+7.0710673119E-01*DETOR( 1)  
+7.0710673119E-01*DETOR( 2)
```

NUMBER OF INSTRUCTIONS USED ON EXIT FROM SUBPROGRAM SECDAT = 4447

SOLUTION OF S

ENERGIES OF S

-7.4540361952E+01

EIGENVECTORS FOR

1.0000000000E+00

NUMBER OF INSTRUCTIONS USED ON EXIT FROM SUBPROGRAM SECSOL
NUMBER OF INSTRUCTIONS USED ON ENTRY TO SUBPROGRAM TDFILE

TDFILE PARAMETER VALU

CONTENTS OF PRIVATE

OXYGEN ATOM INTEGRALS.	FROM BLOCK	1 WORD	0.
OXYGEN ATOM CI P DETOR MATRIX.	FROM BLOCK	2 WORD	164.
OXYGEN ATOM CI 3 P SOLUTION.	FROM BLOCK	2 WORD	168.
**** 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			

EQUULAR EQUATION

TATES 1 TO 1

STATES 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

NATURAL SPIN ORBI
COEFFICIENTS OF

C(1)= 7.0710678119E-01 C(2)= 7.0710678119
NUMBER OF INSTRUCTIONS USED ON ENTRY TO SUBPROGRAM FOJM
NUMBER OF INSTRUCTIONS USED ON EXIT FROM SUBPROGRAM FOJM
NUMBER OF INSTRUCTIONS USED ON ENTRY TO SUBPROGRAM TDFI

TDFILE PARAMETER V

CONTENTS OF PRIV

OXYGEN ATOM INTEGRALS. FROM BLOCK 1 WORD
OXYGEN ATOM CI 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 EXIT FROM SUBPROGRAM TDFI

RESULTS OF NATJR

OCCUPATION NUMBE

1.0000000000E+00

1.0000000000E+00

TRANSFORMATION

1.0000000000E+00
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00

0.0000000000E+00
1.0000000000E+00
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0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00

OCCUPATION NUMBE

5.0000000000E-01

5.0000000000E-01

TRANSFORMATION

0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
1.0000000000E+00
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
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0.0000000000E+00

0.0000000000E+00
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0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
1.0000000000E+00
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00
0.0000000000E+00

SUM OF OCCUPATION

NUMBER OF EL

NUMBER OF INSTRUCTIONS USED ON EXIT FROM SUBPROGRAM NATO

- 272 -

TAL ANALYSIS OF LEVEL 1
INDIVIDUAL DETERMINANTS

1-01 CC

A4 = 4486

K = 1

K = 2

A4 = 4491

LE = 4492

ALUES, IFILE = 3 JFILE = 4

ATE FILE FROM BLOCK 1

0. LOOP PARAMETER =	25. RECORD TYPE = 1.	SEQUENCE NUMBER = 1
4. LOOP PARAMETER =	3. RECORD TYPE = 2.	SEQUENCE NUMBER = 2
8. 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 = 4511

AL SPIN ORBITAL ANALYSIS

RS OF ORBITALS 1 TO 5

1.0000000000E+00	1.0000000000E+00	5.0000000000E-01
------------------	------------------	------------------

MATRIX COLUMNS 1 TO 5

0.0000000000E+00	0.0000000000E+00	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00	0.0000000000E+00
1.0000000000E+00	0.0000000000E+00	0.0000000000E+00
0.0000000000E+00	1.0000000000E+00	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00	1.0000000000E+00
0.0000000000E+00	0.0000000000E+00	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00	0.0000000000E+00

RS OF ORBITALS 6 TO 10

5.0000000000E-01	1.0000000000E+00	1.0000000000E+00
------------------	------------------	------------------

MATRIX COLUMNS 6 TO 10

0.0000000000E+00	0.0000000000E+00	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00	0.0000000000E+00
1.0000000000E+00	0.0000000000E+00	0.0000000000E+00
0.0000000000E+00	1.0000000000E+00	0.0000000000E+00
0.0000000000E+00	0.0000000000E+00	1.0000000000E+00

NUMBERS = 8.0000000001E+00

ELECTRONS = 8

RB = 4552

NUMBER OF INSTRUCTIONS USED ON ENTRY TO SUBPROGRAM TDFI

TDFILE PARAMETER V

CONTENTS OF MAST

OXYGEN ATOM INTEGRALS.	FROM BLOCK	100 WORD
OXYGEN ATOM CI 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

CONTENTS OF PRIV

OXYGEN ATOM INTEGRALS.	FROM BLOCK	1 WORD
OXYGEN ATOM CI 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 EXIT FROM SUBPROGRAM TDFI

**** JOB COMPLETE - TIM

LE = 4556

ALUES,IFILE = 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
8. 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

0. LOOP PARAMETER =	25.	RECORD TYPE =	1.	SEQUENCE NUMBER =	1
4. LOOP PARAMETER =	3.	RECORD TYPE =	2.	SEQUENCE NUMBER =	2
8. 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

SPECTRØ. A PROGRAM FOR COMPUTING THE
SPECTROSCOPIC CONSTANTS OF DIATOMIC MOLECULES

SPECTRØ 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 SPECTRØ

Card 1 NCØNF, NDEG, NR, NØ

 FØRMAT (4I5)

NCØNF = number of energy levels of the molecule to
 be investigated for the symmetry and spin
 defined by Card 4. If NCØNF = 0 execution
 ceases.

NDEG = degree of fitted polynomial

NR = number of values of the bond length to which
 polynomial is to be fitted.

NØ { = 0 to suppress diagnostic output.
 ≠ 0 to obtain diagnostic output, including
 residuals

Card 2 TITLE

 FØRMAT (9A8/6A8)

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

Card 3 RMASS

 FØRMAT (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

FØRMAT (2I5, 2A4)

ISPIN = value of total spin eigenvalue for this state

LAMBDA = value of axial angular momentum for this state

INVERS	{	Gbbb for gerade states
		Ubbb for ungerade states
		bbbb for heteronuclear diatomic molecules
REFLEC	{	+bbb for Σ^+ states
		-bbb for Σ^- states
		bbbb for all other states

(Note : b = blank)

Card 6 (R(I), I = 1, NR)

FØRMAT (1PE20.10)

R(I) is the value of the I-th bond length in bohrs.

(1 ≤ I ≤ NR) Repeat, as required.

Card 7 ((E(I,J), J = 1, NR), I = 1, NCØNF)

FØRMAT (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 NCØNF = 0.

Restrictions

1 ≤ NR ≤ 20

1 ≤ NDEG ≤ NR

1 ≤ NCØNF ≤ 5

0 ≤ LAMBDA ≤ 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,
1REFLEC,RMASS,TITLE(15),F(20),P(20),R(20),BE(5),DE(5),DO(5),FC(5),
2MINR(5),RMIN(5),WE(5),X(20),XX(20,20),A(5,10),YLJ(5,15),E(5,20)

DIMENSION ANGMOM(5)

DATA ANGMOM/3H SIGMA ,3H PI ,8H DELTA ,8H 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) RMASS

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 FORMAT(9A8/6A8)

2 FORMAT(1PE20.10)

3 FORMAT(16I5)

4 FORMAT(2I5,2A4)

C.....PRINT DATA

I=2*ISPIN+1

LAMBDA=LAMBDA+1

WRITE(LP,5) TITLE

WRITE(LP,6) RMASS

WRITE(LP,7) NCONF,NR

WRITE(LP,13) NDEG

WRITE(LP,3) I,ANGMOM(LAMBDA),INVERS,REFLEC,(I,I=1,5)

5 FORMAT(1H1/1H0,44X,31HSPECTROSCOPIC CONSTANTS PROGRAM/1H0,15A8)

6 FORMAT(1H0,35X,14HREDUCED MASS =,1PE17.10,19HAMU (UNIFIED SCALE))

7 FORMAT(1H0,32X,25HNUMBER OF ENERGY LEVELS =,I2,26H, NUMBER OF BOND

1 LENGTHS =,I3)

8 FORMAT(1H0,41X,26HTHE SPECTROSCOPIC STATE IS,I2,A6,1X,2A1/1H0,47X,
125HENERGIES AND BOND LENGTHS/1H0,5X,9HR (BOHRS),6X,5(9X,1HE,I1,9X)

2)

DO 10 I=1,NR

WRITE(LP,9) R(I),(E(J,I),J=1,NCONF)

9 FORMAT(1H0,F11.1,9X,1PE20.10)

10 CONTINUE

13 FORMAT(1H0,44X,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,
1REFLEC,RMASS,TITLE(15),F(20),P(20),R(20),BE(5),DE(5),DO(5),FC(5),
2MINR(5),RMIN(5),WE(5),X(20),XX(20,20),A(5,10),YLJ(5,15),E(5,20)

DIMENSION FL(20),FD(20)

EQUIVALENCE (P(3),A0),(P(4),A1),(P(5),A2),(P(6),A3),(P(7),A4),
1(P(3),A5),(P(9),A6),(P(10),A7)

DATA EPS/1.0E-10/

```

NTERM=NDEG+1
NM1=NDEG-1
NM2=NDEG-2
BPA=R(NR)+R(1)
BMA=1.0/(R(NR)-R(1))
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
DO 13 ICONF=1,NCONF
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,I2,14H 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 CRLIN2(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)
W=F(I)-D
B=B+W*W
IF(NO.NE.0) WRITE(LP,7) X(I),F(I),D,W
6 CONTINUE
7 FORMAT(1H ,13X,2HX=,1PE17.10,6H F(X)=,1PE17.10,6H D(X)=,1PE17.10,
111H 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).
DO 9 I=3,NTERM
IM1=I-1
IM2=I-2
FL(IM1)=IM1*P(I)
FD(IM2)=IM2*FL(IM1)
9 CONTINUE
FL(1)=P(2)
I=MINR(ICONF)
RE=X(I)
ITER=0
10 ITER=ITER+1
D=POLYVA(RE,FL,NM1)/POLYVA(RE,FD,NM2)
IF(NO.NE.0) WRITE(LP,19) ITER,RE,D
IF(ABS(D)-EPS) 15,11,11
11 IF(ITER-100) 12,13,13
12 RE=RE-D
GO TO 10
13 WRITE(LP,14) ICONF,D

```

```

14 FORMAT(1H0,39X,5HLEVEL,I2,26H NEWTON-RAPHSON FAILED, D=,1PE9.2)
15 D=POLYVA(RE,P,NDEG)
    IF(NO.NE.0) WRITE(LP,16) D,RE
16 FORMAT(1H0,25X,34HMINIMUM OF NORMALIZED POLYNOMIAL =,1PE17.10,7H A
    1T X =,OPF13.10)
C.....TRANSFORM POLYNOMIAL TO DUNHAM FORM.
    D=RE+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
    IM1=MINO(10,NTERM)
    DO 17 I=1,IM1
    A(ICONF,I)=FL(I)
    P(I)=FL(I)
17 CONTINUE
    RE=0.5*(RE/BMA+BPA)
    RMIN(ICONF)=RE
C.....COMPUTE SPECTROSCOPIC CONSTANTS AND YLJ.
    BE(ICONF)=60.2014/(RMASS*RE*RE)
    IF(BE(ICONF).LE.0.0.OR.AO.LE.0.0) GO TO 18
    WE(ICONF)=2.0*SQRT(AO*BE(ICONF))
    DE(ICONF)=4.0*(BE(ICONF)/WE(ICONF))**2*BE(ICONF)
    FC(ICONF)=5.891461E-02*RMASS*WE(ICONF)**2
C.....DEFINE B,W AND BW FOR EASE OF WRITING FORMULAE.
