

Exchange Energy Calculation of He-He
with Supermolecular One-Matrix

by

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ABSTRACT

Exchange energy of the He-He system is calculated using the one-density matrix which has been modified according to the supermolecular density formula quoted by Kołos. The exchange energy integrals are computed analytically and by the Monte Carlo method. The results obtained from both ways compared favourably with the results obtained from the SCF program HONDO.

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Chapter 1

INTRODUCTION

The intermolecular forces are of fundamental importance for understanding the dynamic and static properties of gases, liquids, and solids [1]. The theory of intermolecular forces can be extended to difficult systems (e.g. hydrogen-bonded systems, adsorbates, macromolecules, etc.), and serious work on the problem of three body forces in dense phases can be started when the intermolecular forces between two closed systems are known precisely [2]. The quantum mechanical methods like SCF, CI, or perturbation theory can be applied at most to medium size atoms or molecules, and even for simple systems such calculations become very tedious if one wishes to obtain accurate results.

The first successful a priori prediction of the intermolecular repulsive potentials between closed-shell atoms, ions, and molecules has been proposed by Gaydaenko, Nikulin [3] and by Kim and Gordon [4]. The method is based on the statistical model of the atom, and mostly known as the Electron Gas Approximation (EGA). The agreement between theory and experiment was pretty good, except for the case of the He-He system. In the case of He-He, the potential energy curve obtained was too negative and had a very deep well.

The EGA theory of intermolecular forces has been modified by Rae [5], removing the self-exchange energy part from the exchange energy which was estimated in the EGA method. He also introduced the long-range dispersive interaction, to improve the long-range potential energy curve. Rae's method gives a better potential energy curve for the He-He system than the Gordon-Kim method; however, Rae's method is not without its difficulties. It predicts too repulsive interatomic potentials at small intermolecular distances.

Therefore one can conclude that neither the original method nor the corrected one succeeds in yielding reliable results for all systems. This deficiency in the electron gas calculation encouraged Waldman and Gordon to correct the exchange energy in an electron gas calculation. They decided that only the self-exchange energy should be removed by subtracting contributions of the separate atoms in a molecular calculation and proposed a scaled correction for the exchange energy [6]. Even in its scaled form, the EGA not only fails to predict the noble gas pure and mixed interactions with useful precision but also shows error trends that are not consistent with the basic approximation of the method.

However, the electron gas model has been properly criticized because atomic and molecular densities are far from uniform. Brual and Rothstein have the statistical model with a rational function used for the correlation energy density and they have opted for an entirely different approach to the exchange energy which was developed by Handler [7]. The results are a significant improvement over those available from competing electron gas models.

A simple reliable method for the prediction of intermolecular potentials is presented for the lighter noble gases and the mixtures by Hepburn, Penco and Scoles [8]. This method is the hybrid SCF plus damped dispersion models of the Hartree-Fock Dispersion (HFD). The interaction potentials can be found with a sufficient precision to obtain information of value comparable to experimental potential.

A recent and promising effort is the Approximate Exchange Energy (AEE). This model has been developed by Ng et al. [9] and shown to be very accurate for He-He, Ne-Ne, Ar-Ar, and Kr-Kr, but suffers from the shortcoming that one of its parameters has to be determined by fitting to experimental property.

The exchange energy is a purely quantum mechanical effect and can not

be related directly to any observable property of the interacting systems. There is thus a great interest in ab initio methods capable of providing accurate estimates of this effect.

An approximate ab initio approach for calculation of the exchange repulsion energy between closed shell systems described by Hartree-Fock determinants has been proposed by Bulski et al. [10].

The first order exchange energy for the Ar-Ar interaction has been reported using SCF wavefunction for Ar in a large gaussian basis set by Chalasinski et al. [11].

In the present work the supermolecular one-matrix $P_{AB}(1;2)$ of two closed shells A and B is modified from the supermolecular density of two-closed shell system. The supermolecular density $P_{AB}(1;1)$ is quoted by Kołos [12] after Fröman and Löwdin [13] and Jeziorski et al. [14]. The supermolecular one-matrix will be substituted for the spinless one-matrix in the exchange energy formula.

This supermolecular one-matrix formalism will be applied to the He-He system which is the simplest two-closed shell system, to calculate the exchange energies of He-He at different internuclear distances. The results of the exchange energies of He-He at different internuclear distances obtained analytically and by the Monte Carlo method will be compared with those obtained from a SCF program HONDO [15].

In Chapter 2, the SCF theory and the SCF program HONDO are presented in detail together with our modifications to HONDO, which were necessary to get it to run on Brock University's BURROUGH's B6700 computer.

In Chapter 3, the density matrix and the exchange energy for the supermolecule is given in a form appropriate for rare gas systems. The proposed supermolecular one-matrix is applied to the He-He system. The

necessary integrations are done analytically. Comparison with the true results from HONDO is presented.

For a large system, e.g. Ar-Ar, the two electron integral which must be evaluated for the exchange energy is complicated. To facilitate its calculation, it is evaluated by the Monte Carlo simulation. Chapter 4 gives the evaluation of the exchange energy integral for the He-He system. Extensions to the larger systems are discussed therein.

In Chapter 5, the summary and conclusions are presented. The applicability of this method to the other systems is also discussed.

CHAPTER 2

SELF-CONSISTENT FIELD THEORY

2.1 Introduction

The Schrödinger equation

$$\hat{H}\Psi = E\Psi \quad (2-1)$$

gives the analytic solutions for the atoms and the molecules with one-electron. For an N electron system one must turn to approximate solutions to obtain a property such as the total electronic energy E.

One of the approaches to approximate solutions of the Schrödinger equation is the variational principle, which says that if Ψ is a trial many-electron ground-state wave function, and if $W = \langle \Psi | \hat{H} | \Psi \rangle / \langle \Psi | \Psi \rangle$, then $W \geq E_0$ where \hat{H} is the complete Hamiltonian, and E_0 is the exact energy. Since W is always above E_0 , Ψ may be varied to minimize W . The most common application of the variational principle is the self-consistent-field method (SCF) which will be outlined in this section.

For a molecule having A nuclei of charge Z_k and N electrons, neglecting magnetic interactions and other higher-order effects, the purely electronic Hamiltonian, in atomic units (electronic mass m_e , electronic charge e , and $h/2\pi$ set to unity) is

$$\hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \sum_k \frac{Z_k}{r_{ik}} + \sum_{j>i} \frac{1}{r_{ij}} \quad (2-2)$$

The first sum in Eq. (2-2) contains the kinetic energy operators for the N electrons; the second sum is the potential energy for the attractions between the electrons and nuclei. r_{ik} is the distance between electron i and the kth nucleus; the last sum is the potential energy of the interelectronic repulsions between pairs of electrons; r_{ij} is the distance between electron i and electron j. The restriction $j>i$ avoids counting the same interelectronic repulsion twice.

The "best" possible variation function that has the form of an anti-symmetrized product of spin orbitals is the Hartree-Fock SCF wave function [16, 17]. For closed-shell systems the Hartree-Fock wave function is of the form

$$\Psi_{\text{HF}} = A(N) \phi_1(1) \phi_2(2) \dots \phi_N(N) \quad (2-3)$$

in which $A(N)$ is the antisymmetrizer for N electrons and the ϕ 's are spin orbitals, products of a spatial orbital and a one electron spin function α (for $m_s = +\frac{1}{2}$) or β (for $m_s = -\frac{1}{2}$).

$$\phi_i = \begin{array}{l} X_i \alpha \\ \text{or} \\ X_i \beta \end{array} \quad (2-4)$$

The Hartree-Fock wave function is the best function of the single determinant form which can be written as a Slater determinant [18].

$$\Psi_{\text{HF}}(1, \dots, N) = \frac{1}{(N!)^{1/2}} \begin{vmatrix} \phi_1(1) \phi_2(1) \dots \phi_N(1) \\ \phi_1(2) \phi_2(2) \dots \phi_N(2) \\ \vdots \\ \phi_1(N) \phi_2(N) \dots \phi_N(N) \end{vmatrix} \quad (2-5)$$

It is usually the case that all the orbitals in the Slater determinant in Eq. (1-5) are orthogonal

$$S_{ij} = \int dv(1) \phi_i(1) \phi_j(1) = \delta_{ij} \quad (2-6)$$

where $dv(1)$ indicates integration over the space and spin coordinates of electron 1 and δ_{ij} is the kronecker delta.

The exclusion principle is accounted for since the determinant vanishes identically unless the N spin orbitals form a linearly independent set.

Using the wave function Eq. (2-5) and the purely electronic Hamiltonian Eq. (2-2) in the expression $E_{\text{HF}} = \langle \Psi_{\text{HF}} | \hat{H} | \Psi_{\text{HF}} \rangle / \langle \Psi_{\text{HF}} | \Psi_{\text{HF}} \rangle$ gives the expecta-

tion value of the energy, E_{HF} , which is as close to E_0 as possible with a single determinant form.

$$E_{\text{HF}} = \sum_{i=1}^N H_i + \sum_{j>i} \sum_{i=1}^N (J_{ij} - K_{ij}) \quad (2-7)$$

This formula was derived by Slater [19] [Appendix I].

The first summation in Eq. (2-7) goes over the one-electron integrals; the second sum represents the electron repulsion integrals or two-electron integrals where

$$H_i = \int dv(1) \phi_i^*(1) \left\{ -\frac{\nabla_1^2}{2} - \sum_k^A \frac{Z_k}{r_{1k}} \right\} \phi_i(1) \quad (2-8)$$

$$J_{ij} = \iint dv(1) dv(2) \phi_i^*(1) \phi_j^*(2) \frac{1}{r_{12}} \phi_j(2) \phi_i(1) \quad (2-9)$$

$$K_{ij} = \iint dv(1) dv(2) \phi_i^*(1) \phi_j^*(2) \frac{1}{r_{12}} \phi_j(1) \phi_i(2) \quad (2-10)$$

The spin integrations in Eqs. (2-8, 9, 10) drop out immediately since none of the terms in our electrostatic Hamiltonian is spin dependent.

