

MULTICONFIGURATION SELF CONSISTENT FIELD
THEORY USING NON-ORTHOGONAL ORBITALS
BERYLLIUM ATOM

by

A.V. ANANTARAMAN

B.Sc., Madras University, 1950
M.Sc., Madras University, 1956
Ph.D., Calcutta University, 1962

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APPROVAL

Name: A.V. Anantaraman

Degree: Doctor of Philosophy

Title of Thesis: "MULTICONFIGURATIONAL SCF THEORY
USING NON-ORTHOGONAL ORBITALS"

Examining Committee:

Chairman: B. L. Funt

M. L. Benston
Senior Supervisor

Y. L. Chow
Committee

E. M. Veigt
Committee

L. E. Ballentine
Committee

D. P. Cheng, External Examiner
Associate Professor
University of British Columbia

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Author:

(signature)

A. V. Anantaraman

(name)

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ABSTRACT

The thesis presents a comprehensive analysis of Multi-Configurational Self Consistent Field Theory using non-orthogonal orbitals based on the formalism proposed by Benston and Chong (Mol. Phys. 14,449,1968). Their prescription for obtaining a pseudo-eigenvalue equation is shown to be inconsistent and a modified approach to the solution of the Fock equations is described. The "coupling operator" methods such as that of Birss and Fraga are incomplete and do not afford a practical means of arriving at a satisfactory convergent solution.

The modified scheme is applied to the calculation of the ground state energy of Beryllium atom. A complete MC-SCF program using non-orthogonal orbitals has been developed and implemented. Some of the existing configuration interaction calculations on Be atom are analyzed and it is shown that a partial relaxation of the orthogonality constraint on the orbitals has a pronounced effect on the ground state energy of Be atom.

An additional aspect of the present theory concerns the non-orthogonality parameter V . The problem of obtaining V has not been adequately exposed by Benston and Chong. A method is proposed for the evaluation of the parameter V from physically acceptable overlap matrices W . The effect of V on the total energy is also discussed.

THIS THESIS IS DEDICATED TO
MY MOTHER
WHO PASSED AWAY ON
SEPTEMBER 28, 1972

खल्वाटो दिवसेश्वरस्य किरणैः संतापितो मस्तके
वाञ्छन्देशमनातपं विधिवंशात्तालस्य मूलं गतः ।
तत्राप्यस्य महाफलेन पतता भयं सशब्दं शिरः
प्रायो गच्छति यत्र भाग्यरहितस्तत्रैवं यान्त्यापदः ॥

भर्तृहरिः

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CHAPTER I

REVIEW OF CLASSICAL METHODS

1.1 INTRODUCTION

The electronic structure and properties of any atom in the ground state can be determined, in principle, by solving the Schrödinger equation. In the non-relativistic quantum theory of many particle systems, the Schrödinger equation refers to a configuration space having a dimension proportional to the number of particles. Apart from the formidable task of finding a solution to this problem, the resulting wave function may be too complicated to have any physical significance. Although there have been many attempts to reduce the problem by the use of density matrices, a satisfactory understanding of many particle systems still remains a challenge both to physicists and chemists.

Quantum mechanics of one- and two- electron systems may be said to be reasonably well understood with the possible exception of relativistic effects. Attempts to extend these methods to many electron systems have been less successful.

The question is one of finding approximate eigenfunctions and energies that come reasonably close as solutions of the Schrödinger equations and which also provide some insight into the actual physical situation. Although the total energy is not in any sense a complete index as to the accuracy of the approximation, it is a simple and perhaps the best place to start. There are a number of reasons for this: the most important being (a) the convenience of the variational principle, (b) the general good correlation between reasonable values for the energy and those for various other properties calculated with energy optimized

wave functions and (c) the interest that the stationary state energy holds for chemists.

In the past few years it has become clear that the classical Hartree-Fock method represents an unbalanced situation when we consider the dynamics of electrons. It is true that the Hartree-Fock approximation gives "reasonable" values for the energy and a high degree of physical insight. However the energy cannot be calculated to a sufficient accuracy to lead to chemically interesting effects. A considerable stabilizing influence is imparted to an atomic or molecular system by the electronic correlation energy which is not taken into account by the Hartree-Fock method. Recently a number of methods have been proposed to include electron correlation into the Hartree-Fock scheme through such expansion methods as configuration interaction or multi-configurational self consistent field. Even with the use of sophisticated computers, these methods have certain fundamental difficulties, particularly the number of configurations required to achieve a desired accuracy, makes physical interpretation difficult and computation lengthy.

By using non-orthogonal orbitals, we have achieved a significant improvement in the convergence of the configuration interaction expansion, that is, the number of configurations required to achieve a desired degree of accuracy in the energy. This is a major improvement over the existing Configuration Interaction (CI) or Multi-Configurational Self Consistent Field (MC-SCF) methods using orthogonal orbitals. In the following sections we outline the various methods of improving the Hartree-Fock scheme and then describe the MC-SCF method using non-orthogonal orbitals.

1.2 INDEPENDENT PARTICLE MODELS

Perhaps the most widely used and most successful approach to quantum theory of many electron systems is the independent particle model. The Hartree-Fock approximation is simply a variational formulation of this intuitive concept. Physically this approximation amounts to the assumption that each particle moves in an average field of the other particles. Mathematically one approximates the state function as the simplest antisymmetrized product of one-particle functions.

(a) HARTREE-FOCK METHOD^{1,2,3,4}

In view of the fundamental importance of the Hartree-Fock model, it may be appropriate to start with a brief review of this approximation. Essentially, the Hartree-Fock wave function is the best wave function (in the variational sense) that can be constructed based on a one-to-one correspondence between particles and orbitals.

The Hamiltonian for a system of N electrons, in atomic units, can be written as

$$\mathcal{H} = \sum_i^N \left[-\frac{1}{2} \nabla_i^2 - \sum_{\alpha} \frac{Z_{\alpha}}{r_{i\alpha}} + \sum_{k \neq i} \frac{1}{r_{ik}} \right] \quad (1.2.1)$$

where r_i is the distance of the electron i from the nucleus α and r_{ik} is the distance between electrons i and k . In atomic units, the unit of length is the bohr where 1 bohr = 5.2917×10^{-9} cm. and the unit of energy is the hartree where 1 hartree is equal to twice the ionization potential of hydrogen, that is, 27.210 eV. According to the Hartree-Fock model, the trial wave function is taken as the Slater determinant

$$\Phi = \begin{vmatrix} \varphi_1(x_1) & \varphi_2(x_1) & \dots & \varphi_N(x_1) \\ \varphi_1(x_2) & \varphi_2(x_2) & \dots & \varphi_N(x_2) \\ \dots & \dots & \dots & \dots \\ \varphi_1(x_N) & \varphi_2(x_N) & \dots & \varphi_N(x_N) \end{vmatrix} \quad (1.2.2)$$

In this expression $\varphi_1, \varphi_2, \dots, \varphi_N$ are N linearly independent spin orbitals of the form

$$\varphi_k(X) = \varphi_k(r) \begin{cases} \alpha(\sigma) \\ \beta(\sigma) \end{cases} \quad (1.2.3)$$

The Hamiltonian operator of eq. (1.2.1) is

$$\mathcal{K} = \sum_i f_i + \sum_{i>j} g_{ij} \quad (1.2.4)$$

where f_i is the Hamiltonian of electron i moving in the field of the nucleus and g_{ij} is the electrostatic interaction between electrons i and j . The energy of the system is given by

$$E = \langle \Phi | \mathcal{K} | \Phi \rangle \quad (1.2.5)$$

where the orbitals are chosen by variational method so as to give the lowest possible energy. This minimization of energy resulting from a single determinant wave function eq. (1.2.2) gives a set of integro-differential equations called the Hartree-Fock equations.

It is convenient to define two operators J_i and K_i , called coulomb and exchange operators respectively, associated with a particular orbital i

$$J_i(1)\varphi_k(1) = \varphi_k(1) \int \varphi_i(2)^* \frac{1}{r_{12}} \varphi_i(2) dv_2 \quad (1.2.6)$$

$$K_i(1)\varphi_k(1) = \varphi_i(1) \int \varphi_i(2)^* \frac{1}{r_{12}} \varphi_k(2) dv_2 \quad (1.2.7)$$

The energy expression (1.2.4) can now be written as

$$\begin{aligned}
 E &= \langle \Phi | \mathcal{K} | \Phi \rangle \\
 &= 2 \sum_i H_i + \sum_{i,j} (2 J_{ij} - K_{ij})
 \end{aligned}
 \tag{1.2.8}$$

where the integrals are defined by

$$\begin{aligned}
 H_i &= \langle \varphi_i | f | \varphi_i \rangle \\
 J_{ij} &= \langle \varphi_j | J_i | \varphi_j \rangle = \langle \varphi_i | J_j | \varphi_i \rangle \\
 K_{ij} &= \langle \varphi_j | K_i | \varphi_j \rangle = \langle \varphi_i | K_j | \varphi_i \rangle
 \end{aligned}
 \tag{1.2.9}$$

The factor 2 in eq. (1.2.8) appear because of the double occupation of the orbitals. The one particle functions are determined by means of the variational principle

$$\delta \langle \Phi | \mathcal{K} | \Phi \rangle = 0
 \tag{1.2.10}$$

and we obtain the condition

$$\left(\sum_i f_i + \sum_j (2 J_i - K_j) \right) \varphi_i = \sum_j \epsilon_{ji} \varphi_j
 \tag{1.2.11}$$

where the Lagrange multipliers ϵ_{ji} are included in order to take account of the orthogonality of orbitals. If we define the Hartree-Fock operator as

$$F_{\text{op}}(i) = \sum_i f_i + \sum_j (2 J_i - K_j)
 \tag{1.2.12}$$

the Hartree-Fock equation can be written as

$$F_{op} \varphi_i = \sum_j \epsilon_{ji} \varphi_j \quad (1.2.13)$$

since the coulomb and exchange operators are invariant against arbitrary unitary transformation of the "occupied" orbitals φ , the Fock Hamiltonian itself is invariant against unitary transformation. This important property allows us to make a further simplification of the equations. We multiply eq. (1.2.11) by $\sum_k t_{ik}$, where t_{ik} is the (i,k)th element of a unitary matrix T, and put

$$\begin{aligned} \varphi_i' &= \sum_k t_{ik} \varphi_k \\ \epsilon'_{ij} &= \sum_k \sum_j t_{ik} \epsilon_{kj} \end{aligned} \quad (1.2.14)$$

As a result we obtain relations of the form (1.2.11) in which φ and ϵ are simply replaced by φ' and ϵ' . In matrix notation eq. (1.2.14) can be written as

$$\| \epsilon'_{ij} \| = T \| \epsilon_{ij} \| T^{-1} \quad (1.2.15)$$

so that the Hermitian matrix $\| \epsilon' \|$ can be made diagonal by suitable choice of matrix T. We can label the diagonal elements which are real as ϵ_k and dropping the primes

$$F_{op} \varphi_k = \epsilon_k \varphi_k \quad (1.2.16)$$

Equation (1.2.16) is the final form of the Hartree-Fock equations.

The Hartree-Fock equations are usually treated in the eigen-value form (1.2.16) and the solutions are referred to as "Hartree-Fock equations". They are characterized by the fact that they are delocalized over the entire system. It may be noted that a wave function defined by a Slater determinant of the form (1.2.2) is invariant under linear transformation of the set $\varphi_1 \varphi_2 \dots \varphi_N$ and depends only on the linear manifold spanned by this set.

The Hartree-Fock equations represent systems of non-linear integro-differential equations. The self consistent field scheme can be shown as

$$\{ \varphi_k \} \longrightarrow v_i \longrightarrow H_{\text{eff}} \longrightarrow \{ \varphi_k \} \quad (1.2.17)$$

where v_i is called the Hartree-Fock potential given by the coulomb terms, and H_{eff} is the sum of kinetic energy and coulomb terms.

(b) EXPANSION METHODS^{5,6} - (Hartree-Fock-Roothaan)

In attempting to solve the Hartree-Fock equations (1.2.16) it has been found convenient to expand the Hartree-Fock functions in the set

$$\Psi = \{ \varphi_1 \varphi_2 \dots \varphi_N \} \quad (1.2.18)$$

as linear combinations of the form

$$\varphi_k = \sum_{\mu=1}^M \chi_{\mu} Q_{\mu k} \quad (1.2.19)$$

or

$$\varphi = \chi Q \quad (1.2.20)$$

where Q is a rectangular matrix of order $M \times N$. Assuming the basis to be non-orthogonal, we can write

$$\langle \chi | \chi \rangle = S \quad (1.2.21)$$

where S is the overlap matrix and is a measure of non-orthogonality. Since the effective Hamiltonian is self-adjoint, the eigenfunctions of eq. (1.2.16) are orthonormal.

Since the Hartree-Fock wave function is invariant to a unitary transformation we can write

$$\langle \varphi' | \varphi' \rangle = Q^{\dagger} S Q = I \quad (1.2.22)$$

If the effective Hamiltonian is considered as fixed one may solve the eigenvalue problem (1.2.16) by means of the variational method

$$\delta \langle H_{\text{eff}} \rangle = 0 \quad (1.2.23)$$

leading to a set of linear equations

$$\sum_{\nu} (H_{\mu\nu} - \epsilon S_{\mu\nu}) Q_{\nu} = 0 \quad (1.2.24)$$

where

$$H_{\mu\nu} = \langle \varphi_{\mu} | H_{\text{eff}} | \varphi_{\nu} \rangle \quad (1.2.25)$$

This system of equations has non-trivial solution only if the secular equation

$$\det \{ H_{\text{eff}} - \epsilon S \} = 0 \quad (1.2.26)$$

is satisfied and this gives the orbital energies ϵ . Once the ϵ 's are known, the equation can be solved for Q 's. The best determinantal wave function, within the limitation of a truncated basis set, is obtained by varying the expansion coefficients $Q_{\mu k}$. In the limit of infinite basis set, this wave function approaches the Hartree-Fock function.

In 1951, Roothaan and Hall^{6,7} independently proposed a systematic approach to the expansion method. According to the Roothaan formalism, the iterative cycle is

$$\{ Q_{\mu k} \} \longrightarrow H_{\text{eff}} \longrightarrow \{ H_{\mu\nu} \} \longrightarrow \{ Q_{\mu k} \} \quad (1.2.27)$$

Much of the current atomic and molecular calculations make use of the Roothaan method.

The important simplification in the Hartree-Fock method lies in the expression (1.2.2) which consists of products of single particle functions. There is a one-to-one correspondence between particles and one-particle wave functions which impart a considerable amount of physical meaning to the Hartree-Fock model. The

expression contains only occupied states and not the complete system of single particle functions and hence cannot provide a rigorous solution. A pure product function is inadequate chiefly because here the position of an electron which is described by its function $\varphi(\lambda)$ is completely independent of the other electrons, while the electrons are really connected with each other through coulomb interaction. This correlation in motion which thus arise is excluded in single particle product functions. It would for example be quite possible for several electrons to be located in the same position whilst the effect of coulomb repulsion is to keep them apart. Because of this repulsion the coulomb potential e^2/r_{12} becomes infinite at $r_{12} = 0$ which means that each electron is surrounded by a "Coulomb hole" with respect to other electrons. On the other hand a certain amount of correlation appears with a determinantal expression since this takes account of Pauli principle. However this correlation has nothing to do with coulomb interaction. On the whole therefore, in the Hartree-Fock treatment, the electron correlation is hardly taken into account. However it has become evident in recent years that electron correlation is of fundamental importance in chemical binding and therefore the one-electron approximation is inherently too inaccurate to provide a satisfactory basis for an understanding of problems of chemical interest. The problem of electron correlation has been discussed extensively by Lowdin⁸ and others⁹.

A further limitation of the Hartree-Fock method is that it is not in general applicable to open shell systems. An open shell system requires more than one configuration and gives rise to off-diagonal Lagrange multipliers which cannot be easily eliminated.

1.3 IMPROVED METHODS OF DETERMINING ELECTRONIC STRUCTURE OF ATOMS

So far we have confined ourselves to the basic Hartree-Fock formalism in a form applicable to atoms whose wave functions can be developed in terms of closed shell configurations so that the quantum numbers m_l and m_s do not have to be specified. The resulting wave function is a singlet and satisfies certain so called equivalence restrictions¹⁰. An example of the equivalence restrictions is that the spatial part of the orbital $\varphi_1(r) \alpha$ and $\varphi_1(r) \beta$ must be identical. The equivalence restrictions are satisfied whenever the radial part of the orbitals are independent of m_s and m_l quantum numbers and the orbitals are associated with definite l quantum numbers. This means that the resulting wave function is an eigenfunction of S^2 , L^2 and S_z , L_z .

The Hartree-Fock method in which the equivalence restrictions are satisfied or are imposed is known as "restricted" Hartree-Fock method. A single determinant of doubly occupied orbitals represent a totally symmetric 1S state, and a state that can be represented in this manner is called a closed shell state.

If the orbitals are singly occupied (i.e., partially occupied) such a state is called an open shell. In general both closed- and open-shell variational wave functions are based on independent particle model having certain symmetric properties consistent with the effective Hamiltonian. In the closed shell case the radial orbitals of spin paired electrons are constrained to be identical while in the open shell case this condition is relaxed. The proper symmetry can always be obtained in the closed shell procedure with a single determinant, but in the open shell procedure a multideterminantal wave function may be required.

Based on the equivalence restrictions, several modified schemes have been attempted on the conventional Hartree-Fock method. The important cases are discussed by Nesbet ¹¹ and Nesbet and Watson ¹². In the case of configurations arising from open shells, Slater ¹³ has proposed dropping the restriction that the radial functions be independent of m_s . This means that orbitals of opposite spins need not have the same spatial functions. This variant is called spin-polarized Hartree-Fock method.

If the trial function which is a single determinant is free from all restrictions other than the variational principle

$$\delta \langle \Phi | \mathcal{H} | \Phi \rangle = 0 \quad (1.3.1)$$

one obtains the so called unrestricted Hartree-Fock scheme.

Another variation of the Hartree-Fock method is one where the trial function is obtained from the Slater determinant of an open shell configuration by use of L^2 and S^2 projection operators ¹⁴.

Here the total wave function can be written as

$$\Psi \approx P \Phi \quad (1.3.2)$$

where P denotes the desired projection operator and Φ is a single determinant wave function. The energy is given by

$$\langle \mathcal{H} \rangle_{Av} = \frac{\langle \Phi | P^\dagger \mathcal{H} P | \Phi \rangle}{\langle \Phi | P | \Phi \rangle} \quad (1.3.3)$$

Neither the Hartree-Fock method nor those related methods that satisfy one or other of the many equivalent restrictions can account for electron correlation in many electron systems. In order to overcome this fundamental deficiency, we have to go beyond the Hartree-Fock scheme.

There are three "Classical" variational methods of introducing correlation in a wave function

- (a) Open Shell Procedure
- (b) Configuration Interaction
- (c) Interelectron coordinates r_{ij} in the wave function.

a) OPEN SHELL PROCEDURE - (Generalized Hartree-Fock-Roothaan)

Among the three methods, the open shell procedure is the simplest but the most limited in scope since it cannot be extended *per se* to yield any desired accuracy. In general the effect of open shell calculation is to improve the corresponding closed shell energies by an amount approximately independent of the number of

electrons N while on the other hand the correlation energy increases rather rapidly with increasing N . From the practical standpoint, it is more difficult to obtain SCF wave functions for open shells than for closed shell systems¹⁵. In most cases the open shell procedures are direct generalizations of the closed shell method. An important shortcoming of this approach is that the resulting wave function is not an eigenfunction of S^2 , but is a mixture of wave functions with different spin multiplicities. Nevertheless the open shell procedure provides a supplementary technique for gaining some correlation when used in conjunction with other types of correlation methods.

The generalized Hartree-Fock-Roothaan formalism^{16,17} makes a limited improvement on the wave function and energy of closed shell atoms and extends the Hartree-Fock formalism to include open shell atoms and molecules. There are a number of difficulties associated with open shell systems and these are discussed by several authors^{18,19}.

A symmetry operator, operating on any determinantal wave function Φ gives a new function Φ' . In the case of doubly occupied orbitals (closed shell), the new function Φ' are linear combinations of orbitals in the old function Φ . In other words a closed shell determinant describes a totally symmetric state if the orbitals $\varphi_1 \varphi_2 \dots \varphi_N$ provide a basis for representation of any symmetry point group.

In general an open shell single determinant wave function does

not represent a totally symmetric state and will not be an eigenfunction of total spin operators S_z and S^2 . However a linear combination of determinants can be made to satisfy these conditions.

The total wave function ψ is, in general a sum of several Slater determinants

$$\psi = \sum_k L_k \Phi_k \quad (1.3.4)$$

where each Φ_k is an antisymmetrized product of spin orbitals and the coefficients are determined by the above-mentioned symmetry requirements.

Since an open shell implies the presence of both doubly occupied and singly occupied orbitals, it is convenient to assign an occupation number $N_{i\lambda}$ to a particular shell. Here i refers to the orbital and λ refers to the symmetry species. The density matrices corresponding to a general shell, closed shell (c) and open shell (o) can be written as

$$D_{i\lambda} = N_{i\lambda} Q_{i\lambda} Q_{i\lambda}^\dagger \quad (1.3.5)$$

$$D_{c\lambda} = \sum_k D_{k\lambda}$$

$$D_{o\lambda} = \sum_m D_{m\lambda}$$

here the expansion coefficients Q_{ip} are given by

$$\varphi_{i\lambda\alpha} = \sum_p x_{p\lambda\alpha} Q_{ip} \quad (1.3.6)$$

α denotes the symmetry subspecies. In eq. (1.3.5) the indices $k = c$ closed shell and $m = i$ open shell. Since C is a column vector, CC^\dagger represents a matrix.

In order to bring out the basic idea of the formalism, the energy can be written as the sum of two terms corresponding to the one-electron contribution and the two electron contribution:

$$E = E^{(1)} + E^{(2)} \quad (1.3.7)$$

The first term $E^{(1)}$ can easily be obtained as

$$\begin{aligned} E^{(1)} &= \langle \Phi | f | \Phi \rangle \\ &= \sum_{\lambda} \left(\sum_k N_{\lambda k} \sum_{pq} f_{\lambda pq} Q_{\lambda kq} Q_{\lambda kp} \right. \\ &\quad \left. + \sum_m N_{\lambda m} \sum_{pq} f_{\lambda pq} Q_{\lambda mp} Q_{\lambda mq} \right) \end{aligned} \quad (1.3.8)$$

In matrix notation, this reduces to

$$\begin{aligned} E^{(1)} &= \sum_{\lambda} H_{\lambda} D_{c\lambda} + \sum_{\lambda} H_{\lambda} D_{o\lambda} \\ &= H D_{T\lambda} \end{aligned} \quad (1.3.9)$$

where we have used

$$D_{T\lambda} = D_{c\lambda} + D_{o\lambda} \quad (1.3.10)$$

$$D_{c\lambda} = \sum_k D_{k\lambda} \quad \text{and} \quad D_{o\lambda} = \sum_m D_{m\lambda}$$

It may be noted that $E^{(1)}$ does not depend on the symmetry of sub-species α but only on $i\lambda$

The two electron Hamiltonian is more difficult since in this case the matrix elements will depend on the subspecies and the coefficients L_k will have to be considered. The problem is relatively simple for a closed shell where the contribution to the two-electron energy is given by

$$E_c^{(2)} = \frac{1}{2} D_c^\dagger P D_c \quad (1.3.11)$$

where P is a supermatrix whose elements are the two-electron integrals.

In extending these ideas to open shell systems, we follow the method of Roothaan and Bagus²⁰. The following points should be noted:

1. The total wave function is in general a sum of several antisymmetrized products each of which contains a doubly occupied closed shell core Φ_c and a partially occupied open shell chosen from a set Φ_o , the different antisymmetrized products containing different subsets of Φ_o . The combined set of orbitals is given by

$$\Phi = (\Phi_c \Phi_o) \quad (1.3.12)$$

and is assumed to be orthonormal. Eq. (1.3.12) assumes that each configuration Ψ contains a doubly occupied closed shell core Φ_c and partially occupied open shell chosen from a set Φ_o .

2. The expectation value of the energy would contain interaction contributions from the closed-shell, the open-shell and

closed-shell-open-shell.

In the form initially reported by Roothaan, certain restrictions were imposed on the symmetry and occupation of the open shells e.g. only one open-shell was considered and for half closed shells the spins were assumed parallel. Huzinaga²¹ extended this formalism to include two open shells of general symmetry species. We follow the Roothaan-Bagus procedure which is completely general.

The idea is the following: As in the case of a closed shell we construct a supermatrix P, but subtract out another supermatrix Q which represents fictitious interaction terms that were added in the P matrix. In this way, we express the energy $E^{(2)}$ in terms of two supermatrices, the P supermatrix for the case of the closed-shell configurations and the Q supermatrix for the case of open-shell-open-shell interactions.

$$P_{\lambda pq, \mu rs} = \mathcal{J}_{\lambda pq, \mu rs}^0 - \frac{1}{2} \sum_{\nu=|\lambda-\mu|}^{|\lambda+\mu|} A_{\lambda\mu\nu} K_{\lambda pq, \mu rs}^{\nu} \quad (1.3.13)$$

$$Q_{\lambda pq, \mu rs} = \sum_{\nu=0}^{2(\lambda, \mu)} J_{\lambda\mu\nu} \mathcal{J}_{\lambda pq, \mu rs}^{\nu} - \frac{1}{2} \sum_{\nu=|\lambda-\mu|}^{|\lambda+\mu|} K_{\lambda\mu\nu} \kappa_{\lambda pq, \mu rs}^{\nu} \quad (1.3.14)$$

where $\mathcal{J}_{\lambda pq, \mu rs}$ and $\kappa_{\lambda pq, \mu rs}$ are elements of coulomb and exchange supermatrices \mathfrak{J} and \mathfrak{K} respectively. $J_{\lambda\mu\nu}$ and $K_{\lambda\mu\nu}$ are the vector coupling coefficients which vary from state to state and configuration to configuration and are the standard coulomb and exchange integrals. For atoms or ions belonging to the same symmetry species,

that is, for $\lambda = \mu$, these coefficients are not unique²². For a closed shell, supermatrix P is the only one that occurs, and in this case $J_{\lambda\mu\nu} = 0$.

Analogous to the closed shell, we can therefore write down the expression for the two-electron energy in terms of supermatrix P and O, and density matrices D

$$E^{(2)} = \frac{1}{2} D_{T\lambda}^\dagger P D_{T\lambda} - \frac{1}{2} D_O O D_O \quad (1.3.15)$$

Equation (1.3.14) expresses the energy of a system with a wave-function of appropriate symmetry and determinant of known spin properties. Our task now is to incorporate this idea in a practical way into the Hartree-Fock formalism.

Self Consistent Field Technique

Assuming that we have chosen a set of satisfactory basis functions, the usual procedure makes use of the variational method for the density matrices so that the energy is stationary. In fact, a proper choice of the basis function, is by no means easy, and requires an optimization of the orbital exponent. However at the moment, we will assume this has been done. The best function for a given basis set, is the one that minimizes the energy expression

$$\begin{aligned} E &= E^{(1)} + E^{(2)} \\ &= H^\dagger D_T + \frac{1}{2} D_{T\lambda}^\dagger P D_{T\lambda} - \frac{1}{2} D_O^\dagger O D_O \end{aligned} \quad (1.3.16)$$

We subject every orbital φ_i to an infinitesimal variation $\delta\varphi_i$; since the basis set is fixed, this is tantamount to an infinitesimal variation on the expansion coefficients Q_λ . Furthermore since the orbitals φ_i are constrained to be orthogonal, the variation $\delta Q_{i\lambda p}$ is restricted by those conditions which are obtained by subjecting eq. (1.3.1) to an infinitesimal variation. We take the sum of all possible orbital constraints, \sum_{ij} for all possible symmetries \sum_λ , and multiply the resulting expression by the Lagrange Multipliers $\theta_{\lambda ji}$ and $\theta_{\lambda ij}$ and we get

$$2 \sum_{\lambda ij pq} | \delta Q_{\lambda pi} | S_{\lambda pq} Q_{\lambda qj} \theta_{\lambda ji} \quad (1.3.17)$$

where S is the overlap matrix between basis functions.

The standard procedure is to add the term (1.3.16) to the variation in energy δE . The resulting term $\delta E' = 0$ for any choice of the δQ , without any restriction and at the same time should give suitable values for the undertermined Lagrange multipliers.

It is important to realize that for the general case of open shells, we shall have Lagrange multipliers between orbitals in closed shells, between orbitals of open-shells and between orbitals of closed and open shells. In the closed shell case, the orbitals can always be subjected to a unitary transformation

$$\varphi' = \varphi U \quad (1.3.18)$$

which brings the matrix of Lagrange multipliers into diagonal form.

When this has been done, the orbitals all reduce to a simple pseudo eigenvalue equation. In the presence of open shells, we have available only a unitary transformation of the form

$$\varphi'_c = \varphi_c U \quad \varphi'_o = \varphi_o U \quad (1.3.19)$$

which transforms the open and closed shells within themselves. Such a transformation can eliminate only the off-diagonal multipliers θ_{lk} and θ_{nm} but not the multipliers θ_{nk} and θ_{lm} , which couple the closed and open shells. There is however one exception to this, namely, when the closed and open shell orbitals belong to different symmetry; in that case θ_{nk} and θ_{lm} vanish automatically.

There are methods of eliminating the off-diagonal Lagrange multipliers of the type mentioned above²³. Roothaan adopts a different procedure for removing the off-diagonal multipliers where he introduces a new set of operators R_c and R_o for closed and open shells which result in absorbing those terms in a set of regular pseudo eigenvalue equations for closed and open-shells. The advantage is that these coupling operators R_c and R_o can be expressed in terms of previously defined quantities such as P and O.

$$R_{c,\lambda pq} = [N_{c\lambda} / (N_{c\lambda} - N_{o\lambda})] \sum_1 \left(\sum_{uw} S_{\lambda pu} Q_{1\lambda u} O_{\lambda wq} Q_{1\lambda w} + \sum_{uw} O_{\lambda pu} Q_{1\lambda u} S_{\lambda wq} Q_{1\lambda w} \right) \quad (1.3.20)$$

$$R_{O,\lambda pq} = [N_{O\lambda} / (N_{c\lambda} - N_{O\lambda})] \sum_1 \left(\sum_{uw} S_{\lambda pu} Q_{n\lambda u} O_{\lambda wq} Q_{n\lambda w} + \sum_{uw} O_{\lambda pq} Q_{n\lambda u} S_{\lambda wq} Q_{n\lambda w} \right) \quad (1.3.21)$$

Both the operators R_c and R_o are Hermitian by definition. If we define

$$F_{c,\lambda pq} = H_{\lambda pq} + P_{\lambda pq} + R_{O,\lambda pq}$$

$$F_{O,\lambda pq} = H_{\lambda pq} + P_{\lambda pq} + R_{c,\lambda pq} - O_{\lambda pq} \quad (1.3.22)$$

the basic Hartree-Fock equations reduce to the following form

$$F_{c,\lambda pq} Q_{k\lambda q} = \sum_{1q} S_{\lambda pq} Q_{\lambda q1} \theta_{\lambda 1k}$$

$$F_{O,\lambda pq} Q_{m\lambda q} = \sum_{mq} S_{\lambda pq} Q_{\lambda qn} \theta_{\lambda mn} \quad (1.3.23)$$

By making a unitary transformation on the closed and open shells separately, we can bring the θ matrices into diagonal form. By designating as $\epsilon_{m\lambda}$ the diagonal elements of the transformed θ matrices, we can finally arrive at

$$\sum_q F_{c,\lambda pq} Q_{k\lambda q} = \epsilon_{k\lambda} \sum_q S_{\lambda pq} Q_{k\lambda q}$$

$$\sum_q F_{O,\lambda pq} Q_{m\lambda q} = \epsilon_{m\lambda} \sum_q S_{\lambda pq} Q_{m\lambda q} \quad (1.3.24)$$

which in matrix notation can be written as

$$\begin{aligned} F_c Q &= \epsilon S Q \\ F_o Q &= \epsilon S Q \end{aligned} \quad (1.3.25)$$

Equations (1.3.25) are the Hartree-Fock equations for closed and open shells. They are called pseudo eigenvalue equations because the matrices F_c and F_o depend on the solution Q . This demands an iterative procedure and self-consistency is achieved when the same vectors from which these matrices are constructed according to equations (1.3.24), are solutions of equations (1.3.25).

(b) CONFIGURATION INTERACTION ²⁴

Probably the most widely used method of improving the Hartree-Fock approximation is configuration interaction (CI), in which a state function is expressed as a linear combination of Slater determinants

$$\psi = \phi_o + \sum_k \phi_k c_k \quad (1.3.26)$$

where ϕ_o is the Hartree-Fock solution. The other determinants can be constructed from the Hartree-Fock orbitals, including those not occupied in the ground state.