    B=BE(ICONF)
    W=WE(ICONF)
    BW=(B/W)**2
    A1SQ=A1*A1
    A2SQ=A2*A2
    A3SQ=A3*A3
    YLJ(ICONF, 1)=0.125*B*(3*A2-1.75*A1SQ)
    YLJ(ICONF, 2)=W*(1+0.25*BW*(25*A4-16.75*A2SQ-0.5*A1*(95*A3-0.25*A1
1      *(459*A2-144.375*A1SQ))))
    YLJ(ICONF, 3)=0.5*B*(3*(A2-1.25*A1SQ)+0.5*BW*(0.5*A1*(-1365*A5+
1      3667.5*A2*A3+0.25*A1*(3535*A4-15503.25*A2SQ+0.5*A1*
2      (-23865*A3+0.125*A1*(239935*A2-52263.75*A1SQ))))+
3      245*A6-0.5*A2*(335*A4-426.75*A2SQ)-271.25*A3SQ))
    YLJ(ICONF, 4)=0.5*W*BW*(10*A4-8.5*A2SQ-A1*(35*A3-0.25*A1*(225*A2-
1      33.125*A1SQ)))
    YLJ(ICONF, 5)=5*BW*B*(0.25*A1*(-63*A5+241.5*A2*A3+0.25*A1*(543*A4-
1      1247.25*A2SQ+0.5*A1*(-1953*A3+0.125*A1*(23265*A2-
2      5737.75*A1SQ))))-0.25*A2*(33*A4-13.75*A2SQ)-3.5*(
3      2.25*A3SQ-A6))
    YLJ(ICONF, 6)=B*(1+0.5*BW*(15*(1+A3)-9*A2+A1*(14-23*A2+10.5*A1*(1+
1      A1))))
    YLJ(ICONF, 7)=W*BW*(6*(1+A1)+BW*(A1*(235-459*A2+356.25*A3-397.5*A4
1      +534.625*A2SQ+0.25*A1*(1147.5-2409.75*A2+2572.5*A3+
2      A1*(1155-3564.75*A2+974.53125*A1*(1+A1))))-0.5*A2*
3      (335+715*A3-251.25*A2)+190*A3-112.5*A4+175*(1+A5)))
    YLJ(ICONF, 8)=6*B*BW*(5*(1+A3)-3*A2+A1*(10-13*A2+7.5*A1*(1+A1)))
    YLJ(ICONF, 9)=20*BW*BW*W*(A1*(21-45*A2+26.25*A3-25.5*A4+51.375*
1      A2SQ+0.25*A1*(112.5-236.25*A2+217.5*A3+A1*(141-
2      377.25*A2+113.96375*A1*(1+A1))))-0.5*A2*(17+45*A3-
3      12.75*A2)+14*A3-4.5*A4+7*(1+A5))
    YLJ(ICONF,10)=-4*B*BW*(1+0.5*BW*(A1*(190-207*A2+102.5*A3+A1*(-A2*
1      166.5+173.25+126*A1*(1+0.5*A1))))-A2*(119-46*A2)+90*

```

```

2          A3-45*A4+163))
  YLJ(ICONF,11)=-12*BW*BW*W*(9.5-4*A2+9*A1*(1+0.5*A1))
  YLJ(ICONF,12)=-24*BW*BW*B*(A1*(125-117*A2+47.5*A3+A1*(123.75-103.5
1          *A2+90*A1*(1+0.5*A1)))-A2*(61-26*A2)+30*A3-15*A4+65)
  YLJ(ICONF,13)=16*BW*BW*B*(3+A1)
  YLJ(ICONF,14)=12*BW**3*W*(233+A1*(279-88*A2+A1*(139+63*A1))-120*A2
1          +30*A3/3)
  YLJ(ICONF,15)=-64*BW**3*B*(13+9*A1*(1+0.25*A1)-A2)
  DO(ICONF)=YLJ(ICONF,1)+0.5*(YLJ(ICONF,2)+0.5*(YLJ(ICONF,3)+0.5*
1(YLJ(ICONF,4)+0.5*YLJ(ICONF,5))))
13 CONTINUE
19 FORMAT(1H ,21X,9HITERATION,I4,19H CURRENT ESTIMATE =,1PE17.10,11HI
INCREMENT =,1PE17.10)
  RETURN
  END

```

*FORTRAN

```

  SUBROUTINE FINDRE
C.....DETERMINES WHICH LEVELS ARE BOUND.
  COMMON /SPEC/ ICR,INVER,ISPIN,LAMBDA,LOGIC,LP,NCONF,NDEG,NR,NO,
1REFLEC,RMASS,TITLE(15),F(20),P(20),R(20),BE(5),DE(5),DO(5),FC(5),
2MINR(5),RMIN(5),WE(5),X(20),XX(20,20),A(5,10),YLJ(5,15),E(5,20)
  NRMI=NR-1
  DO 4 I=1,NCONF
  MINR(I)=NR
1 EMIN=E(I,NR)
  DO 3 J=1,NRMI
  IF(EMIN-E(I,J)) 3,3,2
2 EMIN=E(I,J)
  MINR(I)=J
  RE=R(J)
3 CONTINUE
  RMIN(I)=RE
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
  DO(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,NROW,NCOL,EPS,ITFAIL)
C.....ORLIN2 GIVES THE LEAST SQUARES SOLUTION FOR A SYSTEM OF N LINEAR
C.....EQUATIONS IN M UNKNOWN. A IS THE N*M-MATRIX OF THE 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.
C.....THE METHOD IS DESCRIBED BY F.L.BAUER IN NUM.MATH.7,333-352(1965).
  DIMENSION A(NROW,NCOL),B(NROW),X(NROW),U(20,20),P(20),Q(210),
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
51 CONTINUE
C.....END OF FORMATION OF THE MATRICES R AND U AND THE VECTOR V.
C.....BACK SUBSTITUTION.
LL=L
MM=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-MM
7 CONTINUE
C.....END OF BACK SUBSTITUTION.
C.....INTERATIVE IMPROVEMENT OF THE SOLUTION.
EPS2=EPS*EPS
SO=0.0

```

```

      8 I=LL
      S1=0.0
      S2=0.0
C.....RESIDUAL VECTOR STORED IN P
      DO 9 J=1,N
      P(J)=-SCPROD(-B(J),A,J,X,M,NROW,NCOL)
      9 CONTINUE
C.....VECTOR ON THE RIGHT SIDE STORED IN PP.
      DO 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-MM
      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
      S0=S1
      GO TO 8
      15 RETURN
      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
      FOFK=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 OF P(X) WHERE X=A*T+B.
      W(1)=1.0
      Z(1)=W(1)
      D(1)=C(1)
      NP1=N+1
      DO 1 I=2,NP1
      W(I)=1.0
      Z(I)=B*Z(I-1)
      D(I)=D(I)+C(I)*Z(I)
1 CONTINUE
      DO 2 J=2,NP1
      W(1)=W(1)*A
      D(J)=C(J)*W(1)
      IF(J.EQ.NP1) RETURN
      K=2
      JP1=J+1
      DO 2 I=JP1,NP1
      W(K)=A*W(K)+W(K-1)
      D(J)=D(J)+C(I)*W(K)*Z(K)
      K=K+1
2 CONTINUE
      RETURN
      END

```

*FORTRAN

SUBROUTINE RFILE

C.....OUTPUT OF RESULTS.

LOGICAL LOGIC

```

COMMON /SPEC/ ICR,INVERS,ISPIN,LAMBDA,LOGIC,LP,NCONF,NDEG,NR,NO,
1REFLEC,RMASS,TITLE(15),F(20),P(20),R(20),BE(5),DE(5),DO(5),FC(5),
2MINR(5),RMIN(5),WE(5),X(20),XX(20,20),A(5,10),YIJ(5,15),E(5,20)
      DIMENSION T(31,2)
      DATA T /8H      RE,8HE(RE) (H,8H      WE(CM,8H      KE(DY,8H      BE(CM
1,8H      DE(CM,8H      Y00,8H      Y10,8H      Y20,8H      Y30,8H      Y40
2,8H      Y01,8H      Y11,8H      Y21,8H      Y31,8H      Y02,8H      Y12
3,8H      Y22,8H      Y03,8H      Y13,8H      Y04,8H      E(R,8H      LIN
4,8H      A0 ,8H      A1 ,8H      A2 ,8H      A3 ,8H      A4 ,8H      A5
5,8H      A6 ,8H      A7 ,8H (BOHRS),CHARTREES),8H-1)      ,SHNE.CM-1)
6,8H-1)      ,SH-1)      ,SH      ,SH=WE      ,SH=-WEX      ,SH=WEY
7,8H=WEZ      ,SH=BE      ,SH=-ALPHAE,SH=GAMMAE ,SH=DELTA E ,SH=-DE
8,8H=BETA E ,SH      ,SH=FE      ,SH      ,SH=HE      ,SHE)(CM-1)
9,8HEAR TERM,SH(CM-1) ,7*8H      /
      DATA T1,T2/8H      ZO(CM,8H-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(1,1),T(1,2),(RMIN(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,(DO(I),I=1,NCONF)
      WRITE(LP,6)

```

```

2 FORMAT(1H1/1H0,15A8/1H0,48X,23HSPECTROSCOPIC CONSTANTS)
3 FORMAT(1H0,20X,5(6X,5HLEVEL,I3,6X))
4 FORMAT(1H ,4X,2A8,1P5E20.10)
5 FORMAT(1H0,48X,33HCLASSICAL SPECTROSCOPIC CONSTANTS/1H )
6 FORMAT(1H0,40X,40HCORRECTED SPECTROSCOPIC CONSTANTS (CM-1)/1H )
   DO 7 I=1,15
     J=I+6
     WRITE(LP,4) T(J,1),T(J,2),(YLJ(K,I),K=1,NCONF)
7 CONTINUE
   WRITE(LP,3)
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,NROW,NCOL)
  DIMENSION A(NROW,NCOL),P(NROW)
  ICUBLE PRECISION T
  T=S
  DO 1 J=1,N
    T=T+DBLE(A(I,J))*DBLE(P(J))
1 CONTINUE
  SCPROD=T
  RETURN
  END

```

FORTRAN STATEMENT										IDENTIFICATION AND SEQUENCE NO.
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100										1
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A. D. THIT

21.3.72

[illegible]

SPECTROSCOPIC CONSTANTS PROGRAM

SPECTRO TEST DATA - SPECTROSCOPIC CONSTANTS FROM KOLOS-ROOTHAAN H2 WAVE FUNCTION.

REDUCED MASS = 5.0391261000E-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

R (BOHRS)	E1	E2	E3	E4	E5
0.8	-1.0201750000E+00				
1.0	-1.1245170000E+00				
1.2	-1.1649300000E+00				
1.4	-1.1744420000E+00				
1.6	-1.1685380000E+00				
2.0	-1.1379990000E+00				
2.4	-1.1020840000E+00				
2.8	-1.0699560000E+00				

LEVEL 1 MEAN ENERGY =-1.1203301250E+00
X=-1.000000000E+00 F(X)= 2.1981508002E+04 D(X)= 2.1981508002E+04 F(X)-D(X)= 1.7881393432E-07
X=-7.999999999E-01 F(X)= -9.1891279909E+02 D(X)= -9.1891279920E+02 F(X)-D(X)= 9.6857547760E-08
X=-6.000000000E-01 F(X)= -9.7885406191E+03 D(X)= -9.7885406191E+03 F(X)-D(X)= -5.9604644775E-08
X=-3.999999998E-01 F(X)= -1.1876183202E+04 D(X)= -1.1876183202E+04 F(X)-D(X)= 0.000000000E+00
X=-2.000000000E-01 F(X)= -1.0580405048E+04 D(X)= -1.0580405048E+04 F(X)-D(X)= 5.9604644775E-08
X= 2.000000000E-01 F(X)= -3.8778696280E+03 D(X)= -3.8778696280E+03 F(X)-D(X)= 1.4901161194E-08
X= 6.000000001E-01 F(X)= 4.0045613525E+03 D(X)= 4.0045613525E+03 F(X)-D(X)= 0.000000000E+00
X= 1.000000000E+00 F(X)= 1.1055841942E+04 D(X)= 1.1055841942E+04 F(X)-D(X)= -5.9604644775E-08

L2 NORM OF SOLUTION = 5.22E-14
ITERATION 1 CURRENT ESTIMATE =-3.999999998E-01 INCREMENT =-1.2643958335E-03
ITERATION 2 CURRENT ESTIMATE =-3.9873560415E-01 INCREMENT =-2.6865127708E-06
ITERATION 3 CURRENT ESTIMATE =-3.9873291764E-01 INCREMENT =-1.2119934818E-11

MINIMUM OF NORMALIZED POLYNOMIAL =-1.1876248322E+04 AT X =-0.3987329176

SPECTRO TEST DATA - SPECTROSCOPIC CONSTANTS FROM KOLOS-ROOTHAAN H2 WAVE FUNCTION.