The two electron integrals in Eq. (2-9) and Eq. (2-10) are called Coulomb integrals and exchange integrals, respectively. The exchange integrals Eq. (2-9) differ from Eq. (2-10) only by interchange of the last two indices i and j . These terms arise from the permutations inherent in the determinantal form. K_{ij} vanishes, due to the spin orthogonality, unless $\phi_i(1)$ and $\phi_j(1)$ have the same spin component. Exchange integrals account for energy differences between singlet and triplet configurations.

By minimizing the energy Eq. (2-7) resulting from the single determinant wave function Eq. (2-5) a set of N coupled integrodifferential equations can be derived [see Appendix II]. These Hartree-Fock integrodifferential equations may also be put in the form of effective one-particle Schrödinger

equations

$$\hat{H}_i^{\text{eff}}(1)\phi_i(1) = \varepsilon_i\phi_i(1) \quad i = 1, \dots, N \quad (2-11)$$

In the Hartree-Fock approximation, the motion of each electron is solved for in the presence of the average potential created by the remaining (N-1) electrons. The effective Hartree-Fock Hamiltonian may be written as follows

$$\hat{H}_i^{\text{eff}}(1) = H_i(1) + V_i^{\text{av}}(1) \quad (2-12)$$

where

$$\hat{H}_i(1) = -\frac{1}{2}\nabla_1^2 - \sum_k \frac{Z}{r_{1k}} \quad (2-13)$$

and

$$V_i^{\text{av}}(1) = \sum_{j \neq i} \int dv(2)\phi_j^*(2) \frac{1}{r_{12}} (1-P_{ij})\phi_j(2) \quad (2-14)$$

in which P_{ij} is an operator which exchanges the subscripts i and j occurring to the right of it, e.g. $P_{ij}\phi_j(2)\phi_i(1) = \phi_i(2)\phi_j(1)$. From Eq. (2-14), the Coulomb and the exchange operators can be defined, respectively

$$\hat{J}_j(1) = \sum_{j \neq i} \int dv(2)\phi_j^*(2) \frac{1}{r_{12}} \phi_j(2) \quad (2-15)$$

$$\hat{K}_j(1) = \sum_{j \neq i} \int dv(2) \phi_j^*(2) \frac{1}{r_{12}} P_{ij}\phi_j(2) . \quad (2-16)$$

Since the exchange integrals K_{ij} are always positive [20], the total energy E_{HF} is lowered by the operation of exchange forces Eq. (2-7) [21]. In the Hartree-Fock equation Eq. (2-11), the "exchange forces" between electrons of parallel spin are given as follows

$$- \sum_{j \neq i} \left[\int dv(2)\phi_j^*(2) \frac{1}{r_{12}} \phi_i(2) \right] \phi_j(1) . \quad (2-17)$$

The effect of the exchange term is to reduce the Coulombic repulsions between electrons with the same spin. Physically, its effects may be simulated by surrounding each electron with a small spherical volume within which other electrons of the same spin may not intrude; the excluded volume is often referred to as the Fermi hole. This mutual avoidance of electrons with the same spin permits the space orbitals to be closer to the atomic nucleus and therefore more strongly bound in these instances [22].

The eigenvalues, $\epsilon_1, \dots, \epsilon_N$ of the Hartree-Fock equations Eq. (2-11) may be related to the integrals Eq. (2-8), Eq. (2-9) and Eq. (2-10), evaluated using the minimized spin orbital functions $\phi_i(1)$. Multiplying the i th equation in Eq. (2-11) by $\phi_i^*(1)$ and integrating over $dv(1)$ the following equation can be obtained

$$\epsilon_i = H_i + \sum_{j=1}^N (J_{ij} - K_{ij}) \quad (2-18)$$

ϵ_i are known as orbital energies. Koopmans' theorem states that these orbital energies ϵ_i may be associated with the ionization potentials of the closed shell atom or molecule. For closed shell systems $-\epsilon_i$ equals the ionization potential for the i th electron minus the total energy of the ion formed by removing electron i . It should be noted that the total electronic energy Eq. (2-7) is not equal to the sum of one-electron energies. This is because the sum of one-electron energies is greater than the total energy since interelectronic repulsion terms $J_{ij} - K_{ij}$ are counted twice over.

$$\begin{aligned} \sum_{i=1}^N \epsilon_i &= \sum_{i=1}^N H_i + \sum_{j \neq i} \sum_{i=1}^N (J_{ij} - K_{ij}) \\ &= \sum_{i=1}^N H_i + 2 \sum_{j>i} \sum_{i=1}^N (J_{ij} - K_{ij}) \\ &= E_{\text{HF}} + \sum_{j>i} \sum_{i=1}^N (J_{ij} - K_{ij}) \end{aligned}$$

E_{HF} can be written as follows

$$E_{\text{HF}} = \sum_{i=1}^N \epsilon_i - \sum_{j>i} \sum_{i=1} (J_{ij} - K_{ij}) \quad (2-19)$$

and we also have Eq. (2-7) for E_{HF} .

Since all the orbitals appear in \hat{V}_i^{av} , Eq. (2-14), they occur in each equation of Eq. (2-11). Therefore the Hartree-Fock equations cannot be solved without making an initial guess at the ϕ_i . One can solve for the ϕ_i and use these as input for another calculation (iteration). Iteration is continued until the calculated set agrees with the input set as closely as desired. The calculation is then said to be self-consistent, that is, the orbitals calculated from Eq. (2-11) are consistent with the orbitals which supply the field \hat{V}_i^{av} for the calculation; thus the term "self-consistent-field (SCF) calculation". If the variation has been complete, the final orbitals are not only self-consistent, but they are the Hartree-Fock orbitals of the atom.

The average potential \hat{V}_i^{av} mostly takes care of the mutual inter-electronic repulsion between electrons. Furthermore, this discussion of the Hartree-Fock method identifies \hat{V}_i^{av} as the source of the screening which reduces the nuclear charge to Z_{eff} and depends on the other occupied orbitals in the atom or molecule. However, Z_{eff} is only one parameter per orbital; in general, several variational parameters should be introduced and varied to achieve an orbital of Hartree-Fock accuracy.

The Hartree-Fock equations, Eq. (2-11), were originally solved by numerical methods which yield orbitals as tables of radial functions. The Hartree-Fock equations reduce to ordinary differential equations in r (rather than partial differential equations in r , ϕ and ψ) because \hat{V}_{av} is spherically symmetric (for atoms). As a result the angular solutions must be the

spherical functions and the Hartree-Fock equations need only be solved for $R_{n\ell}(r)$. When highly refined, this is probably the most accurate method, but it is seldom used. The Hartree-Fock-Roothan procedure is easily adapted to rapid calculation on electronic computers and is very widely applied in atomic and molecular calculations.

2.2 SCF LCAO-MO Approach

The Hartree-Fock Roothaan procedure provides an approximate Hartree-Fock solution for a molecular system [23]. One obtains a set of orthonormal molecular orbitals which minimize the energy of a single Slater determinant representing the ground state molecular wave function. These molecular orbitals are formed as linear combinations of the chosen basis set [24] of one electron atomic orbitals

$$\phi_i(1) = \sum_{\beta=1}^{N'} C_{i\beta} X_{\beta}(1) \quad (2-20)$$

where the linear coefficients, $C_{i\beta}$ are evaluated variationally and are solutions of the following equation

$$\sum_{\beta}^{N'} (H_{\alpha\beta} - \epsilon S_{\alpha\beta}) C_{i\beta} = 0 \quad \alpha = 1, \dots, N' \quad (2-21)$$

and where N' is the number of linearly independent functions $X_1, \dots, X_{N'}$. If N is the number of atomic or molecular spin orbitals, it is necessary that $N' \geq N$.

If we insert Eq. (2-20) into Eq. (2-11), multiply on the left hand side by $X_{\alpha}^*(1)$, and integrate over $dv(1)$, we obtain Eq. (2-21) where

$$\begin{aligned}
H_{\alpha\beta} &= \int dv(1) X_{\alpha}^{*}(1) H_{\mathbf{i}}^{\text{eff}}(1) X_{\beta}(1) \\
&= [\alpha|\beta] + \sum_j \sum_{\gamma\delta} C_{j\gamma}^{*} C_{j\delta} ([\alpha\beta|\gamma\delta] - [\alpha\delta|\gamma\beta])
\end{aligned} \tag{2-22}$$

and

$$S_{\alpha\beta} = \int dv(1) X_{\alpha}^{*}(1) X_{\beta}(1) . \tag{2-23}$$

The total molecular wave function is obtained by solving Eq. (2-21), that is by finding the solution of the secular equation

$$\det(H_{\alpha\beta} - \epsilon S_{\alpha\beta}) = 0 . \tag{2-24}$$

This secular equation determines the orbital energies, $\epsilon_{\mathbf{i}}$; Eq. (2-21) determines the corresponding coefficients.