There are theoretical reasons to believe ²⁵ that the CI method and the Hylleraas procedure are both general methods capable of yielding variational solutions which converge to the exact non-relativistic energy for any desired degree of accuracy by the addition

of sufficient number of terms.

A determinantal configuration differing from the ground state by one spin orbital is said to be singly excited; one differing by two spin orbitals is doubly excited and so on. Assuming that the Hartree-Fock orbitals are orthonormal, we can write

$$E = \langle \Phi_0 | \mathcal{H} | \Phi_0 \rangle + \sum_k \sum_{k'} C_k^{k'} \langle \Phi_0 | \mathcal{H} | \Phi_k^{k'} \rangle + \sum_{k>1} \sum_{k'>1} C_k^{k' 1'} \langle \Phi_0 | \mathcal{H} | \Phi_k^{k' 1'} \rangle \quad (1.3.27)$$

where $\Phi_k^{k'}$ denotes a singly excited configuration in which an orbital k from the Hartree-Fock determinant is replaced by an orbital k' , and similarly for the double notation. It is not necessary that the orbitals used to represent the excited states be themselves eigenfunctions of the Hartree-Fock operator. The fact that the solutions of the Hartree-Fock equations form a complete set of orthogonal functions demands that the excited orbitals be orthogonal to the occupied orbitals. Furthermore these solutions can be divided into two sets, those occupied in the ground state and those not occupied in the ground state, which span mutually orthogonal subspaces²⁶.

There are some fundamental restrictions on the determinants that appear in the CI function. The various configurations that are included in eq(1.3.27) should be symmetry adapted, that is, the chosen linear combination of determinants must possess all the symmetry properties of the Hamiltonian. A further restriction arises from the so-called Brillouin theorem which states that matrix elements of the Hamiltonian operator between the Hartree-Fock and all the singly excited determinants are zero^{27,28}.

$$\int \Phi_{\text{SCF}} \mathcal{H} \Phi_{\text{S}} d\tau = 0 \quad (1.3.28)$$

Here Φ_{S} differs from Φ_{SCF} by a single spin orbital. An important corollary to Brillouin theorem is that singly excited configurations constructed from spin-orbitals orthogonal to the occupied Hartree-Fock orbitals give no first order contributions to the total energy²⁹.

As a consequence of Brillouin theorem the second term in eq. (1.3.27) vanishes so that

$$E = E_{\text{HF}} + E_{\text{Corr}} \quad (1.3.29)$$

where

$$E_{\text{HF}} = \langle \Phi_0 | \mathcal{H} | \Phi_0 \rangle \quad (1.3.30)$$

and

$$E_{\text{Corr}} = \sum_{k>1} \sum_{k'>1'} \langle \Phi_0 | \mathcal{H} | \Phi_{k1}^{k'1'} \rangle C_{k1}^{k'1'} \quad (1.3.31)$$

The matrix elements of the Hamiltonian between Φ_0 and $\Phi_{k1}^{k'1'}$ can be expressed in terms of spin orbitals

$$\langle \Phi_0 | \mathcal{H} | \Phi_{k1}^{k'1'} \rangle = \langle k1 | g | k'1' \rangle - \langle k1 | g | 1'k' \rangle \quad (1.3.32)$$

where

$$\langle ij | g | kl \rangle = \iint i^*(1)j^*(2) r_{12}^{-1} k(1)l(2) d\tau_1 d\tau_2$$

It may be pointed out that Brillouin theorem does not say that singly excited configurations do not contribute to the total energy since it is possible that matrix elements between singly excited configurations do not vanish and thus contribute to the total energy.

Although the correlation energy has been expressed in terms of a seemingly simple integral (1.3.32), the actual computations are difficult. The expansion coefficients C_k of eq. (1.3.26) are determined by variational methods and leads to the secular equation

$$(H - E I)C = 0 \quad (1.3.33)$$

where H is composed of matrix elements between configurations

$$H_{IJ} = \int \phi_I \mathcal{H} \phi_J d\tau \quad (1.3.34)$$

The solution of eq. (1.3.33) is greatly simplified if one notes that matrix elements H_{IJ} between configurations I and J of different symmetries are zero. This means that we need consider only such configurations which have the total symmetry of the particular electronic state being investigated. Special methods for solving dimensionally large equations of the type (1.3.33) are available ^{30,31}.

Difficulties in the CI Method

The expansion of a state function in terms of Slater deter-

minants, eq. (1.3.26) in principle can lead to the exact solution of the correlation problem, provided one includes all possible configurations in the expansion. This difficulty is what is usually referred to as "convergence problem" in configuration interaction approach, that is, many configurations must be superposed in order to achieve a significant lowering of energy. In practice, one truncates the expansion, taking only a finite set of orbitals and builds all the determinants that belong to a given irreducible representation of the symmetry group. However one often finds that such "symmetry-adapted" functions can no longer be represented by a single determinant and may often be linear combination of Slater determinants.

Apart from symmetry considerations, one reduces the size of the CI expansion by discarding configurations which seem unlikely to contribute significantly to the total energy. Unfortunately there is no general rule available for choosing such configurations and one usually resorts to intuition. The "length" of the expansion (that is the number of terms whose coefficients are substantial) is found to be critically dependent on the choice of spin orbital basis ($\varphi_1, \varphi_2, \dots$) from which the Slater determinants Φ are constructed³². The fundamental problem is to find the best set of orbitals that lead to accurate CI functions of moderate length corresponding to rapidly convergent expansions.

(c) HYLLERAAS METHOD

In a series of papers³³ Hylleraas presented three different methods for studying electron-electron correlation

1. Superposition of configurations
2. Correlated wave functions
3. Different orbitals for different spins

The method that is more often attributed to him is (2) where electron correlation is introduced through a parameter that is related to the distance between electrons.

In his pioneering work on Helium atom, Hylleraas showed that the explicit use of r_{12} as one of the variables improved the accuracy of the wavefunction substantially and gave results of much higher accuracy for the eigenvalues than the Hartree-Fock approach. The Hylleraas type of wavefunction is of the form

$$\psi = N e^{-ks} \sum c_{lmn} k^{l+m+n} s^l t^m u^n \sigma(s_1 s_2) \quad (1.3.35)$$

where s , t and u are related to the distances r_1 , r_2 and r_{12} of the two electrons from the nucleus and from each other respectively by

$$\begin{aligned} s &= r_1 + r_2 \\ t &= r_2 - r_1 \\ u &= r_{12} \end{aligned} \quad (1.3.36)$$

N is a normalizing constant and $\sigma(s_1 s_2)$ is a spin function.

k and C_{lmn} are constants to be adjusted so that the energy is minimized.

The ground state of the Helium atom is a 1S state and is an eigenfunction of L^2 and L_z with zero as the eigenvalues of both these operators. The operator associated with L_z is

$$-i\hbar \left(\frac{\partial}{\partial \phi_1} + \frac{\partial}{\partial \phi_2} \right) \quad (1.3.37)$$

if this operator is to have zero as the eigenvalue, it implies that the wave function should depend on the difference between the azimuthal angles and not individually on ϕ_1 and ϕ_2 . In other words, the wave function should depend on the angle between the radius vectors to the two electrons and not separately on the angle to each radius vector. By applying the same argument to the x and y axes, it follows that the wave function for an atomic S state should depend on the relative positions of the two electrons, but not on the orientation of the system in space. The relative positions of the two electrons with respect to the nucleus may be described by r_1, r_2, θ_{12} or alternatively by r_1, r_2 and r_{12} .

For large values of r the deviation of the expression $F\varphi_i/\epsilon_i\varphi_i$ from unity gives a measure of the accuracy of the wave function. A sensitive test for the region $r \rightarrow 0$ is the "cusp" value $(\partial\varphi_i/\partial r_\beta)_{r \rightarrow 0}$. According to Gilbert³⁴ the introduction of r_{12} speeds up convergence not because it describes the cusp conditions better but because the coulomb hole has relatively simple structure when viewed relative to one of the electrons.

On the other hand the coulomb hole has a rather complex structure when considered to a fixed set of axes, and this may be the reason why configuration interaction method is slowly convergent.

The most accurate wave functions for two-electron systems have been obtained by the use of r_{12} ³⁵. The Hylleraas method has been applied with remarkable success not only for the ground state of Helium atom, but for some excited states of Helium, ground states of two-electron ions such as H^- , Li^+ , Be^{++} etc.³⁶. However the method has not been extended to atoms beyond Be because of the difficulty of evaluating complicated integrals involving many particle systems.

1.4 MORE RECENT METHODS

(a) NATURAL ORBITALS^{24,38,32}

The concept of natural orbitals was first introduced by Lowdin, and provides a practical approach to the calculation of CI wave functions. The idea was developed in terms of density matrices and an excellent treatment of this can be found in the review by McWeeny⁴⁰.

The one-electron density matrix $\rho_1(x_1, x'_1)$ is given by

$$\rho_1(x_1, x'_1) = N \int \psi^*(x_1, x_2, \dots, x_N) \psi(x_2, x_3, \dots, x_N) dx_2 \dots dx_N \quad (1.4.1)$$

where the integration has been done over the coordinates of all but the first electron. If we write the total wave function as

$$\psi(x_1, \dots, x_N) = \sum_K C_K \Phi_K(x_1, \dots, x_N) \quad (1.4.2)$$

where

$$\Phi_K(x_1, \dots, x_N) = (N!)^{-\frac{1}{2}} \det \{ \varphi_k(x_j) \}$$

substituting (1.4.2) in (1.4.1) we get

$$\rho(x_1, x'_1) = \sum_{k, l} \varphi_l(x_1) \gamma(l|k) \varphi_k^*(x'_1)$$

where

$$\gamma(l|k) = \sum_K \sum_L C_K C_L^* \Phi_{KL}(k|l) \quad (1.4.3)$$

where

$$\Phi_{KL}(k|l) = \int \Phi_K(x_1, \dots, x_{k-1}, x_{k+1}, \dots, x_N) \Phi_L^*(x_1, \dots, x_{l-1}, x_{l+1}, \dots, x_N) dx \quad (1.4.4)$$

The set of natural spin-orbitals is defined as that orthogonal basis, in terms of which the first order reduced density matrix is diagonal. Since the matrix formed by the coefficients $\gamma(l|k)$ is hermitian, it can be reduced to the diagonal form by an unitary transformation

$$U \gamma U^\dagger = n \quad (1.4.5)$$

where n is a diagonal matrix with eigenvalues n_1, n_2, \dots .

Introducing a new basic set $\{\chi_k\}$ defined by

$$\chi_k = \sum_\alpha U_{k\alpha} \varphi_\alpha \quad (1.4.6)$$

or in matrix form

$$\chi = U \varphi \quad (1.4.7)$$

the inverse transformation of (1.4.7) is

$$\varphi = U^\dagger \chi \quad (1.4.8)$$

substituting these in (1.4.3), we get

$$\begin{aligned} \rho(x_1, x'_1) &= \varphi^\dagger \gamma \varphi = \chi^\dagger U \gamma U^\dagger \chi \\ &= \sum_k n_k \chi_k^*(x'_1) \chi_k(x_1) \end{aligned} \quad (1.4.9)$$

The functions χ_1, χ_2, \dots are known as natural spin orbitals associated with a given state. The first function χ_1 has the highest occupation number possible, the second function χ_2 has the same property within the class orthogonal to χ_1 and so on. From eq. (1.4.9) the basic set χ_k has the occupation number n_k and since these are eigenvalues of γ , they have extremum properties⁴¹.

If we substitute (1.4.6) in (1.4.2) we get the following expansion of ψ into configurations of natural orbitals

$$\psi = (N!)^{-\frac{1}{2}} \sum_K C_K \det \{ \chi_k, \chi_1, \dots \} \quad (1.4.10)$$

Eq. (1.4.10) is called the natural expansion.

The reason for the importance of natural orbitals arises from the fact they give the most rapidly convergent CI expansion; any spin orbital whose population is negligible may be omitted

from a CI expansion without affecting the accuracy of the expansion.

The mathematical justification for the above ideas has been given by Coleman⁴².

The concept of natural orbitals affords an excellent basis for configuration interaction calculations. However, it must be pointed out, that the existence of rapidly convergent expansions for CI does not necessarily mean that they can be found easily. The reason for this can be found in the very definition of natural orbitals, which are derived through an exact density matrix. This means that we should perform a complete CI or some such related scheme for energy optimization which in turn can lead to the exact one-particle density matrix. Nevertheless it has been found that by diagonalization of an approximate single particle density matrix at any stage of a CI calculation and including only those configurations that correspond to large occupation numbers, lead to a considerable decrease in the number of terms in the CI expansion.^{43,44}

There exist a number of calculations on the ground state of the Helium isoelectronic series using natural orbitals^{45,46,47,48}. Most of these papers discuss the convergence properties of quantities other than the energy. The general conclusion is that the quantity r_{12}^{-1} is reduced by correlation by about twice the energy improvement and $\langle -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 \rangle$ is increased by about half as much³⁸.

Attempts to extend the same approach to systems with more than two electrons have been less satisfactory. The only advantage of natural orbitals for these systems appears in a shortened CI expansion⁵⁰. Hurley⁵¹ has reported natural orbitals for carbon

monoxide and Barnett, Linderberg and Shull⁴¹ have calculated natural orbitals for Be using the data of several workers. Smith and Fogel⁵³ have analyzed Watson's Be data, using natural orbitals. Kouba and Öhrn⁵⁴ have reported a configuration interaction study of boron carbide using natural orbitals.

The major problems in a CI calculation are the choice of orbitals and the selection of appropriate configurations. Both these problems are far from being simple. Furthermore, in order to be able to use natural orbitals, a good initial guess would be required. Three different schemes have been proposed:

- (i) Lowdin and Shull method⁵⁵
- (ii) Natural orbitals using Hylleraas type functions⁴⁴
- (iii) Direct calculation from Schrödinger equation²⁴

Although natural orbital based CI method imparts a certain physical meaning to the CI method, the difficulty in implementing the scheme far out-weighs this advantage, particularly for systems for more than two electrons.

(b) MANY ELECTRON THEORY OF SINANOGLU^{58,59,60}

In the previous sections we presented methods of improving the independent particle model. In principle the configuration interaction treatment can yield an accurate solution but in practice the rate of convergence is slow. The Hylleraas method is very appealing from this point of view, but extension to systems containing more than two electrons has proved to be difficult. Sinanoglu's approach tries to combine the advantages of these two

methods within the framework of the Hartree-Fock method.

The exact wave function can be expressed in the form

$$\psi = \Phi_0 + \chi \quad (1.4.11)$$

where Φ_0 is the Hartree-Fock function

$$\Phi_0 = A \varphi_1 \varphi_2 \dots \varphi_N \quad (1.4.12)$$

and χ is orthogonal to Φ_0 . $\varphi_1, \varphi_2 \dots \varphi_N$ denote one particle orbitals and are eigenfunctions of the Hartree-Fock operator

$$F_{op} \varphi_i = \epsilon_i \varphi_i$$

where

$$F_{op}(i) = -\frac{1}{2} \nabla_i^2 - \sum_{\alpha} \frac{Z_{\alpha}}{r_{\alpha i}} + \sum_{i>j} g_{ij} \quad (1.4.13)$$

The total Hamiltonian is then expressed in terms of a perturbation

$$\mathcal{K} = \sum_{i=1}^N H_i + \sum_{i<j} g_{ij} \quad (1.4.14)$$

$$= H_0 + H_1$$

$$H_0 = \sum_{i=1}^N (H_i + V_i(i)) \quad (1.4.15)$$

for the independent electrons in the total Hartree-Fock potential

V_i and

$$\begin{aligned} H_1 &= \sum_{i<j} g_{ij} - \sum_{k=1}^N V_k(k) \\ &= \sum_{i<j} g_{ij} - S_i(j) - S_j(i) \end{aligned} \quad (1.4.16)$$

is a residual fluctuation potential part. The total Hartree-Fock potential is thus separated into those of orbital

$$\sum_k^N v_k(x_k) = \sum_{i < j}^N S_i(j) + \sum_{i < j}^N S_j(i) \quad (1.4.17)$$

where $S_i(j)$ is the coulomb-exchange operator defined by

$$S_i(j) = \int \varphi_i r_{ij}^{-1} (1 - P_{ij}) \varphi_i d\tau_j \quad (1.4.18)$$

where P_{ij} is a permutation operator which interchanges coordinates i and j .

According to Sinanoglu, the Hartree-Fock potential, eq. (1.4.17) takes the long-range correlation into account, and the difference of the actual Hamiltonian and the Hartree-Fock one is composed of "fluctuating potentials" m_{ij} which are of short range. These fluctuating potentials are defined as

$$m_{ij} = r_{ij}^{-1} - S_i(j) - S_j(i) + J_{ij} - K_{ij} \quad (1.4.19)$$

where J_{ij} and K_{ij} are the coulomb and exchange integrals respectively.

The correction to the Hartree-Fock function can be expanded in the form

$$\chi = \sum_{i=1}^N \{ \hat{f}_i \} + \sum_{i < j} \{ \hat{U}_{ij} \} + \sum_{ijk} \{ \hat{U}_{ijk} \} + \dots \quad (1.4.20)$$

where

$$\begin{aligned} \{ \hat{f}_i \} &= A (1,2 \dots N) \hat{f}_i (i) \\ \{ U_{ij} \} &= A (1,2 \dots N) \hat{w}_{ij} (\sqrt{2} \varphi_i \varphi_j)^{-1} \end{aligned} \quad (1.4.21)$$

where $f_i(i)^{-1}$ refers to the inverse of the normalization integral with components (i,i) . In the language of configuration interaction, the first term in eq. (1.4.20) corresponds to the set of singly excited configurations, and the second term corresponds to doubly excited configurations and so on. The role of \hat{f}_i is to modify the starting orbitals and in the case of Hartree-Fock orbitals, their importance is quite small. The dominant term is the one that involves \hat{w}_{ij} , the two-particle linked cluster. In terms of cluster expansion, Sinanoglu discusses the relative contribution from various terms and that contributions from "unlinked clusters" are the most important. For example, in a four electron system, \hat{U}_{ij} of eq. (1.4.20) is given by

$$\hat{U}_{ij} = A (\hat{w}_{12} \hat{w}_{34} + \hat{w}_{13} \hat{w}_{24} + \hat{w}_{14} \hat{w}_{23}) \quad (1.4.22)$$

Physically this means that the probability of finding three or more electrons in the neighborhood of the same point is very small. The probability of finding two electrons with same spin around the same point in space is small (Fermi hole). With three or more electrons, the spins of at least two are parallel, so the anti-symmetry principle prevents the occurrence of large clusters. The

fluctuating potential is of short range and its effect is appreciable only over a range which is smaller than the Fermi hole⁶¹.

As a practical means of evaluating $\hat{\omega}_{ij}$, Sinanoglu writes for the correlation energy

$$E \approx E_{\text{HF}} + \sum \epsilon'_{ij} \quad (1.4.23)$$

where the pair energy for the orbitals i and j is given by

$$\epsilon'_{ij} = \frac{2\langle \mathbb{P}(i,j) | m_{ij} | \hat{\omega}_{ij}(i,j) + \langle \hat{\omega}_{ij}(i,j) | e_i + e_j + m_{ij} | \hat{\omega}_{ij}(i,j) \rangle}{1 + \langle \hat{\omega}_{ij}(i,j) | \hat{\omega}_{ij}(i,j) \rangle}$$

where $\mathbb{P}(i,j) = \frac{1}{\sqrt{2}} (\varphi_i \varphi_j - \varphi_j \varphi_i)$

and $e_i = h_i - \epsilon_i$ (1.4.24)

The basic problem now is to optimize the wave function by variational adjustment of the pair functions $\hat{\omega}_{ij}$, subject to the condition that they remain strongly orthogonal to the occupied orbitals in the Hartree-Fock function

$$\langle \hat{\omega}_{ij}(i,j) | \varphi_j \rangle_{x_j} = 0 \quad (1.4.25)$$

The most significant aspect of the method appears to be the decomposition of the correlation energy into pairwise contributions. Similar cluster expansion techniques have been given by Szasz⁶² and McWeeny and Steiner⁶³.

CHAPTER II

MULTI - CONFIGURATIONAL

SELF CONSISTENT FIELD THEORY

2.1 INTRODUCTION

The most physically meaningful methods of calculating atomic wave functions have been those that refer to an independent particle model. On the other hand, single determinantal wave functions are inherently incapable of describing the correlation associated with the mutual repulsion of electrons. Although the configuration interaction scheme offers in principle, a method of refining the wave function to any degree of accuracy, progress along this path has been unsatisfactory due to the notoriously slow convergence of the CI expansion.

In the multi-configurational SCF method, one approximates the total wave function of an N-particle system by using M one-particle functions ($M > N$)

$$\psi_M = \{ \varphi_1 \varphi_2 \dots \varphi_M \} \tag{2.1.1}$$

this allows us to construct $\binom{M}{N}$ Slater determinants ψ_K corresponding to ordered configurations $K = (k_1 k_2 \dots k_N)$. The total wave function which is an eigenfunction of the Hamiltonian \mathcal{K} can be expressed in the form eq. (1.3.26). Keeping ψ_M fixed, the optimum coefficients C_K are determined using variational principle $\delta \langle \mathcal{K} \rangle = 0$ which gives

$$\sum_K (\mathcal{K}_{KL} - E \delta_{KL}) C_L = 0 \tag{2.1.2}$$

If one simultaneously varies the set ψ_M and the C's for fixed M,

one obtains better and better energies until finally a certain minimum is achieved. This formalism leads to the multi-configurational self consistent field (MC-SCF) method and was first suggested by Frenkel⁶⁴. The motivation for doing a multiconfigurational SCF calculation is to give the most rapidly convergent configuration expansion functions. This is accomplished by minimizing the energy not only with respect to the configuration mixing coefficients but also with respect to the orbital expansion coefficients. Recently, there has been a revival of interest in this approach and has been studied from a variety of points of view^{65,66,67,68,69,70}.

Wahl and Das⁷¹ have developed a MC-SCF formalism that omits the changes in the core functions as a function of internuclear distance. In their method called the optimized valence configuration method (OVC) one builds up the molecule according to the Hartree-Fock formalism. The valence orbitals are then adjusted by introducing appropriately optimized valence configurations which are constructed by promoting a valence electron pair from the Hartree-Fock ground state to an allowed excited state. Slight readjustments in the added valence orbitals and the unchanged core orbitals is achieved through the usual SCF procedure. This method has been primarily used with a view to explaining the nature of chemical binding^{72,73}.

Another method which is very appealing also from a chemical point of view has been suggested by Adams^{74,69}. Adams' procedure involves the construction of a projection operator that projects

the multiconfigurational N-particle wave function ψ from a set of M spin orbitals. The spin orbitals and ψ are optimized so as to make

$$\frac{\langle \psi | \mathcal{K} | \psi \rangle}{\langle \psi | \psi \rangle} \quad (2.1.3)$$

stationary. For a fixed set of spin orbitals, the Schrödinger equation with an effective Hamiltonian can be written as

$$O \mathcal{K} O \psi = E \psi \quad (2.1.4)$$

where O is the projection operator. This equation (2.1.4) has as many different eigenfunctions as there are different Slater determinants of the M orbitals. Any variation in the orbitals will correspond to a change in the projection operator. To extremize the energy, Adams derives an equation in terms of a fundamental invariant²⁴ and the first- and second- order density matrices, for the vanishing first order correction to the energy

$$(1 - \rho_1) [h_1 \gamma_1 + \text{Tr} (V_{12} \Gamma_{12})] = 0 \quad (2.1.5)$$

Here γ_1 is the one particle density matrix, Γ_{12} represents the two particle density matrix, ρ_1 is the fundamental invariant (which is also a projection operator) and h_1 and V_{12} are the one- and two- electron operators respectively. By means of some simple modification this equation can be expressed as a Hartree-Fock

pseudo eigenvalue equation. These equations can be solved self consistently starting with a set of trial coefficients for the determinants. These coefficients correspond to density matrices which in turn can be identified with the orbitals.

Gilbert⁷⁵ has given a general formalism for MC-SCF where he attempts to obtain the best possible eigenfunction by simultaneous variation of linear expansion coefficients for the determinants and for the orbitals. The intradeterminantal orbitals are not assumed to be orthogonal

$$\frac{\partial E}{\partial C_p^*} = \sum_q \frac{(H_{pq} - ES_{pq}) C_p}{\langle \psi^* | \psi \rangle}$$

where the total energy E is given by (2.1.6)

$$E = \frac{\langle \psi^* \mathcal{H} \psi \rangle}{\langle \psi^* \psi \rangle}$$

and $H_{pq} = \langle \psi^* \mathcal{H} \psi_q \rangle$

and $S_{pq} = \langle \psi_p^* \psi_q \rangle$

For a finite expansion, the variational principle can be applied so that the energy be stationary with respect to the linear expansion coefficients and simultaneously of the orbitals.

The intramanifold orbital overlap constraints may be taken into account in terms of an energy functional (within a

determinantal manifold p)

$$\Omega = E - \sum_{i,j} \langle \varphi_i^{p*} \varphi_j^p \rangle \lambda_{ji}^p \quad (2.1.7)$$

where λ_{ji} are Lagrange multipliers. The variational equations are

$$\frac{\partial \Omega}{\partial C_p^*} = 0 \quad (2.1.8)$$

$$\frac{\partial \Omega}{\partial \varphi_i^{p*}} = 0 \quad (2.1.9)$$

While eq. (2.1.8) leads to the familiar eigenvalue problem of eq. (2.1.6), there is no simple way of solving eq. (2.1.9) Gilbert expresses eq. (2.1.9) in a form resembling the Hartree-Fock equation

$$G^p \varphi_i^p = \sum_{j=1}^N \varphi_j^p \lambda_{ji}^p \quad (2.1.10)$$

where the one-particle operator G can be written as

$$G = \frac{C_p^*}{\langle \psi^* \psi \rangle} \sum_{q=1} \left\{ C_q G'_{\rho}{}^{qp} + (1 - \delta_{pq}) \frac{C_q \rho^{qp} G'_{\rho}{}^{qp}}{S_{pq}} + (1 - \delta_{pq}) [H_{pq} - ES_{pq}] \frac{C_q \rho^{qp}}{S_{pq}} \right\}$$

where G' is the Hartree-Fock operator (2.1.11)

$$G' = h + \frac{\langle v (1-P_{12}) \rho^{qp} \rangle}{S_{pq}} \quad (2.1.12)$$

h and v are one- and two-particle operators, ρ^{qp} is the kernel of first order density matrix and P_{12} is the permutation operator.

Although eq. (2.1.10) appears to be simple, the form of the variational functional is complicated. In a later paper⁷⁶ Gilbert has reformulated the problem in slightly different manner by including the concept of localized orbitals in the MC-SCF scheme and derives the equation.

$$(G' - \rho_F G' \rho_F + G) \varphi_i = \lambda_i \varphi_i \quad (2.1.13)$$

where the localization potential A is defined as

$$A = - G' + G \quad (2.1.14)$$

and ρ is the first order density operator.

The method proposed by Yutsis and coworkers is based on numerical Hartree-Fock formalism and has given satisfactory results for simple atoms⁶⁵.

Based on the open-shell SCF procedure, Hinze and Roothaan⁷⁷ have given a general MC-SCF formalism for orthogonal orbitals. This method is computationally feasible and has been applied to a number of systems by Sabelli and Hinze⁷⁸. Further generalization of this procedure has been done by Huzinaga⁷⁹.

2.2 GENERAL THEORY OF MC-SCF

Following the ideas of Lowdin²⁴ and Slater,²⁵ Benston and Chong⁸⁰ proposed a general formalism for multiconfigurational SCF theory with non-orthogonal orbitals. The general MC-SCF procedure when applied to all configurations simultaneously is cumbersome, expensive and slowly convergent. It is hoped that use of non-orthogonal orbitals would achieve a more rapid convergence and hence somewhat more intuition to the CI expansion.

As in the Hartree-Fock approximation, the many electron wave functions are constructed from one-electron orbitals. These orbitals are classified according to symmetry and are not assumed to be orthogonal. In what follows we will use φ to denote such general orbitals.

$$\varphi_{i\lambda}(r, \theta, \phi) = r^{-1} R_{\lambda i}(r) Y(\theta, \phi) \quad (2.2.1)$$

$$\int_0^{\infty} dr R_{\lambda i}(r) R_{\lambda j}(r) = S_{ij}$$

The index λ denotes the symmetry species, i and j denote the orbital labels that are not distinguishable by symmetry. The spin orbitals are obtained by multiplying the spatial orbitals by the appropriate spin functions.

From the spin orbitals we obtain determinantal wave functions which are non-orthogonal. Each of the Slater determinants can be identified by the spin-orbitals that are used in forming the particular Slater determinant. This allows us to define an occupation number of a particular electron shell as the number of

occupied spin-orbitals of that shell. The occupation number of a closed shell λ_i is equal to $(4\lambda + 2)$. Otherwise it corresponds to an open shell. The collection of all Slater determinants that have the same occupation numbers constitute an electron configuration. The total wave function, called configuration state function (CSF) is expressed as a linear combination of determinantal functions.

$$\psi_K = \sum_A \phi_A Y_{AK} \quad (2.2.2)$$

The MC-SCF wave function is a linear combination of several CSF's.

$$\Psi = \sum_K \psi_K A_K = \sum_K \sum_A \phi_A Y_{AK} A_K = \sum_A \phi_A C_A \quad (2.2.3)$$

It may be pointed out that in the classical Hartree-Fock method, the wave function for each component of a degenerate atomic state is approximated by a single determinant CSF; the Hartree-Fock orbitals are those orbitals for which the total energy calculated from the single determinant CSF has a minimum. According to the present scheme, the total energy is optimized with respect to the functional form, (or in practice with respect to the expansion coefficients) and simultaneously with respect to the expansion coefficients of the CSF's.

This method is also distinct from the usual configuration interaction where the orbitals are determined such that they yield an extremum for the energy for a single configuration state function.

Since in CI, the functional form of the orbitals are not subjected to the variational principle, the orbitals cannot adjust themselves to the best possible form in the actual electronic environment. The present method allows this additional degree of freedom.

The energy of a system represented by a multiconfigurational wave function ψ is given by

$$\begin{aligned} E &= \langle \psi | \mathcal{H} | \psi \rangle \\ &= \sum_{A B} C_A \langle \phi_A | \mathcal{H} | \phi_B \rangle C_B \end{aligned} \quad (2.2.4)$$

In the MC-SCF method, two independent variations of the energy are performed one with respect to the orbitals through the expansion coefficients and the other with respect to the configuration mixing coefficients. Strictly speaking these two variations are not independent; however we assume that the two variational parameters are not strongly coupled and can be treated separately. Furthermore since both these parameters are determined self-consistently, we believe that this procedure is justified.

Equation (2.2.4) is suitable for the variation of configuration mixing coefficients and leads to the familiar eigenvalue equations

$$H \underline{C} = E T \underline{C} \quad (2.2.5)$$

where T denotes the overlap matrix between configurations,

$$H_{AB} = \langle \phi_A | \mathcal{H} | \phi_B \rangle \quad (2.2.6)$$

and \tilde{c} is the column vector of the expansion coefficients.

Using the Hamiltonian of eq. (1.2.4) we obtain

$$\langle \phi_A | \mathcal{H} | \phi_B \rangle = h_{AB} + g_{AB} \quad (2.2.7)$$

where

$$h_{AB} = \sum_i^A \sum_j^B p(i,j) D_{AB}(i,j) \quad (2.2.8)$$

$$g_{AB} = \sum_i^A \sum_j^B \sum_k^A \sum_l^B q(i,j,k,l) D_{AB}(i,j,k,l) \quad (2.2.9)$$

$$p(i,j) = \langle \varphi_i | h | \varphi_j \rangle$$

$$q(i,j,k,l) = \langle \varphi_i(1) \varphi_k(2) r_{12}^{-1} \varphi_j(1) \varphi_l(2) \rangle \quad (2.2.10)$$

In the above equations i, j, k, l refer to orbitals, $D_{AB}(i, j)$ and $D_{AB}(k, j, k, l)$ are the first- and second-order cofactors of the determinant of transitional overlap matrix between the orbitals in ϕ_A and ϕ_B . This transition overlap matrix Γ_{AB} is defined by

$$\Gamma_{AB}(i^+, j^+) = \Gamma_{AB}(i^-, j^-) = \langle \varphi_i, \varphi_j \rangle$$

$$\Gamma_{AB}(i^+, j^-) = \Gamma_{AB}(i^-, j^+) = 0 \quad (2.2.11)$$

where i and j refer to purely spatial orbitals φ_i and φ_j . Including spin explicitly in eq.(2.2.8) we can write

$$h_{AB} = \left[\sum_{i^+}^A \sum_{j^+}^B p(i^+j^+) D_{AB}(i^+j^+) + \sum_{i^-}^A \sum_{j^-}^B p(i^-j^-) D_{AB}(i^-j^-) \right]$$

$$\begin{aligned} g_{AB} = & \sum_{i^+}^A \sum_{j^+}^B \sum_{k^+}^A \sum_{l^+}^B q(i^+j^+k^+l^+) D_{AB}(i^+j^+k^+l^+) \Delta(i^+k^+) \Delta(j^+l^+) + \\ & \sum_{i^+}^A \sum_{j^+}^B \sum_{k^-}^A \sum_{l^-}^B q(i^+j^+k^-l^-) D_{AB}(i^+j^+k^-l^-) + \\ & \sum_{i^-}^A \sum_{j^-}^B \sum_{k^+}^A \sum_{l^+}^B q(i^-j^-k^+l^+) D_{AB}(i^-j^-k^+l^+) + \end{aligned} \quad (2.2.12)$$

$$\sum_{i^-}^A \sum_{j^-}^B \sum_{k^-}^A \sum_{l^-}^B q(i^-j^-k^-l^-) D_{AB}(i^-j^-k^-l^-) \Delta(i^-k^-) \Delta(j^-l^-) \quad (2.2.13)$$

The Δ factors are introduced so as to eliminate terms arising from $m = n$

$$\Delta(m,n) = 1 - \delta_{mn} \quad (2.2.14)$$

The summation sign $\sum_{i^+}^A$ denotes that summation is carried out over spin orbitals $\subset \phi_A$

Applying the variational principle, varying each orbital by an infinitesimal amount $\delta\phi_i$ in eq. (2.2.4), we obtain

$$\delta E = \sum_A \sum_B C_A^* C_B [\delta h_{AB} + \delta g_{AB}] \quad (2.2.15)$$

Details of the algebra for the expansion of eq. (2.2.15) in terms of orbitals are given in Appendix I.