SPECTROSCOPIC CONSTANTS

LEVEL

LEVEL 1

RE (BOHRS) 1,4012670824E+00
E(RE) (HARTREES) -1,1744422967E+00

CLASSICAL SPECTROSCOPIC CONSTANTS

WE(CM-1) 4,3994526819E+03
KE(DYNE.CM-1) 5,7461311684E+05
BE(CM-1) 6,0842846589E+01
DE(CM-1) 4,6546953692E-02
Z0(CM-1) 2,1809659866E+03

CORRECTED SPECTROSCOPIC CONSTANTS (CM-1)

Y00	1.0750560943E+01
Y10=WE	4.3939515377E+03
Y20=-WEX	-1.0434405417E+02
Y30=WEY	-5.4227486096E+00
Y40=WEZ	5.6221518275E-02
Y01=BE	6.0800301634E+01
Y11=-ALPHA	-2.8337208123E+00
Y21=GAMMA	-3.2167071652E-02
Y31=DELTA	-3.0576539895E-02
Y02=-DE	-4.6628897998E-02
Y12=BETA	2.2471739842E-03
Y22	-8.3602912307E-04
Y03=FE	5.1091724295E-05
Y13	-5.3969321117E-06
Y04=HE	-6.8786602704E-08

DUNHAM ANALYSIS EXPANSION COEFFICIENTS

E(RE)(CM-1)	-2.5776027678E+05
LINEAR TERM	-1.3187527657E-06
A0 (CM-1)	7.9529414654E+04
A1	-1.5652456248E+00
A2	1.9003468697E+00
A3	-2.4778954686E+00
A4	2.3905957811E+00
A5	-9.5918684303E-01
A6	0.0000000000E+00
A7	0.0000000000E+00

APPENDIX IX

SPECIFICATION OF DETORS AND CODETORS FOR

THE $^3\Sigma^-_g$, $^1\Sigma^+_g$, AND $^1\Delta_g$ STATES

The detors are specified by using the identifiers of the valence shell molecular spin-orbitals according to the rules

$$ns \sigma_g \alpha = 1, ns \sigma_g \beta = 2,$$

$$ns \sigma_u \alpha = 3, ns \sigma_u \beta = 4,$$

$$np_0 \sigma_g \alpha = 5, np_0 \sigma_g \beta = 6,$$

$$np_0 \sigma_u \alpha = 7, np_0 \sigma_u \beta = 8,$$

$$np_- \pi_g \alpha = 9, np_- \pi_g \beta = 10,$$

$$np_- \pi_u \alpha = 11, np_- \pi_u \beta = 12,$$

$$np_+ \pi_g \alpha = 13, np_+ \pi_g \beta = 14,$$

$$np_+ \pi_u \alpha = 15, np_+ \pi_u \beta = 16.$$

In the oxygen molecule calculations $n = 2$, and for the sulphur molecule $n = 3$. To obtain the data required for SECSOL 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 $\underline{T}_{S\sigma}$ (chapters 7 and 8), and n_I is the normalization factor for Ψ_I . The value of n_I is calculated in the routine SECDAT (see Appendix VII), and

$$n_I = \left(\sum_J t_{JI}^2 \right)^{-1/2}$$

(In Tables IX.1 and IX.3, D_I 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. Σ_g DETORS.

D(1)=(1)(2)(3)(4)(5)(6)(7)(8)(9)(10)(13)(14)
D(2)=(1)(2)(3)(4)(5)(6)(7)(8)(9)(10)(15)(16)
D(3)=(1)(2)(3)(4)(5)(6)(7)(8)(11)(12)(13)(14)
D(4)=(1)(2)(3)(4)(5)(6)(7)(8)(9)(11)(14)(16)
D(5)=(1)(2)(3)(4)(5)(6)(7)(8)(10)(11)(13)(16)
D(6)=(1)(2)(3)(4)(5)(6)(7)(8)(9)(12)(13)(16)
D(7)=(1)(2)(3)(4)(5)(6)(7)(8)(10)(12)(13)(15)
D(8)=(1)(2)(3)(4)(5)(6)(7)(8)(9)(12)(14)(15)
D(9)=(1)(2)(3)(4)(5)(6)(7)(8)(10)(11)(14)(15)
D(10)=(1)(2)(3)(4)(5)(6)(7)(8)(11)(12)(15)(16)
D(11)=(1)(2)(3)(4)(5)(6)(9)(10)(11)(13)(14)(16)
D(12)=(1)(2)(3)(4)(5)(6)(9)(10)(12)(13)(14)(15)
D(13)=(1)(2)(3)(4)(5)(6)(9)(11)(12)(14)(15)(16)
D(14)=(1)(2)(3)(4)(5)(6)(10)(11)(12)(13)(15)(16)
D(15)=(1)(2)(3)(4)(5)(7)(9)(10)(12)(14)(15)(16)
D(16)=(1)(2)(3)(4)(6)(7)(9)(10)(11)(14)(15)(16)
D(17)=(1)(2)(3)(4)(5)(8)(9)(10)(11)(14)(15)(16)
D(18)=(1)(2)(3)(4)(6)(8)(9)(10)(11)(13)(15)(16)
D(19)=(1)(2)(3)(4)(5)(8)(9)(10)(12)(13)(15)(16)
D(20)=(1)(2)(3)(4)(6)(7)(9)(10)(12)(13)(15)(16)
D(21)=(1)(2)(3)(4)(6)(7)(9)(11)(12)(13)(14)(16)
D(22)=(1)(2)(3)(4)(5)(8)(9)(11)(12)(13)(14)(16)
D(23)=(1)(2)(3)(4)(6)(8)(9)(11)(12)(13)(14)(15)
D(24)=(1)(2)(3)(4)(5)(8)(10)(11)(12)(13)(14)(15)
D(25)=(1)(2)(3)(4)(6)(7)(10)(11)(12)(13)(14)(15)
D(26)=(1)(2)(3)(4)(5)(7)(10)(11)(12)(13)(14)(16)
D(27)=(1)(2)(3)(4)(7)(8)(9)(10)(11)(13)(14)(16)
D(28)=(1)(2)(3)(4)(7)(8)(9)(10)(12)(13)(14)(15)
D(29)=(1)(2)(3)(4)(7)(8)(9)(11)(12)(14)(15)(16)
D(30)=(1)(2)(3)(4)(7)(8)(10)(11)(12)(13)(15)(16)
D(31)=(1)(2)(3)(4)(9)(10)(11)(12)(13)(14)(15)(16)
D(32)=(1)(2)(3)(5)(6)(7)(9)(10)(12)(13)(14)(16)
D(33)=(1)(2)(4)(5)(6)(7)(9)(10)(11)(13)(14)(16)
D(34)=(1)(2)(3)(5)(6)(8)(9)(10)(11)(13)(14)(16)
D(35)=(1)(2)(4)(5)(6)(8)(9)(10)(11)(13)(14)(15)
D(36)=(1)(2)(3)(5)(6)(8)(9)(10)(12)(13)(14)(15)
D(37)=(1)(2)(4)(5)(6)(7)(9)(10)(12)(13)(14)(15)
D(38)=(1)(2)(3)(5)(6)(7)(10)(11)(12)(14)(15)(16)
D(39)=(1)(2)(4)(5)(6)(7)(9)(11)(12)(14)(15)(16)
D(40)=(1)(2)(3)(5)(6)(8)(9)(11)(12)(14)(15)(16)
D(41)=(1)(2)(4)(5)(6)(8)(9)(11)(12)(13)(15)(16)
D(42)=(1)(2)(3)(5)(6)(8)(10)(11)(12)(13)(15)(16)
D(43)=(1)(2)(4)(5)(6)(7)(10)(11)(12)(13)(15)(16)
D(44)=(1)(2)(3)(5)(7)(8)(9)(10)(12)(14)(15)(16)
D(45)=(1)(2)(4)(5)(7)(8)(9)(10)(11)(14)(15)(16)
D(46)=(1)(2)(3)(6)(7)(8)(9)(10)(11)(14)(15)(16)
D(47)=(1)(2)(4)(6)(7)(8)(9)(10)(11)(13)(15)(16)
D(48)=(1)(2)(3)(6)(7)(8)(9)(10)(12)(13)(15)(16)
D(49)=(1)(2)(4)(5)(7)(8)(9)(10)(12)(13)(15)(16)
D(50)=(1)(2)(4)(5)(7)(8)(9)(11)(12)(13)(14)(16)
D(51)=(1)(2)(3)(6)(7)(8)(9)(11)(12)(13)(14)(16)
D(52)=(1)(2)(4)(6)(7)(8)(9)(11)(12)(13)(14)(15)
D(53)=(1)(2)(3)(6)(7)(8)(10)(11)(12)(13)(14)(15)
D(54)=(1)(2)(4)(5)(7)(8)(10)(11)(12)(13)(14)(15)
D(55)=(1)(2)(3)(5)(7)(8)(10)(11)(12)(13)(14)(15)
D(56)=(1)(2)(3)(5)(9)(10)(11)(12)(13)(14)(15)(16)
D(57)=(1)(2)(4)(7)(9)(10)(11)(12)(13)(14)(15)(16)
D(58)=(1)(2)(5)(6)(7)(8)(9)(10)(11)(13)(14)(16)
D(59)=(1)(2)(5)(6)(7)(8)(9)(10)(11)(13)(14)(15)

TABLE IX.1. $\sum_g$ DETORS (Continued).