In Eq. (2-22) the one-electron integrals $[\alpha|\beta]$ and the two-electron integrals $[\alpha\beta|\gamma\delta]$ can be expressed as follows:

$$[\alpha|\beta] \equiv \int dv(1) X_{\alpha}^{*}(1) \left\{ -\frac{1}{2} \nabla^2 - \sum_k \frac{Z_k}{r_{1k}} \right\} X_{\beta}(1) \tag{2-25}$$

$$[\alpha\beta|\gamma\delta] \equiv \iint dv(1) dv(2) X_{\alpha}^{*}(1) X_{\beta}(1) \frac{1}{r_{12}} X_{\gamma}^{*}(2) X_{\delta}(2) \tag{2-26}$$

Hence, the problem of determining the wave functions for a closed shell molecule comprised of N electrons is reduced to the straightforward solution of a secular equation. In practice an initial $C_{\mathbf{i}\beta}$ is chosen, $H_{\alpha\beta}$ and $S_{\alpha\beta}$ are computed from Eq. (2-22) and Eq. (2-23), respectively, and Eq. (2-24) is solved. Using the first improved $C_{\mathbf{i}\beta}$, $H_{\alpha\beta}$ and $S_{\alpha\beta}$ are solved again. The procedure is repeated until the total energy and eigenvectors are unchanged to the extent of some accuracy.

2.3 Program HONDO

The SCF program HONDO which is reported by Dupuis, Rys and King [15] has been used to calculate the exchange energy between two closed shell systems. HONDO calculates RHF and UHF SCF molecular wave functions, optimizes molecular geometries using the gradient of RHF or UHF energy with respect to the $3*N$ nuclear coordinates and calculates the following properties of RHF and UHF wave function: (a) dipole moment, (b) Mulliken population analysis. This program uses Gaussian type basis functions. Pople's STO-NG and N-31G basis sets are available.

Calculation of an ab initio wave function by the Roothaan LCAO-SCF method involves two major computational steps; SCF iteration and calculation of two-electron integrals, each of which can be made more efficient if the molecular system possesses some point group symmetry. By considering symmetry one can reduce the number of two-electron integrals to be manipulated, and speed up calculation of the Fock matrix during each SCF cycle [25].

In HONDO orbital basis functions are grouped into shells and integrals into blocks for efficient integral evaluation. The shell structure of HONDO is ideally suited for use with Dacre-Elder scheme [26,27] for treating point group symmetry. The SCF program HONDO efficiently computes blocks of integrals using a formula based on the properties of orthogonal polynomials. An entire block of two electron integrals is eliminated if it is symmetrically equivalent to another block with a higher index. Using the "petite list" of block of integrals, a skeleton matrix is formed from which the true Fock matrix is generated by "symmetrization". In order to

reduce the amount of input data to be supplied, all symmetry information in input data is the Schönflies point group symbol and the coordinates of three points which specify the symmetry frame. It can be used for any closed shell molecule and requires negligible computer time to carry out the symmetry-related computations.

HONDO employs Cartesian Gaussian type basis functions. Angular dependence of a basis function may be introduced by a factor $Y_{\ell m}(\theta, \phi)$. However for Gaussians the angular dependence is more frequently introduced, as suggested by S. F. Boys [28], by a primitive basis function of the form

$$C x^p y^q z^s e^{-\alpha r^2} \quad (2-27)$$

where p , q and s are integers. The sum of powers, λ ,

$$\lambda = p + q + s \quad (2-28)$$

is closely related to the total angular momentum quantum number. Functions of this type Eq. (2-27) are usually called Cartesian Gaussian.

As has been mentioned the Roothaan procedure is iterative and large basis sets may need more iterations in order to reach convergence. It is possible to reduce the number of integrals to be evaluated while only slightly reducing the flexibility of the basis set, by using contracted Gaussians, linear combinations of Gaussians with fixed coefficients

$$\chi = x^p y^q z^s \sum_k C_k \exp(-a_k r^2) .$$

In HONDO a shell of functions is a collection of χ all on the same centre and all made up from the same set of exponential parameters a_k . To achieve the necessary flexibility without making the χ basis needlessly large, the construction of a small number of well-chosen, highly contracted

low angular momentum inner shell functions and a lightly contracted valence shell set with high- λ functions have been used by Dupuis, Rys and King [29].

A shell structure is computationally advantageous and particularly simple if an integral over primitives can be written as a product of three factors corresponding to the three Cartesian coordinates. Dupuis and King proved that the two-electron Coulomb repulsion integral can be expressed as a finite sum of such products of three factors. Each term corresponds to one root of a Rys polynomial, the degree of which depends upon the sum of four λ values. The Coulomb repulsion integral is evaluated by an exact numerical Rys quadrature formula [30].

The method of Rys quadrature is applicable to a wide variety of molecular integrals over Gaussian basis functions including those for all the usual one-electron properties as well as for the three and four electron integrals that arise in certain treatments of electron correlation. This method is simple, accurate and applies to any positive integer values of p , q , and s in Eq. (1).

2.4 Modifications to HONDO

HONDO is written in FORTRAN IV for the CDC 6400 by Dupuis, Rys and King.

To get HONDO to work for the Burroughs B 6700/B 7700 several changes have been made. In this section all modifications to HONDO will be given.

Mass storage input/output (MSIO) subroutines in CDC allow the user to create, access, and modify files on a random basis without regard for their physical positioning. Mass storage subroutines which are used in the CDC version of HONDO are OPENMS, CLOSMS, READMS and WRITMS.

OPENMS opens the mass storage file and informs the system that it is

a random (word addressable) file. By creating the files in the job file the same work can be done in Burroughs so that there is no need to have an OPENMS subroutine in Burroughs.

CLOSMS writes the master index from central memory to the file and closes the file. CLOSMS is provided to close a file so that it can be returned to the operating system before the end of a FORTRAN run. To achieve that the CLOSE statement can be used in Burroughs, the CLOSE statement is given for a disk file as follows:

```
CLOSE(n,DISP=KEEP)
```

where n is an arithmetic expression and represents a file designator and DISP stands for DISPOSITION.

READMS transmits data from the file to the central memory. In order to transfer data from the file to the central memory the executable READ statement which is used in the Burroughs of HONDO is given as follows:

```
READ(n=r)m
```

where n and r are arithmetic expressions representing a file designator and record number, respectively, and m is an input list.

WRITMS transmits data from central memory to the file. In the Burroughs version of HONDO, the WRITE statement has been used. The executable WRITE statement causes data to be written from internal storage to one or more records of a program file. The WRITE statement which is used in the new version can be given

```
WRITE(n=r)m
```

where n and r are arithmetic expressions representing a file designator and record number, respectively, and m is an output list.

OVERLAYS have been changed into subroutines.

The READ statement, READ(IS)XX,IX,NX in subroutine PREAD has been changed as follows:

```

:
:
READ(IS)NX
INX=IABS(NX)
READ(IS)(XX(I),I=1,INX)
READ(IS)(IX(I),I=1,INX)
:
:

```

The same modification to READ has been applied to the WRITE statement in SUBROUTINE PWRIT.

The subroutines, ISOIN, ISOOUT and HSTAR have been subjected to several changes, since the proper library function SHIFT is not on the B 6700. This problem has been taken over by introducing a new external function, IPACK, to HONDO [see Appendix III]. In subroutine SCFOP the Burroughs CONCAT intrinsic has been used instead of SHIFT.

The DATA statements with MASK15 and MASK30 have been changed into MASK12 and MASK24 respectively.

Statements SECOND, DATE, and TIME have been changed into Burroughs versions as well.

In order to get the exchange energy from modified HONDO, another subroutine has been introduced to HONDO. This subroutine is called KSTAR which is derived from HSTAR by eliminating F(NIJ) and F(NKL) statements, to compute the exchange operator only. Just after WRITE(IW,9991) the following changes have been added to HONDO:

```

:
:
WRITE(IW,9991)
CALL KSTAR(DA,FA,XX,IX,NINTMX)
CALL SYMH(FA,HO,IA)
EX=TRACEP(DA,FA,NUMSCF)/TWO
WRITE(6,8888) EX
8888 FORMAT(/,15X,"EXCHANGE ENERGY",F20.12)
:
:

```

CHAPTER 3

DENSITY MATRICES AND THE EXCHANGE ENERGY

3.1 Introduction

The total Hamiltonian operator for an N-electron system, Eq. (2-2), can be rewritten in the following form:

$$\hat{H} = \sum_i^N \hat{H}_i + \frac{1}{2} \sum_{i,j}^{N'} \frac{1}{r_{ij}} \quad (\text{a}) \quad (3-1)$$

where the first sum in this equation represents the one-electron term for each electron; the second sum is the electron repulsion term for each electron pair.

The expectation value of the one-electron part is given as follows:

$$\langle \sum_i \hat{H}_i \rangle = \int \dots \int dv(1) \dots dv(N) \Psi_i^*(1,2,\dots,N) \left[\sum_i^N \hat{H}_i \right] \Psi_i(1,2,\dots,N) \quad (3-2)$$

From the symmetry of $\Psi^* \Psi$ each value of i must give the same contribution; therefore the result for the one-electron part is expressed as N times the result for the first term in the sum:

$$\langle \sum_i^N \hat{H}_i \rangle = N \int_{1'=1}^N dv(1), \dots, dv(N) \hat{H}_1 \Psi_1(1,2,\dots,N) \Psi^*(1',2,\dots,N) \quad (3-3)$$

where H_1 works on functions of 1 only and the name of the variables are changed from 1 to $1'$ to protect Ψ^* from the effect of H_1 . After operating with H_1 , but before completing the integration, $1'$ can be equalized to 1 . Thus Eq. (3-3) can be expressed as follows:

$$\langle \sum_i \hat{H}_i \rangle = \int_{1'=1}^N dv(1) H_1 \rho_1(1;1') \quad (3-4)$$

where the one-electron density matrix is

$$\rho_1(1;1') = N \int \dots \int dv(2) \dots dv(N) \Psi(1,2,\dots,N) \Psi^*(1',2,\dots,N) \quad (3-5)$$

(a) $\sum_{i,j}^{N'}$ means $\sum_i^N \sum_j^N$ where $i \neq j$

In a similar way the expectation value of two-electron part may be written in terms of the two-electron density matrix $\rho_2(1,2;1',2')$ [31,32,33]

$$\left\langle \frac{1}{2} \sum_{ij}^N \frac{1}{r_{ij}} \right\rangle = \frac{1}{2} \int_{1'=1} \int_{2'=2} dv(1)dv(2) \frac{1}{r_{12}} \rho_2(1,2;1',2') \quad (3-6)$$

where

$$\rho_2(1,2;1',2') = N(N-1) \int \int dv(3) \dots dv(N) \Psi(1,2,\dots,N) \Psi^*(1',2',\dots,N) \quad (3-7)$$

...