Following Benston and Chong,⁸⁰ we can define an operator

$$\begin{aligned} R_{ij} = & \sum_A \sum_B C_A^* C_B \left\{ N_A^+(i) N_B^+(j) [A_{AB}^+(i,j) + B_{AB}^+(i,j)] \right. \\ & \left. + N_A^-(i) N_B^-(j) [A_{AB}^-(i,j) + B_{AB}^-(i,j)] \right\} \end{aligned} \quad (2.2.16)$$

where $A_{AB}^\pm(i,j)$ is given by

$$\begin{aligned} A_{AB}^\pm(i,j) = & D_{AB}(i^\pm j^\pm)h + \sum_{k^\pm} \sum_{l^\pm} p(i^\pm j^\pm) \Delta(i^\pm k^\pm) \Delta(j^\pm i^\pm) \\ & D_{AB}(i^\pm j^\pm k^\pm l^\pm) + \sum_{k^\mp} \sum_{l^\mp} p(i^\pm j^\pm) D_{AB}(i^\pm j^\pm k^\mp l^\mp) \end{aligned} \quad (2.2.17)$$

Similarly $B_{AB}^\pm(i,j)$ can be defined as

$$\begin{aligned} B_{AB}^\pm(i,j) = & \sum_{k^\pm} \sum_{l^\pm} \left\{ 2 D_{AB}'(i^\pm j^\pm k^\pm l^\pm) \Delta(j^\pm l^\pm) \Delta(i^\pm k^\pm) Y(k^\pm l^\pm) \right. \\ & + \sum_{m^\pm} \sum_{n^\pm} q(m^\pm n^\pm k^\pm l^\pm) D_{AB}''(m^\pm n^\pm k^\pm l^\pm i^\pm j^\pm) \Delta'(m^\pm k^\pm i^\pm) \Delta(n^\pm i^\pm j^\pm) \\ & \left. + \sum_{m^\mp} \sum_{n^\mp} q(m^\mp n^\mp k^\pm l^\pm) D_{AB}''(m^\mp n^\mp k^\pm l^\pm i^\pm j^\pm) \Delta(k^\pm i^\pm) \Delta(l^\pm j^\pm) \right\} \end{aligned}$$

$$+ \sum_{\bar{k}^{\pm}}^A \sum_{\bar{l}^{\pm}}^B \left\{ 2 D_{AB}'(i^{\pm} j^{\pm} \bar{k}^{\mp} \bar{l}^{\mp}) Y(\bar{k}^{\mp} \bar{l}^{\mp}) + \sum_{\bar{m}^{\mp}}^A \sum_{\bar{n}^{\mp}}^B q(\bar{m}^{\mp} \bar{n}^{\mp} \bar{k}^{\mp} \bar{l}^{\mp}) \right.$$

$$D_{AB}''(\bar{m}^{\mp} \bar{n}^{\mp} \bar{k}^{\mp} \bar{l}^{\mp} i^{\pm} j^{\pm}) \Delta(\bar{m}^{\mp} \bar{k}^{\mp}) \Delta(\bar{n}^{\mp} \bar{l}^{\mp})$$

$$+ \left. \sum_{\bar{m}^{\pm}}^A \sum_{\bar{n}^{\pm}}^B q(\bar{m}^{\pm} \bar{n}^{\pm} \bar{k}^{\mp} \bar{l}^{\mp}) D_{AB}''(\bar{m}^{\pm} \bar{n}^{\pm} \bar{k}^{\mp} \bar{l}^{\mp} i^{\pm} j^{\pm}) \Delta(\bar{n}^{\pm} j^{\pm}) \right\}$$

(2.2.18)

where

$$\Delta'(a,b,c) = (1 - \delta_{ab})(1 - \delta_{bc})(1 - \delta_{ca})$$

$D_{AB}''(a,b,c,d,e,f)$ is the cofactor of $\Gamma_{AB}(e,f)$ in the determinant $D_{AB}'(a,b,c,d)$ and $Y(\bar{k}^{\pm} \bar{l}^{\pm}) = \int \varphi_{\bar{k}}^*(2) \xi(1,2) \varphi_{\bar{l}}(2) d\tau$

In terms of the operator R_{ij} , the expression for the variation in energy corresponding to eq. (2.2.15) becomes

$$\begin{aligned} \delta E &= \sum_i \sum_j \langle \delta \varphi_i R_{ij} \varphi_j \rangle + \langle \delta \varphi_i R_{ij} \varphi_j \rangle^* \\ &= \sum_i \langle \delta \varphi_i \sum_j R_{ij} \varphi_j \rangle + \sum_i \langle \delta \varphi_i \sum_j R_{ij} \varphi_j \rangle^* \end{aligned}$$

(2.2.19)

If we define an operator

$$\mathfrak{I}_i = \sum_j R_{ij} | \varphi_j \rangle \langle \varphi_i | \quad (2.2.20)$$

then eq. (2.2.19) becomes

$$\delta E = \sum_i \langle \delta \varphi_i \mathfrak{I}_i \varphi_i \rangle + \sum_i \langle \delta \varphi_i \mathfrak{I}_i \varphi_i \rangle^* \quad (2.2.21)$$

adding eq. (A.I.16) to (2.2.21), we get

$$\begin{aligned} \delta E' = & \sum_i [\langle \delta \varphi_i \mathfrak{I}_i \varphi_i \rangle - \sum_j \epsilon_{ji} \langle \delta \varphi_i | \varphi_j \rangle] \\ & + \sum_i [\langle \delta \varphi_i \mathfrak{I}_i \varphi_i \rangle^* - \sum_j \epsilon_{ij} \langle \delta \varphi_i | \varphi_j \rangle^*] = 0 \end{aligned} \quad (2.2.22)$$

For equation (2.2.22) to be true, we should have

$$\begin{aligned} \langle \delta \varphi_i \mathfrak{I}_i \varphi_i \rangle - \sum_j \epsilon_{ji} \langle \delta \varphi_i | \varphi_j \rangle &= 0 \\ \langle \delta \varphi_i \mathfrak{I}_i \varphi_i \rangle^* - \sum_j \epsilon_{ij} \langle \delta \varphi_i | \varphi_j \rangle^* &= 0 \end{aligned} \quad (2.2.23)$$

Taking the complex conjugate of the second of eq. (2.2.23) and subtracting from the first, we get the well known relation

$$\sum_j (\epsilon_{ji} - \epsilon_{ij}^*) | \varphi_j \rangle = 0$$

or

$$\epsilon_{ji}^* = \epsilon_{ij} \tag{2.2.24}$$

It may be pointed out that eq. (2.2.24) is not a relation that was derived and found to be satisfied by the variational equations. On the other hand, it is fundamental to the very method of Lagrange Multipliers that they be symmetric. The Lagrange multiplier method is concerned with the problem of finding the stationary points of a real function of n variables subject to a set of m conditions.

$$\begin{aligned} \delta \rho (x_1 - \dots - x_n) &= 0 \\ g (x_1 - \dots - x_n) &= 0 \end{aligned} \tag{2.2.25}$$

This is equivalent to solving a system of $m + n$ equations in $m + n$ unknowns (n number of x 's and m number of λ 's)

$$\begin{aligned} \frac{\partial \rho}{\partial x_k} + \sum_i^m \sum_j^m \lambda_{ij} \frac{\partial g_{ij}}{\partial x_k} &= 0 \\ g_{ij} (x_1 - \dots - x_n) &= 0 \end{aligned} \tag{2.2.26}$$

The two equations in (2.2.23) are equivalent and should hold true for the variation of any of the orbitals. We thus obtain the MC-SCF equations for non-orthogonal orbitals

$$\mathfrak{S}_i \varphi_i = \sum_j \epsilon_{ji} \varphi_j \quad (2.2.27)$$

2.3 SOLUTION OF THE SCF EQUATIONS BY COUPLING OPERATOR METHODS

In eq. (2.2.27) we have reduced the non-linear variational problem of determining the orbitals φ_i to the solution of a set of pseudo linear equations, one for each orbital φ_i . The non linearity occurs in the operators \mathfrak{S}_i and, as described in connection with the Hartree-Fock equations in p. 19, in general the solution is attempted by means of iteration until self-consistency is achieved.

Unlike the single determinantal Hartree-Fock problem, eq. (2.2.27) cannot be reduced to simple eigenvalue form for the same reasons that the equations derived for the open shell case cannot, that is, the Hartree-Fock operator in such cases is not invariant to a unitary transformation.

There are two main approaches that have been suggested for solving equations such as (2.2.27). One, which involves reducing eq. (2.2.27) to pseudo eigenvalue form using some coupling operator, will be discussed in this section. The other, the one used in this calculation, involves a direct attack on the equation in the form given and will be discussed in the following section.

Following the early ideas of Roothaan¹⁶, a number of general SCF methods involving the use of coupling operators have been proposed^{17,21}. Birss and Fraga^{82,83} proposed a coupling operator for general SCF methods, which they claimed to be independent of the number and nature of open shells. In developing their theory, Birss and Fraga make no distinction between closed and open shells which, although satisfactory in principle, may lead to difficulty in applying the variational principle³⁷. Dyadyusha and Kuprievich³⁹ have pointed out that the Birss-Fraga formalism satisfies only the necessary but not sufficient condition for a proper variational energy extremum. Other difficulties in these early formulations arise from improper mixing of the various orbitals and hence inadequate form of the coupling operators.

Goddard et.al.⁸¹ and Dahl et. al.⁴⁹ have pointed out that the coupling operator approach for obtaining SCF equations for open shell systems and MC-SCF methods are incomplete and unsatisfactory. The difficulty arises from the fact that for the general case of open shells, the wave function Ψ involves a number of excited states that do not necessarily form a complete set. A proper orbital variational representation must take into account mixing among occupied orbitals, mixing among virtual orbitals and mixing between occupied and virtual orbitals. By identifying the total Fock space in terms of two mutually orthogonal subspaces consisting of occupied orbitals and unoccupied orbitals respectively, Dahl et. al and Goddard et. al derive the necessary conditions on the Hartree-Fock orbitals for correct general variational form as

$$\langle \varphi_\lambda | \mathcal{J}_i | \varphi_i \rangle = \langle \varphi_i | \mathcal{J}_\lambda | \varphi_\lambda \rangle \quad (2.3.1)$$

where λ and i belong to different sub-spaces, and

$$\langle \varphi_k | \mathcal{J}_i | \varphi_i \rangle = \langle \varphi_k | \mathcal{J}_k | \varphi_i \rangle \quad (2.3.2)$$

where the subscripts k and i belong to the same sub-spaces.

This simply means that the elements defined as

$$\xi_{ki} = \langle \varphi_k | \mathcal{J}_i | \varphi_i \rangle \quad (2.3.3)$$

form a Hermitian matrix, that is, $\xi_{ki} = \xi_{ik}^*$.

Most of the workers in the field have proposed coupling operators which assume that the conditions (2.3.1) and (2.3.2) are already satisfied before convergence^{68,72,82}. This assumption is incorrect and may explain some of the difficulties in solving the general SCF equations by pseudo eigenvalue methods.

Hunt et.al.⁵² have proposed an alternative method called orthogonality constrained basis set expansion (OCBSE) method, where the basis set expansion for a given orbital is constrained so that it remains orthogonal to all of the other occupied orbitals. OCBSE appears to be a direct and relatively efficient method for solving open shell problems. In this procedure, separate Hamiltonians are defined for open and closed shells and the corresponding Hartree-Fock equations for each are solved over a reduced space until convergence is achieved. Another simple method proposed by Peters⁵⁶ involves the idea of solving the general SCF equations in two steps iteratively, first the open shell eigenvalue equations and then the closed shell equations until

a convergence criterion is met. The OCBSE and Peters methods have certain similarities. However, Albat and Gruen¹⁰⁴ have shown that neither of these methods allows a general variation in the occupied orbitals and unoccupied orbitals.

The general ideas concerning coupling operators in SCF theory have been elegantly discussed by Huzinaga⁵⁷. There is no particular advantage in unifying the open shell and closed shell eigenvalue equations by means of a coupling operator, for this does not guarantee any recipe for a quick solution to the problem. Huzinaga has reformulated the Birss-Fraga coupling operator although it appears that the variational requirement on the Lagrange multipliers has not been properly included in the formalism.

Hirao and Nakatsuji⁹⁶ have proposed a coupling operator which they claim takes into account the variational conditions on the orbitals and Lagrange multipliers satisfactorily. Their formalism appears to be general and seems to offer a means of expressing the MC-SCF Fock equations in a pseudo eigenvalue equation form.

In general, however, coupling operator methods offer no particular advantage other than mathematical generality and a certain physical significance to the Fock equations. The most serious difficulty appears to be the fact that in many cases the usual methods of solving eigenvalue problems do not lead to converged solutions^{114,115}.

Benston and Chong⁸⁰ have derived a pseudo eigenvalue equation from eq. (2.2.27) using the Birss-Fraga approach. Besides the general difficulties associated with the Birss-Fraga and coupling

operator methods, Benston and Chong's equation (27) suffers from a fundamental inconsistency. This arises from the method of construction of the matrix F which is artificially built from different columns of the matrices $F^{(i)}$ belonging to different orbitals.

The result of this is that F is in general a non-Hermitian matrix. Benston and Chong then use a similarity transformation to obtain an explicit identity between F in an orthogonal basis (\hat{F}) and the matrix of the Lagrange multipliers in the same basis. Since the latter must be Hermitian and F in general is not, their equation (27) is clearly inconsistent. This relationship has been used in obtaining a pseudo eigenvalue equation (Benston and Chong eq. 31).

It may be possible to circumvent the inconsistency in Benston-Chong method by a different set of operations and obtain a matrix to take the place of F ; however, the general problems of using coupling operators would still remain.

For these reasons, we choose to attack the equation (2.2.27) directly. We transform this equation into a set of matrix equations in terms of orbital expansion coefficients and solve these by means of an iterative method.

2.4 SOLUTION OF SCF EQUATIONS BY AN ITERATIVE METHOD

It may be noted that the operator \mathfrak{J}_i in eq. (2.2.27) has been defined in terms of a specific orbital i . The non-orthogonal orbitals φ_i can be expanded in a basis set $\{\chi\}$

$$\varphi_i = \sum_p \chi_p B_{pi} \quad (2.4.1)$$

so that equation (2.2.27) becomes

$$\mathfrak{I}_i \sum_p \chi_p B_{pi} = \sum_j \sum_p \chi_p B_{pj} \epsilon_{ji} \quad (2.4.2)$$

The complete set of basis functions form a row vector and can be written as

$$\underline{\chi} = (\chi_1 \chi_2 \dots \chi_p) \quad (2.4.3)$$

Equation (2.3.6) reduces to

$$\mathfrak{I}_i \underline{\chi} \underline{B}_i = \sum_j \underline{\chi} \underline{B}_j \epsilon_{ji} \quad (2.4.4)$$

where \underline{B}_i is a column vector of expansion coefficients

$$\underline{B}_i = \begin{bmatrix} B_{1i} \\ B_{2i} \\ \vdots \\ B_{pi} \end{bmatrix} \quad B = \begin{bmatrix} B_{11} & B_{12} & \dots \\ \vdots & \vdots & \vdots \\ B_{p1} & B_{p2} & \dots \end{bmatrix} \quad (2.4.5)$$

Equation (2.3.8) now becomes, after multiplication by $\underline{\chi}^*$

$$\langle \underline{\chi} | \mathfrak{I}_i | \underline{\chi} \rangle \underline{B}_i = \sum_j \langle \underline{\chi} | \underline{\chi} \rangle \underline{B}_j \epsilon_{ji}$$

Define

$$h_i = (\underline{\chi} | \mathfrak{I}_i | \underline{\chi}) \quad (2.4.6)$$

where h_i represents a matrix having elements of the form

$$(h_i)_{kj} = \langle \chi_k | \mathcal{O}_i | \chi_j \rangle \quad (2.4.7)$$

then, equation (2.2.27) can be expressed as

$$h_i \underline{B}_i = S \sum_j \underline{B}_j \epsilon_{ji} \quad (2.4.8)$$

where S is the overlap matrix between basis functions.

The method that we propose to use for solving the SCF equations is based on a hybrid method given by Levenberg⁸⁴ and Marquardt⁸⁵. Powell⁸⁶ later modified the method in a series of papers and we have adopted Powell's algorithm. The actual method is a combination of Newton-Raphson and steepest descent methods.

The principles of the Newton-Raphson method used by Roothaan and Bagus and the method of steepest descent used by McWeeny have been described elsewhere^{118,119}. The basic idea in both methods is the following:

Starting with a certain set of vectors B_i in equation (2.4.8) we consider all changes resulting from a change in these vectors. The first order correction to these vectors are included in the next iteration and the process is continued until the SCF cycle converges to the true solution. It is important to note that the elements of the vectors B_i are non-linear variables of the integrals involved in constructing the Fock matrix and can only be determined by

methods which involve corrections both in direction and magnitude.

In deriving the non-linear equations which determine the correction vectors, following Hinze and Roothaan,⁷⁷ we consider only one symmetry at a time. This means that we neglect in each cycle of iteration the effects on the Fock matrix caused by changes in the vectors which belong to different symmetry. The only justification for this procedure that we offer is the fact that because of strong orthogonality between orbitals of different symmetry (such as s and p) there is little or no coupling between them. This results in a considerable simplification of the Newton-Raphson equations, since these can be solved in blocks of different symmetry. In the following it is implied that the set of equations are applied to one symmetry at a time.

Equation (2.4.8), namely,

$$h_i B_i = S \sum_j B_j \epsilon_{ji}$$

represents a set of simultaneous equations in the expansion coefficients B_i . Furthermore, they are non-linear and are actually cubic in the coefficients B_i . Since the present formalism assumes the orbitals to be non-orthogonal, the expansion coefficients B_i do not form an orthonormal set.

Equation (2.4.8) represents the fundamental equation that we are attempting to solve by means of an iterative procedure. Note that h_i is a matrix corresponding to the orbital i and so we get one such equation for each orbital.

Starting with an initial guess of vectors B_i° , the corrected set of vectors are obtained as

$$\tilde{B}_i = \tilde{B}_i^{\circ} + \delta \tilde{B}_i \quad (2.4.9)$$

where the superscript^o refers to the starting values.

If we define W as the overlap matrix between non-orthogonal orbitals

$$\langle \varphi_i | \varphi_j \rangle = W_{ij} \quad (2.4.10)$$

then we can write

$$\tilde{B}_i^{\circ} S \tilde{B}_j^{\circ} = W_{ij} \quad (2.4.11)$$

The corrected Fock matrix can be written as

$$h_i = h_i^{\circ} + \delta h_i \quad (2.4.12)$$

using (2.4.9) in (2.4.11) we get

$$\tilde{B}_i S \delta \tilde{B}_j + \tilde{B}_j S \delta \tilde{B}_i = 0_2 \quad (2.4.13)$$

where O_2 denotes terms of second and higher order in the correction vector δB . In deriving eq. (2.4.13) we have used the relation

$$\underline{B}_i^{\circ} S \underline{B}_j^{\circ} = \underline{B}_i S \underline{B}_j = W_{ij} \quad (2.4.14)$$

Since the Lagrange multipliers have to be symmetric, we need the further constraint that (we assume only real values)

$$\epsilon_{ik} = \epsilon_{ki} \quad (2.4.15)$$

However in the course of the iterative process, the constraint (2.4.15) may be violated and may eventually lead to divergence. For this reason, we include a mathematical set up to enforce this condition. Multiplying eq. (2.4.8) by B_k^+

$$\begin{aligned} \underline{B}_k^+ h_i \underline{B}_i &= \underline{B}_k^+ S \sum_j \underline{B}_j \epsilon_{ji} \\ &= W_{kk} \epsilon_{ki} + \sum_{j \neq k} W_{kj} \epsilon_{ji} \end{aligned} \quad (2.4.16)$$

If W is assumed to be a unit matrix, the second term on the right hand side can be taken to be zero and the first term becomes ϵ_{ki} . This enables us to express the Lagrange multipliers simply as

$$\underline{B}_k^+ h_i \underline{B}_i = \epsilon_{ki} \quad (2.4.17)$$

and similarly

$$\tilde{B}_i^+ h_i \underline{B}_k = \epsilon_{ik} \quad (2.4.18)$$

The approximations involved in eq. (2.4.17) and (2.4.18) are valid if one considers an orthogonal vector space. As W deviates from a unit matrix, the validity of this approximation becomes questionable. Nevertheless, we have used this approximation even when W was quite different from a unit matrix. As will be discussed below, in view of the fundamental requirement of maintaining linear independence among the vectors, we have obtained approximate solutions to eq. (2.4.8) in terms of orthogonal vectors. Because of this constraint on the solution vectors, the expressions (2.4.17) and (2.4.18) are used in the following derivation.

For starting values of the Lagrange multipliers, we use

$$\epsilon_{ki}^{\circ} = \tilde{B}_k^{\circ+} h_i \underline{B}_i^{\circ} \quad (2.4.19)$$

and in order to maintain the condition (2.4.15) we have taken

$$\epsilon_{ki} = \epsilon_{ik} = \frac{1}{2} \left(\tilde{B}_k^+ h_i \underline{B}_i + \tilde{B}_i^+ h_i \underline{B}_k \right) \quad (2.4.20)$$

Since ϵ_{ik} 's depend on B 's, corrections similar to (2.4.1) will have to be applied to ϵ_{ik}

$$\epsilon_{ik} = \epsilon_{ik}^{\circ} + \delta\epsilon_{ik} \quad (2.4.21)$$

Expanding eq. (2.4.8) using eq. (2.4.9) and eq. (2.4.12) we get

$$\begin{aligned} (h_i^\circ + \delta h_i) (\underline{B}_i^\circ + \delta \underline{B}_i) = \\ S \sum_j \frac{1}{2} (\underline{B}_j h_i \underline{B}_i + \underline{B}_i h_i \underline{B}_j) \end{aligned} \quad (2.4.22)$$

Eq. (2.4.22) can be reduced to

$$h_i^\circ \underline{B}_i^\circ - S \sum_j \epsilon_{ji}^\circ \underline{B}_j^\circ = g \delta B \quad (2.4.23)$$

where g represents the Jacobian of the left hand side of eq. (2.4.23).

Equation (2.4.23) then provides the basis for an approximate solution of eq. (2.4.8) by our iterative procedure. Details of this hybrid of Newton-Raphson and steepest descent methods are given in section 3.3.

We replace an estimate B_i of the solution of equation

$$h_i \underline{B}_i^k - S \sum_j \underline{B}_j^k \epsilon_{ji} = 0 \quad (2.4.24)$$

by the estimate

$$\underline{B}_i^{k+1} = \underline{B}_i^k + \delta \underline{B}_i^k \quad (2.4.25)$$

where $\delta \underline{B}_i^k$ solves the linear system of equations

$$h_i \underline{B}_i^k - S \sum_j \underline{B}_j^k \epsilon_{ji} - g_i^k \delta \underline{B}_i^k = 0 \quad (2.4.26)$$

The reason for obtaining orthogonal solutions arises because there are certain conditions which we would like to maintain and which we have introduced in the iterative algorithm. The search direction of our displacement vector δB_i is a linear combination of the steepest descent direction and the Newton direction. The problem of optimizing a function of n -dimensions (with n large) is extremely difficult. Given a hyperspace of n dimensions, it is difficult to find satisfactory and economical multi-dimensional search procedures. The difficulty resides in the fact that we must search each minute fractional volume of the n dimensional space if we hope to find an optimum value for the function. The choice of appropriate directions for the displacement vector δB_i is primarily decided by the fundamental requirement of linear independence among the vectors. A simple way to fulfill this requirement is to maintain near orthogonality between the sets of vectors. Although there may be methods that retain linear independence without any need for orthogonal search directions, such methods are likely to be more difficult to implement and may have poor convergence.

Particularly when the non-orthogonality is small, it is believed that our procedure is a reasonable one. Even for large values of the overlap, this method appears to be satisfactory (with the possible exception of results in Table XII) as indicated by the results based on this procedure.

Since the solution vectors are obtained in mutually orthogonal form, it is probably more appropriate to call the vectors that

result from the iteration by another symbol Q . The orthogonal orbitals which we will call $\hat{\phi}$, can be expanded in the basis functions

$$\hat{\phi}_i = \sum_p x_p Q_{pi} \quad (2.4.27)$$

and it is the Q_i that are obtained as solutions of our equation. If we define a transformation matrix Λ relating orthogonal and non-orthogonal orbitals by

$$\hat{\phi}_i = \sum_a \varphi_a \Lambda_{ai} \quad (2.4.28)$$

then we get the relationship

$$B = QV \quad (2.4.29)$$

Using (2.4.29) we transform the output matrix Q into non-orthogonal form B , and then proceed to the next iteration.

It may be recalled that the starting Fock matrix h_i constructed from initial vectors B_i is updated during each cycle of iteration. The final Fock matrix h_i is given by

$$h_i = h_i^{\circ} + \delta h_i \quad (2.4.30)$$

where δh_i is given by

$$\delta h_i \approx \sum_{j=1}^n J_{ij} \delta B_j \quad (2.4.31)$$

where J_{ij} represents an element of the matrix of Jacobian.

Apart from the approximations involved in obtaining solutions in orthogonal space, we have used an approximate Jacobian in the process of optimization. This latter procedure was adopted because of the fact that a test run using an exact Jacobian did not affect the convergence point. It is possible that there may be other situations where an approximate Jacobian would not be satisfactory. However, an input parameter DSTEP in the algorithm prevents any large changes in this approximation and attempts to make the necessary corrections.

CHAPTER III

PRINCIPLES OF COMPUTATION

3.1 GENERAL COMMENTS

Hartree-Fock equations can be solved in two ways, either by numerical integration or by matrix methods of the integrated Hartree-Fock equations. We have used the latter method which is identified as the Roothaan procedure.

It may be appropriate to make a few general comments about the numerical vs analytical procedures. While the Roothaan method depends heavily on the nature and number of basis functions used, the numerical method is not limited by the basis functions. Despite this difficulty most of the current atomic and molecular calculations make use of the analytic procedure. One important reason for this is the fact that numerical integrations take excessive time and since most of the calculations require the evaluation of multicentre integrals, the numerical method may be expensive. Yet another reason is that numerical wave functions are essentially tabulations of numbers vs electron coordinates and apart from being voluminous and cumbersome, they do not offer any physically intuitive meaning.

The Roothaan method on the other hand is well suited for the calculation of multicenter integrals. A further advantage is that in a configuration interaction calculation the Roothaan method provides an easy means of choosing a starting wave function.

The analytic procedure involves a number of matrix manipulations and an iterative process so as to arrive at an appropriate solution. The numerical method on the other hand

performs a numerical integration during each cycle of iteration until self consistency is achieved. One serious difficulty with the Roothaan procedure is the proper choice of basis functions. This problem is not at all simple and require a number of trial calculations. Any practical calculation in general is limited to a relatively small number of basis functions because of computer time.

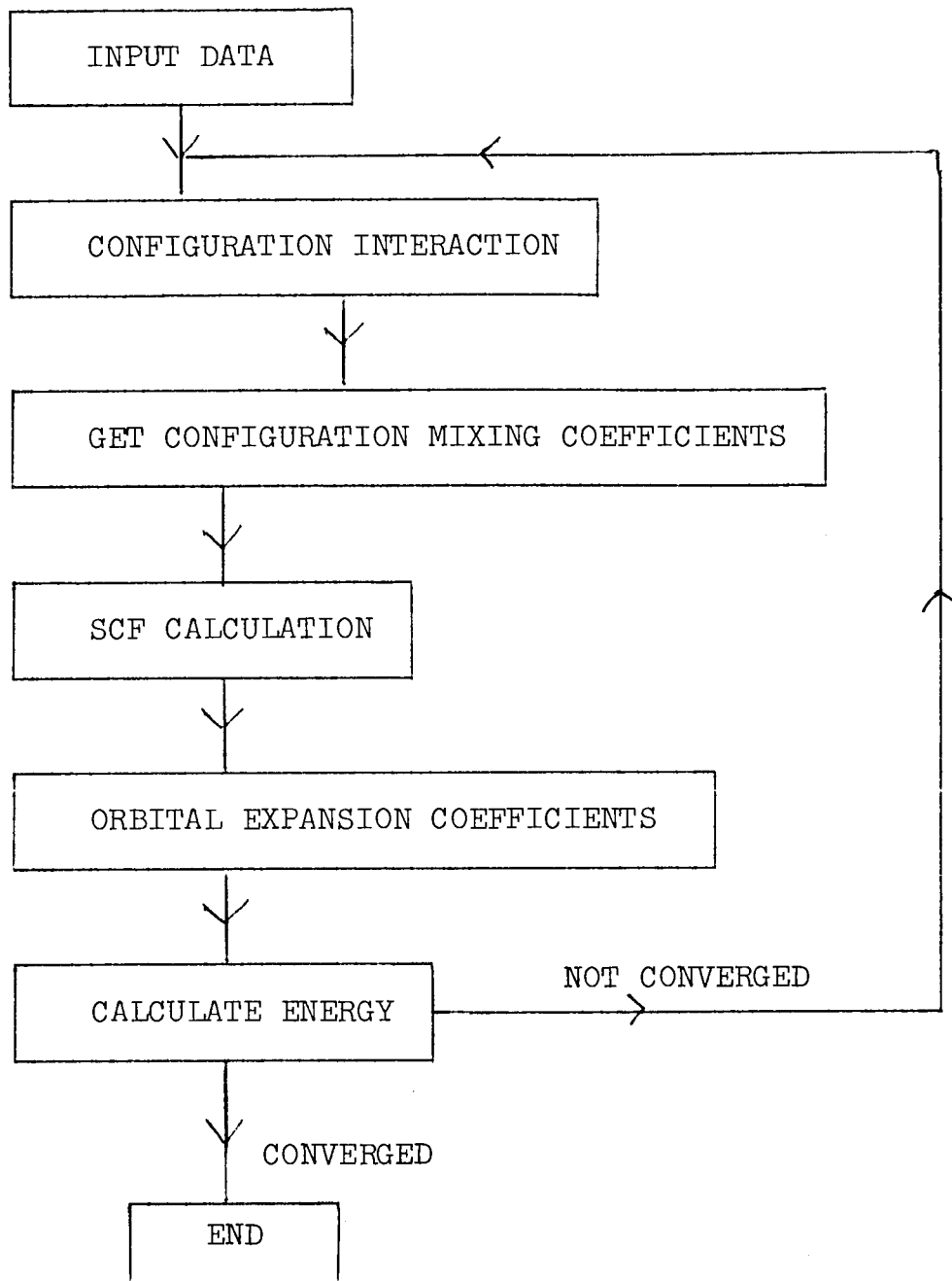
A multi-configurational wave function ψ for a N-electron system is a linear combination of Slater determinants Φ_k of spin orbitals φ_α . As has been mentioned in the theory, this involves two sets of coefficients

$$\psi = \sum_k c_k \Phi_k \{ \varphi_\alpha \} \quad (3.1.1)$$

In elaborating the practical aspects of the problem, it is convenient to separate the procedure into two categories:

- (i) Configuration interaction part in which we build configurations from linear combination of determinants.
- (ii) Self consistent field theory part in which the various determinants are built up from basis functions and expansion coefficients.

We will consider the computational aspects of each of the steps separately. The overall scheme can be summarized as follows:



3.2 CONFIGURATION INTERACTION

A major question in any truncated CI procedure is what type of excited configurations have to be mixed in the total wave function in order to obtain the most significant improvement in energy. The situation is relatively simple in two-electron systems where the inclusion of a few lower excited configurations is able to account for a large part of the correlation. The problem becomes more difficult as the number of electrons in the system increases.