D(60)=(1)(2)(5)(6)(7)(8)(9)(11)(12)(14)(15)(16)
D(61)=(1)(2)(5)(6)(7)(8)(10)(11)(12)(13)(15)(16)
D(62)=(1)(2)(5)(6)(9)(10)(11)(12)(13)(14)(15)(16)
D(63)=(1)(2)(7)(8)(9)(10)(11)(12)(13)(14)(15)(16)
D(64)=(1)(3)(4)(5)(6)(7)(9)(10)(12)(14)(15)(16)
D(65)=(2)(3)(4)(5)(6)(7)(9)(10)(11)(14)(15)(16)
D(66)=(1)(3)(4)(5)(6)(8)(9)(10)(11)(14)(15)(16)
D(67)=(2)(3)(4)(5)(6)(8)(9)(10)(11)(13)(15)(16)
D(68)=(1)(3)(4)(5)(6)(8)(9)(10)(12)(13)(15)(16)
D(69)=(2)(3)(4)(5)(6)(7)(9)(10)(12)(13)(15)(16)
D(70)=(2)(3)(4)(5)(6)(7)(9)(11)(12)(13)(14)(16)
D(71)=(1)(3)(4)(5)(6)(8)(9)(11)(12)(13)(14)(16)
D(72)=(2)(3)(4)(5)(6)(8)(9)(11)(12)(13)(14)(15)
D(73)=(1)(3)(4)(5)(6)(8)(10)(11)(12)(13)(14)(15)
D(74)=(2)(3)(4)(5)(6)(7)(10)(11)(12)(13)(14)(15)
D(75)=(1)(3)(4)(5)(6)(7)(10)(11)(12)(13)(14)(16)
D(76)=(1)(3)(4)(5)(7)(8)(9)(10)(12)(13)(14)(16)
D(77)=(2)(3)(4)(5)(7)(8)(9)(10)(11)(13)(14)(16)
D(78)=(1)(3)(4)(6)(7)(8)(9)(10)(11)(13)(14)(16)
D(79)=(2)(3)(4)(6)(7)(8)(9)(10)(11)(13)(14)(15)
D(80)=(1)(3)(4)(6)(7)(8)(9)(10)(12)(13)(14)(15)
D(81)=(2)(3)(4)(5)(7)(8)(9)(10)(12)(13)(14)(15)
D(82)=(1)(3)(4)(5)(7)(8)(10)(11)(12)(14)(15)(16)
D(83)=(2)(3)(4)(5)(7)(8)(9)(11)(12)(14)(15)(16)
D(84)=(1)(3)(4)(6)(7)(8)(9)(11)(12)(14)(15)(16)
D(85)=(2)(3)(4)(6)(7)(8)(9)(11)(12)(13)(15)(16)
D(86)=(1)(3)(4)(6)(7)(8)(10)(11)(12)(13)(15)(16)
D(87)=(2)(3)(4)(5)(7)(8)(10)(11)(12)(13)(15)(16)
D(88)=(1)(3)(4)(6)(9)(10)(11)(12)(13)(14)(15)(16)
D(89)=(2)(3)(4)(5)(9)(10)(11)(12)(13)(14)(15)(16)
D(90)=(1)(3)(5)(6)(7)(8)(9)(10)(12)(14)(15)(16)
D(91)=(2)(3)(5)(6)(7)(8)(9)(10)(11)(14)(15)(16)
D(92)=(1)(4)(5)(6)(7)(8)(9)(10)(11)(14)(15)(16)
D(93)=(2)(4)(5)(6)(7)(8)(9)(10)(11)(13)(15)(16)
D(94)=(1)(4)(5)(6)(7)(8)(9)(10)(12)(13)(15)(16)
D(95)=(2)(3)(5)(6)(7)(8)(9)(10)(12)(13)(15)(16)
D(96)=(2)(3)(5)(6)(7)(8)(9)(11)(12)(13)(14)(16)
D(97)=(1)(4)(5)(6)(7)(8)(9)(11)(12)(13)(14)(16)
D(98)=(2)(4)(5)(6)(7)(8)(9)(11)(12)(13)(14)(15)
D(99)=(1)(4)(5)(6)(7)(8)(10)(11)(12)(13)(14)(15)
D(100)=(2)(3)(5)(6)(7)(8)(10)(11)(12)(13)(14)(15)
D(101)=(1)(3)(5)(6)(7)(8)(10)(11)(12)(13)(14)(16)
D(102)=(1)(3)(6)(8)(9)(10)(11)(12)(13)(14)(15)(16)
D(103)=(2)(3)(5)(8)(9)(10)(11)(12)(13)(14)(15)(16)
D(104)=(1)(4)(5)(8)(9)(10)(11)(12)(13)(14)(15)(16)
D(105)=(2)(4)(5)(7)(9)(10)(11)(12)(13)(14)(15)(16)
D(106)=(1)(4)(6)(7)(9)(10)(11)(12)(13)(14)(15)(16)
D(107)=(2)(3)(6)(7)(9)(10)(11)(12)(13)(14)(15)(16)
D(108)=(1)(6)(7)(8)(9)(10)(11)(12)(13)(14)(15)(16)
D(109)=(2)(5)(7)(8)(9)(10)(11)(12)(13)(14)(15)(16)
D(110)=(3)(4)(5)(6)(7)(8)(9)(10)(11)(13)(14)(16)
D(111)=(3)(4)(5)(6)(7)(8)(9)(10)(12)(13)(14)(15)
D(112)=(3)(4)(5)(6)(7)(8)(9)(11)(12)(14)(15)(16)
D(113)=(3)(4)(5)(6)(7)(8)(10)(11)(12)(13)(15)(16)
D(114)=(3)(4)(5)(6)(9)(10)(11)(12)(13)(14)(15)(16)
D(115)=(3)(4)(7)(8)(9)(10)(11)(12)(13)(14)(15)(16)
D(116)=(3)(5)(6)(8)(9)(10)(11)(12)(13)(14)(15)(16)
D(117)=(4)(5)(6)(7)(9)(10)(11)(12)(13)(14)(15)(16)
D(118)=(5)(6)(7)(8)(9)(10)(11)(12)(13)(14)(15)(16)

TABLE IX.2

${}^3\Sigma_g^-$ Codetors constructed from detors in Table IX.1.

$$\Psi_1 = 2^{-1/2}(D_4 - D_7)$$

$$\Psi_2 = 2^{-1/2}(D_5 - D_8)$$

$$\Psi_3 = 2^{-1/2}(D_{11} + D_{12})$$

$$\Psi_4 = 2^{-1/2}(D_{13} + D_{14})$$

$$\begin{aligned} \Psi_5 = 8^{-1/2}(& - D_{16} - D_{17} + D_{19} + D_{20} \\ & + D_{21} + D_{22} - D_{24} - D_{25}) \end{aligned}$$

$$\begin{aligned} \Psi_6 = 24^{-1/2}(& - 2D_{15} - D_{16} + D_{17} + 2D_{18} + D_{19} - D_{20} \\ & - D_{21} + D_{22} + 2D_{23} + D_{24} - D_{25} - 2D_{26}) \end{aligned}$$

$$\begin{aligned} \Psi_7 = 12^{-1/2}(& - D_{15} + D_{16} - D_{17} + D_{18} - D_{19} + D_{20} \\ & + D_{21} - D_{22} + D_{23} - D_{24} + D_{25} - D_{26}) \end{aligned}$$

$$\Psi_8 = 2^{-1/2}(D_{27} + D_{28})$$

$$\Psi_9 = 2^{-1/2}(D_{29} + D_{30})$$

$$\Psi_{10} = 12^{-1/2}(-2D_{32} - D_{33} + D_{34} + 2D_{35} + D_{36} - D_{37})$$

$$\Psi_{11} = 6^{-1/2}(-D_{32} + D_{33} - D_{34} + D_{35} - D_{36} + D_{37})$$

$$\Psi_{12} = 12^{-1/2}(-2D_{38} - D_{39} + D_{40} + 2D_{41} + D_{42} - D_{43})$$

$$\Psi_{13} = 6^{-1/2}(-D_{38} + D_{39} - D_{40} + D_{41} - D_{42} + D_{43})$$

$$\begin{aligned} \Psi_{14} = 8^{-1/2}(& - D_{45} - D_{46} + D_{48} + D_{49} \\ & + D_{50} + D_{51} - D_{53} - D_{54}) \end{aligned}$$

TABLE IX.2 (continued)

$$\begin{aligned}\psi_{15} = 24^{-1/2} (& - 2D_{44} - D_{45} + D_{46} + 2D_{47} + D_{48} - D_{49} \\ & - D_{50} + D_{51} + 2D_{52} + D_{53} - D_{54} - 2D_{55})\end{aligned}$$

$$\begin{aligned}\psi_{16} = 12^{-1/2} (& - D_{44} + D_{45} - D_{46} + D_{47} - D_{48} + D_{49} \\ & + D_{50} - D_{51} + D_{52} - D_{53} + D_{54} - D_{55})\end{aligned}$$

$$\psi_{17} = 2^{-1/2} (D_{58} + D_{59})$$

$$\psi_{18} = 2^{-1/2} (D_{60} + D_{61})$$

$$\begin{aligned}\psi_{19} = 8^{-1/2} (& - D_{65} + D_{66} + D_{68} + D_{69} \\ & + D_{70} + D_{71} - D_{73} - D_{74})\end{aligned}$$

$$\begin{aligned}\psi_{20} = 24^{-1/2} (& - 2D_{64} - D_{65} + D_{66} + 2D_{67} + D_{68} - D_{69} \\ & - D_{70} + D_{71} + 2D_{72} + D_{73} - D_{74} - 2D_{75})\end{aligned}$$

$$\begin{aligned}\psi_{21} = 12^{-1/2} (& - D_{64} + D_{65} - D_{66} + D_{67} - D_{68} + D_{69} \\ & + D_{70} - D_{71} + D_{72} - D_{73} + D_{74} - D_{75})\end{aligned}$$

$$\psi_{22} = 12^{-1/2} (- 2D_{76} - D_{77} + D_{78} + 2D_{79} + D_{80} - D_{81})$$

$$\psi_{23} = 6^{-1/2} (- D_{76} + D_{77} - D_{78} + D_{79} - D_{80} + D_{81})$$

$$\psi_{24} = 12^{-1/2} (- 2D_{82} - D_{83} + D_{84} + 2D_{85} + D_{86} - D_{87})$$

$$\psi_{25} = 6^{-1/2} (- D_{82} + D_{83} - D_{84} + D_{85} - D_{86} + D_{87})$$

$$\begin{aligned}\psi_{26} = 8^{-1/2} (& - D_{91} - D_{92} + D_{94} + D_{95} \\ & + D_{96} + D_{97} - D_{99} - D_{100})\end{aligned}$$

TABLE IX.2 (continued)

$$\begin{aligned}\Psi_{27} = 24^{-1/2}(& - 2D_{90} - D_{91} + D_{92} + 2D_{93} + D_{94} - D_{95} \\ & - D_{96} + D_{97} + 2D_{98} + D_{99} - D_{100} - 2D_{101})\end{aligned}$$

$$\begin{aligned}\Psi_{28} = 12^{-1/2}(& - D_{90} + D_{91} - D_{92} + D_{93} - D_{94} + D_{95} \\ & + D_{96} - D_{97} + D_{98} - D_{99} + D_{100} - D_{101})\end{aligned}$$

$$\Psi_{29} = 2^{-1/2}(D_{110} + D_{111})$$

$$\Psi_{30} = 2^{-1/2}(D_{112} + D_{113})$$

¹ Σ_g^+ Codetors constructed from detors in Table IX.1.