The two-density matrix $\rho_2(1,2;1',2')$ reduces to $\rho_2(1;2)$ when it is taken $1'=1$ and $2'=2$. Since $\frac{1}{r_{12}}$ is just a factor in the integrand, the primes may be dropped at once.

Now, the total energy for an N-electron system becomes

$$E_{\text{HF}} = \int_{1'=1} dv(1) \hat{H}_1 \rho_1(1;1') + \frac{1}{2} \iint dv(1)dv(2) \frac{1}{r_{12}} \rho_2(1;2) \quad (3-8)$$

Considering the one-determinant approximation [see Appendix IV for details], the two-density matrix can be determined by the one-density matrix

$$\rho_2(1,2;1',2') = \rho_1(1;1')\rho_1(2;2') - \rho_1(2;1')\rho_1(1;2') \quad (3-9)$$

where the one-density matrix [31] is

$$\rho_1(1;1') = \sum_{i(\text{occ})} \phi_i(1)\phi_i^*(1') \quad (3-10)$$

ϕ stands for the spin orbital. Thus the total Hartree-Fock energy can be expressed in terms of the one-density matrix

$$E_{\text{HF}} = \int_{1'=1} dv(1) \hat{H}_1 \rho_1(1;1') + \frac{1}{2} \iint dv(1)dv(2) \frac{1}{r_{12}} \rho_1(1;1)\rho_1(2;2) - \frac{1}{2} \iint dv(1)dv(2) \frac{1}{r_{12}} \rho_1(2;1)\rho_1(1;2) \quad (3-11)$$

The second term in Eq. (3-11) is the coulomb energy term; the third term represents the exchange energy.

The spinless counterparts of the one-electron and the two-electron densities are obtained by integrating over spins,

$$P_1(1;1') = \int_{s_1, s_1'} ds(1) \rho_1(1;1') \quad (3-12)$$

$$P_2(1,2;1',2') = \int_{s_1, s_1'} \int_{s_2, s_2'} ds(1) ds(2) \rho_2(1,2;1',2') \quad (3-13)$$

Using Eqs. (3-12) and (3-13) the total Hartree-Fock energy becomes

$$E_{\text{HF}} = \int_{1'=1} dr(1) \hat{H}_1 P_1(1;1') + \frac{1}{2} \iint dr(1) dr(2) \frac{1}{r_{12}} P_2(1;2) \quad (3-14)$$

where the spinless two-density matrix can be represented entirely in terms of the spinless one-density matrix for a closed shell [32]

$$P_2(1,2;1',2') = P_1(1;1') P_1(2;2') - \frac{1}{2} P_1(2;1') P_1(1;2') \quad (3-15)$$

By inserting Eq. (3-15) into Eq. (3-11) the total Hartree-Fock energy is found in terms of the spinless one-density matrix

$$E_{\text{HF}} = \int_{1'=1} dr(1) H_1 P_1(1;1') + \frac{1}{2} \iint dr(1) dr(2) \frac{1}{r_{12}} P_1(1;1) P_1(2;2) - \frac{1}{4} \iint dr(1) dr(2) \frac{1}{r_{12}} P_1(2;1) P_1(1;2) \quad (3-16)$$

The second term and the third term in Eq. (3-16) are the spinless counterparts of the coulomb energy and the exchange energy in Eq. (3-11), respectively, and where

$$P_1(1;1') = 2 \sum_{\mu_{\text{occ}}} X_{\mu}(1) X_{\mu}^*(1'), \quad (3-17)$$

and μ_{occ} indicates the summation over the occupied MO's.

3.2 Method

The exchange energy for an N-electron system has been defined in Eq. (3-16) in the following way:

$$E_X = -\frac{1}{4} \iint dr(1)dr(2) \frac{P_1(1;2)P_1(2;1)}{r_{12}} \quad (3-18)$$

where $P_1(1;2)$ is the spinless one-matrix.

In the present work, the spinless one-matrix is approximated by the supermolecular density for two-closed shell systems A and B. The supermolecular density is calculated according to the formula given by Fröman, Löwdin [13] and Jeziorski et al. [14], as quoted by Kołos [12]

$$P_{AB}(1;1) = 2 \sum_{\mu, \nu} X_{\mu}(1) (\Delta^{-1})_{\mu\nu} X_{\nu}(1) \quad (3-19)$$

where X_{μ} and X_{ν} stand for atomic orbitals of both constituents. The summation goes over the occupied atomic orbitals of both A and B atoms. Δ^{-1} is the inverse of the total overlap matrix Δ which may be decomposed into two parts

$$\Delta = 1 + S \quad (3-20)$$

where 1 is the unit matrix (1's on the diagonal, zeros elsewhere) and S denotes the matrix of the intermolecular overlap integrals, vanishing as the intermolecular distances tend to infinity and the matrix elements of S are given as follows:

$$S_{\mu\nu} = \int dr X_{\mu} X_{\nu} - \delta_{\mu\nu} \quad (3-21)$$

The matrix Δ^{-1} can be expanded in the following power series

$$\Delta^{-1} = 1 - S + S^2 - S^3 + \dots \quad (3-22)$$

and it is convenient to express the matrix

$$\Delta^{-1} = 1 + D \quad (3-23)$$

where

$$D = -S(1 + S)^{-1} \quad (3-24)$$

Hence, the supermolecular density P_{AB} can be expressed as follows [12]

$$\begin{aligned} P_{AB}(1;1) = & P_A + P_B + 2 \sum_{\mu, \nu}^A D_{\mu\nu} X_{\mu}(1) X_{\nu}(1) \\ & + 2 \sum_{\mu, \nu}^B D_{\mu\nu} X_{\mu}(1) X_{\nu}(1) + 4 \sum_{\mu}^A \sum_{\nu}^B D_{\mu\nu} X_{\mu}(1) X_{\nu}(1) \end{aligned} \quad (3-25)$$

where P_A and P_B are the electron densities of both constituent atoms A and B, respectively, and $D_{\mu\nu}$ are the matrix elements of D.

3.3 Application to He-He System

Using the method mentioned in the previous section the exchange energy for two-closed shell systems can be calculated. In this present work, the He-He system has been considered. For the He-He system which has four electrons and two orbitals, the supermolecular density can be written as

$$\begin{aligned} P_{\text{He-He}}(1;1) = & P_{\text{He}_1}(1;1) + P_{\text{He}_2}(1;1) + P_{\text{He}_1}(1;1)D_{11} \\ & + P_{\text{He}_2}(1;1)D_{22} + 2X_1(1)X_2(1)D_{12} + 2X_2(1)X_1(1)D_{21} \end{aligned} \quad (3-26)$$

where

$$\begin{aligned} P_{\text{He}_1}(1;1) &= 2X_1(1)X_1(1) \\ P_{\text{He}_2}(1;1) &= 2X_2(1)X_2(1) \end{aligned} \quad (3-27)$$

For the calculation of the exchange energy we will hypothesize that

$$\begin{aligned} P_{\text{He-He}}(1;2) = & 2X_1(1)X_1(2) + 2X_1(1)X_1(2)D_{11} + 2X_2(1)X_2(2) \\ & + 2X_2(1)X_2(2)D_{22} + 2X_1(1)X_2(2)D_{12} + 2X_2(1)X_1(2)D_{21} \end{aligned} \quad (3-28)$$

D_{11} and D_{22} are equal to each other because of the indistinguishability of the He atoms. For simplicity we can represent X_1 and X_2 as a and b , respectively

$$P_{\text{He-He}}(1;2) = A2[a(1)a(2) + b(1)b(2)] + C2[a(1)b(2) + b(1)a(2)] \quad (3-29)$$

$$\text{where } A = (1 + D_{11}) \text{ and } C = D_{12} \quad (3-30)$$

Using the idempotency condition [34]:

$$\int dr(3)P_1(1;3)P_1(3;2) = 2P_1(1;2) \quad (3-31)$$

the correctness of A and C has been verified. Details are provided in Appendix VI.