No definite guidelines are available in determining the dominant configurations among the many that are possible. Second order perturbation theory has been used in obtaining energy estimates, but such estimates were found to be poor⁸⁷. Most of the authors have depended on results of previous calculations^{87, 88}. The magnitude of the eigenvectors of each configuration can provide an accurate value for the energy contribution from each configuration. If one is interested in accurate wave functions, it would be necessary to include such configurations that have large eigenvectors. But the problem is difficult and involves a considerable amount of experimentation.

From the available spin-orbitals, we construct Slater determinants to obtain a N-electron wave function. Each Slater determinant is completely characterized by the spin orbitals that are used for its construction. The number of occupied spin orbitals of a shell in a particular Slater determinant is called the occupation number of the shell in that Slater determinant.

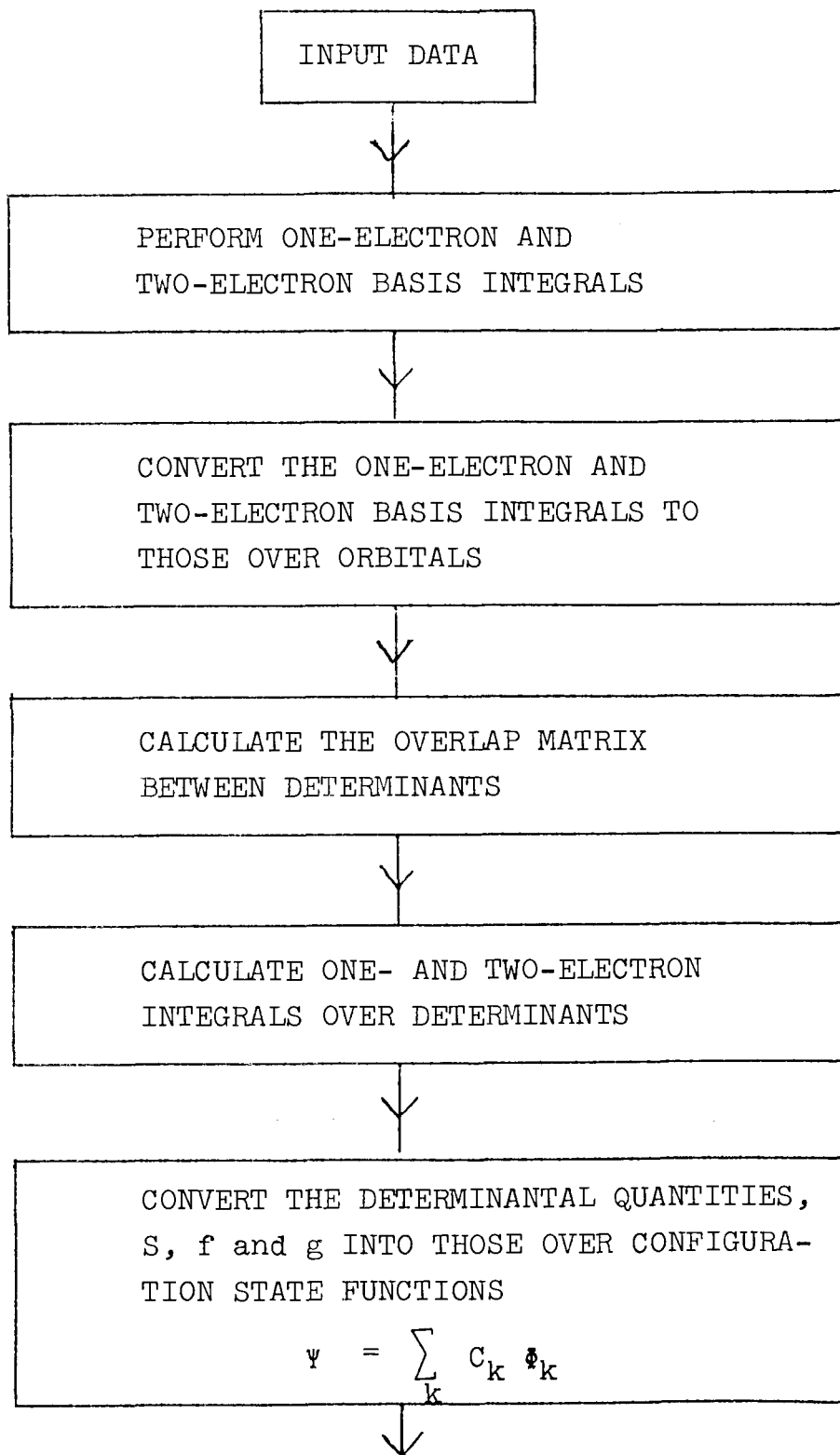
The collection of all Slater determinants which have the same shell occupation numbers constitute an electron configuration. This enables us to define a configuration in terms of a set of occupation numbers.

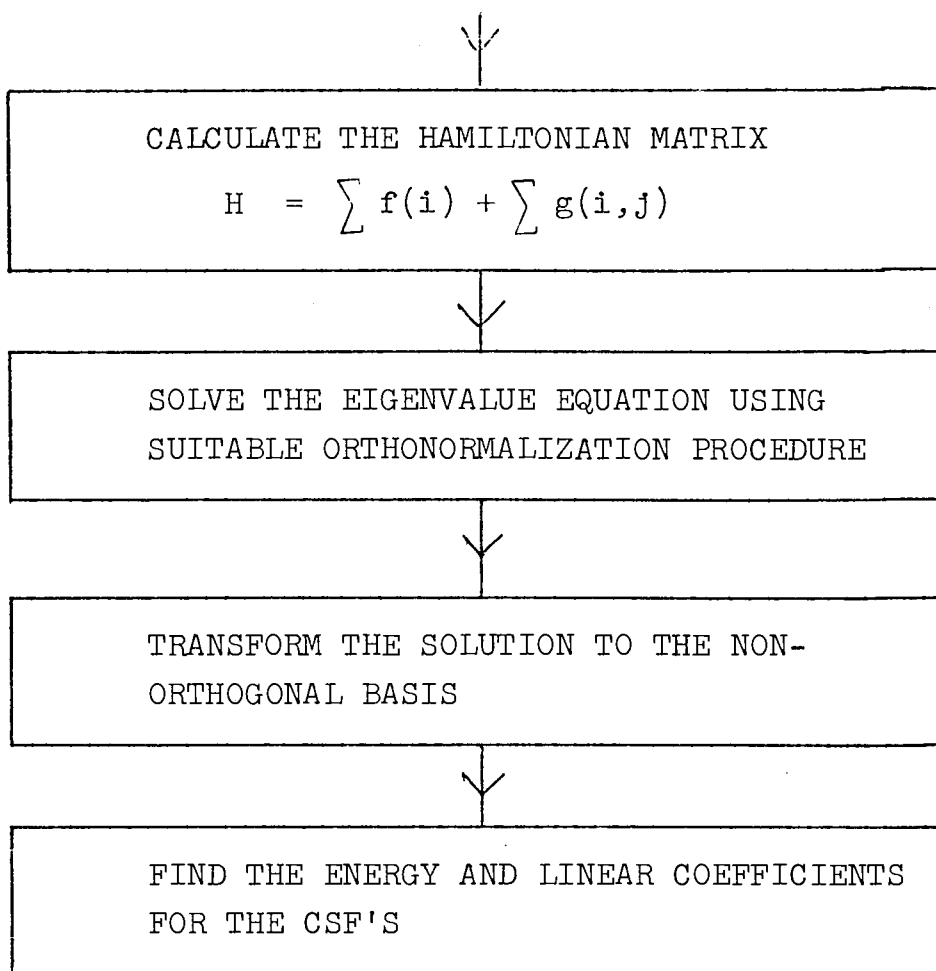
We construct configuration state functions (CSF) which are specific linear combinations of Slater determinants with the coefficients chosen such that the CSF's correspond to the same symmetry species and subspecies as the state for which the total wave function is to be constructed. Since we do not assume any orthogonality property for the orbitals, the same applies for the configuration state functions

$$\langle \psi_I | \psi_J \rangle = \Delta_{IJ} \tag{3.2.1}$$

According to the analytical procedure the spin orbitals are expanded in terms of basis functions. In order to solve the CI problem, we must therefore start with a set of appropriate orbital expansion coefficients and construct the one- and two-electron integrals over basis functions. Details of this procedure can be found in Roothaan's paper and is discussed briefly in Section (1.2). The sequence of computational procedures may best be described by means of a flow chart.

FLOW CHART OF CI PART





Choice of Basis Sets

One of the most important considerations in evaluating the reliability of an electronic structure calculation is the choice of basis set. There are three main criteria for a good basis set.

- (a) The functions must be of correct general behavior.
- (b) The functions must lead to integrals that can be evaluated.
- (c) The number of functions needed must be small.

To stress the importance of the third condition, it becomes clear if we consider a basis of m real atomic functions. In such a case, we will have to perform $n = \frac{1}{2} m (m + 1)$ distinct integrals of each type $\langle \chi_p | \chi_q \rangle$ and $\langle \chi_p | h | \chi_q \rangle$ and $k = \frac{1}{2} n(n+1)$ distinct integrals of the type $\langle \chi_p \chi_q | g | \chi_r \chi_s \rangle$. The calculation and storage of such a large number of values can be tedious.

As for the functions themselves, exponential or gaussian functions are the most common. The use of exponential function was first suggested by Slater and functions of the type

$$A r^n e^{-\xi r} \tag{3.2.2}$$

are usually called Slater type orbitals, where A is a normalizing constant, n is the principal quantum number, and ξ is the orbital exponent or screening parameter. Note that a function of this kind gives only a radial dependence and angular dependence is introduced through spherical harmonic functions.

To obtain accurate results without an excessively large number of basis functions, the individual functions must be chosen with great care; this is accomplished by variation of the parameter ξ . In fact, there is no easy way of obtaining an optimum basis set except by repeated calculation using different values of ξ .

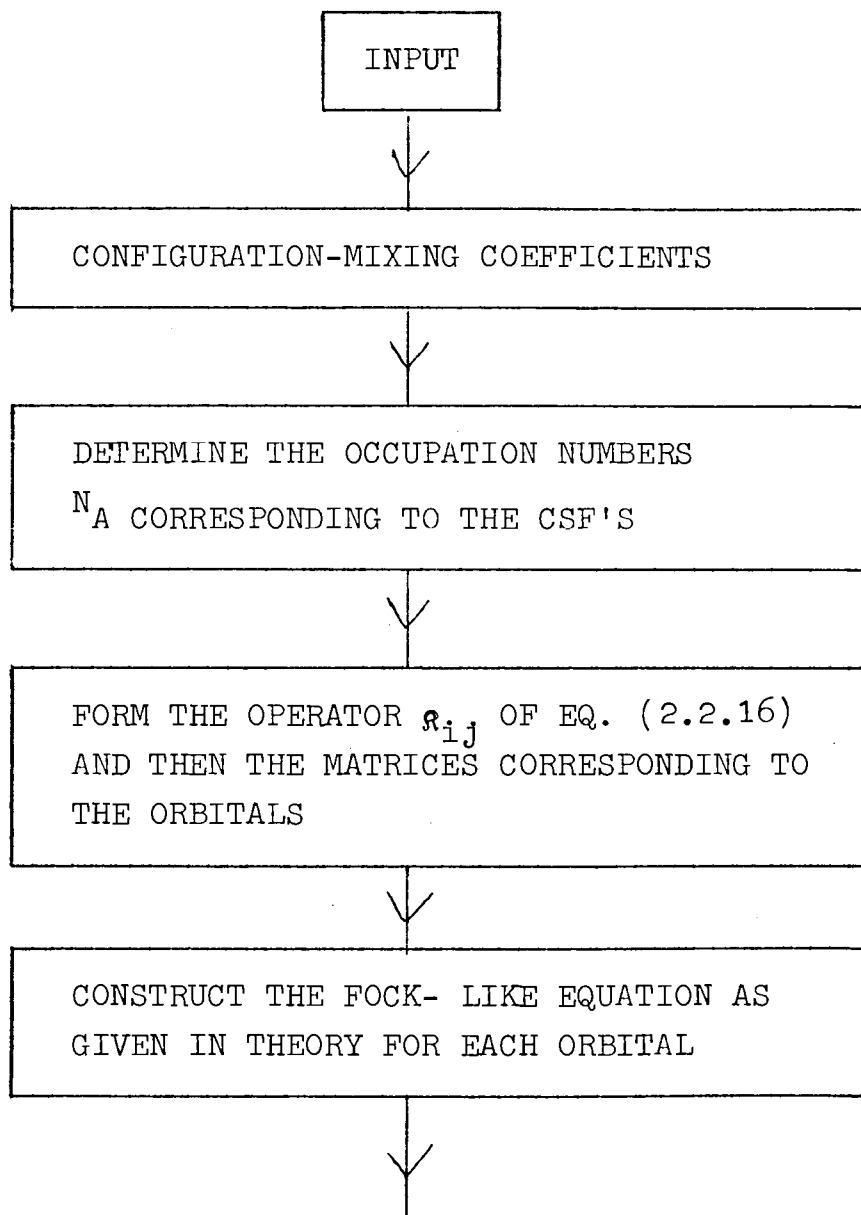
As indicated before, the main difficulty arises from the calculation and storage of two-electron integrals. Analytical methods have been developed in order to evaluate certain types of repulsion integrals by Coulson and Barnett⁸⁹ and Harris and Michels⁹⁰.

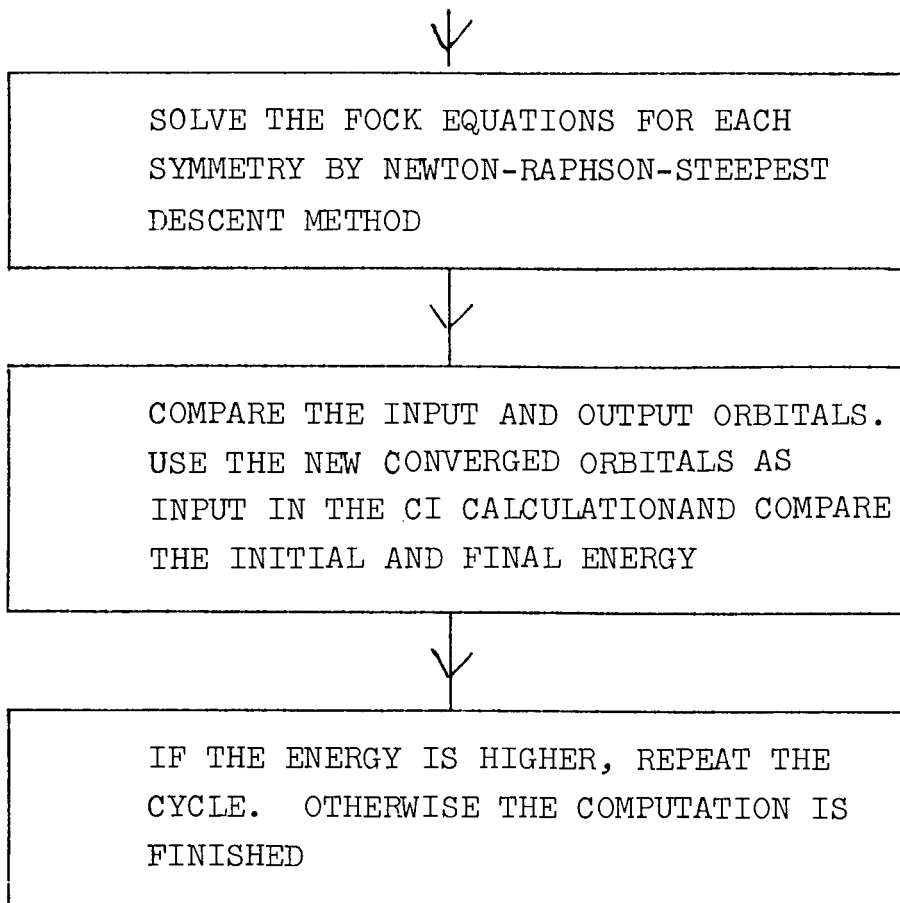
The most advantageous choice of basis functions can generally be obtained by two different methods: (a) choose as many basis functions as possible (saturation) and do not optimize the basis function exponents (b) choose a small set of basis functions and optimize the exponents carefully. Most often the choice falls on (b) for the following reasons:

1. A smaller basis set gives a more compact wave function
2. The convergence in the solution of the SCF equations is more stable with few basis functions.
3. From the computational stand point, a smaller basis is more economical.

3.3. THE SELF CONSISTENT FIELD PART

The orbital optimization and SCF procedure can be clearly represented by means of a flow chart. Corresponding to the ground state energy (from the CI part) of the total wave function, we get a set of coefficients which are the input for this step.





Solution of the CI eigenvalue problem as outlined in the previous section gives the ground state energy and the eigenvectors corresponding to this energy. Since the orbitals are allowed to be non-orthogonal, we arbitrarily assign an input matrix V which is essentially a non-orthogonality parameter

$$V^+V = W \tag{3.3.1}$$

where W is the overlap matrix between orbitals.

The total wave function is expressed as a linear combination of determinantal functions (CSF's), eq. (3.1.1)

The presence of a certain determinant in the total wave function is indicated by the occupation numbers N_A, N_B, \dots which are used in the construction of the Fock like operator.

The actual computation follows the theory which is described in the previous section. In the following we will describe the computational aspects of the method of solving the Fock equations.

The Fock operator is obtained in orbital form, one for each orbital and is transformed to the basis vector space by means of expansion methods. The matrix h_i which occurs for each orbital i is constructed from a set of initial guess expansion coefficients. The Newton-Raphson equations are formed using these initial vectors

$$h_i \tilde{B}_i - \sum_{j=1}^N \epsilon_{ij} S \tilde{B}_j \tag{3.3.2}$$

where i and j refer to orbitals and the summation is over all the orbitals. Since the Lagrange multipliers ϵ_{ji} are explicitly dependent on the expansion coefficients, the former must be reconstructed after each iterative correction of the latter.

These equations are treated in sets of symmetry blocks, that is, orbitals of s symmetry are not mixed with p, d, \dots . This means that the number of equations in each block will be equal to $(n \times m)$ where n is the number of orbitals of that particular symmetry and m is the number of basis set used.

The method used to solve the Fock equations (3.3.2) is

based on a scheme suggested by Powell⁹¹. It is a hybrid method in the sense that the algorithm selects either the Newton-Raphson method or the steepest descent method depending on the values of certain parameters.

The classical Newton-Raphson method of solving a set of simultaneous equations

$$f_i(x) = f_i(x_1, x_2, \dots, x_n) = 0 \tag{3.3.3}$$

is explained in many texts on numerical analysis¹¹⁹. An initial guess of the set of variables x_1, x_2, \dots, x_n is replaced by a corrected estimate

$$x_i^{k+1} = x_i^k + \delta_i^k \tag{3.3.4}$$

where the correction terms δ_i solve the linear system of equations

$$f_i(x_i^k) + \sum_{j=1}^n J_{ij}^{(k)} \delta_j^{(k)} = 0 \tag{3.3.5}$$

Here J_{ij} is the Jacobian defined by

$$J_{ij}^{(k)} = \left[\frac{\partial f_i}{\partial x_j} \right]_{x = x^{(k)}} \tag{3.3.6}$$

Analytically one approximates the function $f(x)$ in the vicinity of x_0 by its first order Taylor expansion and then seeks the zero of the linear function (3.3.5).

Newton-Raphson method suffers from two serious disadvantages from the point of view of practical calculations. The first of these is the difficulty of computing the Jacobian matrix. Even if the functions f_j are sufficiently simple for their partial derivatives to be obtained analytically, the amount of labour required to evaluate all n^2 of these may be excessive. In the majority of problems, however, the f_j 's are far too complicated for this and an approximation to the Jacobian matrix must be found numerically. This is often carried out directly, i.e., $\partial f_j / \partial x_k$ is computed by evaluating f_j for two different values of x_k while holding the remaining $n-1$ independent variables constant. Although this direct approach gives an immediate approximation to the partial derivative, it is not without its disadvantages, the most serious of which is the amount of labour involved. For in order to compute the Jacobian in this manner, the vector function f must be evaluated for at least $n + 1$ sets of independent variables.

The second disadvantage of the Newton-Raphson method is the fact that without some modifications it frequently fails to converge. Conditions for convergence are well known but they rely on the initial estimate of the solution being good, a requirement that is often impossible to realize in practice.

Despite these disadvantages, the method has much to commend. The algorithm is simple even though it does require the solution of n linear equations at every step, it has a sound theoretical basis and for many problems it is rapidly convergent.

Descent techniques of functional minimization involve iterations which consists of three parts: first, a direction δ^k is found, then a descent step length λ^k is determined and finally the descent step

$$x^{k+1} = x^k + \lambda^k \delta^k \quad (3.3.7)$$

The descent direction is an n-dimensional vector

$$\delta = (\delta_1 \ - \ - \ - \ \delta_n) \quad (3.3.8)$$

At the k th iteration, the direction vector δ^k originates at the current point x^k . The value of the objective function $f_i(x)$ decreases from x^k to a point at some distance in that direction. A unit vector δ^k is said to be a descent direction with respect to the objective function $f_i(x)$ at x^k if there is a $\lambda' > 0$ such that for all λ satisfying $\lambda' \geq \lambda > 0$ we have

$$f_i(x^{k+1}) = f_i(x + \lambda \delta^k) < f_i(x^k) \quad (3.3.9)$$

If $f_i(x)$ is differentiable, δ^k is a descent direction if

$$\begin{aligned} \lim_{\lambda \rightarrow 0} \frac{f_i(x^k + \lambda \delta^k) - f_i(x^k)}{\lambda} &= \left. \frac{f_i(x^k + \lambda \delta^k)}{d\lambda} \right|_{\lambda=0} \\ &= \underline{(\delta^k)} \nabla f_i(x^k) < 0 \end{aligned} \quad (3.3.10)$$

where $\nabla f_i(x^k)$ denotes the gradient of the objective function $f_i(x)$ evaluated at the point x^k . If this directional derivative, $\nabla f_i(x^k)$, exists, and is negative, then δ^k is a descent direction.

The descent techniques differ from each other in the type of descent directions and in the strategy used to determine the lengths of the descent steps. They also differ in the order of partial derivatives of $f_i(x)$ involved in the computation.

While the convergence rate of Newton-Raphson method is quadratic, that of the steepest descent is linear. If only a poor

initial estimate of the solution is available, Newton's method becomes unpredictable and always fails if the Jacobian at any stage becomes singular. For some problems where a good initial estimate of the solution is not available, the method of steepest descent has been found to be effective and for this reason, hybrid algorithms based on the method of steepest descent followed by the application of Newton-Raphson method have been recommended. In the present algorithm we retain the fast convergence of Newton's method, but we modify the iteration so that it is progressive even if the guess x is far from the solution. A detailed description of the algorithm is given by Powell ⁹¹.

Haselgrove ⁹² observes that it is often worthwhile to use the correction δ , calculated from equation (3.3.5) as a search direction in the space to the variables. Haselgrove's iteration replaces x by $(x + \lambda \delta)$ where the value of the parameter λ is calculated by a search process, which tries to make the estimate $(x + \lambda \delta)$ better than the estimate x , the criterion being the inequality

$$F(x + \lambda \delta) < F(x) \tag{3.3.11}$$

where $F(x)$ is the sum of squares of residuals

$$F(x) = \sum_{k=1}^n [f_k(x)]^2 \tag{3.3.12}$$

Following Marquardt ⁸⁵ and Levenberg, ⁸⁴ Powell ⁹¹ modifies

the Newton iteration so that it converges from a poor initial

estimate of the required vector x , by introducing a parameter λ^* into the "normal least square" formulation of equation (3.3.5)

$$\sum_{j=1}^n \left\{ \sum_{k=1}^n J_{ki} J_{kj} \right\} \delta_j = - \sum_{k=1}^n J_{ki} f_k(x) \quad (3.3.13)$$

Specifically, a correction vector δ^* is obtained by solving the set of linear equations

$$\sum_{j=1}^n \left\{ \lambda^* I_{ij} + \sum_{k=1}^n J_{ki} J_{kj} \right\} \delta_j^* = - \sum_{k=1}^n J_{ki} f_k(x) \quad (i = 1, \dots, n) \quad (3.3.14)$$

where I is the unit matrix. The Levenberg - Marquardt iteration changes an estimate of x to the estimate $(x + \delta^*)$, the length of the correction being regulated by the value of λ^* . The inequality

$$F(x + \delta^*) < F(x) \quad (3.3.15)$$

can be achieved if λ^* , the positive parameter, is sufficiently large provided that the functions $f_k(x)$ have continuous first derivatives and that the components of the gradient of $F(x)$ are not all equal to zero at the initial estimate x of the iteration.

To begin the k^{th} iteration, an estimate of the solution $x^{(k)}$, a step length $\Delta^{(k)}$ and two numbers E and M are required. The step length can be changed on each iteration and its purpose

is to restrict the length of the displacement $(x^{k+1} - x^k)$ in order that the iteration decrease the value of $F(x)$. However, provided $F(x)$ is decreased substantially, Δ^k may be kept large as otherwise unnecessarily large number of iterations would be applied. The numbers E and M are assigned fixed positive values before the iteration begins and they govern the conditions for completing the iteration process. It finishes if the value of $F(x)$ is reduced to less than E or alternately if the gradient of $F(x)$ is so small that the distance from x to a solution is predicted to exceed M . Therefore E is set to a very small value in order that the condition

$$\sum_{i=1}^n [f_i(x)]^2 < E \quad (3.3.16)$$

implies that x is acceptably close to the nonlinear equations and M is usually set to an overestimate of the distance from $x^{(1)}$ to the solution

First the k^{th} iteration calculates the elements of the Jacobian matrix (3.3.6) at x^k and then it evaluates both the full Newton-Raphson correction $\delta^{(k)}$ (by solving the linear system of equations (3.3.5) and also the gradient $g^{(k)}$ of $F(x)$ at $x^{(k)}$, by calculating the components

$$\begin{aligned} g_j^{(k)} &= \left[\frac{\partial}{\partial x_j} F(x) \right]_{x = x^{(k)}} \\ &= 2 \sum_{i=1}^n \left[f_i(x) \frac{\partial}{\partial x_j} f_i(x) \right]_{x = x^{(k)}} \end{aligned} \quad (3.3.17)$$

It then tries the test

$$F(x^{(k)}) \geq M \|g^{(k)}\|_2 \quad (3.3.18)$$

and if it holds we finish iterating because of the likelihood that the sequence of estimates of $x^{(k)}$ is converging not to a solution of the equations, but to a local minimum of $F(x)$. This test is justified because $\|g^{(k)}\|_2$ is the steepest slope of $F(x)$ at $x^{(k)}$ and therefore it seems that the length of the change in $x^{(k)}$ that is needed to reduce $F(x)$ to zero will have to exceed M which is wrong if M is specified in the recommend way.

If the condition (3.3.18) does not hold then we calculate the displacement $\delta^{(k)}$ to add to the vector $x^{(k)}$. This displacement is the classical correction $\delta^{(k)}$ if $\Delta^{(k)} \geq \|\delta^{(k)}\|_2$.

But if $\Delta^{(k)} < \|\delta^{(k)}\|_2$ then we make the length $\bar{\delta}^{(k)}$ equal to $\Delta^{(k)}$. In this case the displacement has the form

$$\bar{\delta}^{(k)} = \alpha_1 \delta^{(k)} + \beta_1 g^{(k)} \quad (3.3.19)$$

where α_1 and β_1 are scalars. In fact we let $\alpha_1 = 0$ if the step along the steepest descent vector of $F(x)$

$$\bar{\delta}^{(k)} = -\Delta^{(k)} g^{(k)} / \|g^{(k)}\|_2 \quad (3.3.20)$$

does not go beyond the predicted minimum of $F(x)$ along the steepest descent vector from $x^{(k)}$. This predicted minimum is at the

$$x^{(k)} - \left\{ \frac{1}{2} \|g^{(k)}\|_2^2 / \|J^{(k)} g^{(k)}\|_2^2 \right\} \quad (3.3.21)$$

so we try the condition

$$\Delta^{(k)} < \frac{1}{2} \|g^{(k)}\|_2^3 / \|J^{(k)} g^{(k)}\|_2^2 \quad (3.3.22)$$

and if (3.3.18) and (3.3.22) hold good, then $\bar{\delta}^{(k)}$ is defined by equation (3.3.20). In the case that condition (3.3.18) holds, but condition (3.3.22) does not, then we let the point $\{x^{(k)} + \bar{\delta}^{(k)}\}$ be on the straight line joining the point (3.3.21) to the point $\{x^{(k)} + \delta^{(k)}\}$, the actual components of $\delta^{(k)}$ being determined using the extra condition $\|\bar{\delta}^{(k)}\|_2 = \Delta^{(k)}$.

The next stage of the iteration is to try to estimate $(x^{(k)} + \bar{\delta}^{(k)})$, so we calculate the functions $f_i(x)$, ($i = 1, \dots, n$) at this point. If the expected inequality

$$F(x^{(k)} + \delta^{(k)}) < F(x^{(k)}) \quad (3.3.23)$$

holds, then the iteration defines $x^{(k+1)} = x^{(k)} + \bar{\delta}^{(k)}$ and we try the convergence test (3.3.15) at $x^{(k+1)}$. However if (3.3.23) fails we let $x^{(k+1)} = x^{(k)}$ and test (3.3.24)

$$F(x^{(k)} + \bar{\delta}^{(k)}) > (1 - \zeta) F(x^{(k)}) + \zeta \Phi^{(k)} \quad (3.3.24)$$

leads to a reduction in the step length $\Delta^{(k)}$. Thus the iteration revises the estimate $x^{(k)}$ using only one calculation of the left hand sides of the system of equations (3.3.3).

The last stage of the iteration revises the step length $\Delta^{(k)}$. This calculation depends on the predicted value of the sum of squares of the residuals at $x^{(k)} + \bar{\delta}^{(k)}$, namely

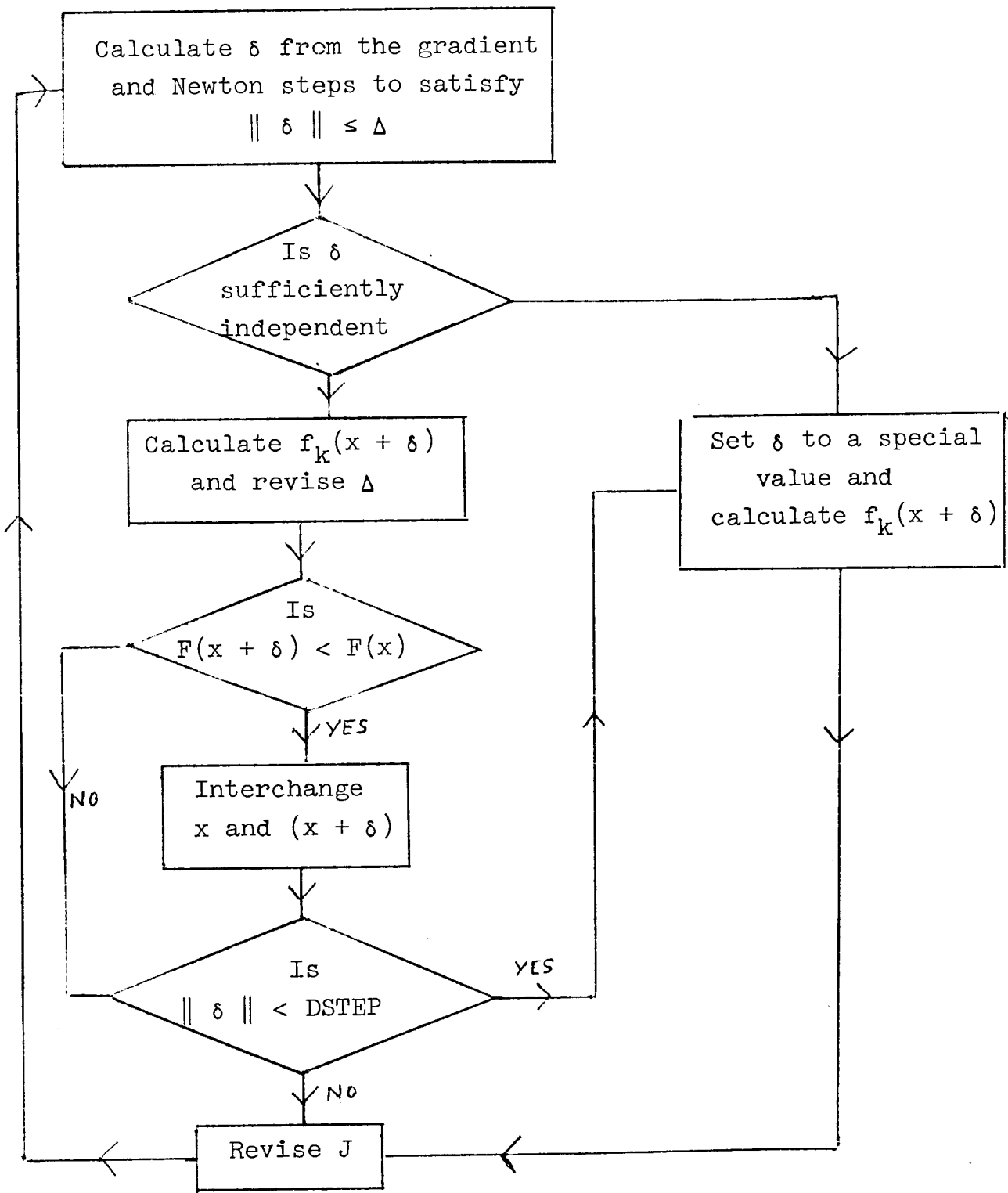
$$\Phi^{(k)} = \left\{ f_i(x^{(k)}) + \sum_{ij} J_{ij}^{(k)} \bar{\delta}_j^{(k)} \right\}^2 \quad (3.3.25)$$

which is less than $F(x^{(k)})$. If it is found that this prediction is so bad that the actual value of the sum of squares satisfies the inequality (3.3.24) then it is assumed that the linear approximations to the functions $f_i(x)$, derived from the Jacobian elements (3.3.6) are not adequate over the distance $\| \delta^{(k)} \|_2$. Therefore $\Delta^{(k)}$ is reduced and is multiplied by a constant in the interval $[0,1]$.