$$\Psi_1 = D_1$$

$$\Psi_2 = 2^{-1/2}(D_2 + D_3)$$

$$\Psi_3 = 2^{-1}(- D_5 + D_6 - D_8 + D_9)$$

$$\Psi_4 = 12^{-1/2}(2D_4 - D_5 - D_6 + 2D_7 - D_8 - D_9)$$

$$\Psi_5 = D_{10}$$

$$\Psi_6 = 2^{-1/2}(D_{11} - D_{12})$$

$$\Psi_7 = 2^{-1/2}(D_{13} - D_{14})$$

$$\begin{aligned}\Psi_8 = 8^{-1/2}(& - D_{16} + D_{17} - D_{19} + D_{20} \\ & - D_{21} + D_{22} - D_{24} + D_{25})\end{aligned}$$

$$\begin{aligned}\Psi_9 = 24^{-1/2}(& 2D_{15} - D_{16} - D_{17} + 2D_{18} - D_{19} - D_{20} \\ & + D_{21} + D_{22} - 2D_{23} + D_{24} + D_{25} - 2D_{26})\end{aligned}$$

$$\Psi_{10} = 2^{-1/2}(D_{27} - D_{28})$$

TABLE IX.2 (continued)

$$\Psi_{11} = 2^{-1/2}(D_{29} - D_{30})$$

$$\Psi_{12} = D_{31}$$

$$\Psi_{13} = 2^{-1}(-D_{33} + D_{34} - D_{36} + D_{37})$$

$$\Psi_{14} = 2^{-1}(-D_{39} + D_{40} - D_{42} + D_{43})$$

$$\begin{aligned}\Psi_{15} = 8^{-1/2}(&-D_{45} + D_{46} - D_{48} + D_{49} \\ &- D_{50} + D_{51} - D_{53} + D_{54})\end{aligned}$$

$$\begin{aligned}\Psi_{16} = 24^{-1/2}(&2D_{44} - D_{45} - D_{46} + 2D_{47} - D_{48} - D_{49} \\ &+ D_{50} + D_{51} - 2D_{52} + D_{53} + D_{54} - 2D_{55})\end{aligned}$$

$$\Psi_{17} = 2^{-1/2}(D_{56} - D_{57})$$

$$\Psi_{18} = 2^{-1/2}(D_{58} - D_{59})$$

$$\Psi_{19} = 2^{-1/2}(D_{60} - D_{61})$$

$$\Psi_{20} = D_{62}$$

$$\Psi_{21} = D_{63}$$

$$\begin{aligned}\Psi_{22} = 8^{-1/2}(&-D_{65} + D_{66} - D_{68} + D_{69} \\ &- D_{70} + D_{71} - D_{73} + D_{74})\end{aligned}$$

$$\begin{aligned}\Psi_{23} = 24^{-1/2}(&2D_{64} - D_{65} - D_{66} + 2D_{67} - D_{68} - D_{69} \\ &+ D_{70} + D_{71} - 2D_{72} + D_{73} + D_{74} - 2D_{75})\end{aligned}$$

$$\Psi_{24} = 2^{-1}(-D_{77} + D_{78} - D_{80} + D_{81})$$

$$\Psi_{25} = 2^{-1}(-D_{83} + D_{84} - D_{86} + D_{87})$$

TABLE IX.2 (continued)

$$\Psi_{26} = 2^{-1/2} (D_{88} - D_{89})$$

$$\Psi_{27} = 8^{-1/2} (-D_{91} + D_{92} - D_{94} + D_{95} \\ - D_{96} + D_{97} - D_{99} + D_{100})$$

$$\Psi_{28} = 24^{-1/2} (2D_{90} - D_{91} - D_{92} + 2D_{93} - D_{94} - D_{95} \\ + D_{96} + D_{97} - 2D_{98} + D_{99} + D_{100} - 2D_{101})$$

$$\Psi_{29} = 2^{-1} (-D_{103} + D_{104} - D_{106} + D_{107})$$

$$\Psi_{30} = 12^{-1/2} (2D_{102} - D_{103} - D_{104} + 2D_{105} - D_{106} - D_{107})$$

$$\Psi_{31} = 2^{-1/2} (D_{108} - D_{109})$$

$$\Psi_{32} = 2^{-1/2} (D_{110} - D_{111})$$

$$\Psi_{33} = 2^{-1/2} (D_{112} - D_{113})$$

$$\Psi_{34} = D_{114}$$

$$\Psi_{35} = D_{115}$$

$$\Psi_{36} = 2^{-1/2} (D_{116} - D_{117})$$

$$\Psi_{37} = D_{118}$$

TABLE IX.3. Δ_g DETORS.

D(1)=(1)(2)(3)(4)(5)(6)(7)(8)(9)(14)(15)(16)
D(2)=(1)(2)(3)(4)(5)(6)(7)(8)(10)(13)(15)(16)
D(3)=(1)(2)(3)(4)(5)(6)(7)(8)(11)(13)(14)(16)
D(4)=(1)(2)(3)(4)(5)(6)(7)(8)(12)(13)(14)(15)
D(5)=(1)(2)(3)(4)(5)(6)(9)(10)(13)(14)(15)(16)
D(6)=(1)(2)(3)(4)(5)(6)(11)(12)(13)(14)(15)(16)
D(7)=(1)(2)(3)(4)(5)(7)(10)(12)(13)(14)(15)(16)
D(8)=(1)(2)(3)(4)(6)(7)(9)(12)(13)(14)(15)(16)
D(9)=(1)(2)(3)(4)(5)(8)(9)(12)(13)(14)(15)(16)
D(10)=(1)(2)(3)(4)(6)(8)(9)(11)(13)(14)(15)(16)
D(11)=(1)(2)(3)(4)(5)(8)(10)(11)(13)(14)(15)(16)
D(12)=(1)(2)(3)(4)(6)(7)(10)(11)(13)(14)(15)(16)
D(13)=(1)(2)(3)(4)(7)(8)(9)(10)(13)(14)(15)(16)
D(14)=(1)(2)(3)(4)(7)(8)(11)(12)(13)(14)(15)(16)
D(15)=(1)(2)(3)(5)(6)(8)(9)(10)(13)(14)(15)(16)
D(16)=(1)(2)(4)(5)(6)(7)(9)(10)(13)(14)(15)(16)
D(17)=(1)(2)(3)(5)(6)(8)(11)(12)(13)(14)(15)(16)
D(18)=(1)(2)(4)(5)(6)(7)(11)(12)(13)(14)(15)(16)
D(19)=(1)(2)(3)(5)(7)(8)(10)(12)(13)(14)(15)(16)
D(20)=(1)(2)(4)(5)(7)(8)(9)(12)(13)(14)(15)(16)
D(21)=(1)(2)(3)(6)(7)(8)(9)(12)(13)(14)(15)(16)
D(22)=(1)(2)(4)(6)(7)(8)(9)(11)(13)(14)(15)(16)
D(23)=(1)(2)(3)(6)(7)(8)(10)(11)(13)(14)(15)(16)
D(24)=(1)(2)(4)(5)(7)(8)(10)(11)(13)(14)(15)(16)
D(25)=(1)(2)(5)(6)(7)(8)(9)(10)(13)(14)(15)(16)
D(26)=(1)(2)(5)(6)(7)(8)(11)(12)(13)(14)(15)(16)
D(27)=(1)(3)(4)(5)(6)(7)(10)(12)(13)(14)(15)(16)
D(28)=(2)(3)(4)(5)(6)(7)(9)(12)(13)(14)(15)(16)
D(29)=(1)(3)(4)(5)(6)(8)(9)(12)(13)(14)(15)(16)
D(30)=(2)(3)(4)(5)(6)(8)(9)(11)(13)(14)(15)(16)
D(31)=(1)(3)(4)(5)(6)(8)(10)(11)(13)(14)(15)(16)
D(32)=(2)(3)(4)(5)(6)(7)(10)(11)(13)(14)(15)(16)
D(33)=(1)(3)(4)(6)(7)(8)(9)(10)(13)(14)(15)(16)
D(34)=(2)(3)(4)(5)(7)(8)(9)(10)(13)(14)(15)(16)
D(35)=(1)(3)(4)(6)(7)(8)(11)(12)(13)(14)(15)(16)
D(36)=(2)(3)(4)(5)(7)(8)(11)(12)(13)(14)(15)(16)
D(37)=(1)(3)(5)(6)(7)(8)(10)(12)(13)(14)(15)(16)
D(38)=(2)(3)(5)(6)(7)(8)(9)(12)(13)(14)(15)(16)
D(39)=(1)(4)(5)(6)(7)(8)(9)(12)(13)(14)(15)(16)
D(40)=(2)(4)(5)(6)(7)(8)(9)(11)(13)(14)(15)(16)
D(41)=(1)(4)(5)(6)(7)(8)(10)(11)(13)(14)(15)(16)
D(42)=(2)(3)(5)(6)(7)(8)(10)(11)(13)(14)(15)(16)
D(43)=(3)(4)(5)(6)(7)(8)(9)(10)(13)(14)(15)(16)
D(44)=(3)(4)(5)(6)(7)(8)(11)(12)(13)(14)(15)(16)

TABLE IX.4

$^1\Delta_g$ Codetors constructed from detors in Table IX.3.

$$\psi_1 = 2^{-1/2}(D_1 - D_2)$$

$$\psi_2 = 2^{-1/2}(D_3 - D_4)$$

$$\psi_3 = D_5$$

$$\psi_4 = D_6$$

$$\psi_5 = 2^{-1}(-D_8 + D_9 - D_{11} + D_{12})$$

$$\psi_6 = 12^{-1/2}(2D_7 - D_8 - D_9 + 2D_{10} - D_{11} - D_{12})$$

$$\psi_7 = D_{13}$$

$$\psi_8 = D_{14}$$

$$\psi_9 = 2^{-1/2}(D_{15} - D_{16})$$

$$\psi_{10} = 2^{-1/2}(D_{17} - D_{18})$$

$$\psi_{11} = 2^{-1}(-D_{20} + D_{21} - D_{23} + D_{24})$$

$$\psi_{12} = 12^{-1/2}(2D_{19} - D_{20} - D_{21} + 2D_{22} - D_{23} - D_{24})$$

$$\psi_{13} = D_{25}$$

$$\psi_{14} = D_{26}$$

$$\psi_{15} = 2^{-1}(-D_{28} + D_{29} - D_{31} + D_{32})$$

$$\psi_{16} = 12^{-1/2}(2D_{27} - D_{28} - D_{29} + 2D_{30} - D_{31} - D_{32})$$

$$\psi_{17} = 2^{-1/2}(D_{33} - D_{34})$$

$$\psi_{18} = 2^{-1/2}(D_{35} - D_{36})$$

TABLE IX.4 (continued)

$$\psi_{19} = 2^{-1}(-D_{38} + D_{39} - D_{41} + D_{42})$$

$$\psi_{20} = 12^{-1/2}(2D_{37} - D_{38} - D_{39} + 2D_{40} - D_{41} - D_{42})$$

$$\psi_{21} = D_{43}$$

$$\psi_{22} = D_{44}$$

TABLE IX.5. PART 1, Σ_g SPATIAL ORBITAL CONFIGURATIONS.

	$ns\sigma_g$	$ns\sigma_u$	$np\sigma_g$	$np\pi_u$	$np\pi_g$	$np\sigma_u$	Present $3\Sigma_g^-$ Codetors	Present $1\Sigma_g^+$ Codetors	Ref. 42 $3\Sigma_g^-$	Ref. 42 $1\Sigma_g^+$
1	2	2	2	-	4	2		1		d
2	2	2	2	2	2	2		2		e
3	2	2	2	2	2	2	1,2	3,4	a,b	a,b
4	2	2	2	4	-	2		5		c
5	2	2	2	2	4	-	3	6	d	g
6	2	2	2	4	2	-	4	7	c	f
7	2	2	1	3	3	1	5,6,7	8,9	g,h,i	h,i
8	2	2	-	2	4	2	8	10	f	k
9	2	2	-	4	2	2	9	11	e	j
10	2	2	-	4	4	-		12		l
11	2	1	2	2	4	1	10,11	13		
12	2	1	2	4	2	1	12,13	14		
13	2	1	1	3	3	2	14,15,16	15,16		
14	2	1	-	4	4	1		17		
15	2	-	2	2	4	2	17	18		
16	2	-	2	4	2	2	18	19		
17	2	-	2	4	4	-		20		
18	2	-	-	4	4	2		21		
19	1	2	2	3	3	1	19,20,21	22,23		
20	1	2	1	2	4	2	22,23	24		
21	1	2	1	4	2	2	24,25	25		
22	1	2	1	4	4	-		26		
23	1	1	2	3	3	2	26,27,28	27,28		
24	1	1	1	4	4	1		29,30		
25	1	-	1	4	4	2		31		
26	-	2	2	2	4	2	29	32		
27	-	2	2	4	2	2	30	33		
28	-	2	2	4	4	-		34		
29	-	2	-	4	4	2		35		
30	-	1	2	4	4	1		36		
31	-	-	2	4	4	2		37		

TABLE IX.5. PART 2, Δ_g SPATIAL ORBITAL CONFIGURATIONS.