Inserting Eq. (3-28) into Eq. (3-18), the exchange energy, E_X , for He-He becomes

$$E_X = -\frac{1}{4} \iint dr(1)dr(2) \frac{P_{\text{He-He}}(1;2)P_{\text{He-He}}(2;1)}{r_{12}} \quad (3-32)$$

After some algebraic manipulations we have

$$E_X = -\frac{1}{4} \{A^2[aa|aa] + 2A^2[ab|ab] + 4AC[aa|ab] + 4AC[ab|bb] + A^2[bb|bb] + 2C^2[aa|bb] + 2C^2[ab|ab]\} \quad (3-33)$$

where a and b are the minimum basis set of the Slater functions

$$a(1) = (\alpha_1^3/\pi)^{1/2} \exp(-\alpha_1 r_{a1}) \quad (3-34)$$

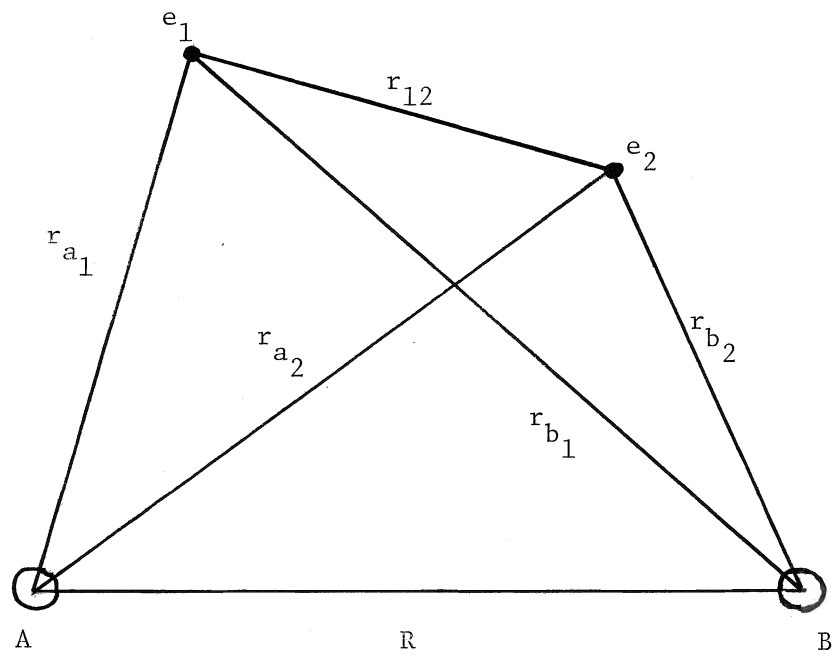
$$b(1) = (\alpha_2^3/\pi)^{1/2} \exp(-\alpha_2 r_{b1}) \quad (3-35)$$

where r_{a1} is the distance between electron 1 and the centre A and r_{b1} is the distance between electron 1 and the centre B as they are shown in Fig. 1.

α_1 is the optimized orbital exponent from atomic SCF calculations using minimum basis sets and given by Clementi and Raimondi [35]. In most cases

Figure 1. Diatomic Molecule Coordinate Systems

R represents the internuclear distance; r_{12} the electron-electron distance; and r_{a_1} and r_{b_1} the electron-nuclear distances.



the energy-optimized exponents are not a great deal different from those obtained by Slater's rules [36]. The parameter α_1 is equal to α_2 because of the homonuclear case; hence, the results of integrals $[aa|aa]$ and $[aa|ab]$ are equal to $[bb|bb]$ and $[bb|ba]$, respectively, considering symmetry of a and b. Then Eq. (3-33) can be re-arranged as

$$E_X = -\frac{1}{4}\{2A^2[aa|aa] + 2(A^2 + C^2)[ab|ab] + 8AC[aa|ab] + 2C^2[aa|bb]\} \quad (3-36)$$

where

$$[aa|aa] = 4 \iint dr(1)dr(2) a(1)a(1) \frac{1}{r_{12}} a(2)a(2) \quad (3-37)$$

$$[ab|ab] = 4 \iint dr(1)dr(2) a(1)b(1) \frac{1}{r_{12}} a(2)b(2) \quad (3-38)$$

$$[aa|ab] = 4 \iint dr(1)dr(2) a(1)a(1) \frac{1}{r_{12}} a(2)b(2) \quad (3-39)$$

$$[aa|bb] = 4 \iint dr(1)dr(2) a(1)a(1) \frac{1}{r_{12}} b(2)b(2) \quad (3-40)$$

The analytical solutions of two-centre integrals $[ab|ab]$, $[aa|ab]$, and $[aa|bb]$ are given by Slater [37]. Integrals are in atomic units; the factor of 4 in front of above integrals comes from the supermolecular one-matrix definition, Eq. (3-28).

The results of the exchange energies of He-He at different R obtained by this method and HONDO are given in Table 1. As it is shown in Figure 2 the exchange energy results from this work are in good agreement with HONDO.

TABLE 1

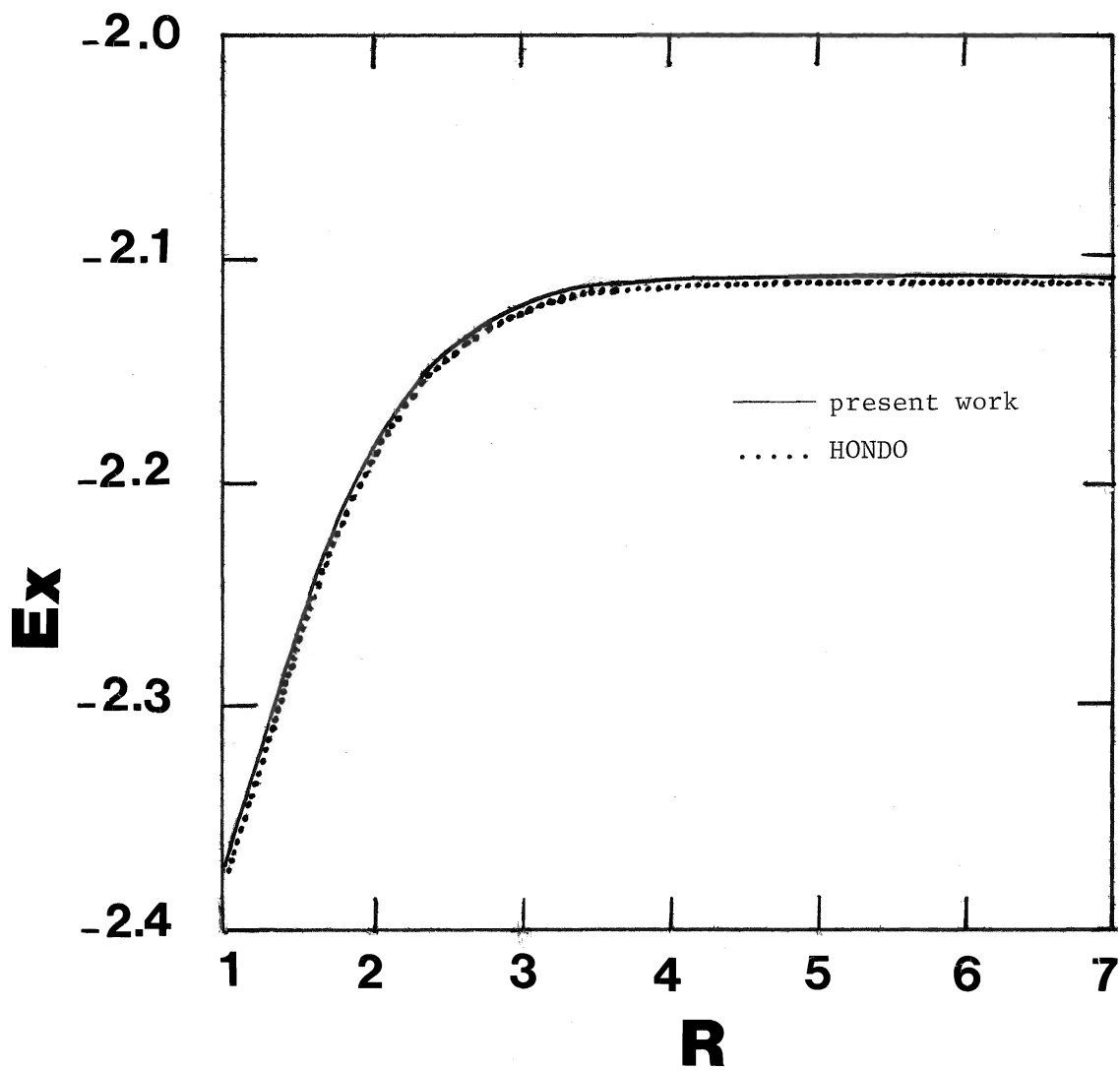
Exchange Energy of He-He^a

R(a ₀)	Exchange Energy	
	Present Work	HONDO
1.0	-2.37108	-2.37417
1.5	-2.25624	-2.25916
2.0	-2.18138	-2.18427
2.5	-2.14036	-2.14332
3.0	-2.12123	-2.12426
3.5	-2.11348	-2.11656
4.0	-2.11069	-2.11379
4.5	-2.10977	-2.11288
5.0	-2.10945	-2.11260
5.5	-2.10940	-2.11252
6.0	-2.10938	-2.11250
6.5	-2.10938	-2.11250
7.0	-2.10938	-2.11250

^aAll values are in atomic units.

Figure 2. Comparison of the exchange energy
results of this work with HONDO.

He-He



CHAPTER 4

MONTE CARLO METHOD

4.1 Introduction

The Monte Carlo method solves the mathematical and physical problems approximately by the simulation of random quantities [38].

Integrals can be evaluated by the Monte Carlo method. For simplicity, we can choose the one-dimensional integral as an example to exhibit the fundamental features of the Monte Carlo method.

$$I = \int_a^b dx f(x) \quad (4-1)$$

where $f(x)$ is an arbitrary continuous function which is defined on the interval $a \leq x \leq b$. In fact, such integrals can be computed by quadrature formulas, a more precise technique, but for multidimensional integrals the situation is different: quadrature formulas become tedious while the Monte Carlo remains principally unchanged.

In the Monte Carlo method the essential feature is that at some point we have to substitute for a random variable a corresponding set of actual values having the statistical properties of the random variable. The values that we substitute are called random numbers. There are several ways to generate random numbers which have also been subjected to a number of statistical tests to check that these numbers are correctly distributed over the interval or not [39].

In order to compute the integral Eq. (4-1) we need to know the values of random variables v which are distributed over the interval $[a,b]$ with probability density $p_v(x)$. The values of random variable v can be constructed transforming one or more values of random number G is given by the following formula

$$\int_a^v dx p_v(x) = G \quad (4-2)$$

where the probability density $p_v(x)$ must satisfy the following two conditions:

(1) the probability density $p_v(x)$ is positive,

$$p_v(x) > 0 \quad (4-3)$$

(2) the integral of the density $p_v(x)$ over the whole interval $[a,b]$ is equal to 1,

$$\int_a^b dx p_v(x) = 1 \quad (4-4)$$

Each value of G gives the solution of Eq. (4-2) for the corresponding v value.