To begin an iteration, the following data are required:

- (a) a vector of variables x which is an estimate of the solution of the equations (3.1.3) and the corresponding function values $f_i(x)$ ($i = 1, \dots, n$),
- (b) an approximation to the Jacobian J ,
- (c) the inverse matrix J^{-1} ,
- (d) a matrix Ω of n directions in the space of variables and an associated vector of integers ω ,
- (e) a step length Δ .

The iteration process is outlined in the flow chart :



The functions $f_k(x)$ ($k = 1, 2, \dots, n$) defining the system of non-linear equations is defined by a separate subroutine.

For the majority of practical problems it is not possible to express the Jacobian explicitly and in these cases it is necessary to use an approximation J to the Jacobian. A simple method for obtaining this is by using the forward difference formula to approximate the partial derivative. If $J = J_{ij}$

$$J_{ij} = \frac{f_i(x + \text{DSTEP} \cdot e_j) - f_i(x)}{\text{DSTEP}} \quad (3.3.26)$$

where e_j is the normalized j th coordinate vector.

A fundamental difficulty inherent in this form of approximation is the choice of DSTEP. This parameter has been chosen arbitrarily, but required adjustment by trial and error so that it is not so small as to cause rounding error or so large to cause truncation error. In order to begin the k th iteration we require the matrix elements of $J_{ij}^{(k)}$ and we also require the elements of the inverse of $J^{(k)}$ which can be defined as the matrix

$$H^{(k)} = \{ J_{ij}^{(k)} \}^{-1} \quad (3.3.27)$$

Before the first iteration, $J^{(1)}$ is obtained from finite differences along the coordinate directions and then $H^{(1)}$ is calculated using a matrix inversion subroutine.

Given the elements $J_{ij}^{(k)}$ and $H_{ij}^{(k)}$ and given the other quantities that are needed to commence an iteration, we first

calculate the components

$$g_{ij}^{(k)} = 2 \sum_{j=1}^n f_i(x^{(k)}) J_{ij}^{(k)} \quad (j = 1, \dots, n) \quad (3.3.28)$$

and then instead of solving the linear system of equations (3.3.5), the components of $\delta^{(k)}$ are calculated by using the formula

$$\delta_i^{(k)} = - \sum_{j=1}^n H_{ij}^{(k)} f_j(x^{(k)}) \quad (3.3.29)$$

The method of revising the Jacobian approximation depends on the vector δ and on the differences γ^k

$$\gamma^k = f_k(x + \delta) - f_k(x) \quad (k = 1, \dots, n) \quad (3.3.30)$$

The revised matrices J^* and H^* are

$$J^* = J + (\gamma - J \delta) \underline{\delta} / \|\delta\|^2 \quad (3.3.31)$$

$$H^* = H + (\delta - H \gamma) \underline{\delta} H / (\delta H \gamma) \quad (3.3.32)$$

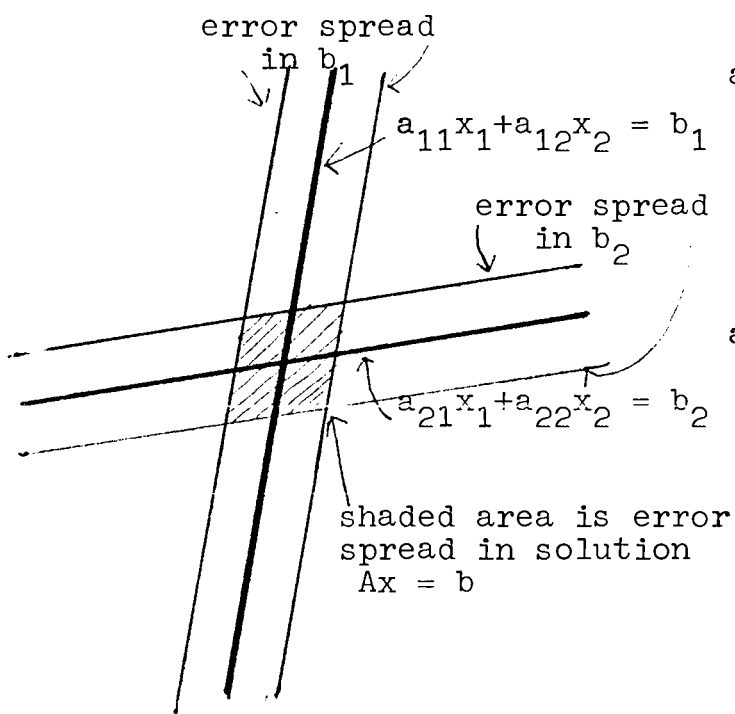
The method used for revising the Jacobian requires that the correction vector δ are linearly independent. In the course of iterations it might happen that the dependent directions are introduced and it is necessary that the program maintains a linear independence.

In any set of linear equations the solution when it exists is the point of intersection between the straight lines. Furthermore a unique solution exists if and only if the lines are not parallel or equivalently if and only if their normals are linearly independent or non-collinear. In particular one may have diffi-

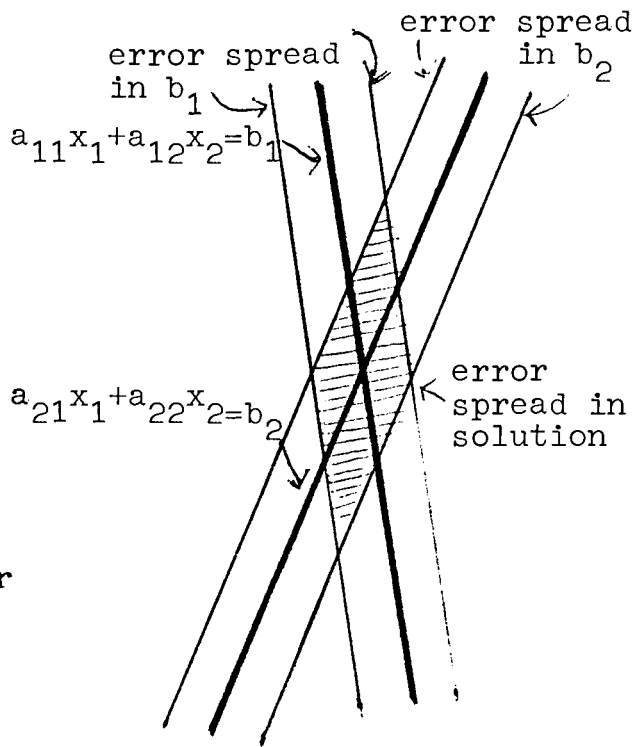
culty if the lines are nearly parallel because the solution may be highly sensitive to small changes in the positions of the lines caused by round off errors in computation. Diagrammatically, for the set of two equations

$$a_{11}x_1 + a_{12}x_2 = b_1 \tag{3.3.33}$$

$$a_{21}x_1 + a_{22}x_2 = b_2$$



Well conditioned case



Ill conditioned case

This kind of numerical instability might lead to poor resolution of the solution of the problem. With this in mind, we ensure that the correction vector δ is independent of a set of directions only if the least angle between δ and some vector in the space spanned by the directions is not less than, say, 30 degrees.

Since we start with a set of orthonormal vectors, the problem can be simplified and we ensure that the new directions are also orthonormal.

3.4 THE PARAMETER V

An important aspect of the present method concerns the parameter V and its evaluation. The orbital overlap matrix W is related to V by eq.(2.2.15)

$$W = V^\dagger V$$

For a given W , there are infinite values of V and choice of the optimum V from among them is difficult. On the other hand for a given V there is only one unique value for the overlap matrix W ; however the initial choice of V is difficult.

In view of the fact that W is physically meaningful, we have followed a method by which a V is obtained from an arbitrary W by a diagonalization procedure. It must be pointed out that such a choice of V may not lead to an optimum value of the parameter with respect to the total energy.

CHAPTER IV

APPLICATION TO BERYLLIUM

4.1 GENERAL COMMENTS

Viewed from the broad perspective, a theoretical understanding of the many body problem obviously requires a fundamental knowledge of the electronic structure of atoms. Although complex in itself, considerable progress has been made in the calculation of the electronic properties of simple atoms, particularly those with few electrons. With the help of high speed computers it is now possible to calculate almost any electronic property of two electron systems with a high degree of accuracy.

The problem becomes more complicated as the number of electrons in the system increase. The Hylleraas method which has been so successful for two electron systems becomes computationally formidable for systems with $Z > 3$. On the other hand the CI method offers a better scope in terms of computational feasibility, but the limits of accuracy depend on the number of configurations included in the expansion. Because of this convergence difficulty the CI wave function loses much of the physical meaning attributed to the Hartree-Fock model on which it is based.

As a test of our MC-SCF formalism with non-orthogonal orbitals, we have calculated the ground state energy of Be atom. Beryllium was chosen for the following reasons:

- (a) As a test case, Be retains all the complications of a many body problem beyond the simple He atom;
- (b) A number of highly sophisticated calculations on Be exist making it possible for a meaningful comparison with our

results.

4.2 PREVIOUS WORK ON BERYLLIUM

Boys⁹³ in his pioneering work on configuration interaction has published a 10 configuration wave function for Be. By a careful choice of exponents and configurations, Boys was able to obtain nearly two-thirds of the correlation energy and reported an energy of -14.637 a.u.

Kibartas, Kavetskis and Yutsis⁶⁵ used a numerical Hartree-Fock procedure in their three configuration calculation. Their surprisingly close value of -14.642 accounts for about 70% of the correlation energy. From the point of view of the present work, the result of Kibartas et.al. is particularly significant because the three configurations they used are non-orthogonal. Another important aspect of their calculation is the excellent choice of configurations involved in the build up of their total wave function. Apart from the basis $1s^2 2s^2$, the other two configurations are $1s^2 p_I^2$ and $2s^2 p_{II}^2$ where the p_I is a numerical Hartree-Fock one-electron solution for a p function in Be $1s^2 p_I^2$ and similarly for the p_{II} .

Another calculation involving non-orthogonal orbitals has been reported by Brigman et.al.⁹⁴ where singlet open shells are formed by linear combination of s-type Slater determinants. Of particular interest to us are the following:

TABLE I

Configuration	Energy(a.u)
Hartree-Fock single config. ¹²²	-14.570
$1s^2 2s^2$	-14.557
$1s^2 2s 2s'$ *	-14.558
$1s 1s' 2s^2$	-14.580
$1s 1s' 2s 2s'$	-14.5815

It may be noted that the opening of the 1s level makes an appreciable improvement in the energy whereas opening of the 2s level makes little improvement.

Szasz and Byrne⁹⁵ have used the Hylleraas method with a starting Hartree function for Be and obtained an energy of -14.6175 a.u. Only binary correlations are included in their calculation and even in this case the mathematical complexity of evaluating the integrals is apparent.

A number of configuration interaction calculations on Be have been done by various authors and these are summarized in table II.

* The primes indicate orbitals that are virtually identical to the corresponding unprimed ones. The overlap between the 2s and 2s', for example, would be large, probably of the order of 0.9.

TABLE II

Method	Type of orbitals	Number of configs.	% correlation	Energy (a.u)
Boys ⁹³	Orthogonal	10	66	-14.637
Yutsis ⁶⁵	Non-orthogonal	3	73.4	-14.642
Matsen ⁹⁴	Non-orthogonal	1		-14.5815
Watson ⁸⁷	Orthogonal	37	89.5	-14.6574
Weiss ⁹⁷	Orthogonal	55	94.5	-14.6609
Yutsis ⁹⁸	Non-orthogonal		96.5	-14.666

There are some second order perturbation calculations which are of poor accuracy in comparison with the CI method^{99,100}.

Recently there have been several calculations on the correlation energy of Be atom using perturbation theory or Bethe-Goldstone procedure, where generally only pair correlations are included. Although the results obtained by these methods are undeniably more accurate, there are some fundamental questions that may be raised regarding the validity of the additivity of pair functions. The separation of the total correlation energy into intra- and inter shell correlations does not seem to be unique and strongly depends on the order in which the correlating configurations are added⁷⁸.

TABLE III

Comparison of Be atom calculations using perturbation methods

Method	Correlation energy			Total	%	Energy (a.u)
	$1s^2$	$2s^2$	$1s-2s$			
Kelly ⁹⁹	0.04212	0.04387	0.00497	0.09096	96.5	-14.66307
Nesbet ¹⁰⁰	0.04183	0.04535	0.00586	0.09212	97.6	-14.66514
Geller ¹⁰¹ et.al	0.04208	0.04438	0.00497	0.09143	97.0	-14.66439
Byron ¹⁰² et.al	0.0425	0.0448	0.0052	0.0925	97.9	-14.6655

One of the first exhaustive CI studies of Be atom was carried out by Watson⁸⁷ using 37 terms in the expansion and taking $1s^2 2s^2$ Hartree-Fock function as the leading term. The orthogonal basis included 6 s-type functions, 5 p-type functions, 4 d-type functions, 2 f-type functions and 2 g-type functions. The final wave function gives an energy of -14.65740 corresponding to about 89.5% of the correlation energy.

Weiss⁹⁷ has published a 55 term configuration interaction study of Be using 7 of s-type, 5 of p-type, 3 of d-type and 2 of f-type functions. In this case the basis functions are non-orthogonal. Weiss obtains an energy of -14.66090 corresponding to about 93% of the correlation energy.

Sims and Hagstrom¹⁰³ have recently carried out an extensive calculation on Be using a combination of Hylleraas and CI methods. Their method is a hybrid one in the sense that an

additional correlation factor r_{ij} is introduced in the configuration that make the largest contribution to the total wave function. Only unlinked type of interelectronic coordinates have been considered. Using 107 configurations, Sims and Hagstrom were able to obtain an energy of -14.66654 which differs from the exact value by only 0.0002 atomic units. Although their results are the most accurate to date, such a large number of configurations are included that physical intuition becomes particularly difficult to apply in trying to understand their results.

TABLE IV
Results of Sims and Hagstrom¹⁰³

Number of terms	Type	Energy(a.u)
59 term	Hylleraas	-14.66325
92 term	Hylleraas	-14.66358
107 term	Hylleraas + CI	-14.66654

One of the most sophisticated and rapidly convergent configuration interaction wave function for Be has been obtained by Bunge¹⁰⁴. Bunge's calculations are based on natural orbital concepts and involve a number of new ideas. As a first step, Bunge makes an ordinary SCF calculation using a large set of

Slater type basis functions. Then a CI calculation is carried out including the restricted Hartree-Fock configuration $1s\alpha 1s\beta 2s\alpha 2s\beta$ plus all possible doubly excited configurations whose orbital occupancies may be specified $x_i x_j 2s^2$ and $1s^2 x_i x_j$ where x_i and x_j are all orbitals in the basis set other than the SCF orbitals $1s$ and $2s$. From the expansion coefficients of this wave function the density matrix is formed which is diagonalized to give a set of natural orbitals.

One of the most difficult aspects of a CI calculation is the choice of configurations that make important contributions to the total wave function. Bunge uses perturbation methods in the search for such important configurations and performs a CI calculation using 180 configurations and the natural orbitals obtained in the first step of the calculation.

Bunge's calculation suggests an important application of natural orbitals in performing a CI calculation. Although his calculation accounts for 99.6% of the correlation energy, this requires inclusion of p, d, f and g type of orbitals in achieving the claimed accuracy. Consequently physical insight about the nature of the wave function is lost. Furthermore, the calculations are very complicated and inconceivable without the aid of a large computer.

The most important single configuration has been found to be $1s^2 2p^2$ in agreement with the results of Watson. Bunge's detailed analysis enabled him to assign upper limits to the energy and correlation energy.

TABLE V

Contributions of orbitals with different l values
to the correlation energy of Be

Energy (s limit)	-14.59202 a.u
% Correlation energy	20.3
Energy (sp limit)	-14.66080 a.u
% Correlation energy	94.0
Energy (spd limit)	-14.66453 a.u
% Correlation energy	98.0
Energy (spdf limit)	-14.66570 a.u
% Correlation energy	99.3
	-
Energy (spdfg limit)	-14.66598 a.u
% Correlation energy	99.6
* Exact non-relativistic energy =	-14.66731 a.u

Sabelli and Hinze⁷⁸ have performed an MC-SCF calculation on a number of atoms including Be. Their calculations are based on the MC-SCF formalism of Hinze and Roothaan⁷⁷. Using 10 configurations Sabelli and Hinze obtain an energy of -14.65464 a.u corresponding to 86.5% of the correlation energy. Apart from the $1s^2 2s^2$, the major contribution arises from the configuration $1s^2 2p^2$.

* Obtained by subtracting relativistic corrections from the experimental value.

In concluding this section, we may say that MC-SCF calculations in general are able to improve energy values and show excellent agreement with experimental results. Unfortunately the accuracy of the results seem to demand inclusion of a large number of independent configurations in the wave function. Apart from being computationally expensive, fundamental questions regarding the significance of many "virtual configurations" remain unanswered.

Most of the Be calculations we have reviewed use orthogonal orbitals. It is hoped that our non-orthogonal MC-SCF formalism may provide answers to some of these questions.

4.3 DETAILS OF THIS CALCULATION

As described in the theory, the MC-SCF procedure involves solution of two self consistent equations

$$h_i B_i = S \sum_j B_j \epsilon_{ji} \quad (4.3.1)$$

$$H C = E T C \quad (4.3.2)$$

The notations are the same as mentioned before and are given in pertinent sections.

Since the matrix elements of the operator h_i and the Hamiltonian \mathcal{K} are constructed from one- and two-electron integrals, our main purpose in this section is to describe the method used in evaluating these integrals. The rest of the calculation is straightforward and follows the theory very closely.

Consider a set of basis functions of the form

$$\chi_i = \left| R_{i\lambda}(r_\alpha)/r_\alpha \right| Y(\theta, \phi) \sigma_i(s) \quad (4.3.3)$$

where Y is a spherical harmonic and σ is a spin function with eigenvalues $m_s = +\frac{1}{2}$ or $-\frac{1}{2}$. The radial functions $R_{i\lambda}(r)$ can be completely arbitrary except that they are assumed to be linearly independent within sets of common symmetry λ (angular quantum number). These functions are chosen to be of the Slater type and are of the normalized form

$$R_{j\lambda} = N_j r^{\ell+n_j+1} e^{-\zeta_j r} \quad (4.3.4)$$

ℓ is the angular momentum quantum number, ζ_j and n_j are assigned parameters and N_j is the normalization constant given by

$$N_j = \frac{(2\zeta_j)^{2\ell+2n_j+3}}{(2\ell+2n_j+3)!} \quad (4.3.5)$$

The choice of the various parameters (particularly the screening parameter ζ) for a particular ℓ value is by no means simple.

The determination of optimum values of ζ_j is difficult and generally requires the computation of energies for several values of ζ_j 's followed by an interpolation. There appears to be no way of avoiding these repeated calculations to obtain a truly optimum orbital exponent. This obviously increases the labour of a CI calculation. Unfortunately it appears that accurate CI wave

functions using small numbers of basis functions require near optimum values of ζ^{105} .

For the ground state of Beryllium, the spherical symmetry of the atomic wavefunction allows the separation of the Hartree-Fock equations so that they depend on a single radial variable only. This statement is precisely true only in closed shell configurations^{10,11}, but it is generally a good approximation for atoms to express the orbitals as products of radial functions $R_\alpha(r)$, spherical harmonics $Y_{\ell m}(\theta, \phi)$ and spin eigenfunctions, so that we would use the same approximation even for excited state calculations on Be atom. Furthermore, use of the spherical symmetry enables us to apply the j-j coupling scheme in evaluating the two-electron integrals.

In general the choice of the various parameters for a particular calculation relies heavily on earlier work by others. In the present calculation we have used the basis functions given by Watson in his CI calculations on Be atom. This implies that we have adopted a modified form of option (a) mentioned in page 78, that is, that of choosing not very well optimized ζ 's and a relatively large number of basis functions. The values for ζ used by Watson^{87,111} are based on earlier work on He atom. Watson's results indicate that optimization of ζ is not very critical in the case of Be atom, provided one includes a sufficiently large number of basis functions. Additional care must be taken to ensure that no two basis functions are similar.

Having made a choice of basis functions, the next task is to assign appropriate coefficients B_{ij} to these functions to form initial guesses for the corresponding one electron orbitals. In the present calculation, we have used the expansion coefficients given by Watson^{87,111}.

The various parameters used in our calculation are summarized in tables VI and VII.

Evaluation of Integrals

In calculation the integrals, we have followed the method suggested by Nesbet¹⁰⁶ and Boys¹⁰⁷. Atomic units are used throughout.

In order to make the notation clear, let us define the following:

$$\langle i|K|j\rangle = \int \chi_i^*(1) K(1) \chi_j(1) d\tau \quad (4.3.6)$$

$$\langle ij|Q|kl\rangle = \int \int \chi_i^*(1) \chi_k^*(2) Q(1,2) \chi_j(1) \chi_l(2) d\tau_1 d\tau_2 \quad (4.3.7)$$

The matrix elements between orbitals can be easily expressed in terms of the primitive integrals (4.3.6) and (4.3.7) and expansion coefficients B_{ij} of eq.(2.4.1). For the one-electron

integral between orbitals φ_k and φ_1 we have

$$\langle \varphi_k | K | \varphi_1 \rangle = \sum_p \sum_r B_{kp} B_{1r} \langle \chi_p(1) | K(1) | \chi_r(1) \rangle \quad (4.3.8)$$

Similarly for the two electron integrals between orbitals, we have

$$\langle \varphi_i \varphi_j | Q | \varphi_k \varphi_1 \rangle = \sum_p \sum_q \sum_r \sum_s B_{ip} B_{1s} B_{jq} B_{kr} \langle \chi_i(1) \chi_1(2) | Q(1,2) | \chi_j(1) \chi_k(2) \rangle \quad (4.3.9)$$

In view of equations (4.3.8) and (4.3.9), we need consider only details of the evaluation of primitive integrals.

Using eq.(4.3.3) we can write for the overlap integral

$$\begin{aligned} \langle i | 1 | j \rangle &= \int \chi_i^* \chi_j \, dr \\ &= \delta_{\ell_i \ell_j} \delta_{m_{\ell_i} m_{\ell_j}} \delta_{m_{s_i} m_{s_j}} \int_0^{\infty} R_i(r) R_j(r) \, dr \end{aligned} \quad (4.3.10)$$

Similarly the one-electron integrals can be expressed in terms of the radial functions.

$$\langle i | -\frac{\nabla^2}{2} | j \rangle = \delta_{\ell_i \ell_j} \delta_{m_{\ell_i} m_{\ell_j}} \delta_{m_{s_i} m_{s_j}} \int_0^{\infty} R_i \left| -\frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{r^2} \right| R_j \, dr^2 \quad (4.3.11)$$

$$\langle i | \frac{Z}{r} | j \rangle = \delta_{\ell_i \ell_j} \delta_{m_{\ell_i} m_{\ell_j}} \delta_{m_{s_i} m_{s_j}} \int_0^{\infty} R_i \left| \frac{Z}{r} \right| R_j \, dr^2 \quad (4.3.12)$$

The two-electron operator $Q = 1/r_{ij}$ is more difficult to handle. In this case, in addition to the trivial orbital expansion coefficients, we will have to include the vector coupling coefficients. The derivation of these equations can be found in Condon and Shortley¹⁰⁹ or Rose¹¹⁰. In terms of the radial functions, the integral can be written as

$$\begin{aligned} \langle \chi_i(1)\chi_j(2) | Q(1,2) | \chi_k(1)\chi_l(2) \rangle = & \\ & \delta_{m_{s_i} m_{s_k}} \delta_{m_{s_j} m_{s_l}} \delta_{m_{l_i} + m_{l_j}, m_{l_k} + m_{l_l}} \sum_{k=0}^{\infty} \\ & C^k(l_i m_{l_i}, l_k m_{l_k}) C^k(l_l m_{l_l}, l_j m_{l_j}) R^k(ij,kl) \end{aligned} \quad (4.3.13)$$

where

$$\begin{aligned} R^k(ij,kl) &= R^K(n_i l_i n_j l_j, n_k l_k n_l l_l) \\ &= \int_0^{\infty} \int_0^{\infty} R_i(r_1) R_j(r_2) R_k(r_1) R_l(r_2) \frac{r_1^k}{r_2^{k+1}} dr_1 dr_2 \end{aligned} \quad (4.3.14)$$

The sum over k does not go to infinity since $k + l + l'$ must be even and $|l - l'| \leq k \leq |l + l'|$.

The coefficients C^k are integrals of products of three Legendre functions and are given by

$$C^k(l m_l, l' m_{l'}) = \sqrt{\frac{2}{2k+1}} \int_0^{\pi} \Theta(k, m_l - m_{l'},) \Theta(l m_l) \Theta(l' m_{l'}) \sin \theta d\theta \quad (4.3.15)$$

The Gaunt coefficients C^k are related to the Wigner coefficients by

$$\begin{aligned}
 C^k(\ell m_\ell \ell' m_{\ell'}) &= \left| \frac{2\ell'+1}{2\ell+1} \right|^{\frac{1}{2}} \begin{matrix} k & \ell' & \ell \\ A & 0 & 0 & 0 \\ & & & A \end{matrix} \begin{matrix} k & \ell' & \ell \\ m_\ell & -m_\ell' & m_\ell' & m_\ell \end{matrix} \\
 &= (-1)^{m_\ell} \left| \frac{2\ell'+1}{2\ell+1} \right|^{\frac{1}{2}} \begin{pmatrix} \ell & k & \ell' \\ -m_\ell & m_\ell & -m_\ell' & m_\ell \end{pmatrix} \\
 & \qquad \qquad \qquad \begin{pmatrix} \ell & k & \ell' \\ 0 & 0 & 0 \end{pmatrix} \quad (4.3.16)
 \end{aligned}$$

The main advantage of this formulation is that the angular integrals need be evaluated only once. Values of C^k are stored in 3 dimensional array.

From the foregoing discussion we find that two types of integrals have to be evaluated.

$$(K|ij) = \int d\tau_1 R_i^*(1) K(1) R_j(1) \quad (4.3.17)$$

and $R^k(ij,kl)$.

When the operator K is unity, the integral gives the overlap. When K is equal to $-\frac{1}{2}\nabla^2$ or $1/r$, the integral represents the one electron integral.

The actual evaluation of the integrals is done by means of recursion formulae^{106,107}. Define a function $T(x,y)$

$$T(x,y) = x!/y^{x+1} \quad (4.3.18)$$

$$T(0,y) = 1/y \quad (4.3.19)$$

$$T(x+1,y) = \{(x+1)/y\} T(x,y) \quad (4.3.20)$$

If we rewrite the basis function in a slightly condensed form

$$R_{j\ell} = N_j r^{A+\ell} e^{-\zeta_j r} \quad (4.3.21)$$

the overlap and one-electron integrals can be written as

$$(1 | ij) = T(A+B+2\ell+2, \zeta_i + \zeta_j) \quad (4.3.22)$$

$$\left(\frac{1}{r} | ij\right) = T(A+B+2\ell+1, \zeta_i + \zeta_j) \quad (4.3.23)$$

$$\left(-\frac{1}{2}\nabla^2 | ij\right) = \frac{1}{2} \left[\zeta_i \zeta_j T(A+B+2\ell+2, \zeta_i + \zeta_j) - (A\zeta_j + B\zeta_i) T(A+B+2\ell+1, \zeta_i + \zeta_j) + AB T(A+B+2\ell, \zeta_i + \zeta_j) \right] \quad (4.3.24)$$

Similarly the two-electron integrals are given by

$$R^k(ij, kl) = \sum_{r=0}^{M+1} \frac{(M+1)!}{(M+1-r)!} \frac{1}{u^{r+1}} T(P+Q+3-r, u+v) + \sum_{s=0}^{N+1} \frac{(N+1)!}{(N+1-s)!} \frac{1}{v^{s+1}} T(P+Q+3-s, u+v) \quad (4.3.25)$$

where

$$\begin{aligned} M &= P - k \\ N &= Q - k \\ P &= A + B + \ell_i + \ell_j \\ Q &= C + D + \ell_k + \ell_l \\ u &= \zeta_i + \zeta_j \\ v &= \zeta_k + \zeta_l \end{aligned}$$

We define a recursion formula

$$V_M(0, u) = \frac{1}{u} \quad (4.3.26)$$

$$V_M(r+1, u) = [(M-r)/u] V_M(r, u) \quad (4.3.27)$$

which allows us to express equation(4.3.25) as a sum of terms of the form

$$R^k(ij,kl) = \sum_r V_M(r,u) T(\quad) \quad (4.3.28)$$

The normalization constants can easily be calculated from eq.(4.3.22), $\langle j|1|j \rangle = N_j$, and are stored separately. The one- and two electron integrals will have to be multiplied by $N_p N_q$ and $N_p N_q N_r N_s$ respectively.

The program requires for each value of ℓ , lists of n_j and ζ_j for the basis functions. These are taken from Watson^{87,111} and are given in table VI, for calculations involving s-type functions only, and table VII, for calculations involving p-type functions also.

TABLE VI⁸⁷

Be basis function parameters

For the construction of s functions($\ell = 0$)			For the construction of p functions($\ell = 1$)		
j	n_j	ζ_j	j	n_j	ζ_j
1	1	6.0	10	1	9.0
2	1	1.0	11	1	1.5
3	2	6.0	12	2	9.0
4	2	1.0	13	2	1.5
5	3	6.0	14	3	9.0
6	3	1.0	15	3	1.5
7	4	6.0	16	4	9.0
8	4	1.0			
9	5	6.0			

TABLE VII¹¹¹Be basis function parameters

For the construction of s functions($l = 0$)			For the construction of p functions($l = 1$)		
j	n_j	ζ_j	j	n_j	ζ_j
1	1	6.8783	8	2	2.7633
2	1	4.4293	9	2	1.3601
3	1	3.1111	10	2	0.9909
4	2	2.6147	11	2	0.6044
5	2	1.5166			
6	2	0.9681			
7	2	0.6425			

In eq.(4.3.14) orbitals i and j have the same quantum number l_α and orbitals k and l have the same quantum number l_β . Hence only two kinds of integrals are present: direct integrals of the form $(l_\alpha l_\alpha | Q | l_\beta l_\beta)$ and exchange integrals of the form $(l_\alpha l_\beta | X | l_\alpha l_\beta)$. The entire set of two electron integrals that contribute to the Fock operator can be classified into blocks with common values of l_α and l_β . A natural ordering of these blocks is to arrange them in order of increasing index pairs $(l_\alpha l_\beta)$ where $l_\alpha \geq l_\beta$. The sequential ordering of elements in these blocks takes advantage of the fact that $(ij | Q | kl)$ is sym-

metric in (i,j) , symmetric in (k,l) , and symmetric in $(ij),(kl)$ whenever the corresponding l quantum number is the same.

To deal with the overlap matrix T in the eigenvalue equation arising in the CI part, eq.(4.3.2), a Lowdin transformation matrix $T^{-\frac{1}{2}}$ is constructed in the following way.

Using an arbitrary unitary matrix U , diagonalize T such that

$$U^\dagger T U = \lambda \quad (4.3.29)$$

where λ are the corresponding eigenvalues. Then it is easily seen that

$$U \lambda^{-\frac{1}{2}} U^\dagger = T^{-\frac{1}{2}} \quad (4.3.30)$$

where $\lambda^{-\frac{1}{2}}$ is the inverse of $\lambda^{\frac{1}{2}}$. This method avoids the problem of convergence that is often encountered in the binomial expansion suggested by Lowdin¹⁴.