	$ns\sigma_g$	$ns\sigma_u$	$np\sigma_g$	$np\pi_u$	$np\pi_g$	$np\sigma_u$	Present ${}^1\Delta_g$ Codetors
1	2	2	2	2	2	2	1
2	2	2	2	2	2	2	2
3	2	2	2	2	4	-	3
4	2	2	2	4	2	-	4
5	2	2	1	3	3	1	5,6
6	2	2	-	2	4	2	7
7	2	2	-	4	2	2	8
8	2	1	2	2	4	1	9
9	2	1	2	4	2	1	10
10	2	1	1	3	3	2	11,12
11	2	-	2	2	4	2	13
12	2	-	2	4	2	2	14
13	1	2	2	3	3	1	15,16
14	1	2	1	2	4	2	17
15	1	2	1	4	2	2	18
16	1	1	2	3	3	2	19,20
17	-	2	2	2	4	2	21
18	-	2	2	4	2	2	22

REFERENCES

1. M. Born, and J.R. Oppenheimer, Ann. d. Phys. 84, 457 (1927).
2. C.C.J. Roothaan, Phys. Rev. 23, 69 (1951).
3. G.G. Hall, Rep. Progr. Phys. XXII, 1 (1959).
4. H. Eyring, J. Walter, and G. Kimball, "Quantum Chemistry" (Wiley, New York 1944)
5. G.G. Hall, Proc. Roy. Soc. A208, 328 (1951).
6. R.K. Nesbet, Advan. Chem. Phys. IX, 321 (1965).
7. A.T. Amos, and G.G. Hall, Proc. Roy. Soc. A263, 483 (1961).
8. P-O. Löwdin, Phys. Rev. 97 1474, 1490, 1509 (1955).
9. A.C. Wahl, J. Chem. Phys. 41, 2600 (1964).
10. W.G. Richards, T.E.H. Walker, and R.K. Hinkley, "A Bibliography of Ab Initio Molecular Wave Functions" (Clarendon Press, Oxford 1971)
11. R. McWeeny, and B.T. Sutcliffe, "Methods of Molecular Quantum Mechanics" (Academic Press, London 1969).
12. M. Kotani, A. Ameiya, E. Ishiguro, and T. Kimura, "Tables of Molecular Integrals" (Maruzen Co. Ltd., Tokyo 1963).
13. J.H. Wilkinson, "The Algebraic Eigenvalue Problem" (Clarendon Press, Oxford 1965).
14. J.C. Slater, "Quantum Theory of Molecules and Solids", Vol. 1 (McGraw-Hill Book Co. Inc., New York 1963).
15. J. Hinze, and C.C.J. Roothaan, Progr. Theor. Phys. Supplement No. 40, 37 (1967).
16. G. Das, and A.C. Wahl, J. Chem. Phys. 47, 2934 (1967).
17. G. Das, and A.C. Wahl, J. Chem. Phys. 44, 87 (1966).
18. G. Das, and A.C. Wahl, Phys. Rev. Letters, 24, 440 (1970).
19. W. Kolos, and C.C.J. Roothaan, Rev. Mod. Phys. 32, 219 (1960). See also reference 10.
20. H. Shull, J. Chem. Phys. 30, 1405 (1959).
21. H. Shull, J. Am. Soc. 82, 1287 (1960).
22. R.E. Christoffersen, J. Chem. Phys, 41, 960 (1964).
23. W.C. Price, J. Chem. Phys. 15, 614 (1947).

24. J.N. Shoolery, Discussions Faraday Soc. 19, 215 (1955).
25. K.E. Banyard, and H. Shull, J. Chem. Phys. 44, 384 (1966)
26. See reference 20.
27. R.S. Mulliken, J. Chem. Phys. 23, 1833 (1955).
28. P-O. Löwdin, and H. Shull, Phys. Rev. 101, 1730 (1956).
29. F. Ayres, "Matrices" (Schaum Pub. Co., New York 1962).
30. R. McWeeny, J. Chem. Phys. 19, 1614 (1951); 20, 920 (1952);
Acta Crystallogr. 5 463 (1952).
31. R.E. Christoffersen, and H. Shull, J. Chem. Phys. 48 1790 (1968).
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this paper.
32. R.E. Christoffersen, Private communication; M.E. Schwartz, and
L.J. Schaad, J. Chem. Phys. 47, 5325 (1967).
33. J.D. Hopton, and J.W. Linnett, J. Chem. Soc. 1553 (1962).
34. J.O. Hirschfelder, H. Eyring, and N. Rosen, J. Chem. Phys. 4 130 (1936).
35. H. Shull, J. Am. Chem. Soc. 86, 469 (1964).
36. K. Ruedenberg, Rev. Mod. Phys. 34, 326 (1962).
37. K.E. Banyard, and A. West, J. Chem. Phys. 54, 437 (1971).
38. S.F. Boys, Proc. Roy. Soc. A200, 542 (1950).
39. M. Hammermesh, "Group Theory and its Applications to Physical Problems"
(Pergammon Press, London 1962).
40. J. Todd, "A Survey of Numerical Analysis" (McGraw-Hill Book Co. Inc.,
New York 1962).
41. F.E. Harris, "Computational Methods in Quantum Chemistry" (Quantum
Chemistry Group, Uppsala University, TXVII, 1967).
42. A. Meckler, J. Chem. Phys. 21, 1750 (1953).
43. M. Kotani, Y. Mizuno, K. Kayama, and E. Ishiguro, J. Phys. Soc. Jap.
12, 707 (1957).
44. F.E. Harris, and H.H. Michels, Intern. J. Quantum Chem. 1S 329 (1967).
45. H.F. Schaefer, and F.E. Harris, J. Chem. Phys. 48, 4946 (1968).
46. E.P. Wigner, and E.E. Witmer, Z. Physik, 51 859 (1928).
47. H. Bowlder, R.S. Martin, and J.H. Wilkinson, Num. Math. 11, 293 (1968).
48. R.S. Martin, C. Reinsch, and J.H. Wilkinson, Num. Math. 11, 181 (1968).

49. C.F. Schofield, "FORTRAN V" (ULACSS, 2nd Ed. 1969).
50. I.C.T. Atlas 1 Computer. Programming Manual for A.B.L. List CS 348A. (January 1965).
51. "Usage of Atlas Magnetic Tape in the Hartran System" (Atlas Computer Laboratory). This also applies to FORTRAN V.
52. S.F. Boys, Proc. Roy. Soc. A201, 125 (1950).
53. E. Clementi, and E.R. Davis, J. Comp. Phys. 1, 223 (1966).
54. J. Miller, and J.C. Browne, Tech. Report. Molecular Physics Group. Univ. of Texas. Austin 12. Texas. U.S.A. (January 1962).
55. J.L. Dunham, Phys. Rev. 41, 713, 721 (1932).
56. G. Herzberg, "Molecular Spectra and Molecular Structure" Vol. 1. "Spectra of Diatomic Molecules" (D. Van Norstrand Co. Inc., London 1967).
57. L.A. König, J.H.E. Mattauch, and A.H. Wapstra, Nucl. Phys. 31, 18 (1962).
58. C.L. Beckel, and R. Engelke, J. Chem. Phys. 49, 5199 (1968).
59. C.L. Beckel, and J.R. Sattler, J. Mol. Spectry. 20, 153 (1966).
60. F.L. Bauer, Num. Math. 7 338 (1965).
61. G.T. Anthony. Private Communication.
62. G. Mackinney, ACM Algorithm 29; "Polynomial Transformer".
63. A.D. McLean, J. Chem. Phys. 40, 2774 (1964).
64. B.P. Stoicheff, Can. J. Phys. 35, 730 (1957).
65. A.G. Gaydon, "Dissociation Energies of Diatomic Molecules" (Chapman and Hall, London 1968).
66. H.F. Schaefer, and F.E. Harris, Chem. Phys. Letters, 1, 407 (1967).
67. F.E. Harris, J. Chem. Phys. 46, 2769 (1967).
68. R.F. Barrow, and R.P. Du Parcq, "Elemental Sulphur" p. 251. (Interscience 1965. Ed. B. Meyer).
69. P. Budininkas, R.K. Edwards, and P.G. Wahlbeck, J. Chem. Phys. 48, 2859 (1968).
70. J. Von Neumann, and E.P. Wigner, Physik Z. 30, 467 (1929).
71. M. Dixon, Unpublished work.
72. W. Kauzmann, "Quantum Chemistry" (Academic Press, New York 1964).

- 73. E. Clementi, and D.L. Raimondi, J. Chem. Phys. 38, 2686 (1963).
- 74. E.R. Cohen, and J.W. Du Mond, Rev. Mod. Phys. 37, 537 (1965).
- 75. H. Shull, and G.G. Hall, Nature 184, 1559 (1959).

Quantum-Mechanical Study of Some Three-Center Two-Electron Systems. II. A Natural-Orbital, Electron-Population, and Energy Analysis

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Configuration-interaction wavefunctions for a series of pseudomolecular ions of the form ZHZ^{+2Z-1} , 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 $Z\hat{H}Z$, 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 θ for each value of Z . For $Z=1.0$, i.e., H_3^+ , 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 θ was increased beyond 60° , it was found that the "central" proton within H_3^+ began to dominate the system. For $Z=2.2$, the ions approach most closely to their separated systems of minimum energy as θ tends to 180° . The contour diagrams and the electron-population analysis also show that the ZHZ^{+2Z-1} ions change from a three-center to, basically, a two-center system and a strongly perturbing proton as the values for Z and θ increase and decrease, respectively. The θ 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 θ 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 θ and Z are allowed to vary.

I. INTRODUCTION

In recent years considerable effort has been devoted to the study of the H_3^+ ion.¹ 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.² 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_3^+ to a series of pseudomolecular ions of the form ZHZ^{+2Z-1} . The results were reported in Part I of the present series.³ Several interesting features emerged from these calculations: first, we observed an initial decrease in the optimum value of the bond angle $Z\hat{H}Z$ 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.⁴

In Part I it was tentatively suggested that the behavior of the energy of the ZHZ^{+2Z-1} 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^{+2Z-1} ions, when $Z=1.0$ (0.4) 2.2, are analyzed for various values of the bond angle $Z\hat{H}Z$ ranging from $\theta=30^\circ$ – 180° . The wavefunction is reformulated in terms of natural spin orbitals and the occupation numbers are examined as a function of Z and θ . 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^{+2Z-1} 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 θ 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 Φ for the ZHZ^{+2Z-1} ions,

¹ R. E. Christoffersen, J. Chem. Phys. **41**, 960 (1964); H. Conroy, *ibid.* **41**, 603 (1964); **41**, 1341 (1964); J. R. Hoyland, *ibid.* **41**, 1370 (1964); W. A. Lester, Jr., and M. Krauss, *ibid.* **44**, 207 (1966); B. D. Joshi, *ibid.* **44**, 3627 (1966).

² H. C. Longuet-Higgins, Quart. Rev. (London) **11**, 121 (1957).

³ K. E. Banyard and H. Shull, J. Chem. Phys. **44**, 384 (1966).

⁴ K. E. Banyard, J. Chem. Phys. **44**, 4645 (1966); see also *ibid.* **48**, 2121 (1968).

TABLE I. Transformation matrices $[A_{jk}]$ of the natural orbitals χ_k for selected $Z:\theta$ values where $\chi_k = \sum_j \gamma_j A_{jk}$.