To compute the integral Eq. (4-1) by the Monte Carlo method, besides the random variable v , defined on the interval $[a,b]$ with density $p_v(x)$, we need a random variable such as

$$H = \frac{f(v)}{p_v(v)} \quad (4-5)$$

The expectation value of H is I .

$$E(H) = \frac{\int_a^b dx \left(\frac{f(x)}{p_v(x)} \right) p_v(x)}{\int_a^b dx p_v(x)} = \int_a^b dx \left(\frac{f(x)}{p_v(x)} \right) p_v(x) = I \quad (4-6)$$

Let us consider N independent, identically distributed random variables, H_1, H_2, \dots, H_N , that is, the probability densities of these variables coincide. Applying the central limit theorem [38] [Appendix VII] to the sum of the variables we can write the following relation

$$\text{prob} \left(\left| \frac{1}{N} \sum_{i=1}^N H_i - I \right| < 3 \sqrt{\frac{\text{var}(H)}{N}} \right) \approx 0.997 \quad (4-7)$$

This relation shows that the absolute error between the true result of the integral and the result obtained by the Monte Carlo method will almost certainly not exceed $3 \sqrt{\frac{\text{var}(H)}{N}}$, provided we choose sufficiently large N . Thus we compute

$$\frac{1}{N} \sum_{i=1}^N H_i = \frac{1}{N} \sum_{i=1}^N \frac{f(v_i)}{p_v(v_i)} \approx I \quad (4-8)$$

Any random number v , defined on the interval $[a,b]$ can be used to compute the integral Eq. (4-1) because

$$E(H) = E\left(\frac{f(v)}{p_v(v)}\right) = I \quad (4-9)$$

but the variance of H and hence the estimate of the error of Eq. (4-9) are dependent on what variable v we use.

$$\text{var}(H) = E(H^2) - I^2 = \int_a^b \left(\frac{f^2(x)}{p_v(x)}\right) dx - I^2 \quad (a) \quad (4-10)$$

Since the random variable is extracted from $p_v(x)$ on the interval $[a,b]$ the variance is also dependent on the probability density $p_v(x)$ which we use. The variance can be minimized when $p_v(x)$ is proportional to $|f(x)|$ ("importance sampling") [39,40], but we have to restrict our choice of the probability density $p_v(x)$ to functions that we can integrate analytically, since the values of v are constructed from Eq. (4-2).

4.2 Application to Exchange Energy Integral

In this section our aim is to compute the exchange energy formula given

$$(a) \quad \text{var}(H) \approx \frac{1}{N-1} \left[\sum_{i=1}^N (H_i)^2 - \frac{1}{N} \left(\sum_{i=1}^N H_i \right)^2 \right] .$$

by Eq. (3-29) using the procedure described in the previous section for multidimensional integrals since we have to integrate our Eq. (3-29) over electron 1 and electron 2.

To compute the integral by the Monte Carlo method we have to define the probability density which satisfies two conditions: Eq. (4-3) and Eq. (4-4). Since the product $P_{\text{He-He}}(1;2)P_{\text{He-He}}(2;1)$ appears in Eq. (3-29), we can use it as a guide to choose the probability density. Of course, our choice would not be very complex since the random variable would be constructed from it.

The square of our supermolecular one-matrix for He-He is given as follows:

$$\begin{aligned} P_{\text{He-He}}(1;2) \times P_{\text{He-He}}(2;1) \\ = \{A[2a(1)a(2) + 2b(1)b(2)] + C[2a(1)b(2) + 2b(1)a(2)]\} \\ \times \{A[2a(2)a(1) + 2b(2)b(1)] + C[2a(2)b(1) + 2b(2)a(1)]\} \quad (4-11) \end{aligned}$$

Assuming that the off-diagonal element of the inverse matrix is smaller than the diagonal element of the inverse matrix, that is, C is smaller than A, we can choose our probability density as

$$\begin{aligned} p_{\text{v}}(1;2) = N[a(1)a(2)a(1)a(2) + a(1)a(1)b(2)b(2) \\ + b(1)b(1)a(2)a(2) + b(1)b(2)b(1)b(2)] \quad (4-12) \end{aligned}$$

This expression can be rearranged as follows:

$$p_{\text{v}}(1;2) = N[a(1)a(1) + b(1)b(1)][a(2)a(2) + b(2)b(2)] \quad (4-13)$$

where a and b are the normalized 1s STO's, and N is the normalization constant. ($p_{\text{v}}(1;2)$ has to be normalized to 1, Eq. (4-4).)

$$\iint dr(1)dr(2)p_{\text{v}}(1;2) = 1 \quad (4-14)$$

Our calculations will be in the prolate spheroidal coordinates because of their usefulness in treating "two centre" problems [see Appendix VIII] [41].

$$\mu = (r_a + r_b)/R \quad 1 \leq \mu \leq \infty \quad (4-15)$$

$$\nu = (r_a - r_b)/R \quad -1 \leq \nu \leq 1 \quad (4-16)$$

$$\phi \quad 0 \leq \phi \leq 2\pi \quad (4-17)$$

and the volume element is

$$d\tau = \left(\frac{R}{2}\right)^3 (\mu^2 - \nu^2) d\mu d\nu d\phi \quad (4-18)$$

The 1s STO's a and b can be expressed in the prolate spheroidal coordinates as follows:

$$a(1) = \left(\frac{\alpha}{\pi}\right)^{3/2} \exp[-\alpha \frac{R}{2} (\mu_1 + \nu_1)] \quad (4-19)$$

$$b(1) = \left(\frac{\alpha}{\pi}\right)^{3/2} \exp[-\alpha \frac{R}{2} (\mu_1 - \nu_1)] \quad (4-20)$$

To construct the random variable we recall Eq. (4-2). Our random variables will be μ_1, ν_1, ϕ_1 and μ_2, ν_2, ϕ_2 because the integration is over electron 1 and electron 2. For μ_1 the following equation can be derived from Eq. (4-2):

$$N \int_1^{\mu_1} d\mu_1 \int_1^{\infty} d\mu_2 \int_{-1}^1 d\nu_1 \int_{-1}^1 d\nu_2 \int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\phi_2 \left(\frac{R}{2}\right)^6 (\mu_1^2 - \nu_1^2) (\mu_2^2 - \nu_2^2) \\ [a(1)a(1) + b(1)b(1)][a(2)a(2) + b(2)b(2)] = G_\mu \quad (4-21)$$

Since a and b are the normalized functions Eq. (4-21) turns out to be

$$2N \int_1^{\mu_1} d\mu_1 \int_{-1}^1 d\nu_1 \int_0^{2\pi} d\phi_1 \left(\frac{R}{2}\right)^3 (\mu_1^2 - \nu_1^2) [a(1)a(1) + b(1)b(1)] = G_\mu \quad (4-22)$$

In a similar way ν_1 and ϕ_1 can be constructed:

$$2N \int_1^{\infty} d\mu_1 \int_{-1}^{v_1} dv_1 \int_0^{2\pi} d\phi_1 \left(\frac{R}{2}\right)^3 (\mu_1^2 - \nu_1^2) [a(1)a(1) + b(1)b(1)] = G_v^* \quad (4-23)$$

$$2N \int_1^{\infty} d\mu_1 \int_{-1}^1 dv_1 \int_0^{\phi_1} d\phi_1 \left(\frac{R}{2}\right)^3 (\mu_1^2 - \nu_1^2) [a(1)a(1) + b(1)b(1)] = G_\phi \quad (4-24)$$

After integrating Eqs. (4-22) and (4-23) a nonlinear equation is obtained for μ_1 and ν_1 . To find the roots of this equation an IMSL subroutine ZSCNT has been used. This gives μ_1 and ν_1 . To find ϕ_1 we integrate Eq. (4-24) and obtain

$$\frac{1}{2\pi} \int_0^{\phi_1} d\phi_1 = G_\phi \quad \phi_1 = 2\pi \times G_\phi \quad (4-25)$$

In Eqs. (4-21) to (4-25), G is a random number uniformly distributed between 0 and 1. To generate these an IMSL subroutine GGUBFS has been used.

In a similar way μ_2 , ν_2 and ϕ_2 can be constructed. Since $[a(1)a(1) + b(1)b(1)] \times [a(2)a(2) + b(2)b(2)]$ is symmetric, we do not even have to generate μ_2 , ν_2 and ϕ_2 ; their values are found in the same way as μ_1 , ν_1 , and ϕ_1 . Obviously $\mu_1 \neq \mu_2$, $\nu_1 \neq \nu_2$ and $\phi_1 \neq \phi_2$.

We need to know the r_{12} in the prolate spheroidal coordinates to compute the integral Eq. (3-29). This expression is given by Kołos and Roothaan [42]

$$r_{12}^2 = \frac{1}{4} R^2 \{ \mu_1^2 + \nu_1^2 + \mu_2^2 + \nu_2^2 - 2\mu_1\nu_1\mu_2\nu_2 - 2 [(\mu_1^2 - 1)(1 - \nu_1^2)(\mu_2^2 - 1)(1 - \nu_2^2)]^{1/2} \cos(\phi_1 - \phi_2) \} \quad (4-26)$$

Recalling Eq. (4-8), we can compute the exchange energy integral as follows:

*The expression is not correct. Indeed we should choose ν_1 from the probability of ν conditioned upon the value of μ_1 . That is,

$$\int_0^{\nu_1} p(\nu|\mu_1) d\nu = G_v$$

where $p(\nu|\mu_1) = p(\mu_1, \nu) / p(\mu_1) = \left(\int_0^{2\pi} p_v d\phi / \int_{-1}^1 \int_0^{2\pi} p_v d\nu d\phi \right)_{\mu = \mu_1}$

$$E_X = \frac{1}{N} \sum_{i=1}^N \frac{f(\mu_{1i}, \nu_{1i}, \phi_{1i}, \mu_{2i}, \nu_{2i}, \phi_{2i})}{P_V(\mu_{1i}, \nu_{1i}, \phi_{1i}, \mu_{2i}, \nu_{2i}, \phi_{2i})}$$

where

$$f = -\frac{1}{4} P_{\text{He-He}}(1;2) P_{\text{He-He}}(2;1) / r_{12}$$

and P_V is given by Eq. (4-13).