In each iterative cycle, the Hamiltonian matrix of the eigenvalue equation (4.3.2) is transformed into

$$H' = T^{-\frac{1}{2}} H (T^{-\frac{1}{2}})^\dagger \quad (4.3.31)$$

whose eigenvectors satisfy the standard linear eigenvalue equation

$$H \tilde{C}' = E \tilde{C}' \quad (4.3.32)$$

A fast Jacobi method is used for this procedure. The eigenvectors in the old basis of eq.(4.3.2) obtained by the transformation

$$C = T^{-\frac{1}{2}} C' \quad (4.3.33)$$

4.4 SCF PROCEDURE FOR SOLVING THE HARTREE-FOCK EQUATIONS

The method that we have adopted is due to Powell¹¹⁷ and has some advantages over similar iterative techniques proposed by other workers^{77,112,113}. It belongs to the class of least square methods and uses a Newton-Gauss iteration where the search direction is biased in the steepest descent direction. Details of implementation of the method are given in section 3.3 and the algorithm closely follows the description.

As an initial step, the algorithm calculates a correction δB to apply to B . This correction is a compromise between a Newton iteration and the steepest descent method. The balance between these two methods is governed by the step length Δ , so that if Δ is large, the correction is a pure Newton step and the convergence is quadratic. For very small values of Δ , the vector δB is exactly a multiple of the predicted gradient of $F(B)$ and in general the correction is such that the sum of the squares $F(B+\delta B)$ is predicted to be less than $F(B)$. However the non-linearity in the function $f_k(B)$ may influence the above prediction. Besides, a very small step length means an unnecessarily large number of iterations. Therefore the algorithm includes a method of revising the step length Δ so that the condition

$$F(B + \delta B) < F(B) \quad (4.4.1)$$

is always maintained.

The choice of the input parameter DSTEP is important since its magnitude determines the limit in the course of revision of Δ . Our choice of DSTEP is based on a large number of trials and is performed for each new wavefunction.

Another important point is that the method of revising the Jacobian J depends on the displacement vector δB and on the differences

$$Y_k = f_k(B + \delta B) - f_k(B) \quad (4.4.2)$$

These differences are liable to be dominated by round off errors if δB is too small, so we include the precaution of setting δ to a special value $\|\delta\| < \Delta$

Iterative methods such as these could fail if the matrix of the Jacobian becomes singular. Our method of revising the Jacobian is such that we should avoid linear dependence in the directions that are generated by the successive iterations of the algorithm. The revised Jacobian is required to satisfy the conditions

$$\sum_{j=1}^n J_{kj} \delta B_j = Y_k \quad (4.4.3)$$

which would hold if the Jacobian were exact. According to Broyden¹²¹, the new Jacobian J^* is obtained from the formula

$$J^* = J + (Y - J \delta B) \delta B / \|\delta\|^2 \quad (4.4.4)$$

Formula (4.4.4) demands that we insure sufficient independence of successive displacement δB .

4.5 METHOD OF OBTAINING THE PARAMETER V

An integral part of the present method is the choice of a suitable V which is the parameter that occurs in the inverted form as a transformation matrix in eq.(2.4.28). The overlap matrix W between the orbitals is related to this parameter by

$$W = V^\dagger V \quad (4.5.1)$$

Initial choice of an acceptable V is difficult; on the other hand W is physically meaningful and an acceptable choice of W is relatively easy. We have therefore used the following procedure to obtain the parameter V . The overlap matrix can be written as

$$W = W^{\frac{1}{2}} U^{-1} U W^{\frac{1}{2}} = V^\dagger V \quad (4.5.2)$$

where U is any arbitrary unitary matrix. The right hand side of eq.(4.5.2) is Hermitian regardless of V , since $(V^\dagger V)^\dagger = V V^\dagger$. This necessarily implies the existence of W being Hermitian. If V is non-singular, then, so is W and we get

$$U = V (W^{\frac{1}{2}})^{-1} \quad (4.5.3)$$

Furthermore since W is Hermitian, it is semisimple and its eigenvalues are real.

Equation (4.5.3) enables us to obtain a V

$$V = U W^{-\frac{1}{2}} \quad (4.5.4)$$

where $W^{-\frac{1}{2}}$ is the inverse of $W^{\frac{1}{2}}$.

It is easy to see that W is positive definite (apart from the fact that W is the overlap matrix; this may be treated as a special case) since for any non-null matrix X we have

$$X W X^\dagger = X V^\dagger V X^\dagger = (X V^\dagger)(V^\dagger X)^\dagger = Y Y^\dagger$$

which is real and positive and Y is non-null as long as X is. Hence the eigenvalues of W are positive. This justifies the definition of $W^{\frac{1}{2}}$ as

$$W^{\frac{1}{2}} = S \left[\text{diag}(\lambda_1, \lambda_2, \dots, \lambda_n) \right] S^{-1} \quad (4.5.5)$$

where $\lambda_1^2, \lambda_2^2, \dots, \lambda_n^2$ are the eigenvalues of W and S is unitary.

There is an important theorem which proves that a positive definite Hermitian matrix has a unique square root that is also positive definite.

CHAPTER V

RESULTS AND DISCUSSION

5.1 RESULTS AND DISCUSSION

Watson's data on the configuration interaction study of Be atom forms the basis for comparison with the results of our calculations^{96,111}. As shown in table II, Watson's 37-term expansion accounts for 89.5 % of the correlation energy of Be atom.

Apart from the Hartree-Fock orbital $1s^2 2s^2$, the most important s-type single configuration appears to be $2s^2 s_I^2$. Table VII shows our results for a two configuration calculation both for the orthogonal and non-orthogonal cases.

TABLE VIII

Configuration: $1s^2 2s^2 + 2s^2 s_I^2$

Value of $\langle 1s s_I' \rangle$	Energy(a.u)
0.00000	-14.58370
0.03103	-14.58265
0.08923	-14.58282
0.10596	-14.58401
0.12232	-14.58576
0.13828	-14.58815
0.15408	-14.58548

In general, the primed orbitals are obtained from the corresponding unprimed Watson orbitals. For example, the starting orbital expansion coefficients for the s_I' orbital are obtained from Watson's s_I data

by slight adjustment and subsequent renormalization. The s_I , s_{II} , etc. are virtual orbitals with s-type symmetry.

Removal of the orthogonality constraint on the 1s orbital results in a significant improvement in energy. This means that the charge densities of 1s and s_I orbitals are not strictly localized in their respective orbital regions. It is worthwhile to compare our results with that of Brigman et.al.⁹⁴ shown in table I. Although they claim to have used non-orthogonal orbitals, our results are superior, which among other things may be due to a better choice of basis functions. Brigman et.al.'s paper is only sketchy and a detailed analysis and comparison is not possible.

From Watson's calculations we find that the total contributions to energy from all the s-type orbitals including single and double substitution configurations add up to a total of -14.58640 a.u. Using non-orthogonal orbitals we are able to obtain a much more rapidly convergent energy. For example, with non-orthogonal orbitals a two configuration $1s^2 2s^2 + 2s^2 s_I^2$ provides most of the correlation energy that Watson has reported with all the s-type configurations: $1s^2 2s^2 + 2s^2 s_I^2 + 1s 2s s_I^2 + 2s^2 s_{III}^2 + 2s^2 s_I s_{II} + 2s^2 s_{III} s_{IV} + 2s^2 s_I s_{IV} + 2s^2 s_{IV}^2$. This conclusion is already known from the results of Kibartas et.al.⁶⁵ where their 3 configuration calculation is found to show comparable total energy to Watson's 37-term value.

We have done a number of calculations involving non-orthogonal s-type orbitals. The main aspects of these results

are shown below and detailed tabulations are given in appendix III.

TABLE IX

Configuration: $1s^2 2s^2 + 1s' 2s' s_I^2$

Value of $\langle 1s 1s' \rangle$	Energy(a.u)
1.00000	-14.57303
0.96610	-14.57347
0.87731	-14.57489
0.85503	-14.57528
0.80682	-14.57616
0.77705	-14.57671
0.76516	-14.57671

TABLE X

Configuration: $1s^2 2s^2 + 2s^2 s_I^2 + 1s' 2s' s_I^2$

Value of $\langle 1s 1s' \rangle$	Energy(a.u)
1.00000	-14.58486
0.96610	-14.58519
0.85503	-14.58608
0.80682	-14.58645
0.77705	-14.58666
0.76516	-14.58664

The results of our entire calculations are summarized in table XVI.

TABLE XI

Configuration: $1s^2 2s^2 + 2s^2 s_I'^2 + 2s^2 s_{II}'^2$

Value of $\langle s_I' s_{II}' \rangle$	Energy(a.u)
0.00000	-14.58484
0.02128	-14.58309
0.03723	-14.58592
0.04654	-14.58773
0.06776	-14.59247
0.07140	-14.60486
0.08084	-14.60057

TABLE XII

Configuration: $1s^2 2s^2 + 2s^2 s_I'^2 + 1s^2 s_{II}'^2 + 2s^2 s_{II}'^2$

Value of $\langle 1s s_{II}' \rangle$	Energy(a.u)
0.00000	-14.58636
0.01884	-14.58430
0.05629	-14.58349
0.07493	-14.58732
0.09345	-14.58369

As shown in tables XI and XII, we have obtained energy values below the so-called "limits" set by Bunge in table V. The value reported

by Yutsis et.al.⁹⁸ in table II, presumably using only s- and p-type orbitals, is also below the sp limit shown in table V. Perhaps, such rigorous limits can only be established for orthogonal orbitals.

Among all the configurations considered by Watson, the most important contribution comes from $1s^2 2p^2$. This fact has been reported by many authors^{65,104}, and is believed to be due to a strong mixing of the $1s^2 2s^2$ and $1s^2 2p^2$ configurations arising from the near degeneracy of the 2p and 2s orbitals.

In the case of two electron systems such as helium and its isoelectronic species, the discrepancy between the Hartree-Fock and the "true" wavefunctions can be satisfactorily accounted for in terms of two particle correlations and the correlation energy is nearly independent of nuclear charge. Early estimates of the correlation energy of many electron systems led to the belief that the correlation energy can be expressed in terms of pair correlations. Furthermore, it was believed that the correlation energy per pair of electrons is a constant for electrons that differ only in their m_s values. This view was strengthened by the observation that the correlation energy of Be is almost twice that of a two electron system. This view was shown to be wrong by the studies of Kibartas et.al.⁶⁵, Linderberg and Shull¹¹⁷ and Watson⁸⁷. The superposition of the configuration $1s^2 2p^2$ to the Hartree-Fock $1s^2 2s^2$ improves the energy by 0.04116 a.u. corresponding to 43.5 % of the correlation.

Watson has performed a two configuration calculation¹¹¹ on Be with

$$\psi = a(1s^2 2s^2) + b(1s^2 2p^2)$$

and obtained an energy of -14.61652 a.u. Although this calculation uses only 7 basis functions (table VII), the resulting energy is lower than an earlier calculation using 9 basis functions (table VI). This is perhaps due to a better choice of orbital exponents.

We have performed a number of calculations using two configurations

$$\psi = A(1s^2 2s^2) + B(1s' 2p^2)$$

with 1s and 1s' non-orthogonal to each other. The results of these calculations are shown in table XIII. A very important conclusion that is apparent from the table is that the removal of orthogonality constraint does not lead to a lowering of the energy as might be expected.

TABLE XIII

Configuration: $1s^2 2s^2 + 1s' 2p^2$

Value of $\langle 1s 1s' \rangle$	Energy(a.u)
1.00000	-14.61652
0.99925	-14.61321
0.99625	-14.60790
0.99607	-14.60353
0.99479	-14.60386
0.96835	-14.58021

This is the only calculation where removal of the orthogonality constraint does not lead to a lowering of energy. It may be because of the approximation involved in obtaining solutions to the SCF equations. However, we would to rule out this possibility and accept this as a valid observation. The major arguments in support of this belief are as follows:

As has been mentioned in an earlier paragraph, the major contribution to the Hartree-Fock energy comes from the configuration $1s^2 2p^2$ and has been interpreted as being due to the near degeneracy of the 2s and 2p orbitals. This is shown in figure 1. Following Watson¹¹¹ we may classify the correlation energy of Be atom as

- (a) correlation from 1s shell
- (b) correlation from mixing of $1s^2 2s^2$ and $1s^2 2p^2$ configurations
- (c) correlation arising from 2s shell or additional inter-shell mixing.

It must be pointed out that unlike the Hylleraas or Sinanoglu methods, a CI formalism does not offer a clear and unique method of separating the correlation energy into inter-shell and intra-shell contributions. The major part of electron correlation comes through the radial part of the wavefunction and hence depends on the nature of the orbitals and the configurations that are included in the wavefunction. The above classification of the correlation energy should not therefore

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be taken too seriously and is merely a point of view. Although a direct comparison of the CI results and the results obtained from methods such as those of Hylleraas, Sinanoglu or Bethe-Goldstone is not justified because of the role of pairwise interaction and their additivity in the latter methods, it is worthwhile to consider the correlation energy contributions for Be atom obtained from perturbation methods¹⁰².

TABLE XIV

Contribution of each electron pair to the total correlation energy

1s↑ 1s↓	-0.0425 a.u
1s↑ 2s↓	-0.0052 a.u
2s↑ 2s↓	-0.0448 a.u

Though the major contribution arises from intra-shell electrons, the inter-shell correlation energy is significant.

It appears from our results that the upper bound is reached in the case of a two configuration, $1s^2 2s^2 + 1s^2 2p^2$ with the orbitals being orthogonal. Both the 1s - 1s correlation and the 2s - 2s correlation seem to have attained a maximum by mixing of $1s^2 2s^2$ and $1s^2 2p^2$ configurations. According to our scheme, the orbitals are not constrained to be orthogonal and it may be possible to obtain a certain amount of inter-shell

correlation, (1s - 2s), by an appropriate choice of an orbital $1s'$ in the wavefunction

$$\psi = 1s^2 2s^2 + 1s' 2 2p^2$$

Our attempts to extract this additional correlation energy with only two configurations proved to be unsuccessful. We believe that in the simple two configuration case, it is likely that any attempt to improve the intershell correlation results in decreasing the intra-shell correlation. Since the overall magnitude of the intra-shell correlation energy is larger by an order of 10, it is possible that attempts to gain a small amount of inter-shell correlation results in a large loss of intra-shell correlation so that there is a net increase in energy.

In the configuration interaction approach, one improves the correlation energy by increasing the number of configurations in the total wavefunction. We therefore studied the three configuration wavefunction

$$\psi = 1s^2 2s^2 + 1s^2 2p^2 + 2s' 2 2p^2 \quad (5.1.1)$$

where the $2s'$ orbital is chosen to resemble the 2s orbital. The results of our calculations are shown in table XV.

TABLE XV

Configuration: $1s^2 2s^2 + 1s^2 2p^2 + 2s^1 2p^2$

Value of $\langle 2s 2s' \rangle$	Energy(a.u)
1.00000	-14.61660
0.99465	-14.61676
0.98342	-14.61702
0.98078	-14.61945
0.94086	-14.62323
0.89684	-14.64519
0.89103	-14.61688

It can be seen from table XV that addition of a third configuration, keeping the orbitals orthogonal, does not significantly improve the total energy. Removal of the orthogonality constraint markedly improves the energy. This probably arises from the fact that the 1s and 2s correlations could be obtained independently, thereby extracting some additional inter-shell correlation energy .

The results of our calculation clearly demonstrate the improved convergence due to the relaxing of orthogonality constraints. Our three configuration function of equation (5.1.1) gives a slightly better energy than a function with the four

configurations:

$$\psi = 1s^2 2s^2 + 1s^2 2p_I^2 + 2s^2 2p_{II}^2 + 2s^2 s_I^2 \quad (5.1.2)$$

We mention in passing that we recalculated Watson's results for this configuration of equation (5.1.2) and obtained an energy of -14.64513 a.u. There is a discrepancy between our calculation and that reported by Watson (-14.64253 a.u.) which may be attributed to improved methods of the present calculation and possible round off errors in Watson's computations.

The four configuration calculation uses two different p-functions. Computationally, this demands more time than using the single p-function of equation (5.1.1). The only other comparable three configuration calculation with presumably non-orthogonal orbitals, is by Yutsis et.al⁶⁵. Their paper, based on the numerical Hartree-Fock method, reports an energy of -14.642 a.u. which is slightly worse than ours. Moreover, their calculation requires the use of two different p-functions.

TABLE XVI

Summary of the present calculations

Configurations	Overlap	Energy(a.u)	
		Orthogonal	Nonorthogonal
$1s^2 2s^2 + 2s^2 s_I'^2$	$\langle 1s s_I' \rangle = 0.13828$	-14.58370	-14.58815
$1s^2 2s^2 + 1s'^2 s_I'^2$	$\langle 1s 1s' \rangle = 0.77705$	-14.57303	-14.57671
$1s^2 2s^2 + 2s^2 s_I'^2 + 1s'^2 s_I'^2$	$\langle 1s 1s' \rangle = 0.77705$	-14.58486	-14.58664
$1s^2 2s^2 + 2s^2 s_I'^2 + 2s^2 s_{II}'^2$	$\langle s_I' s_{II}' \rangle = 0.07140$	-14.58484	-14.60486
$1s^2 2s^2 + 2s^2 s_I'^2 + 1s_{II}'^2 s_I'^2 + 2s^2 s_{II}'^2$	$\langle 1s s_{II}' \rangle = 0.07493$	-14.58636	-14.58732
$1s^2 2s^2 + 1s^2 2p^2 + 2s'^2 2p^2$	$\langle 2s 2s' \rangle = 0.89684$	-14.61660	-14.64519

Finally we wish to make a few remarks about the influence of the parameter V on the results of the present calculation. As has been pointed out before, we have preferred to create V from an arbitrarily chosen overlap matrix W . This means that there are infinite possible choices for V , all of which are related by unitary transformations.

The question may be raised, is there an optimum V for each wavefunction that corresponds to the lowest energy? In order to find an answer, we studied the effect of various V 's - (all of which give the same overlap W for a particular case) - on the total energy. These various V 's were obtained by multiplying the initially chosen V by a class of unitary matrices. The results seem to point out that while the total energy is very sensitive to the orbital overlap matrix W , it is relatively unaffected by the parameter V . In other words, the energy tends to reach an optimum depending upon the overlap matrix W and the dependence on V appears to be small if any.

A more emphatic statement about the dependence of energy on the parameter V would require a systematic calculation of the energy with respect to a variation of V .

5.2 SOURCES OF ERROR AND ACCURACY OF THE CALCULATIONS

A few remarks about the sources of errors and accuracy of the present calculations would be appropriate. As in any computer calculations, two major sources of error that are inherent are truncation errors and round off errors. The former arises due to the finite storage capacity of computers and infinite decimal quantities that have to be appropriately truncated. Round off errors can arise even with numbers with finite decimal representation. It is the accumulation of such errors that is the major source of error in atomic and molecular calculations such as the present one. An example of a calculation where this difficulty occurs is in the computation of two-electron integrals. Unfortunately it is often impossible to eliminate round off errors.

The present method of calculation is not adapted to make convergence statements similar to those made in numerical Hartree-Fock calculations where it is often the practice to write the percent change in a wavefunction from one Hartree-Fock iteration to the next. Instead, we have used the calculations based on orthogonal orbitals as indices for the magnitude of errors in other calculations.

The overlap integrals between different occupied orbitals of the same l value (for orthogonal orbitals) never exceed 2.0×10^{-7} . It is believed that this is a reasonable indication of the accumulated error in one electron integrals.

Most of the error in calculations of this kind occurs in the course of evaluation of the two electron integrals. Our values are in excellent agreement with those reported by Watson¹¹¹ to within 5.0×10^{-6} . It is however difficult to compare the accuracy of the present calculation with those of Watson, but a general survey of calculations of this kind together with considerations of the software of the particular computer, seem to indicate that our calculations are accurate at least to the seventh decimal place. The main point to note is that our calculations have converged to an apparently stable energy.

The calculations were all done on IBM 370/155 Computing System using double precision mode.

5.3 CONCLUSIONS

In the foregoing sections, we have presented the theory of Multi-Configurational Self Consistent Field using non-orthogonal orbitals and a practical implementation of the method to the calculation of the ground state energy of Beryllium atom. The traditional Configuration Interaction or MC-SCF procedure when applied to all configurations simultaneously is cumbersome, expensive and slowly convergent. This thesis presents a method of surmounting some of the problems in the traditional approach. The major conclusions are:

- (a) The use of non-orthogonal orbitals results in a significant improvement in the convergence of the CI expansion. The three

configuration function represented by equation (5.1.1) and reported in table XV , appears to give the lowest energy of any three configuration calculation to date on Beryllium. In view of this result and the arguments presented in pages 125 - 126, relaxation of orthogonality constraint on orbitals appears to be justified from the chemical point of view.

(b) The pseudo-eigenvalue approach proposed by Benston and Chong is inconsistent and cannot be satisfactorily applied in the form given. With one possible exception, the orbitals which result from our scheme, give substantial lowering of the energy and hence the approximation we have used appears to be quite good.

(c) While the total energy is very sensitive to the orbital overlap matrix W , it appears to be much less sensitive to the parameter V .

Additional information as to the degree to which the wave function describes the exact electronic configuration could possibly be obtained from expectation values of various one- and two-electron operators. Such calculations are not included in the present study for two reasons: (1) The major point of this investigation is to try to assess the advantages of non-orthogonal orbital expansions as compared to the orthogonal ones. Among the many calculations on Be atom, only Sabelli and Hinze⁷⁸ have reported values for anything other than energy. This would not provide sufficient grounds for comparison, especially since (2) the one-electron operators which are relatively easy to calculate are quite insensitive to the degree of approximation in the wave function. The two-electron operators which are more difficult to calculate are too sensitive to give any unambiguous trends in the light of such limited sources for comparison. Besides, such calculations would involve a considerable amount of computation and can constitute a major study in itself.

APPENDIX I

The general variation in energy with respect to orbitals is given by eq.(2.2.15)

$$\delta E = \sum_A \sum_B C_A^* C_B [\delta h_{AB} + \delta g_{AB}] \quad (\text{A.I.1})$$

where

$$\begin{aligned} \delta h_{AB} = & \sum_{i^\pm} \sum_{j^\pm} [D_{AB}(i^\pm j^\pm) \langle \delta \varphi_{i^\pm}^* h \varphi_{j^\pm} \rangle + \langle \varphi_{i^\pm}^* h \varphi_{j^\pm} \rangle \delta D_{AB}(i^\pm j^\pm)] \\ & + \sum_{i^\pm} \sum_{j^\pm} [D_{AB}(i^\pm j^\pm) \langle \varphi_{i^\pm}^* h \delta \varphi_{j^\pm} \rangle \\ & + \langle \varphi_{i^\pm}^* h \varphi_{j^\pm} \rangle \delta D'_{AB}(i^\pm j^\pm)] \quad (\text{A.I.2}) \end{aligned}$$

$$\begin{aligned} \delta g_{AB} = & \sum_{i^\pm} \sum_{j^\pm} \sum_{k^\pm} \sum_{l^\pm} [D_{AB}(i^\pm j^\pm k^\pm l^\pm) \Delta(i^\pm k^\pm) \Delta(j^\pm l^\pm) \delta q(i^\pm j^\pm k^\pm l^\pm) \\ & q(i^\pm j^\pm k^\pm l^\pm) \delta D_{AB}(i^\pm j^\pm k^\pm l^\pm) \Delta(i^\pm k^\pm) \Delta(j^\pm l^\pm)] + \\ & \sum_{i^\pm} \sum_{j^\pm} \sum_{k^\mp} \sum_{l^\mp} [D_{AB}(i^\pm j^\pm k^\mp l^\mp) \delta q(i^\pm j^\pm k^\mp l^\mp) + \\ & q(i^\pm j^\pm k^\mp l^\mp) \delta D_{AB}(i^\pm j^\pm k^\mp l^\mp)] + \sum_{i^\mp} \sum_{j^\mp} \sum_{k^\pm} \sum_{l^\pm} [\\ & D_{AB}(i^\mp j^\mp k^\pm l^\pm) \delta q(i^\mp j^\mp k^\pm l^\pm) + q(i^\mp j^\mp k^\pm l^\pm) \delta D_{AB}(i^\mp j^\mp k^\pm l^\pm)] \\ & + \sum_{i^\pm} \sum_{j^\pm} \sum_{k^\pm} \sum_{l^\pm} [D_{AB}(i^\pm j^\pm k^\pm l^\pm) \Delta(i^\pm k^\pm) \Delta(j^\pm l^\pm) \delta q'(i^\pm j^\pm k^\pm l^\pm) \\ & + q(i^\pm j^\pm k^\pm l^\pm) \delta D'_{AB}(i^\pm j^\pm k^\pm l^\pm) \Delta(i^\pm k^\pm) \Delta(j^\pm l^\pm)] + \end{aligned}$$

$$\begin{aligned}
 & \sum_{i^\pm} \sum_{j^\pm} \sum_{k^\mp} \sum_{l^\mp} [D_{AB}(i^\pm j^\pm k^\mp l^\mp) \delta q'(i^\pm j^\pm k^\mp l^\mp) + \\
 & q(i^\pm j^\pm k^\mp l^\mp) \delta D'_{AB}(i^\pm j^\pm k^\mp l^\mp)] + \\
 & \sum_{i^\mp} \sum_{j^\mp} \sum_{k^\pm} \sum_{l^\pm} [D_{AB}(i^\mp j^\mp k^\pm l^\pm) \delta q'(i^\mp j^\mp k^\pm l^\pm) + \\
 & q(i^\mp j^\mp k^\pm l^\pm) \delta D'_{AB}(i^\mp j^\mp k^\pm l^\pm)] \quad (A. I. 3)
 \end{aligned}$$

where

$$\begin{aligned}
 \delta D_{AB}(i^\pm j^\pm) &= \sum_{k^\pm}^A \sum_{l^\pm}^B D_{AB}(i^\pm j^\pm k^\pm l^\pm) \Delta(i^\pm k^\pm) \Delta(j^\pm l^\pm) \delta T_{AB}(k^\pm l^\pm) + \\
 & \sum_{k^\mp}^A \sum_{l^\mp}^B D_{AB}(i^\pm j^\pm k^\mp l^\mp) \delta T_{AB}(k^\mp l^\mp) \quad (A. I. 4)
 \end{aligned}$$

$$\delta T_{AB}(k^\mp l^\mp) = \langle \delta \varphi_k^* | \varphi_l \rangle \quad (A. I. 5)$$

$$\begin{aligned}
 \delta D'_{AB}(i^\pm j^\pm) &= \sum_{k^\pm}^A \sum_{l^\pm}^B D_{AB}(i^\pm j^\pm k^\pm l^\pm) \Delta(i^\pm k^\pm) \Delta(j^\pm l^\pm) \delta T'_{AB}(k^\pm l^\pm) + \\
 & \sum_{k^\mp}^A \sum_{l^\mp}^B D_{AB}(i^\pm j^\pm k^\mp l^\mp) \delta T'_{AB}(k^\mp l^\mp) \quad (A. I. 6)
 \end{aligned}$$

$$\delta T'_{AB}(k^\pm l^\pm) = \langle \varphi_k^* | \delta \varphi_l \rangle \quad (A. I. 7)$$

$$\delta q(i^\pm j^\pm k^\pm l^\pm) = \delta q(i^\pm j^\pm k^\mp l^\mp) \quad (A. I. 8)$$

$$= \langle \delta \varphi_i^*(1) \varphi_k^*(2) g(1,2) \varphi_j(1) \varphi_l(2) \rangle + \\ \langle \varphi_i^*(1) \delta \varphi_k^*(2) g(1,2) \varphi_j(1) \varphi_l(2) \rangle$$

$$\delta q'(i^\pm j^\pm k^\pm l^\pm) = \delta q'(i^\pm j^\pm k^\mp l^\mp) \quad (\text{A.I.8})$$

$$= \langle \varphi_i^*(1) \varphi_k^*(2) g(1,2) \delta \varphi_j(1) \varphi_l(2) \rangle + \\ \langle \varphi_i^*(1) \varphi_k^*(2) g(1,2) \varphi_j(1) \delta \varphi_l(2) \rangle$$

$$\delta D_{AB}(i^\pm j^\pm k^\pm l^\pm) = \sum_{m^\pm}^A \sum_{n^\pm}^B D_{AB}(i^\pm j^\pm k^\pm l^\pm / m^\pm n^\pm) \Delta(i^\pm k^\pm m^\pm) \Delta(j^\pm l^\pm n^\pm) \delta T_{AB}(m^\pm n^\pm) \\ + \sum_{m^\mp}^A \sum_{n^\mp}^B D_{AB}(i^\pm j^\pm k^\pm l^\pm m^\mp n^\mp) \delta T_{AB}(m^\mp n^\mp) \quad (\text{A.I.9})$$

$$\delta D_{AB}(i^\pm j^\pm k^\mp l^\mp) = \sum_{m^\pm}^A \sum_{n^\pm}^B D_{AB}(i^\pm j^\pm k^\mp l^\mp m^\pm n^\pm) \Delta(i^\pm m^\pm) \Delta(j^\pm n^\pm) \\ \delta T_{AB}(m^\pm n^\pm) + \sum_{m^\mp}^A \sum_{n^\mp}^B D_{AB}(i^\pm j^\pm k^\mp l^\mp m^\mp n^\mp)$$

$$\Delta(k^\mp l^\mp) \Delta(l^\mp n^\mp) \delta T_{AB}(m^\mp n^\mp) \quad (\text{A.I.10})$$

$$\delta D'_{AB}(i^\pm j^\pm k^\pm l^\pm) = \sum_{m^\pm}^A \sum_{n^\pm}^B D_{AB}(i^\pm j^\pm k^\pm l^\pm m^\pm n^\pm) \Delta(i^\pm k^\pm m^\pm) \Delta(j^\pm l^\pm n^\pm)$$

$$\delta T'_{AB}(m^\pm n^\pm) + \sum_{m^\mp}^A \sum_{n^\mp}^B D_{AB}(i^\pm j^\pm k^\pm l^\pm m^\mp n^\mp)$$

$$\delta T'_{AB}(m^\mp n^\mp) \quad (\text{A.I.11})$$

Because of the Hermitian character of h and g , the primed quantities are simply the complex conjugates of the unprimed ones.