θ	Z								
	1.0			1.8			2.2		
60°	0.40793	0.00000	-0.57826	0.57073	0.00000	-0.37010	0.61715	0.00000	-0.28805
	0.40793	0.00000	1.15652	0.16368	0.00000	1.08571	0.09397	0.00000	1.05970
	0.00000	1.00158	0.00000	0.00000	0.84681	0.00000	0.00000	0.80064	0.00000
120°	0.36089	0.00000	-0.81247	0.56556	0.00000	-0.55863	0.64158	0.00000	-0.41616
	0.52425	0.00000	1.28316	0.28160	0.00000	1.12742	0.16143	0.00000	1.08724
	0.00000	0.79834	0.00000	0.00000	0.73263	0.00000	0.00000	0.71904	0.00000
180°	0.32756	0.00000	-0.90220	0.55900	0.00000	-0.59373	0.64306	0.00000	-0.43061
	0.58345	0.00000	1.32320	0.30709	0.00000	1.13264	0.17026	0.00000	1.08948
	0.00000	0.76029	0.00000	0.00000	0.72000	0.00000	0.00000	0.71250	0.00000

where the bond length $Z-H$ was denoted by R ,⁵ 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

$$\Psi(1, 2) = \sum_i a_i \phi_i(1, 2), \quad (1)$$

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.⁶ Thus, we have

$$\begin{aligned} \phi_1(1, 2) &= 2\gamma_1(1)\gamma_1(2), \\ \phi_2(1, 2) &= 2\gamma_2(1)\gamma_2(2), \\ \phi_3(1, 2) &= 2\gamma_3(1)\gamma_3(2), \\ \phi_4(1, 2) &= [\gamma_1(1)\gamma_2(2) + \gamma_1(2)\gamma_2(1)], \end{aligned} \quad (2)$$

where

$$\begin{aligned} \gamma_1(t) &= [\varphi(1s_B) + \varphi(1s_C)](t), \\ \gamma_2(t) &= [\varphi(1s_A)](t), \\ \gamma_3(t) &= [\varphi(1s_B) - \varphi(1s_C)](t), \end{aligned} \quad (3)$$

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 θ .

A. Natural Spin Orbitals

Natural spin orbitals are defined⁷ as forming a basis set which diagonalizes the generalized first-order density matrix. Further, if a many-particle wavefunction Φ ,

⁵ Unless stated otherwise, the bond length $Z-H$ was held fixed throughout this work at a value of 1.66 a.u. All units in the present article are Hartree atomic units, see H. Shull and G. G. Hall, *Nature* **184**, 1559 (1959).

⁶ The proton was located on center A and the nuclear charges Z were located on centers B and C . The bond angle θ was defined as $BAC = \hat{H}Z$.

⁷ P.-O. Löwdin and H. Shull, *Phys. Rev.* **101**, 1730 (1956).

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 Φ is distinguished as the superposition of configurations of most rapid convergence.⁸ For the special case of two-electron systems, Löwdin and Shull⁷ showed that the natural expansion for the space part of the wavefunction could be expressed as

$$\Psi(1, 2) = \sum_k c_k \chi_k(\bar{r}_1) \chi_k(\bar{r}_2), \quad (4)$$

where the natural orbitals $\chi_k(\bar{r}_k)$ are defined such that the spinless first-order electron density matrix can be written as

$$\gamma(\bar{r}_1' | \bar{r}_1) = 2 \sum_k n_k \chi_k^*(\bar{r}_1') \chi_k(\bar{r}_1). \quad (5)$$

The occupation number of the k th natural orbital is given by $n_k = c_k^2$ and satisfies the relation

$$\sum_k n_k = 1. \quad (6)$$

For the simple basis set⁹ employed in Part I, we obtained natural orbitals of the following form and symmetry

$$\begin{aligned} \chi_1(t) &= [A_{11}(b+c) + A_{21}a](t), & A_1, \\ \chi_2(t) &= [A_{32}(b-c)](t), & B_1, \\ \chi_3(t) &= [A_{13}(b+c) + A_{23}a](t), & A_1. \end{aligned} \quad (7)$$

The coefficients A_{jk} of the natural orbitals are given in Table I, however, for reasons of space, results are quoted only for selected values of Z and θ . The occupation numbers are given in Table II for all the $Z:\theta$ values.

⁸ P.-O. Löwdin, *Advan. Phys.* **5**, 1 (1956).

⁹ 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 $\gamma_j(t)$ of Eq. (3) may be expressed in the abbreviated form used in Eq. (7).

TABLE II. Occupation numbers of the natural orbitals χ_1 , χ_2 , and χ_3 for various Z : θ values.

θ	Z			
	1.0	1.4	1.8	2.2
30°	0.99000	0.99527	0.99482	0.99332
	0.00213	0.00366	0.00507	0.00667
	0.00787	0.00107	0.00011	0.00001
40°	0.98845	0.99137	0.98838	0.98271
	0.00347	0.00692	0.01138	0.01725
	0.00808	0.00171	0.00024	0.00004
50°	0.98699	0.98479 ^a	0.97663 ^a	0.96106
	0.00521	0.01282	0.02294	0.03887
	0.00780	0.00239	0.00043	0.00007
60°	0.98546	0.97954	0.96050	0.92361
	0.00727	0.01773	0.03888	0.07628
	0.00727	0.00273	0.00062	0.00011
70°	0.98378	0.97199	0.93792	0.87080
	0.00956	0.02503	0.06130	0.12906
	0.00666	0.00298	0.00078	0.00014
80°	0.98208	0.96388	0.91129	0.81185
	0.01194	0.03307	0.08784	0.18801
	0.00598	0.00305	0.00087	0.00014
100°	0.97874	0.94780	0.85754	0.71520
	0.01657	0.04934	0.14158	0.28468
	0.00469	0.00286	0.00088	0.00012
120°	0.97589	0.93479	0.81721	0.66180
	0.02045	0.06268	0.18198	0.33810
	0.00366	0.00253	0.00081	0.00010
150°	0.97345	0.92375	0.78601	0.62883
	0.02394	0.07413	0.21327	0.37108
	0.00261	0.00212	0.00072	0.00009
180°	0.97294	0.92084	0.77759	0.62105
	0.02483	0.07719	0.22172	0.37887
	0.00223	0.00197	0.00069	0.00008

^a The occupation numbers quoted here are for $\theta=52.15^\circ$, for $Z=1.4$, and $\theta=50.5^\circ$, for $Z=1.8$.

B. Electron-Population Analysis

Electron-population analysis will be particularly useful in the present work since it will permit us to observe changes in the amount of charge associated with different regions of the molecule as Z and θ are varied.

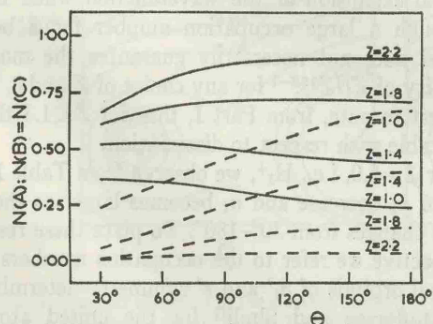


FIG. 1. The total net atomic population for the centers A, B, and C expressed as a function of the bond angle θ . The dotted lines are for center A and the solid lines for centers B or C.

The definitions for overlap and atomic populations have been taken from Mulliken.¹⁰ 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.¹¹ 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 work¹⁰ 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 subtotal overlap population. These quantities may be formulated as follows: from Eq. (5) the electron density $\rho(\bar{r}_1)$ can be written as

$$\rho(\bar{r}_1) = \gamma(\bar{r}_1 | \bar{r}_1) = 2 \sum_{k=1}^3 n_k \chi_k^2(\bar{r}_1), \quad (8)$$

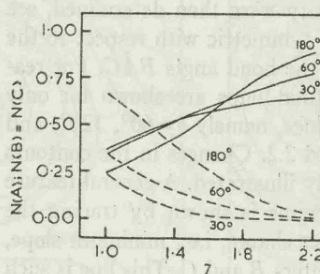


FIG. 2. The total net atomic population for the centers A, B, and C expressed as a function of Z for $\theta=30^\circ$, 60° , and 180° . The dotted lines are for center A and the solid lines for centers B or C.

where

$$\chi_1^2 = A_{11}^2[b^2 + 2bc + c^2] + 2A_{11}A_{21}[ab + ac] + A_{21}^2[a^2],$$

$$\chi_2^2 = A_{32}^2[b^2 - 2bc + c^2],$$

and

$$\chi_3^2 = A_{13}^2[b^2 + 2bc + c^2] + 2A_{13}A_{23}[ab + ac] + A_{23}^2[a^2].$$

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

$$N(A) = 2[n_1 A_{21}^2 + n_3 A_{23}^2];$$

similarly, we may write

$$N(B) = 2[n_1 A_{11}^2 + n_2 A_{32}^2 + n_3 A_{13}^2].$$

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 R. S. Mulliken, J. Chem. Phys. **23**, 1833 (1955).

¹¹ C. W. Scherr, J. Chem. Phys. **23**, 569 (1955), see Appendix II.

tion $S(BC)$ between the centers B and C is defined as

$$S(BC) = 4S_{bc}[n_1A_{11}^2 - n_2A_{32}^2 + n_3A_{13}^2];$$

similarly, we obtain

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

where $S_{ab} = S_{ac}$ and S_{bc} 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 θ 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 available³ which allowed us to study changes in the θ 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) values of the density were obtained in the plane of the molecule for each set of $Z:\theta$. 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 $B\hat{A}C$. For reasons of space, the contour maps are shown for only three groups of $Z:\theta$ values, namely $\theta=60^\circ$, 120° , and 180° for $Z=1.0$, 1.8 , and 2.2 . Changes in the contours as θ 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

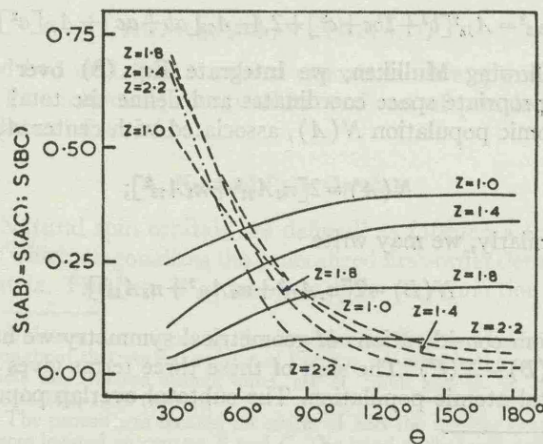


FIG. 3. The subtotal overlap population for $A-B$, $A-C$, and $B-C$ expressed as a function of the bond angle θ for various values of Z . The dotted lines are for $B-C$ and the solid lines for $A-B$ or $A-C$.

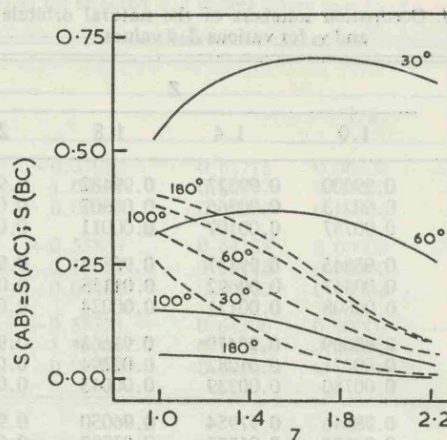


FIG. 4. The subtotal overlap population for $A-B$, $A-C$, and $B-C$ expressed as a function of Z for $\theta=30^\circ$, 60° , 100° , and 180° . The dotted lines are for $A-B$ or $A-C$ and the solid lines for $B-C$.

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,³ Fig. 8 showed the θ 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 function of the bond angle θ is shown for different Z values. Similarly, the θ 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 χ_1 and χ_3 are bonding-type orbitals, whereas χ_2 possesses a form which is antibonding. Reference to the occupation numbers given in Table II reveals that, for all values of θ , χ_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 ZHZ^{+2Z-1} for any choice of Z and θ , it is of interest to note, from Part I, that for $Z < 1.3$ the ions are stable with respect to dissociation.

For $Z=1.0$, i.e., H_3^+ , we observe from Table II that n_1 and n_3 decrease and n_2 becomes larger as the bond angle changes from 30° – 180° . To place these results in perspective we refer to the occupation numbers of the natural orbitals of a_1' and e' symmetry determined by Christoffersen and Shull¹² for the united atom Li^+

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.