The list of the results of the exchange energy of He-He at different R , obtained by the Monte Carlo method, is given in Table 2. If we compare Table 2 with Table 1, we can see that the results from the Monte Carlo method are in good agreement with the results from HONDO.

It has been mentioned that the probability of the absolute value of the error in calculating an integral exceeding the value 3σ is less than 1%. However, in reality as a rule turns out to be noticeably less than this value such as in our exchange integral calculation. Therefore we can use the "probable error".

$$\delta p = 0.675 \sigma$$

The probable error δp gives not the likely upper limit of the error, but rather its order of magnitude. In fact, deviations from the expected value larger and smaller than the probable error 0.675σ are equally probable [38].

$$\int_{I - 0.675 \sigma}^{I + 0.675 \sigma} dx P_z(x) = 0.5$$

In Figure 3 the results from the Monte Carlo method is compared with the results from HONDO. The probable error is also shown in this figure.

The contributions of the exchange energies, ΔE_x , at various internuclear distances are given in Table 3. As it is shown in Figure 4, ΔE_x values obtained from the analytical way are in good agreement with HONDO. The results obtained from Monte Carlo are not far from the others at short distances but

TABLE 2

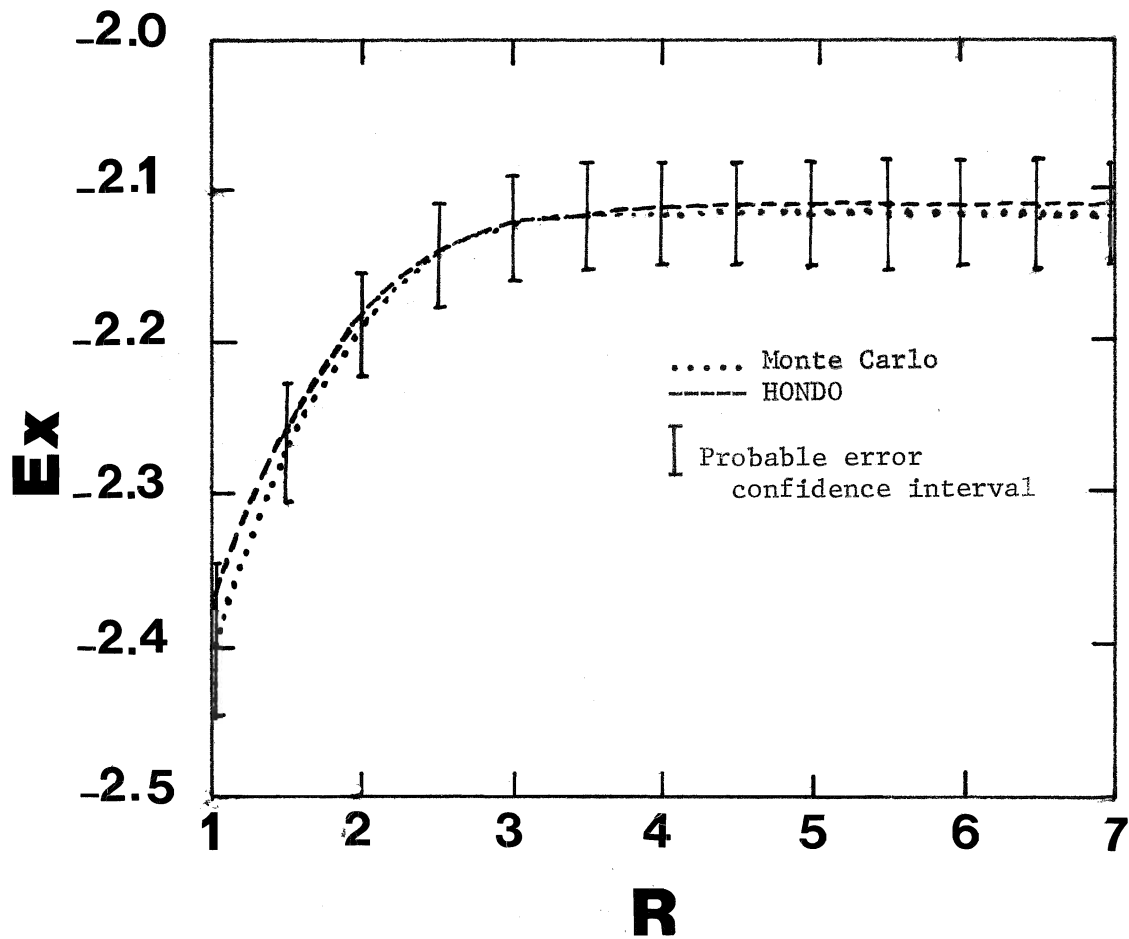
Exchange Energy Results of He-He at different R,
obtained by the Monte Carlo method with probable errors^a

R(a ₀)	Exchange Energy of He-He	Probable Error (δp)
1.0	-2.39746	0.04824
1.5	-2.26792	0.04162
2.0	-2.18542	0.03697
2.5	-2.14253	0.03549
3.0	-2.12386	0.03498
3.5	-2.11727	0.03485
4.0	-2.11581	0.03485
4.5	-2.11598	0.03487
5.0	-2.11646	0.03490
5.5	-2.11688	0.03493
6.0	-2.11721	0.03485
6.5	-2.11744	0.03487
7.0	-2.11761	0.03498

^aAll values are in atomic units.

Figure 3. Comparison of the exchange energy results
from Monte Carlo method with HONDO.

He-He



at long distances Monte Carlo results show some deviations from the others. This shows that exchange energy calculations by Monte Carlo need some improvement which could be done in the future.

TABLE 3

ΔE_x^{anal} (a), ΔE_x^{MC} (b) and $\Delta E_x^{\text{HONDO}}$ (c) of He-He at Different R

R(a ₀)	ΔE_x^{anal}	ΔE_x^{MC}	$\Delta E_x^{\text{HONDO}}$
1.0	-2.61705×10^{-1}	-2.88085×10^{-1}	-2.62274×10^{-1}
1.5	-1.46865×10^{-1}	-1.58545×10^{-1}	-1.47734×10^{-1}
2.0	-7.20050×10^{-2}	-7.60450×10^{-2}	-7.28442×10^{-2}
2.5	-3.09850×10^{-2}	-3.31550×10^{-2}	-3.18942×10^{-2}
3.0	-1.18550×10^{-2}	-1.44850×10^{-2}	-1.28342×10^{-2}
3.5	-4.10500×10^{-3}	-7.89500×10^{-3}	-5.13420×10^{-3}
4.0	-1.31500×10^{-3}	-6.43500×10^{-3}	-2.36420×10^{-3}
4.5	-3.95000×10^{-4}	-6.60500×10^{-3}	-1.45420×10^{-3}
5.0	-7.50000×10^{-5}	-7.08500×10^{-3}	-1.17420×10^{-3}
5.5	-2.50000×10^{-5}	-7.50500×10^{-3}	-1.09420×10^{-3}
6.0	-5.00000×10^{-6}	-7.83500×10^{-3}	-1.07420×10^{-3}
6.5	-5.00000×10^{-6}	-8.06500×10^{-3}	-1.07420×10^{-3}
7.0	-5.00000×10^{-6}	-8.23500×10^{-3}	-1.07420×10^{-3}

(a) $\Delta E_x^{\text{anal}} = E_x$ of He-He (analytical) - 2 x E_x of He (analytical).