Since the operators are Hermitian, the variation in energy can be written as

$$\begin{aligned}
 \delta E = & \sum_A \sum_B C_A^* C_B \left[\sum_{i^\pm} \sum_{j^\pm} \left\{ \langle \delta \varphi_{i^\pm} | h | \varphi_{j^\pm} \rangle D_{AB}(i^\pm j^\pm) + \right. \right. \\
 & p(i^\pm j^\pm) \delta D_{AB}(i^\pm j^\pm) \left. \right\} + \sum_{i^\pm} \sum_{j^\pm} \sum_{k^\pm} \sum_{l^\pm} \left\{ \delta q(i^\pm j^\pm k^\pm l^\pm) \right. \\
 & D_{AB}(i^\pm j^\pm k^\pm l^\pm) \Delta(i^\pm k^\pm) \Delta(j^\pm l^\pm) + q(i^\pm j^\pm k^\pm l^\pm) \\
 & \delta D_{AB}(i^\pm j^\pm k^\pm l^\pm) \left. \right\} + \sum_{i^\mp} \sum_{j^\mp} \sum_{k^\pm} \sum_{l^\pm} \left\{ \delta q(i^\mp j^\mp k^\pm l^\pm) \right. \\
 & D_{AB}(i^\mp j^\mp k^\pm l^\pm) + q(i^\mp j^\mp k^\pm l^\pm) \delta D_{AB}(i^\mp j^\mp k^\pm l^\pm) \left. \right\} + \\
 & \left\{ \langle \delta \varphi_{i^\mp} | h | \varphi_{j^\mp} \rangle D_{AB}(i^\mp j^\mp) + p(i^\mp j^\mp) \delta D_{AB}(i^\mp j^\mp) \right\}^* + \\
 & \sum_{i^\pm} \sum_{j^\pm} \sum_{k^\pm} \sum_{l^\pm} \left\{ \delta q(i^\pm j^\pm k^\pm l^\pm) D_{AB}(i^\pm j^\pm k^\pm l^\pm) \Delta(i^\pm k^\pm) \Delta(j^\pm l^\pm) \right. \\
 & \left. + q(i^\pm j^\pm k^\pm l^\pm) \delta D_{AB}(i^\pm j^\pm k^\pm l^\pm) \right\}^* + \\
 & \sum_{i^\mp} \sum_{j^\mp} \sum_{k^\pm} \sum_{l^\pm} \left\{ \delta q(i^\mp j^\mp k^\pm l^\pm) D_{AB}(i^\mp j^\mp k^\pm l^\pm) + \right. \\
 & \left. q(i^\mp j^\mp k^\pm l^\pm) \delta D_{AB}(i^\mp j^\mp k^\pm l^\pm) \right\}^*
 \end{aligned} \tag{A. I. 12}$$

The complex conjugates are denoted by the symbol *. In writing eq.(A.I.12) we have made use of the Hermitian property

$$\langle \varphi_i | 0 | \delta \varphi_i \rangle = \langle \delta \varphi_i | 0 | \varphi_i \rangle^* \quad (\text{A.I.13})$$

Relation (A.I.13) is subjected to the orbital optimization condition

$$\langle \delta \varphi_i | \varphi_j \rangle + \langle \varphi_i | \delta \varphi_j \rangle = 0 \quad (\text{A.I.14})$$

Note that the first term involves the variation of φ_i while the second term involves the variation of φ_j . We now define an arbitrary set of Lagrange multipliers ϵ_{ij} and sum over both i and j .

$$-\sum_{i=1} \sum_{j=1} \epsilon_{ji} \left(\langle \delta \varphi_i | \varphi_j \rangle + \langle \varphi_i | \delta \varphi_j \rangle \right) = 0 \quad (\text{A.I.15})$$

Using the relation $\langle \varphi_i | \delta \varphi_j \rangle = \langle \delta \varphi_j | \varphi_i \rangle^*$ we get

$$-\sum_{i=1} \sum_{j=1} \epsilon_{ji} \langle \delta \varphi_i | \varphi_j \rangle - \sum_{i=1} \sum_{j=1} \epsilon_{ji} \langle \delta \varphi_i | \varphi_j \rangle^* = 0 \quad (\text{A.I.16})$$

Equation (A.I.16) is now added to eq.(A.I.12). The necessary but not sufficient condition that E reach its absolute minimum is that $\delta E = 0$ for any arbitrary choice of variation $\delta \varphi_i$ in the orbitals. We finally get

$$\begin{aligned}
 \delta E' = 0 = & \sum_A \sum_B C_A^* C_B \left[\sum_{i^\pm} \sum_{j^\pm} \left\{ \langle \delta \varphi_{i^\pm} | h | \varphi_{j^\pm} \rangle D_{AB}(i^\pm j^\pm) \right. \right. \\
 & + p(i^\pm j^\pm) \delta D_{AB}(i^\pm j^\pm) \left. \right\} + \sum_{i^\pm} \sum_{j^\pm} \sum_{k^\pm} \sum_{l^\pm} \left\{ \right. \\
 & \delta q(i^\pm j^\pm k^\pm l^\pm) D_{AB}(i^\pm j^\pm k^\pm l^\pm) \Delta(i^\pm k^\pm) \Delta(j^\pm l^\pm) + \\
 & q(i^\pm j^\pm k^\pm l^\pm) \delta D_{AB}(i^\pm j^\pm k^\pm l^\pm) \left. \right\} + \sum_{i^\pm} \sum_{j^\pm} \sum_{k^\mp} \sum_{l^\mp} \left\{ \right. \\
 & \delta q(i^\pm j^\pm k^\mp l^\mp) D_{AB}(i^\pm j^\pm k^\mp l^\mp) + q(i^\pm j^\pm k^\mp l^\mp) \\
 & \left. \delta D_{AB}(i^\pm j^\pm k^\mp l^\mp) \right\}] - \sum_{i^\pm} \sum_{j^\pm} \epsilon_{ji} \langle \delta \varphi_i | \varphi_j \rangle + \\
 & \sum_A \sum_B C_A^* C_B \left[\sum_{i^\pm} \sum_{j^\pm} \left\{ \langle \delta \varphi_{i^\pm} | h | \varphi_{j^\pm} \rangle D_{AB}(i^\pm j^\pm) + \right. \right. \\
 & p(i^\pm j^\pm) \delta D_{AB}(i^\pm j^\pm) \left. \right\}^* + \sum_{i^\pm} \sum_{j^\pm} \sum_{k^\pm} \sum_{l^\pm} \left\{ \right. \\
 & \delta q(i^\pm j^\pm k^\pm l^\pm) D_{AB}(i^\pm j^\pm k^\pm l^\pm) \Delta(i^\pm k^\pm) \Delta(j^\pm l^\pm) + \\
 & q(i^\pm j^\pm k^\pm l^\pm) \delta D_{AB}(i^\pm j^\pm k^\pm l^\pm) \left. \right\}^* + \\
 & \sum_{i^\pm} \sum_{j^\pm} \sum_{k^\mp} \sum_{l^\mp} \left\{ \delta q(i^\pm j^\pm k^\mp l^\mp) D_{AB}(i^\pm j^\pm k^\mp l^\mp) + \right.
 \end{aligned}$$

$$q(i^\pm j^\pm k^\mp l^\mp) \delta_{AB}(i^\pm j^\pm k^\mp l^\mp) \}^*] -$$

$$\sum_{i^\pm} \sum_{j^\pm} \epsilon_{ij} \langle \delta\varphi_i | \varphi_j \rangle^* \quad (\text{A.I.17})$$

APPENDIX II

II. 1 PROPERTIES OF DETERMINANTS

Let $A = a_{\alpha\beta}$ be a $n \times n$ matrix. The determinant of A is defined by

$$\det A = \sum \epsilon(\alpha, \beta, \dots) a_{1\alpha} a_{2\beta} \dots a_{n\delta} \quad (\text{A.II.1})$$

where $\epsilon(\alpha, \beta, \dots)$ refers to the permutation (sign) of the determinant. The determinant A can be expanded in terms of the matrix elements of the row α explicitly

$$\det A = \sum_{\beta} a_{\alpha\beta} (\text{Cof } a_{\alpha\beta}) \quad (\text{A.II.2})$$

where the cofactor $\text{Cof } a_{\alpha\beta}$ is a number and depends on the matrix elements in other rows.

A determinant vanishes if it has two identical rows or two identical columns. Using this property we can write

$$\sum_{\beta} a_{\alpha\beta} (\text{Cof } a_{\alpha'\beta}) = \det A \cdot \delta_{\alpha\alpha'} \quad (\text{A.II.3})$$

Expanding the cofactors $a_{\alpha\beta}$ in eq.(A.II.2) in terms of row γ , we get

$$\det A = \sum_{\beta} \sum_{\delta} a_{\alpha\beta} a_{\gamma\delta} (\text{Cof } a_{\alpha\beta, \gamma\delta}) \quad (\text{A.II.4})$$

$\text{Cof } a_{\alpha\beta, \gamma\delta}$ is a general cofactor of order 2 and depends on matrix elements on other rows. The proof is as follows:

Let the α th row move up to become the first row and the γ th row move up to become the second row. Then by the usual Laplace expansion of a determinant

$$\det A = (-1)^{\alpha-1} (-1)^{\gamma-2} \begin{vmatrix} a_{\alpha 1} & a_{\alpha 2} & - & - & - \\ a_{\gamma 1} & a_{\gamma 2} & - & - & - \\ - & - & - & - & - \end{vmatrix} \quad (\text{A.II.5})$$

Expanding from the first two rows we get

$$\det A = (-1)^{\alpha+\gamma-3} (-1)^{\beta+\delta+1} \begin{vmatrix} a_{\alpha\beta} & a_{\alpha\delta} \\ a_{\gamma\beta} & a_{\gamma\delta} \end{vmatrix} M(\alpha, \beta; \gamma, \delta) \quad (\text{A.II.6})$$

where $M(\alpha, \beta; \gamma, \delta)$ is the minor of α, β and γ, δ . Note that we have assumed that $\alpha < \gamma$ and $\beta < \delta$. Equation (A.II.6) can be written as

$$\det A = (-1)^{\alpha+\beta+\gamma+\delta} \sum_{\beta, \delta} \begin{vmatrix} a_{\alpha\beta} & a_{\alpha\delta} \\ a_{\gamma\beta} & a_{\gamma\delta} \end{vmatrix} \quad (\text{A.II.7})$$

$$= \sum_{\beta} \sum_{\delta} a_{\alpha\beta} a_{\gamma\delta} (\text{Cof } a_{\alpha\beta, \gamma\delta}) \quad (\text{A.II.8})$$

Making use of the property (A.II.3) we can rewrite eq.(A.II.8) as

$$\begin{aligned} \det A &= \sum_{\beta} \sum_{\delta} a_{\alpha\beta} a_{\gamma\delta} (\text{Cof } a_{\alpha', \beta, \gamma', \delta}) \\ &= \det A [\delta_{\alpha\alpha'} \delta_{\gamma\gamma'} - \delta_{\alpha\gamma'} \delta_{\gamma\alpha'}] \quad (\text{A.II.9}) \end{aligned}$$

Equation (A.II.9) exhibits the property that a determinant vanishes if two rows are identical and changes sign if two rows α

and γ are exchanged.

Another important property which is of use to us is the following. If A is non singular, that is, $\det A \neq 0$, the inverse of A is given by

$$A^{-1} = \frac{1}{\det A} \cdot \text{adj } A \quad (\text{A.II.10})$$

where the adjoint of a square matrix A is the transpose of the matrix of cofactors of A

$$A \text{ adj } A = \left| \sum_{k=1}^n a_{ik} b_{kj} \right| \quad (\text{A.II.11})$$

where b_{kj} is the kj th element of $\text{adj } A$, that is, A_{jk} .

$$\begin{aligned} \text{Therefore } A \text{ adj } A &= \left| \sum_{k=1}^n a_{ik} A_{jk} \right| \\ &= \det A \cdot I \end{aligned} \quad (\text{A.II.12})$$

Since $\det A \neq 0$, we have

$$A \frac{1}{\det A} \cdot \text{adj } A = I$$

$$\text{or } A^{-1} = \frac{1}{\det A} \cdot \text{adj } A \quad (\text{A.II.13})$$

In terms of the components $(a^{-1})_{\beta\alpha}$ of the matrix A^{-1} , we can write eq.(A.II.10) as

$$(a^{-1})_{\beta\alpha} = \frac{(\text{Cof } a_{\alpha\beta})}{\det A} \quad (\text{A.II.14})$$

$$\text{or } (\text{Cof } a_{\alpha\beta}) = (a^{-1})_{\beta\alpha} \cdot \det A \quad (\text{A.II.15})$$

That is, the inverse matrix is $(1/\det A)$ times the transpose of the matrix whose elements are the cofactors of the elements of the original matrix. This statement can be generalized so as to include eq.(A.II.4) and we can write

$$(\text{Cof } a_{\alpha\beta,\gamma\delta}) = \det A [(a^{-1})_{\gamma\alpha}(a^{-1})_{\delta\beta} - (a^{-1})_{\gamma\beta}(a^{-1})_{\delta\alpha}] \quad (\text{A.II.16})$$

II. 2 MATRIX ELEMENTS OF OPERATORS ON DETERMINANTAL FUNCTIONS

We are interested in matrix elements of the general form

$$W = \langle \Phi(1,2,---N) | \Omega(1,2,---N) | \Psi(1,2,---N) \rangle \quad (\text{A.II.17})$$

where Φ and Ψ are antisymmetric functions of N electrons and Ω is a Hermitian N -electron operator. The operator Ω may be written as

$$\Omega(1,2,---N) = \sum_i^N \Omega_i + \sum_{i < j}^N \sum_{i < j}^N \Omega_{ij} + \sum_{i < j < k}^N \sum_{i < j < k}^N \Omega_{ijk} + \dots \quad (\text{A.II.18})$$

where Ω_{ij} represents an operator in electrons i and j etc. In the following we will be concerned with only one- and two particle operators.

(a) Overlap of two Slater determinant functions:

In terms of the one particle functions, the Slater determinant Φ_0 may be written in abbreviated form

$$\Phi_0 = \varphi_1(x_1)\varphi_2(x_2) \dots \varphi_A(x_A) \quad (\text{A.II.19})$$

and similarly for Ψ_0 . The corresponding antisymmetrized Slater determinant wave function is defined by

$$\Phi = N_\Phi \mathcal{D} \Phi_0 \quad (\text{A.II.20})$$

$$\langle \Phi | \Psi \rangle = N_\Phi N_\Psi \langle \mathcal{D} \Phi_0 | \mathcal{D} \Psi_0 \rangle \quad (\text{A.II.21})$$

$$= \frac{1}{A!} N_\Phi N_\Psi \sum \epsilon(\alpha\beta \dots \eta) \langle \varphi_\alpha(1) | \psi_{\alpha'}(1) \rangle \times \\ \langle \varphi_\beta(2) | \psi_{\beta'}(2) \rangle \dots \langle \varphi_\eta(N) | \psi_{\eta'}(N) \rangle \quad (\text{A.II.22})$$

$$= \frac{1}{A!} N_\Phi N_\Psi \det\{ \varphi_\alpha | \psi_{\alpha'} \} \quad (\text{A.II.23})$$

In deriving the above relation we have used the fact that the antisymmetrizer \mathcal{D} is a projection operator and hence idempotent.

The normalization constant is given by

$$\langle \Psi | \Psi \rangle = 1 = \frac{1}{A!} N_\Psi^2 \det\{ \psi_\alpha | \psi_{\alpha'} \}$$

$$N_\Psi = A! \det\{ \langle \psi_\alpha | \psi_{\alpha'} \rangle \} \quad (\text{A.II.24})$$

Combining eq.(A.II.23) and eq.(A.II.24) we get

$$\langle \Phi | \Psi \rangle = \det\{ \langle \varphi_\alpha | \psi_{\alpha'} \rangle \} \left(\det\{ \langle \varphi_\alpha | \varphi_{\alpha'} \rangle \} \det\{ \langle \psi_\alpha | \psi_{\alpha'} \rangle \} \right)^{-\frac{1}{2}} \quad (\text{A.II.25})$$

(b) Matrix elements of a one electron operator

Let $F = \sum_I^A f_\alpha$ where f_α acts only on the coordinates

of the electron α

$$\begin{aligned}
 \langle \Phi | F | \Psi \rangle &= \langle \mathcal{D} \Phi_0 | F | \mathcal{D} \Psi \rangle N_{\Phi} N_{\Psi} \\
 &= N_{\Phi} N_{\Psi} \sum_{\alpha} \langle \Phi_0 | f_{\alpha} | \mathcal{D} \Psi_0 \rangle \\
 &= N_{\Phi} N_{\Psi} \sum_{\alpha} \langle f_{\alpha} \Phi_0 | \mathcal{D} \Psi_0 \rangle \quad (\text{A.II.26})
 \end{aligned}$$

The wave function $f_{\alpha} \Phi_0$ is obtained from Φ_0 by replacing single particle function $\varphi_{\alpha}(x_{\alpha})$ by $f_{\alpha} \varphi_{\alpha}(x_{\alpha})$. Hence the right hand side of eq.(A.II.26) may be evaluated using eq.(A.II.23). It is only necessary to replace the matrix elements $\langle \varphi_{\alpha} | \psi_{\alpha'} \rangle$ in the α th row of $\det\{\langle \varphi_{\alpha} | \psi_{\alpha'} \rangle\}$ by $\langle f_{\alpha} \varphi_{\alpha} | \psi_{\alpha'} \rangle = \langle \varphi_{\alpha} f_{\alpha} | \psi_{\alpha'} \rangle$. The modified determinant may be evaluated by using cofactor expansion. Hence the terms α in the sum (A.II.26) must be

$$\sum \langle \varphi_{\alpha} | f | \psi_{\alpha'} \rangle c_{\alpha\alpha'}$$

where $c_{\alpha\alpha'}$ is the cofactor of $\langle \varphi_{\alpha} | \psi_{\alpha'} \rangle$ in $\det\{\langle \varphi_{\alpha} | \psi_{\alpha'} \rangle\}$. Finally using (A.II.15) and (A.II.23) we get

$$\langle \Phi | F | \Psi \rangle = \langle \Phi | \Psi \rangle \sum_{\alpha\alpha'} \langle \varphi_{\alpha} | f | \psi_{\alpha'} \rangle (B^{-1})_{\alpha\alpha'} \quad (\text{A.II.27})$$

where $B_{\alpha\alpha'} = \langle \varphi_{\alpha} | \psi_{\alpha'} \rangle$ and B^{-1} is the inverse of B .

(c) Matrix elements of two electron operator

Let $V = \sum_{\alpha < \beta} v_{\alpha\beta}$ where $v_{\alpha\beta}$ acts only on the coordinates

x_α and x_β of the electrons α and β . By an argument similar to that given in the case of one electron operator, we can establish

$$\langle \Phi | V | \Psi \rangle = \frac{1}{2} N_\Phi N_\Psi \sum \langle \varphi_\alpha \varphi_\beta | v | \psi_\gamma \psi_\delta \rangle c(\alpha\beta, \gamma\delta) \quad (\text{A. II. 28})$$

where $c(\alpha\beta, \gamma\delta)$ are the generalized cofactors defined in (A. II. 15). Using (A. II. 16) we can write

$$\begin{aligned} \langle \Phi | V | \Psi \rangle = \frac{1}{2} \langle \Phi | \Psi \rangle \sum \langle \varphi_\alpha \varphi_\beta | v | \psi_\gamma \psi_\delta \rangle [(B^{-1})_{\gamma\alpha} (B^{-1})_{\delta\beta} - \\ (B^{-1})_{\gamma\beta} (B^{-1})_{\delta\alpha}] \quad (\text{A. II. 29}) \end{aligned}$$

APPENDIX III
RESULTS

CONFIGURATION: 1S2 2S2 + 2S2 1S2

OPTIMIZED EXPANSION COEFFICIENTS

1S	2S	1S
0.48484699	-0.08112931	-0.94140142
0.21760690	-0.14734551	-0.40747615
0.26416609	-0.05114961	-0.51197534
-0.26830193	1.33291181	0.48963974
0.16822500	-0.04106392	1.87747533
0.16758440	-0.38678023	-0.27675481
0.04512770	-0.00752240	-0.08762587
-0.04528750	0.22482522	0.05847970
0.06688270	-0.02764800	-0.12763148

ORBITAL OVERLAP MATRIX

1.00000000	0.0	0.03102888
0.0	1.00000000	0.13975427
0.03102888	0.13975427	1.00000000

CONFIGURATION MIXING COEFFICIENTS

	1S2 2S2	2S2 1S2
C	0.99983543	-0.01814147

COMPARISON OF RESULTS

	ORTHOGONAL	NON-ORTHOGONAL
ENERGY	-14.58370000	-14.58264715

CCONFIGURATION: 1S2 2S2 + 2S2 SI2

OPTIMIZED EXPANSION COEFFICIENTS

1S	2S	SI
0.48484699	-0.08112932	-0.90758842
0.21760690	-0.14734552	-0.39284053
0.26416609	-0.05114961	-0.49358635
-0.26830192	1.33291181	0.33388876
0.16822500	-0.04106391	1.91008474
0.16758440	-0.38678023	-0.26681440
0.04512770	-0.00752240	-0.08447855
-0.04528750	0.22482522	0.05637924
0.06688270	-0.02764800	-0.12304724

ORBITAL OVERLAP MATRIX

1.00000000	0.0	0.08923167
0.0	1.00000000	0.00615852
0.08923167	0.00615852	1.00000000

CONFIGURATION MIXING COEFFICIENTS

	1S2 2S2	2S2 SI ²
C	0.99983500	-0.01816792

COMPARISON OF RESULTS

	ORTHOGONAL	NON-ORTHOGONAL
ENERGY	-14.5837000	-14.58282283

CONFIGURATION: 1S2 2S2 + 2S2 SI2

OPTIMIZED EXPANSION COEFFICIENTS

1S	2S	SI
0.48484699	-0.08112932	-0.89799461
0.21760690	-0.14734552	-0.38868795
0.26416609	-0.05114961	-0.48836882
-0.26830192	1.33291181	0.33035932
0.16822500	-0.04106390	1.90971446
0.16758440	-0.38678023	-0.26399399
0.04512770	-0.00752240	-0.08358556
-0.04528750	0.22482522	0.05578328
0.06688270	-0.02764800	-0.12174655

ORBITAL OVERLAP MATRIX

1.00000000	0.0	0.10596683
0.0	1.00000000	0.00731353
0.10596683	0.00731353	1.00000000

CONFIGURATION MIXING COEFFICIENTS

	1S2 2S2	2S2 SI'2
C	0.99975270	-0.01932369

COMPARISON OF RESULTS

	ORTHOGONAL	NON-ORTHOGONAL
ENERGY	-14.5837000	-14.58400531

CONFIGURATION: 1S2 2S2 + 2S2 SI2

OPTIMIZED EXPANSION COEFFICIENTS

1S	2S	SI
0.48484699	-0.08112932	-0.88835701
0.21760690	-0.14734552	-0.38451641
0.26416609	-0.05114961	-0.48312747
-0.26830192	1.33291181	0.32681380
0.16822500	-0.04106390	1.90882656
0.16758440	-0.38678023	-0.26116072
0.04512770	-0.00752240	-0.08268849
-0.04528750	0.22482522	0.05518459
0.06688270	-0.02764800	-0.12043993

ORBITAL OVERLAP MATRIX

1.00000000	0.0	0.12231821
0.0	1.00000000	0.00844206
0.12231821	0.00844206	1.00000000

CONFIGURATION MIXING COEFFICIENTS

	1S2 2S2	2S2 SI ²
C	0.99978417	-0.02077542

COMPARISON OF RESULTS

	ORTHOGONAL	NON-ORTHOGONAL
ENERGY	-14.58370000	-14.58575532

CONFIGURATION: 1S2 2S2 + 2S2 SI2

OPTIMIZED EXPANSION COEFFICIENTS

1S	2S	SI
0.48484699	-0.08112928	-0.87869257
0.21760690	-0.14734550	-0.38033305
0.26416609	-0.05114959	-0.47787152
-0.26830200	1.33291179	0.32325596
0.16822502	-0.04106390	1.90745516
0.16758443	-0.38678022	-0.25831688
0.04512770	-0.00752240	-0.08178892
-0.04528752	0.22482522	0.05458385
0.06688200	-0.02764800	-0.11912963

ORBITAL OVERLAP MATRIX

1.0000000	0.0	0.13828591
C.C	1.0000000	0.00954410
0.13828591	0.00954410	1.0000000

CONFIGURATION MIXING COEFFICIENTS

	1S2 2S2	2S2 SI ²
C	0.99974262	-0.02268672

COMPARISON OF RESULTS

	ORTHOGONAL	NON-ORTHOGONAL
ENERGY	-14.58370000	-14.58814640

CONFIGURATION: 1S2 2S2 + 2S2 SI2

OPTIMIZED EXPANSION COEFFICIENTS

1S	2S	SI
0.50192895	-0.08112171	-0.85749155
0.22500119	-0.14734210	-0.37102282
0.27345605	-0.05114546	-0.46633311
-0.27459238	1.33290757	0.31390538
0.13397741	-0.04106096	1.90301070
0.17260793	-0.38677760	-0.25165417
0.04671769	-0.00752169	-0.07981556
-0.04634969	0.22482450	0.05300522
0.06919868	-0.02764695	-0.11623547

ORBITAL OVERLAP MATRIX

1.00000000	0.0	0.15407599
0.0	1.00000000	0.01066914
0.15407599	0.01066914	1.00000000

CONFIGURATION MIXING COEFFICIENTS

	1S2 2S2	2S2 SI'2
C	0.99960634	-0.02805646

COMPARISON OF RESULTS

	ORTHOGONAL	NON-ORTHOGONAL
ENERGY	-14.58370000	-14.58548000

CONFIGURATIONS: 1S2 2S2 + 1S'2 S12

OPTIMIZED EXPANSION COEFFICIENTS

1S	2S	1S'	S1
0.48473638	-0.08136575	0.38236385	-0.95419772
0.22002307	-0.14555985	0.48757265	-0.41245117
0.26411499	-0.05126963	0.20833724	-0.51893186
-0.26994251	1.33140854	-0.21374696	0.35053957
0.16723587	-0.04185799	0.13152590	1.90272717
0.16802002	-0.38640653	0.13274388	-0.28037855
0.04511736	-0.00754445	0.03558727	-0.08881697
-0.04556396	0.22457187	-0.03604495	0.05919099
0.06688927	-0.02765971	0.05277838	-0.12936000

ORBITAL OVERLAP MATRIX

1.00000000	0.00000005	0.96610804	0.00000015
0.00000005	0.99999999	0.23479689	0.00000001
0.96610804	0.23479689	1.00000000	0.06032881
0.00000015	0.00000001	0.06032881	0.99999960

CONFIGURATION MIXING COEFFICIENTS

	1S2 2S2	1S'2 S12
C	0.99999101	-0.00434513

COMPARISON OF RESULTS

	ORTHOGONAL	NON-ORTHOGONAL
ENERGY	-14.57302493	-14.57347122

CONFIGURATIONS: 1S2 2S2 + 1S'2 SI2

OPTIMIZED EXPANSION COEFFICIENTS

1S	2S	1S'	SI
0.48484697	-0.08113000	0.26570115	-0.95417669
0.21760517	-0.14734251	0.70128807	-0.41300549
0.26416607	-0.05114996	0.14476574	-0.51892309
-0.26829898	1.33290932	-0.14703117	0.35102760
0.16822550	-0.04106538	0.09218892	1.90295349
0.16758358	-0.38677967	0.09183769	-0.28051041
0.04512770	-0.00752246	0.02473045	-0.08881500
-0.04528701	0.22482480	-0.02481784	0.05927325
0.06688266	-0.02764806	0.03665239	-0.12936349

ORBITAL OVERLAP MATRIX

1.00000000	0.00000005	0.87730796	0.00000015
0.00000005	0.99999999	0.43653201	0.00000001
0.87730796	0.43653201	1.00000000	0.11216257
0.00000015	0.00000001	0.11216257	0.99999960

CONFIGURATION MIXING COEFFICIENTS

	1S2 2S2	1S'2 SI2
C	0.99996400	-0.00846000

COMPARISON OF RESULTS

	ORTHOGONAL	NON-ORTHOGONAL
ENERGY	-14.57302493	-14.57488971

CONFIGURATIONS: 1S2 2S2 + 1S'2 S12

OPTIMIZED EXPANSION COEFFICIENTS

1S	2S	1S'	S1
0.48484702	-0.08112944	0.24204198	-0.95417669
0.21760657	-0.14734488	0.73754360	-0.41300527
0.26416611	-0.05114968	0.13187518	-0.51892309
-0.26830127	1.33291128	-0.13393971	0.35102746
0.16822501	-0.04106426	0.08297952	1.90295340
0.16758423	-0.38678011	0.08366030	-0.28051038
0.04512770	-0.00752241	0.02252834	-0.08881500
-0.04528739	0.22482513	-0.02260809	0.05927323
0.06688269	-0.02764801	0.03338872	-0.12936349

ORBITAL OVERLAP MATRIX

1.00000000	0.00000005	0.85502999	0.00000015
0.00000005	0.99999999	0.47168785	0.00000001
0.85502999	0.47168785	1.00000000	0.12119550
0.00000015	0.00000001	0.12119550	0.99999960

CONFIGURATION MIXING COEFFICIENTS

	1S2 2S2	1S'2 S12
C	0.99995721	-0.00927112

COMPARISON OF RESULTS

	ORTHOGONAL	NON-ORTHOGONAL
ENERGY	-14.57302493	-14.57528142

CONFIGURATIONS: 1S2 2S2 + 1S'2 SI2

OPTIMIZED EXPANSION COEFFICIENTS

1S	2S	1S'	SI
0.48484696	-0.08112938	0.19464520	-0.95417671
0.21760700	-0.14734523	0.80385037	-0.41300584
0.26416608	-0.05114964	0.10605132	-0.51892310
-0.26830185	1.33291156	-0.10771204	0.35102791
0.16822497	-0.04106402	0.06753498	1.90295361
0.16758438	-0.38678018	0.06727803	-0.28051050
0.04512770	-0.00752241	0.01811683	-0.08881500
-0.04528749	0.22482518	-0.01818105	0.05927330
0.06688269	-0.02764801	0.02685053	-0.12936350

ORBITAL OVERLAP MATRIX

1.00000000	0.00000005	0.80682313	0.00000015
0.00000005	0.99999999	0.53737258	0.00000001
0.80682313	0.53737258	1.00000000	0.13807251
0.00000015	0.00000001	0.13807251	0.99999960

CONFIGURATION MIXING COEFFICIENTS

	1S2 2S2	1S'2 SI2
C	0.99994114	-0.01082497

COMPARISON OF RESULTS

	ORTHOGONAL	NON-ORTHOGONAL
ENERGY	-14.57302493	-14.57616114

CONFIGURATIONS: 1S 2S + 1S' 2 S12

OPTIMIZED EXPANSION COEFFICIENTS

1S	2S	1S'	S1
0.48484696	-0.08112933	0.16735524	-0.95417671
0.21760702	-0.14734556	0.83846699	-0.41300599
0.26416608	-0.05114961	0.09118254	-0.51892310
-0.26830199	1.33291184	-0.09261032	0.35102804
0.16822499	-0.04106385	0.05806646	1.90295367
0.16758442	-0.38678224	0.05784536	-0.28051054
0.04512770	-0.00752240	0.01557679	-0.08881500
-0.04528752	0.22482522	-0.01563198	0.05927332
0.06688270	-0.02764801	0.02308599	-0.12936350

ORBITAL OVERLAP MATRIX

1.00000000	0.00000005	0.77705204	0.00000015
0.00000005	0.99999999	0.57252169	0.00000001
0.77705204	0.57252169	1.00000000	0.14710371
0.00000015	0.00000001	0.14710371	0.99999960

CONFIGURATION MIXING COEFFICIENTS

	1S 2S	1S' 2 S12
C	0.99993221	-0.01166525

COMPARISON OF RESULTS

	ORTHOGONAL	NON-ORTHOGONAL
ENERGY	-14.57302493	-14.57671104

CONFIGURATIONS: 1S2 2S2 + 1S'2 S12

OPTIMIZED EXPANSION COEFFICIENTS

1S	2S	1S'	S1
0.48484702	-0.08112933	0.15679502	-0.95417672
0.21760749	-0.14734512	0.85120086	-0.41300519
0.26416611	-0.05114961	0.08542887	-0.51892311
-0.26830237	1.33291146	-0.08676714	0.35102742
0.16827466	-0.04106406	0.05440198	1.90295335
0.16758453	-0.38678014	0.05419547	-0.28051037
0.04512770	-0.00752240	0.01459388	-0.08881500
-0.04528758	0.22482516	-0.01464570	0.05927322
0.06688271	-0.02764800	0.02162925	-0.12936350

ORBITAL OVERLAP MATRIX

1.00000000	0.00000005	0.76515693	0.00000009
0.00000005	0.99999999	0.58562641	0.00000005
0.76515693	0.58562641	1.00000000	0.15047084
0.00000009	0.00000005	0.15047084	0.99999960

CONFIGURATION MIXING COEFFICIENTS

	1S2 2S2	1S'2 S12
C	0.99992818	-0.01198008

COMPARISON OF RESULTS

	ORTHOGONAL	NON-ORTHOGONAL
ENERGY	-14.57302493	-14.57671324

CONFIGURATIONS: 1S2 2S2 + 2S2 S12 + 1S'2 S12

OPTIMIZED EXPANSION COEFFICIENTS

1S	2S	1S'	S1
0.48471211	-0.08137212	0.38223583	-0.95420636
0.22000555	-0.14557960	0.48754268	-0.41257141
0.26410175	-0.05127318	0.20832192	-0.51893706
-0.26992778	1.33142545	-0.21372149	0.35063609
0.16728752	-0.04183736	0.13158841	1.90276992
0.16801127	-0.38641286	0.13273142	-0.28040708
0.04511509	-0.00754505	0.03558466	-0.08881777
-0.04556148	0.22457472	-0.03604066	0.05920726
0.06688586	-0.02766076	0.05277439	-0.12936237

ORBITAL OVERLAP MATRIX

1.00000000	0.00000005	0.96610804	0.00000015
0.00000005	0.99999999	0.23479689	0.00000001
0.96610804	0.23479689	1.00000000	0.06032880
0.00000015	0.00000001	0.06032880	0.99999960

CONFIGURATION MIXING COEFFICIENTS

	1S2 2S2	2S2 S12	1S'2 S12
C	0.99979299	-0.01972811	-0.00372713

COMPARISON OF RESULTS

	ORTHOGONAL	NON-ORTHOGONAL
ENERGY	-14.58486221	-14.58519113

CONFIGURATIONS: 1S2 2S2 + 2S2 SI2 + 1S'2 SI2

OPTIMIZED EXPANSION COEFFICIENTS

1S	2S	1S'	SI
0.48484695	-0.08112952	0.24204187	-0.95417671
0.21760643	-0.14734476	0.73754349	-0.41300569
0.26416607	-0.05114972	0.13187512	-0.51892311
-0.26830108	1.33291118	-0.13393957	0.35102777
0.16822518	-0.04106425	0.08398013	1.90295355
0.16758416	-0.38678010	0.08366024	-0.28051047
0.04512770	-0.00752242	0.02252833	-0.08881500
-0.04528736	0.22482511	-0.02260807	0.05927328
0.06688268	-0.02764802	0.03338870	-0.12936350

ORBITAL OVERLAP MATRIX

1.00000000	0.00000005	0.85502999	0.00000015
0.00000005	0.99999999	0.47168785	0.00000010
0.85502999	0.47168785	1.00000000	0.12119550
0.00000015	0.00000010	0.12119550	0.99999960