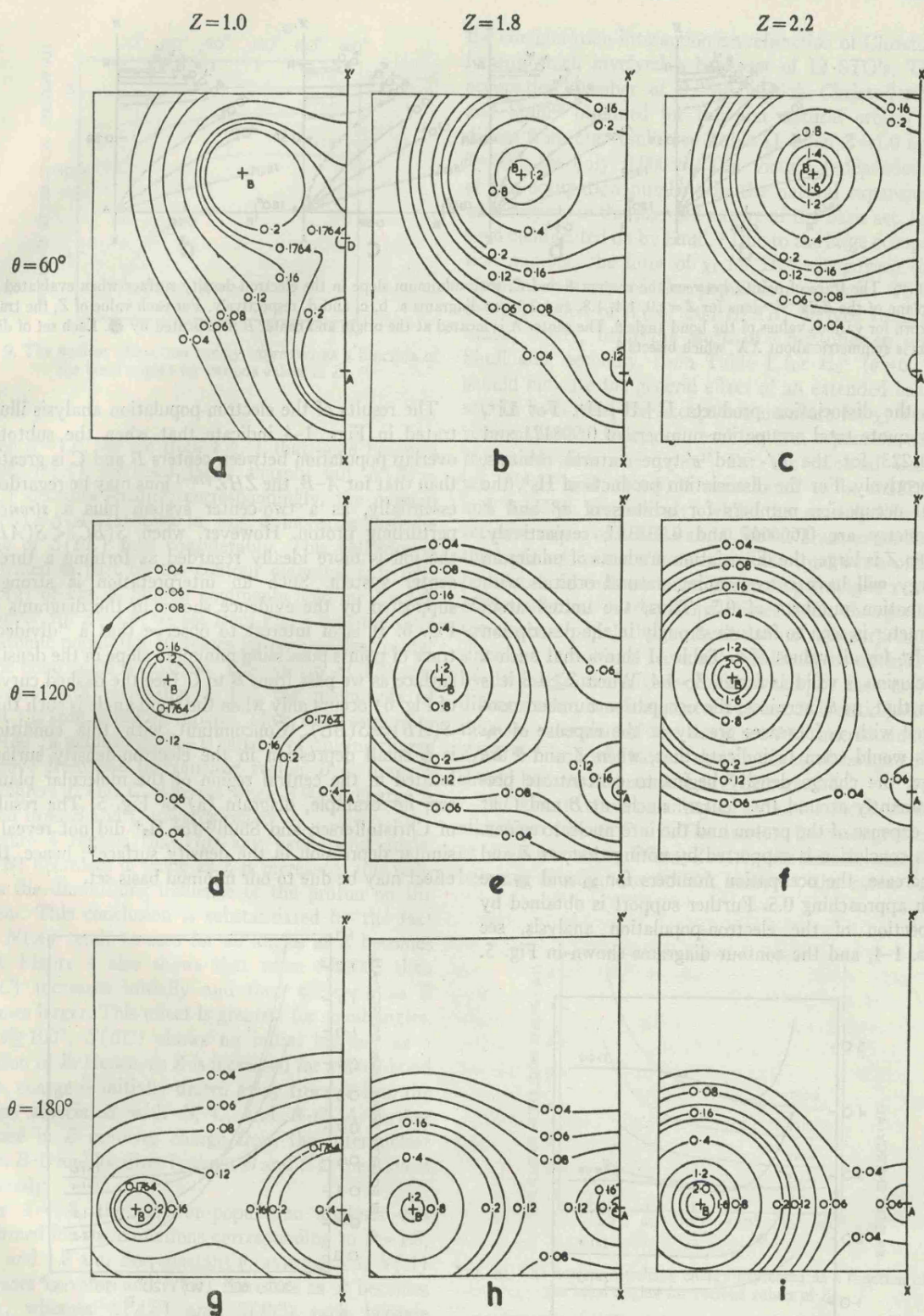


FIG. 5. Contour diagrams of the electron density in the plane of the molecule for selected values of $Z:\theta$. The diagrams are symmetric about the line XX' which bisects the bond angle θ . In (a) the density at D is less than 0.1764.

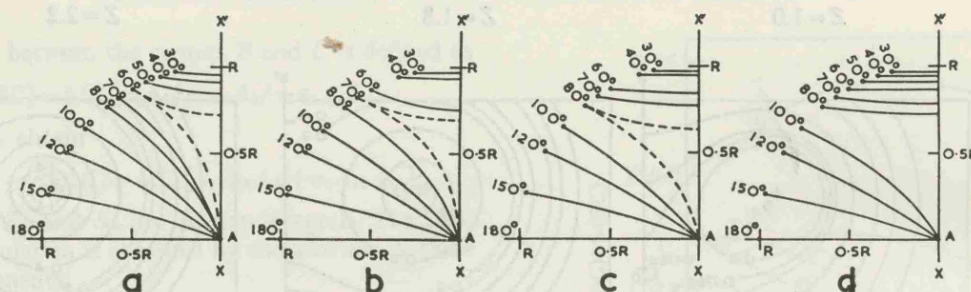


FIG. 6. The trace of points, between the centers B and C , with minimum slope in the electron-density surface when evaluated in the plane of the ZH_2^{+2Z-1} ions for $Z=1.0, 1.4, 1.8$, and 2.2 , see diagrams a, b, c, and d, respectively. For each value of Z , the trace is shown for various values of the bond angle θ . The center A is located at the origin and center B is indicated by $\bullet$. Each set of diagrams is symmetric about XX' which bisects θ .

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' -type natural orbitals, respectively. For the dissociation products of 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 H_3^+ for all values of θ . Table II shows that such a conclusion is valid as far as $Z \sim 1.4$. When $Z \geq 1.8$ it is seen that, as θ increases, the occupation number associated with χ_2 increases greatly at the expense of n_1 . This would seem to indicate that, when Z and θ are large, the charge density begins to concentrate predominantly around the "outer" nuclei at B and C at the expense of the proton and the internuclear regions. This conclusion is supported by noting that, as Z and θ increase, the occupation numbers for χ_1 and χ_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.

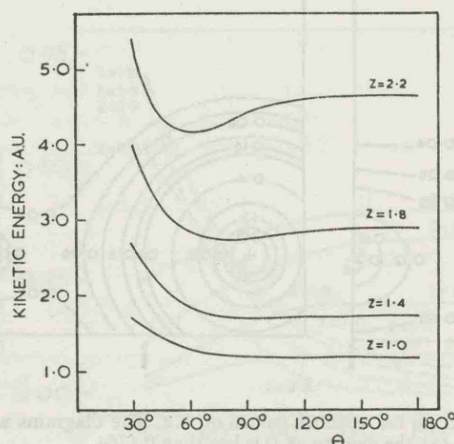


FIG. 7. The kinetic energy expressed as a function of the bond angle θ for various values of Z .

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 ZH_2^{+2Z-1} 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 $S(AB) \approx S(BC)$. 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 Shull¹² for H_3^+ did not reveal a similar depression in the density surface¹³; hence, the effect may be due to our minimal basis set.

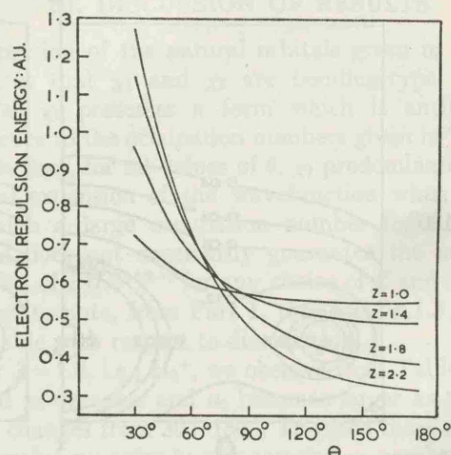


FIG. 8. The electron repulsion energy expressed as a function of the bond angle θ for various values of Z .

¹³ A private communication from R. E. Christoffersen for which we are grateful.

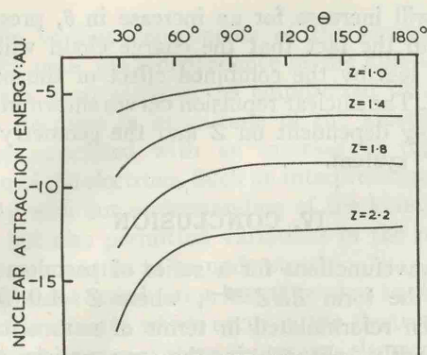


Fig. 9. The nuclear attraction energy expressed as a function of the bond angle θ for various values of Z .

For $Z=1.0$, we see from Fig. 1 that, as θ 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 $S(AB)$ also increases with increasing θ , but the magnitude of $S(BC)$ is seen to fall off rapidly. Thus, as θ varies from 30° – 180° , a value of $Z \geq 1.8$ 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 θ , 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 analysis¹² of

the configuration-interaction wavefunction of Christoffersen¹ which involved a basis set of 12 STO's. The occupation number of 0.98487 which Christoffersen and Shull¹² obtained for the first natural orbital χ_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.¹⁴ Due to the large occupation number, the form of χ_1 for H_3^+ will govern the essential features of the population analysis. Thus, the evaluation of $N(A)$ and $S(AB)$ derived from χ_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 χ_1 were renormalized to unity, i.e., each natural expansion was truncated after one term.¹⁵ For the minimal basis set, $N(A)$ and $S(AB)$ ¹⁶ 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 $1s$ 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 ZH_3^{+2Z-1} 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

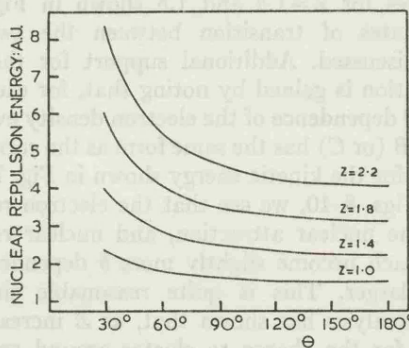


Fig. 10. The nuclear repulsion energy expressed as a function of the bond angle θ for various values of Z .

¹⁴ H. Shull, J. Chem. Phys. **30**, 1405 (1959).

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_3^+ system.

As pointed out by Ruedenberg,¹⁷ 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 θ 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 θ is increased to a value of about 60° , 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 θ , 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 θ approaches 180° . 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 θ . However, a continued increase of θ 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_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. 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 θ 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 θ 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 θ approaches 180° . 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 θ , 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 ZHZ^{+2Z-1} system.

IV. CONCLUSION

The wavefunctions for a series of pseudomolecular ions of the form ZHZ^{+2Z-1} , 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 $Z\hat{H}Z$, 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 θ 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 θ . 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 $Z < 1.3$.

The occupation numbers of the natural orbitals for H_3^+ 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_3^+ . The contour diagrams also showed that, when $\theta=60^\circ$, the "bonds" in H_3^+ were directed from the nuclei towards the centroid of the positive charges. The elaborate wavefunction of Christoffersen, analyzed by Christoffersen and Shull, also revealed this "bonding" arrangement. For fixed bond lengths BA and CA , as θ 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_3^+ 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 θ approaches 180° . 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 θ increases, charge flows from the internuclear region B - C towards the "outer" nuclei. The diagrams and analysis also show that, as Z increases and θ decreases, the ZHZ^{+2Z-1} ions change from a three-center system to what is essentially a two-center system plus a strongly perturbing proton.

¹⁷ K. Ruedenberg, Rev. Mod. Phys. **34**, 326 (1962).

Of the various components of the energy of the ZHZ^{+2Z-1} ions, the θ 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

ZHZ^{+2Z-1} as the bond angle $Z\hat{H}Z$ and the nuclear charges Z are allowed to vary.

ACKNOWLEDGMENTS

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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 ZHZ^{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 ZHZ 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 .