CONFIGURATION MIXING COEFFICIENTS

	1S2 2S2	2S2 SI2	1S'2 SI2
C	0.99979531	-0.01906110	-0.00688023

COMPARISON OF RESULTS

	ORTHOGONAL	NON-ORTHOGONAL
ENERGY	-14.58486221	-14.58608313

CONFIGURATIONS: 1S2 2S2 + 2S2 S12 + 1S'2 S12

OPTIMIZED EXPANSION COEFFICIENTS

1S	2S	1S'	S1
0.48484698	-0.08112936	0.19464523	-0.95417670
0.21760702	-0.14734523	0.80385040	-0.41300575
0.26416609	-0.05114963	0.10605133	-0.51892310
-0.26830187	1.33291156	-0.10771207	0.35102785
0.16822496	-0.04106405	0.06753492	1.90295358
0.16758439	-0.38678017	0.06727805	-0.28051049
0.04512770	-0.00752241	0.01811684	-0.08881500
-0.04528750	0.22482518	-0.01818105	0.05927329
0.06688270	-0.02764801	0.02685053	-0.12936350

ORBITAL OVERLAP MATRIX

1.00000000	0.00000005	0.80682313	0.00000015
0.00000005	0.99999999	0.53737258	0.00000001
0.80682313	0.53737258	1.00000000	0.13807251
0.00000015	0.00000001	0.13807251	0.99999960

CONFIGURATION MIXING COEFFICIENTS

	1S2 2S2	2S2 S12	1S'2 S12
C	0.99979522	-0.01869222	-0.00780245

COMPARISON OF RESULTS

	ORTHOGONAL	NON-ORTHOGONAL
ENERGY	-14.58486221	-14.58645412

CONFIGURATIONS: 1S2 2S2 + 2S2 S12 + 1S'2 S12

OPTIMIZED EXPANSION COEFFICIENTS

1S	2S	1S'	S1
0.48484701	-0.08112928	0.16735527	-0.95417670
0.21760803	-0.14734583	0.83846753	-0.41300589
0.26416611	-0.05114959	0.09118256	-0.51892310
-0.26830285	1.33291207	-0.09261074	0.35102805
0.16822443	-0.04106381	0.05806609	1.90295363
0.16758467	-0.38678030	0.05784548	-0.28051054
0.04512770	-0.00752240	0.01557679	-0.08881500
-0.04528766	0.22482526	-0.01563205	0.05927332
0.06688271	-0.02764800	0.02308600	-0.12936350

ORBITAL OVERLAP MATRIX

1.00000000	0.00000005	0.77705204	0.00000009
0.00000005	0.99999999	0.57252169	0.00000005
0.77705204	0.57252169	1.00000000	0.14710371
0.00000009	0.00000005	0.14710371	0.99999960

CONFIGURATION MIXING COEFFICIENTS

	1S2 2S2	2S2 S12	1S'2 S12
C	0.99979534	-0.01845091	-0.00829685

COMPARISON OF RESULTS

ORTHOAGONAL NON-ORTHOAGONAL

ENERGY -14.58486221 -14.58665896

CONFIGURATIONS: 1S2 2S2 + 2S2 1S2 + 1S'2 1S2

OPTIMIZED EXPANSION COEFFICIENTS

1S	2S	1S'	1S
0.48484701	-0.08112933	0.15679502	-0.95417673
0.21760748	-0.14734512	0.85120086	-0.41300519
0.26416611	-0.05114961	0.08542887	-0.51892311
-0.26830237	1.33291146	-0.08676714	0.35102742
0.16822467	-0.04106406	0.05440199	1.90295334
0.16758453	-0.38678014	0.05419546	-0.28051037
0.04512770	-0.00752240	0.01459388	-0.08881500
-0.04528758	0.22482516	-0.01464569	0.05927322
0.06688271	-0.02764800	0.02162925	-0.12936350

ORBITAL OVERLAP MATRIX

1.00000000	0.00000005	0.76515693	0.00000009
0.00000005	0.99999999	0.58562641	0.00000005
0.76515693	0.58562641	1.00000000	0.15047084
0.00000009	0.00000005	0.15047084	0.99999960

CONFIGURATION MIXING COEFFICIENTS

	1S2 2S2	2S2 1S2	1S'2 1S2
C	0.99979560	-0.01835293	-0.00848109

COMPARISON OF RESULTS

	ORTHOGONAL	NON-ORTHOGONAL
ENERGY	-14.58486221	-14.58664172

CONFIGURATION: 1S2 2S2 + 2S2 SI2 + 2S2 SII2

OPTIMIZED EXPANSION COEFFICIENTS

1S	2S	SI	SII
0.48484698	-0.08112930	-0.95417697	-0.06774234
0.21760689	-0.14734551	-0.41300592	0.10874702
0.26416609	-0.05114960	-0.51892325	-0.02813516
-0.26830185	1.33291179	0.35102803	-1.57815512
0.16822500	-0.04106391	1.90295394	0.34661743
0.16758438	-0.38678023	-0.28051059	0.42657336
0.04512770	-0.00752240	-0.08881502	-0.00634123
-0.04528753	0.22482522	0.05927329	1.32929378
0.06688270	-0.02764800	-0.12936354	0.01129780

ORBITAL OVERLAP MATRIX

1.00000000	0.00000005	0.0	0.0
0.00000005	0.99999999	0.0	0.0
0.0	0.0	1.00000000	0.0
0.0	0.0	0.0	0.99999960

CONFIGURATION MIXING COEFFICIENTS

	1S2 2S2	2S2 SI'2	2S2 SII'2
C	0.99980329	-0.01982602	-0.00055155

COMPARISON OF RESULTS

	ORTHOGONAL	NON-ORTHOGONAL
ENERGY	-14.58483730	0.0

CONFIGURATION: 1S2 2S2 + 2S2 SI2 + 2S2 SII2

OPTIMIZED EXPANSION COEFFICIENTS

1S	2S	SI	SII
0.48484698	-0.08112930	-0.94140142	-0.06886700
0.21760689	-0.14734551	-0.40747616	0.19601148
0.26416609	-0.05114960	-0.51197535	-0.02859921
-0.26830187	1.33291181	0.48963975	-1.60492604
0.16822501	-0.04106392	1.87747533	0.35251448
0.16758439	-0.38678023	-0.27675481	0.43381453
0.04512770	-0.00752240	-0.08762587	-0.00644663
-0.04528750	0.22482520	0.05847970	1.35182500
0.06688270	-0.02764800	-0.12763148	0.01149252

ORBITAL OVERLAP MATRIX

1.00000000	0.00000005	0.02102888	0.04838169
0.00000005	0.99999999	0.13975429	0.06405532
0.03102888	0.13975429	1.00000000	0.02128534
0.04838169	0.06405532	0.02128534	0.99999960

CONFIGURATION MIXING COEFFICIENTS

	1S2 2S2	2S2 SI ²	2S2 SII ²
C	0.99981683	-0.01813111	-0.00612970

COMPARISON OF RESULTS

	ORTHOGONAL	NCN-ORTHOGONAL
ENERGY	-14.58483730	-14.58308818

CONFIGURATION: 1S2 2S2 + 2S2 SI2 + 2S2 SII2

OPTIMIZED EXPANSION COEFFICIENTS

1S	2S	SI	SII
0.48484698	-0.08112930	-0.90758842	-0.06942708
0.21760689	-0.14734551	-0.39284053	0.26218441
0.26416609	-0.05114960	-0.49358635	-0.02883180
-0.26830187	1.23291182	0.33388876	-1.61797845
0.16822501	-0.04106392	1.91008474	0.35538140
0.16758439	-0.38678023	-0.26681440	0.43734262
0.04512770	-0.00752240	-0.08447855	-0.00649906
-0.04528751	0.22482520	0.05627924	1.26281904
0.06688270	-0.02764800	-0.12304724	0.01158600

ORBITAL OVERLAP MATRIX

1.00000000	0.00000005	0.08923167	0.08531170
0.00000005	0.99999999	0.00615852	0.11301084
0.08923167	0.00615852	1.00000000	0.03723544
0.08531170	0.11301084	0.03723544	0.99999960

CONFIGURATION MIXING COEFFICIENTS

	1S2 2S2	2S2 SI'2	2S2 SII'2
C	0.99970482	-0.01809263	-0.01621536

COMPARISON OF RESULTS

	ORTHOGONAL	NON-ORTHOGONAL
ENERGY	-14.58483730	-14.58592000

CONFIGURATION: 1S2 2S2 + 2S2 SI2 + 2S2 SII2

OPTIMIZED EXPANSION COEFFICIENTS

1S	2S	SI	SII
0.48484696	-0.08112931	-0.88835703	-0.06747971
0.21760688	-0.14734551	-0.38451642	0.10837359
0.26416608	-0.05114961	-0.48312748	-0.02802309
-0.26830186	1.23291180	0.32681381	-1.57259538
0.16822505	-0.04106390	1.90882656	0.42935706
0.16758438	-0.38678023	-0.26116072	0.42507549
0.04512770	-0.00752240	-0.08268849	-0.00631677
-0.04528750	0.22482522	0.05518459	1.32459297
0.06688269	-0.02764800	-0.12043993	0.01126103

ORBITAL OVERLAP MATRIX

1.00000000	0.00000005	0.12231821	0.07492983
0.00000005	0.99999999	0.00844206	0.00516478
0.12231821	0.00844206	1.00000000	0.04653576
0.07492983	0.00516478	0.04653576	0.99999960

CONFIGURATION MIXING COEFFICIENTS

	1S2 2S2	2S2 SI'2	2S2 SII'2
C	0.99970206	-0.02069340	-0.01294511

COMPARISON OF RESULTS

	ORTHOGONAL	NON-ORTHOGONAL
ENERGY	-14.58483730	-14.58773000

CONFIGURATION: 1S2 2S2 + 2S2 SI2 + 2S2 SII2

OPTIMIZED EXPANSION COEFFICIENTS

1S	2S	SI	SII
0.48484697	-0.08112930	-0.89799462	-0.06718442
0.21760688	-0.14734551	-0.38868796	0.10789911
0.26416608	-0.05114960	-0.48836883	-0.02790053
-0.26830186	1.33291180	0.33035936	-1.56571089
0.16822503	-0.04106391	1.90571445	0.46926663
0.16758438	-0.38678023	-0.26399400	0.42321457
0.04512770	-0.00752240	-0.08358556	-0.00628909
-0.04528752	0.22482521	0.05578325	1.31879442
0.06688270	-0.02764800	-0.12174655	0.01121115

ORBITAL OVERLAP MATRIX

1.00000000	0.00000005	0.10596683	0.11187390
0.00000005	0.99999999	0.00731353	0.00771458
0.10596683	0.00731353	1.00000000	0.06775998
0.11187390	0.00771458	0.06775998	0.99999960

CONFIGURATION MIXING COEFFICIENTS

	1S2 2S2	2S2 SI'2	2S2 SII'
C	0.99946189	-0.01899804	-0.02673958

COMPARISON OF RESULTS

	ORTHOGONAL	NON-ORTHOGONAL
ENERGY	-14.58483730	-14.59247000

CONFIGURATION: 1S2 2S2 + 2S2 SI2 + 2S2 SII2

OPTIMIZED EXPANSION COEFFICIENTS

1S	2S	SI	SII
0.48484697	-0.08112930	-0.95281687	-0.06685409
0.21760688	-0.14734551	-0.41241722	0.10736885
0.26416608	-0.05114960	-0.51818357	-0.02776329
-0.26830186	1.23291180	0.38663028	-1.55801565
0.16822503	-0.04106391	1.90024162	0.50147350
0.16758438	-0.38678023	-0.28011074	0.42113456
0.04512770	-0.00752240	-0.08868843	-0.00625820
-0.04528751	0.22482521	0.05918882	1.31231251
0.06688270	-0.02764800	-0.12917914	0.01115662

ORBITAL OVERLAP MATRIX

1.00000000	0.00000005	0.00781681	0.14210780
0.00000005	0.99999999	0.03520647	0.00980127
0.00781681	0.03520647	1.00000000	0.07140137
0.14210780	0.00980127	0.07140137	0.99999960

CONFIGURATION MIXING COEFFICIENTS

	1S2 2S2	2S2 SI ²	2S2 SII ²
C	0.99895109	-0.01878056	-0.04176126

COMPARISON OF RESULTS

	ORTHOGONAL	NON-ORTHOGONAL
ENERGY	-14.58483730	-14.60486400

CONFIGURATION: 1S2 2S2 + 2S2 SI2 + 2S2 SII2

OPTIMIZED EXPANSION COEFFICIENTS

1S	2S	SI	SII
0.48484696	-0.08112931	-0.88835703	-0.06699440
0.21760688	-0.14734551	-0.38451642	0.10759417
0.26416608	-0.05114961	-0.48312748	-0.02782156
-0.26830185	1.33291180	0.32681384	-1.56128538
0.16822504	-0.04106390	1.90882655	0.48877471
0.16758438	-0.38678023	-0.26116073	0.42201837
0.04512770	-0.00752240	-0.08268849	-0.00627135
-0.04528751	0.22482522	0.05518457	1.31506659
0.06688269	-0.02764800	-0.12043993	0.01118004

ORBITAL OVERLAP MATRIX

1.00000000	0.00000005	0.12231821	0.13014102
0.00000005	0.99999999	0.00844206	0.00897534
0.12231821	0.00844206	1.00000000	0.08084273
0.13014102	0.00897534	0.08084273	0.99999960

CONFIGURATION MIXING COEFFICIENTS

	1S2 2S2	2S2 SI ²	2S2 SII ²
C	0.99916873	-0.02034977	-0.03532327

COMPARISON OF RESULTS

	ORTHOGONAL	NON-ORTHOGONAL
ENERGY	-14.58483730	-14.60057290

CCNFURATION: 1S2 2S2 + 2S2 SI2 + 1S2 SII2 + 2S2 SIII2

OPTIMIZED EXPANSION COEFFICIENTS

1S	2S	SI	SII	SIII
0.48484699	-0.08112932	-0.95417679	-0.06774393	-2.33884042
0.21760689	-0.14734552	-0.41300617	0.10874649	-1.13406164
0.26416610	-0.05114961	-0.51892319	-0.02813803	4.79355160
-0.26830183	1.33291180	0.35103182	-1.57815572	2.27366100
0.16822497	-0.04106391	1.90295310	0.34662313	-2.21169604
0.16758438	-0.38678032	-0.28051161	0.42657355	-1.08119036
0.04512770	-0.00752240	-0.08881501	-0.00634149	-0.21766832
-0.04528759	0.22482522	0.05927008	1.32929419	-0.13442125
0.06688270	-0.02764800	-0.12936356	0.01129749	-0.33514720

ORBITAL OVERLAP MATRIX

1.00000000	0.0	0.0	0.0	0.0
0.0	1.00000000	0.0	0.0	0.0
0.0	0.0	1.00000000	0.0	0.0
0.0	0.0	0.0	1.00000000	0.0
0.0	0.0	0.0	0.0	1.00000000

CONFIGURATION MIXING COEFFICIENTS

	1S2 2S2	2S2 SI'2	1S2 SII'2	2S2 SIII2
C	0.99931819	-0.01977479	-0.03111847	-0.00193873

COMPARISON OF RESULTS

	ORTHOGONAL	NON-ORTHOGONAL
ENERGY	-14.5638600	0.0

CONFIGURATION: 1S2 2S2 + 2S2 SI2 + 1S2 SII2 + 2S2 SIII2

OPTIMIZED EXPANSION COEFFICIENTS

1S	2S	SI	SII	SIII
0.48484699	-0.08112932	-0.90758840	-0.06770398	-2.33884103
0.21760690	0.14734552	-0.39284053	0.10873373	-1.13406060
0.26416609	-0.05114961	-0.49358637	-0.02811623	4.79355133
-0.26830197	1.33291181	0.33388878	-1.57782145	2.27364581
0.16822500	-0.04106391	1.91008475	0.36761636	-2.21169269
0.16758440	-0.38678023	-0.26681441	0.42648810	-1.08118625
0.04512770	-0.00752240	-0.08447855	-0.00633777	-0.21766835
-0.04528750	0.22482522	0.05637922	1.32899487	-0.13440845
0.06688270	-0.02764800	-0.12304724	0.01129845	-0.33514709

ORBITAL OVERLAP MATRIX

1.00000000	0.0	0.08923167	0.01883828	0.0
0.0	1.00000000	0.00615852	0.00129348	0.0
0.08923167	0.00615852	1.00000000	0.01108897	0.0
0.01883828	0.00129348	0.01108897	1.00000000	0.00000995
0.0	0.0	0.0	0.00000995	0.99999999

CONFIGURATION MIXING COEFFICIENTS

	1S2 2S2	2S2 SI2	1S2 SII2	2S2 SIII2
C	0.99937257	-0.01811734	-0.03038291	-0.00195762

COMPARISON OF RESULTS

	ORTHOGONAL	NON-ORTHOGONAL
ENERGY	-14.58636000	-14.58430000

CONFIGURATION: 1S2 2S2 + 2S2 SI2 + 1S2 SII2 + 2S2 SIII2

OPTIMIZED EXPANSION COEFFICIENTS

1S	2S	SI	SII	SIII
0.48484699	-0.08112932	0.92657136	-0.06758409	-2.33884106
0.21760690	-0.14734552	-0.40105711	0.10854124	-1.13406062
0.26416609	-0.05114961	-0.50391014	-0.02806649	4.79355154
-0.26830193	1.33291181	0.34087234	-1.57502819	2.27364612
0.16822500	-0.04106390	1.90913313	0.40899282	-2.21169277
0.16758440	-0.38678023	-0.27239506	0.42573308	-1.08118634
0.04512770	-0.00752240	-0.08624549	-0.00632655	-0.21766833
-0.04528750	0.22482522	0.05755845	1.32664211	-0.13440871
0.06688270	-0.02764800	-0.12562088	0.01127845	-0.33514709

ORBITAL OVERLAP MATRIX

1.00000000	0.0	0.05461608	0.05628997	0.0
0.0	1.00000000	0.00376946	0.00387830	0.0
0.05461608	0.00376946	1.00000000	0.03129509	0.0
0.05628997	0.00387830	0.03129509	1.00000000	0.00000973
0.0	0.0	0.0	0.00000973	0.99999996

CONFIGURATION MIXING COEFFICIENTS

	1S2 2S2	2S2 SI ²	1S2 SII ²	2S2 SIII ²
C	0.99936920	-0.01727724	-0.03096561	-0.00195954

COMPARISON OF RESULTS

ORTHOGONAL

NON-ORTHOGONAL

ENERGY

-14.58636000

-14.58349000

CONFIGURATION: 1S 2S2 + 2S2 SI2 + 1S2 SII2 + 2S2 SIII2

OPTIMIZED EXPANSION COEFFICIENTS

1S	2S	SI	SII	SIII
0.48484699	-0.08112928	-0.88835700	-0.06747973	-2.33884106
0.21760690	-0.14734550	-0.38451641	0.10837361	-1.13406062
0.26416609	-0.05114959	-0.48312750	-0.02802313	4.79355134
-0.26830194	1.23291180	0.32681382	-1.57259571	2.27364610
0.16822501	-0.04106391	1.90882656	0.42935717	-2.21169276
0.16758441	-0.38678022	-0.26116072	0.42507558	-1.08118633
0.04512770	-0.00752240	-0.08268849	-0.00631678	-0.21766838
-0.04528757	0.22482520	0.05518459	1.32459324	-0.13440869
0.06688270	-0.02764800	-0.12043993	0.01126104	-0.33514709

ORBITAL OVERLAP MATRIX

1.00000000	0.0	0.12231821	0.07492983	0.0
0.0	1.00000000	0.00844206	0.00516478	0.0
0.12231821	0.00844206	1.00000000	0.04653576	0.0
0.07492983	0.00516478	0.04653576	1.00000000	0.00000973
0.0	0.0	0.0	0.00000973	0.99999999

CONFIGURATION MIXING COEFFICIENTS

	1S 2S2	2S2 SI'2	1S2 SII'2	2S2 SIII2
C	0.99924061	-0.02072499	-0.03293763	-0.00194543

COMPARISON OF RESULTS

	ORTHOGONAL	NON-ORTHOGONAL
ENERGY	-14.58636000	-14.58732000

CONFIGURATION: 1S2 2S2 + 2S2 SI2 + 1S2 SII2 + 2S2 SIII2

OPTIMIZED EXPANSION COEFFICIENTS

1S	2S	SI	SII	SIII
0.48484699	-0.08112932	-0.92657136	-0.06734638	-2.33884105
0.21760690	-0.14734552	-0.40105711	0.10815948	-1.13406050
0.26416609	-0.05114961	-0.50391014	-0.02796776	4.79355133
-0.26830193	1.33291181	0.34087234	-1.56948811	2.27364607
0.16822500	-0.04106390	1.90913313	0.44944349	-2.21169272
0.16758440	-0.38678023	-0.27239505	0.42423559	-1.08118632
0.04512770	-0.00752240	-0.08624509	-0.00630429	-0.21766833
-0.04528750	0.22482522	0.05755844	1.32197572	-0.13440867
0.06688270	-0.02764800	-0.12562088	0.01123877	-0.33514705

CRIPITAL OVERLAP MATRIX

1.00000000	0.0	0.05461608	0.09345395	0.0
0.0	1.00000000	0.00376946	0.00644327	0.0
0.05461608	0.00376946	1.00000000	0.05197269	0.0
0.09345395	0.00644327	0.05197269	1.00000000	0.00000973
0.0	0.0	0.0	0.00000973	0.99999999

CONFIGURATION MIXING COEFFICIENTS

	1S2 2S2	2S2 SI ²	1S2 SII ²	2S2 SIII2
C	0.99916821	-0.01727363	-0.03688718	-0.00195914

COMPARISON OF RESULTS

	ORTHOGONAL	NON-ORTHOGONAL
ENERGY	-14.58636000	-14.58369000

CONFIGURATION: 1S2 2S2 + 1S2 2P2 + 2S² 2P2

OPTIMIZED EXPANSION COEFFICIENTS

1S	2S	2S'
0.04574680	-0.00874895	0.0
0.26213913	-0.03494076	0.0
0.74029787	-0.16338958	0.0
-0.05317447	-0.08125703	0.01551497
C.C1791133	0.19720545	-0.13002356
-0.00845937	0.86446870	1.18685880
0.00246533	0.03438955	-0.08992748

ORBITAL OVERLAP MATRIX

0.99999987	0.00000008	0.0
C.CCCCC008	0.99999989	0.0
0.0	0.0	0.99999989

CONFIGURATION MIXING COEFFICIENTS

	1S2 2S2	1S2 2P2	2S2 2P2
C	0.94994026	C.18038205	0.00038749

COMPARISON OF RESULTS

ORTHOGONAL NON-ORTHOGONAL

ENERGY -14.61660000 0.0

CONFIGURATION: 1S2 2S2 + 1S2 2P2 + 2S² 2P2

OPTIMIZED EXPANSION COEFFICIENTS

1S	2S	2S'	2P
0.04574667	-0.00875193	-0.00448823	0.0
0.26213723	-0.03500110	-0.01797452	0.0
0.74029733	-0.16337627	-0.08374821	0.0
-0.05316749	-0.08099393	-0.04138579	0.01551497
0.01789629	0.19663453	0.10051017	-0.13002356
-0.00844044	0.86492329	0.53658363	1.18685880
0.00246272	0.03429037	0.01752779	-0.08992748

ORBITAL OVERLAP MATRIX

1.00000000	0.0	0.10215231	0.0
0.0	1.00000000	0.99464877	-0.0
0.10215231	0.99464877	1.00000000	0.0
0.0	0.0	0.0	1.00000000

CONFIGURATION MIXING COEFFICIENTS

	1S2 2S2	1S2 2P2	2S ² 2P2
C	0.94993600	0.17944161	0.00108669

COMPARISON OF RESULTS

ORTHOGONAL NON-ORTHOGONAL

ENERGY -14.61660000 -14.61676000

CONFIGURATION: 1S2 2S2 + 1S2 2P2 + 2S² 2P2

OPTIMIZED EXPANSION COEFFICIENTS

1S	2S	2S ²	2P
0.04574680	-0.00874895	-0.00627665	0.0
0.26213910	-0.03494096	-0.02506734	0.0
0.74029783	-0.16338998	-0.11721897	0.0
-0.05317440	-0.08125681	-0.05829485	0.01551497
0.01791185	0.19720763	0.46340829	-0.13002356
-0.00845997	0.86446689	0.62018185	1.18685880
0.00246533	0.03438948	0.02467155	-0.08992748

ORBITAL OVERLAP MATRIX

1.00000000	0.0	0.12833785	0.0
0.0	1.00000000	0.98342401	0.0
0.12833785	0.98342401	1.00000000	0.0
0.0	0.0	0.0	1.00000000

CONFIGURATION MIXING COEFFICIENTS

	1S2 2S2	1S2 2P2	2S ² 2P2
C	0.94903208	0.18192378	0.00405460

COMPARISON OF RESULTS

	ORTHOGONAL	NON-ORTHOGONAL
ENERGY	-14.61660000	-14.61702000

CONFIGURATION: 1S2 2S2 + 1S2 2P2 + 2S'2 2P2

OPTIMIZED EXPANSION COEFFICIENTS

1S	2S	2S'	2P
0.04574674	-0.00874995	-0.00061883	0.0
0.26213840	-0.03495843	-0.00248578	0.0
0.74029742	-0.16338758	-0.01153535	0.0
-0.05317212	-0.08118258	-0.00565992	0.01551497
0.01790634	0.19704429	0.01375666	-0.13002356
-0.00845113	0.86459705	0.99202282	1.18685880
0.00246446	0.03436154	0.00239905	-0.08992748

ORBITAL OVERLAP MATRIX

1.00000000	0.0	0.19289802	0.0
0.0	1.00000000	0.98078505	-0.0
0.19289802	0.98078505	1.00000000	0.0
0.0	0.0	0.0	1.00000000

CONFIGURATION MIXING COEFFICIENTS

	1S2 2S2	1S2 2P2	2S'2 2P2
C	0.95016144	0.17658936	0.00328707

COMPARISON OF RESULTS

	ORTHOGONAL	NON-ORTHOGONAL
ENERGY	-14.61660000	-14.61945000

CONFIGURATION: 1S2 2S2 + 1S2 2P2 + 2S'2 2P2

OPTIMIZED EXPANSION COEFFICIENTS

1S	2S	2S'	2P
0.04574680	-0.00874895	-0.00388309	0.0
0.26213912	-0.03494076	-0.01550794	0.0
0.74029787	-0.16338966	-0.07251816	0.0
-0.05317447	-0.08125699	-0.03606464	0.01551497
0.01791154	0.19720584	0.68903794	-0.13002356
-0.00845964	0.86446840	0.38368096	1.18685880
0.00246533	0.03438955	0.01526330	-0.08992748

ORBITAL OVERLAP MATRIX

1.00000000	0.0	0.23979531	0.0
0.0	1.00000000	0.54086133	-0.0
0.23979531	0.94086133	1.00000000	0.0
0.0	0.0	0.0	1.00000000

CONFIGURATION MIXING COEFFICIENTS

	1S2 2S2	1S2 2P2	2S'2 2P2
C	0.95071459	0.17379753	0.00435571

COMPARISON OF RESULTS

	ORTHOGONAL	NON-ORTHOGONAL
ENERGY	-14.61660000	-14.62363000

CONFIGURATION: 1S2 2S2 + 1S2 2P2 + 2S*2 2P2

OPTIMIZED EXPANSION COEFFICIENTS

1S	2S	2S*	2P
0.04610323	-0.00908298	-0.00236769	0.0
0.26460028	-0.03717814	-0.00984908	0.0
0.74529488	-0.16819509	-0.03950040	0.0
-0.05630778	-0.07876382	-0.01475311	0.01551497
-0.00873313	0.21862966	0.83789640	-0.13002356
0.01543472	0.84602420	0.20721699	1.18685880
0.00350847	0.03357918	0.00686062	-0.08992748

ORBITAL OVERLAP MATRIX

1.00000000	0.0	0.31309516	0.0
0.0	1.00000000	0.89684120	-0.0
0.31309516	0.89684120	1.00000000	0.0
0.0	0.0	0.0	0.99999989

CONFIGURATION MIXING COEFFICIENTS

	1S2 2S2	1S2 2P2	2S*2 2P2
C	0.87477023	0.27688319	0.03993382

COMPARISON OF RESULTS

	ORTHOGONAL	NON-ORTHOGONAL
ENERGY	-14.61660000	-14.64517000

CONFIGURATION: 1S2 2S2 + 1S2 2P2 + 2S'2 2P2

OPTIMIZED EXPANSION COEFFICIENTS

1S	2S	2S'	2P
0.04574680	-0.00874896	-0.00003756	0.0
0.26213915	-0.03494079	-0.00014999	0.0
0.74029792	-0.16338968	-0.00070140	0.0
-0.05317447	-0.08125707	-0.00034882	0.01551497
0.01791133	0.19720554	0.00084656	-0.13002356
-0.00845939	0.86446911	0.00371097	1.18685880
0.00246537	0.03438901	0.99634530	-0.08992748

ORBITAL OVERLAP MATRIX

1.00000000	0.0	0.10086893	0.0
0.0	1.00000000	0.89103400	0.0
0.10086893	0.89103400	1.00000000	0.0
0.0	0.0	0.0	1.00000000

CONFIGURATION MIXING COEFFICIENTS

	1S2 2S2	1S2 2P2	2S'2 2P2
C	0.94948507	0.18115787	0.00280347

COMPARISON OF RESULTS

	ORTHOGONAL	NON-ORTHOGONAL
ENERGY	-14.6166000	-14.61688000

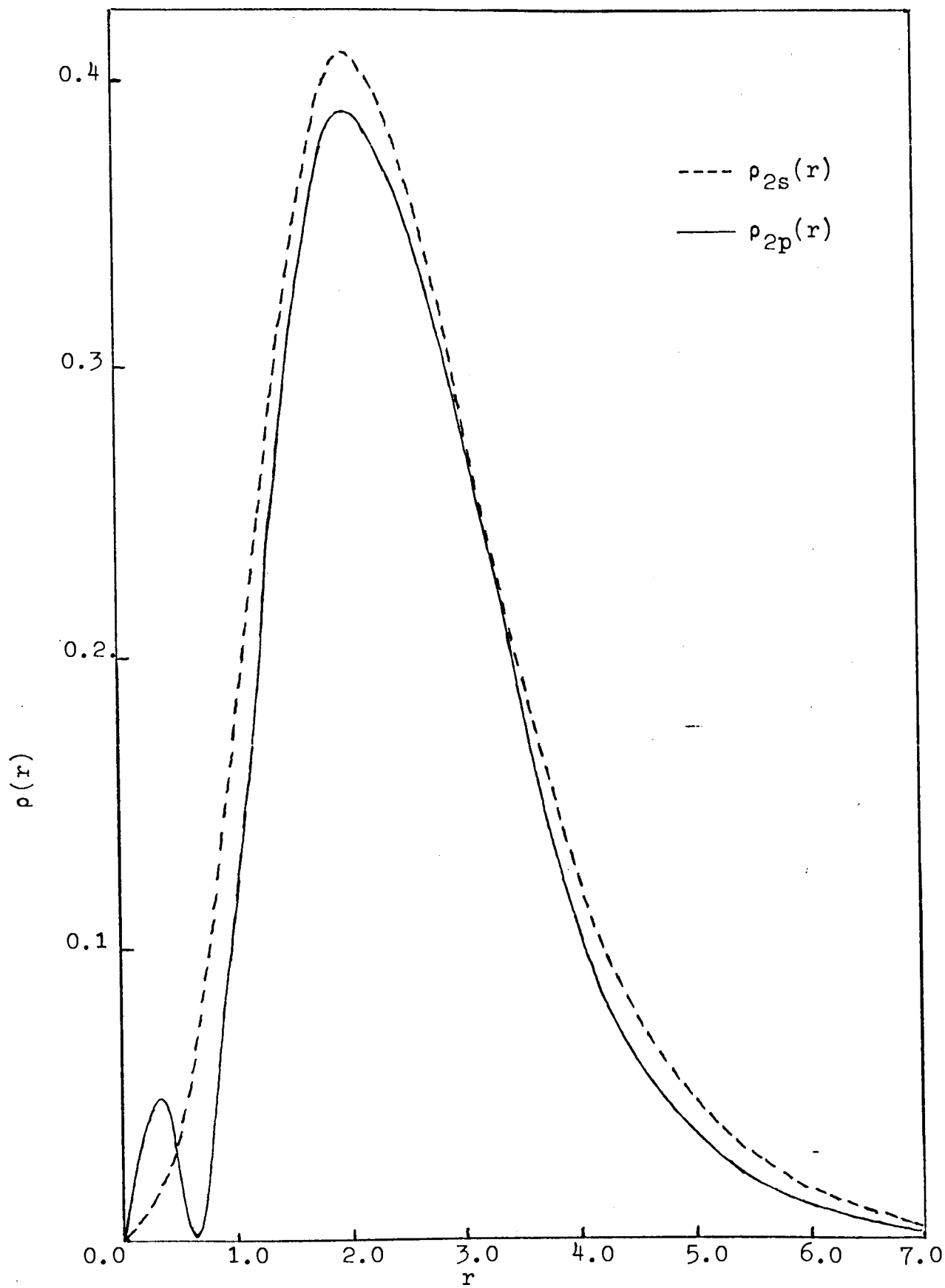


Fig. 1 Be one-electron 2s and 2p charge densities

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