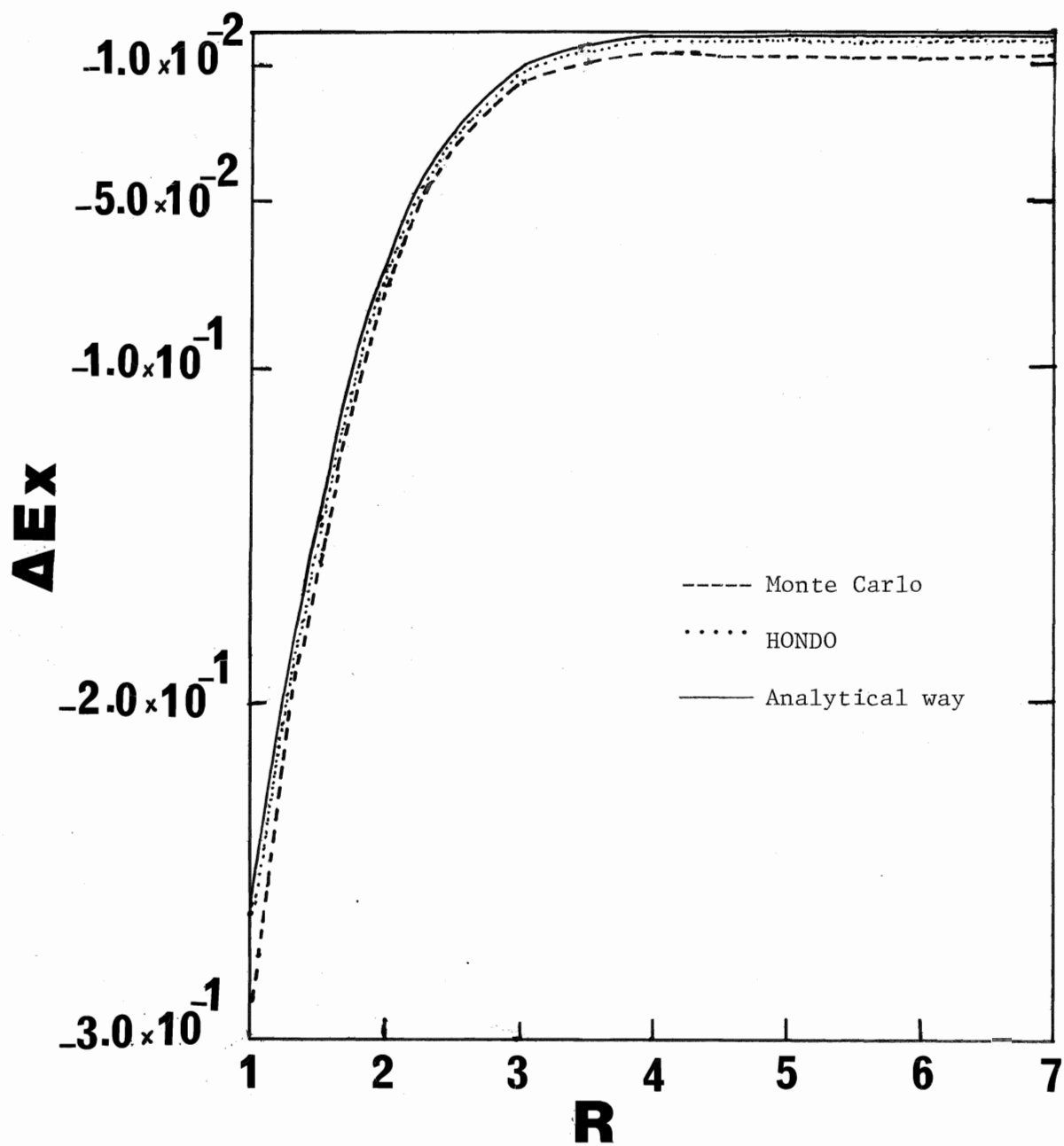
(b) $\Delta E_x^{\text{MC}} = E_x$ of He-He (Monte Carlo) - 2 x E_x of He (analytical).

(c) $\Delta E_x^{\text{HONDO}} = E_x$ of He-He (HONDO) - 2 x E_x of He (HONDO).

E_x of He (HONDO with STO 6G) = -1.05571 a.u.

E_x of He (analytical result with minimum basis set of STO) = -1.05488 a.u.

Figure 4. Comparison of the exchange energy contributions of the He-He system obtained analytically and by the Monte Carlo method with the results obtained HONDO.



CHAPTER 5

SUMMARY AND DISCUSSION

In Chapter 2 the SCF program HONDO has been introduced with some modifications to it.

Our aim is to find the exchange energy of the He-He system as close as possible to results of HONDO by a different way. We generalized the supermolecular density for two interacting closed shells to the supermolecular one-matrix. In Chapter 3, we proved that using the supermolecular one-matrix one can find the exchange energy of He-He correctly. To extend this formula to larger two-closed systems we should find the easiest way to calculate the exchange energy integral. The exchange energy integral is very formidable job because of its unlocal nature. In addition, the supermolecular density should be normalized to the number of electrons and obey the idempotency condition [34]. As the number of electrons increases this job will be more difficult to manage by using analytical and numerical integration .

In Chapter 4 we applied the Monte Carlo method to the exchange energy integral of He-He since the simplicity of the Monte Carlo method for multi-dimensional integral. We found that the results from Monte Carlo are also very close to the results from HONDO for 5000 random points. One can minimize the absolute error of the estimation by increasing the number of random points and/or by taking the probability density which mimics the function we want to integrate. Our aim should be to choose some probability density to reduce the standard error of our estimate and to reduce the variance. Some other variance reduction methods are given by Davis and Rabinowitz [40].

We proved that the Monte Carlo method can provide accurate results for the exchange energy of He-He at different internuclear distances. Our method can be extended to larger two-closed shells using the Monte Carlo method. All we need is to find the probability density which follows closely the integrand. For larger systems such as Ne-Ne, Ar-Ar and Ne-Ar, etc., required overlap integrals can be provided from [47].

APPENDIX I

DERIVATION OF THE HARTREE-FOCK ENERGY EXPRESSION

The antisymmetrizer in the Hartree-Fock wave function Eq. (2-3) is defined as follows:

$$A(N) = (N!)^{-1/2} \sum_{r=1}^{N!} (-1)^r P_r \quad (\text{I-1})$$

The $N!$ permutation operators P_r are so labelled that even(odd) r corresponds to an even(odd) permutation [21].

The antisymmetrizer operators $A(N)$ have three required properties:

$$A^2(N) = (N!)^{1/2} A(N) , \quad (\text{I-2})$$

$$A(N) = A^*(N) , \quad (\text{I-3})$$

and

$$A(N)Q = QA(N) \quad (\text{I-4})$$

where Q is any operator totally symmetrical in the coordinates $1, \dots, N$.

To prove the first property Eq. (I-2) we can write

$$\begin{aligned} A^2(N) &= (N!)^{-1/2} \sum_{r=1}^{N!} (-1)^r P_r (N!)^{-1/2} \sum_{s=1}^{N!} (-1)^s P_s \\ &= (N!)^{-1} \sum_{r=1}^{N!} \sum_{s=1}^{N!} (-1)^{r+s} P_r P_s . \end{aligned} \quad (\text{I-5})$$

Using the fact that the product of two permutation operators is another permutation operator of the same set, we can rewrite Eq. (I-5) as follows:

$$A^2(N) = (N!)^{-1} \sum_{r=1}^{N!} \sum_{t=1}^{N!} (-1)^t P_t = \sum_{t=1}^{N!} (-1)^t P_t = (N!)^{1/2} A(N). \quad (\text{I-6})$$

The Hermitian property of $A(N)$, Eq. (I-3), shows the integral relation

$$\begin{aligned}
& \int \dots \int dv(1) \dots dv(N) \xi^*(1, \dots, N) A(N) \eta(1, \dots, N) \\
& = \int \dots \int dv(1) \dots dv(N) [A(N) \xi(1, \dots, N)]^* \eta(1, \dots, N) \quad (I-7)
\end{aligned}$$

for two arbitrary well-behaved functions $\xi(1, \dots, N)$ and $\eta(1, \dots, N)$. The third property of the antisymmetrization operators is the commutative property, Eq. (I-4).

Considering three properties of $A(N)$ we have

$$\begin{aligned}
& \int \dots \int dv(1) \dots dv(N) \Psi_{HF}^*(1, \dots, N) Q \Psi_{HF}(1, \dots, N) \\
& = \int \dots \int dv(1) \dots dv(N) [A(N) \phi_1(1) \dots \phi_N(N)]^* Q A(N) \phi_1(1) \dots \phi_N(N) \\
& = \int \dots \int dv(1) \dots dv(N) \phi_1^*(1) \dots \phi_N^*(N) A^2(N) Q \phi_1(1) \dots \phi_N(N) \\
& = \int \dots \int dv(1) \dots dv(N) \phi_1^*(1) \dots \phi_N^*(N) \sum_{t=1}^{N!} (-1)^t Q \phi_1(1) \dots \phi_N(N) \quad (I-8)
\end{aligned}$$

Let the totally symmetric operator Q be equal to 1, then we can say that Eq. (2-3) or Eq. (2-5) is normalized.

$$\begin{aligned}
& \int \dots \int dv(1) \dots dv(N) \Psi_{HF}^*(1, \dots, N) \Psi_{HF}(1, \dots, N) \\
& = \int \dots \int dv(1) \dots dv(N) \phi_1^*(1) \dots \phi_N^*(N) \sum_{t=1}^{N!} (-1)^t P_t \phi_1(1) \dots \phi_N(N) \\
& = \int \dots \int dv(1) \dots dv(N) \phi_1(1) \dots \phi_N(N) \phi_1(1) \dots \phi_1(N) \\
& = \left[\int dv(1) |\phi_1(1)|^2 \right] \dots \left[\int dv(N) |\phi_N(N)|^2 \right] = 1 \quad (I-9)
\end{aligned}$$

Only the identity permutation of the Hartree-Fock wave function avoids zero because of the orthonormality of the set $\phi_i(1)$ [Eq.(2-6)].

To evaluate the Hartree-Fock energy expression Eq. (2-7) the operator Q in Eq. (I-8) can be set to

$$\sum_{i=1}^N \hat{H}_i \left[-\sum_{i=1}^N \frac{\nabla_i^2}{2} + \sum_k^A \frac{Z_k}{r_{i,k}} \right] \quad \text{and to} \quad \frac{1}{2} \sum_{j \neq 1} \sum_{i=1} \frac{1}{r_{ij}} .$$

From $\sum_{i=1}^N \hat{H}_i$ we have

$$\begin{aligned}
& \sum_{i=1}^N \int \dots \int dv(1) \dots dv(N) \phi_1^*(1) \dots \phi_N^*(N) \hat{H}_i \sum_{t=1}^{N!} (-1)^t P_t \phi_1(1) \dots \phi_N(N) \\
&= \sum_{i=1}^N \left[\int dv(1) \phi_1^*(1) \phi_1(1) \right] \dots \left[\int dv(i) \phi_i^*(i) \hat{H}_i \phi_i(i) \right] \\
&\quad \dots \left[\int dv(N) \phi_N^*(N) \phi_N(N) \right] = \sum_{i=1}^N \hat{H}_i \tag{I-10}
\end{aligned}$$

and for $\frac{1}{2} \sum_{j \neq i} \sum_{i=1}^N \frac{1}{r_{ij}}$ we have

$$\begin{aligned}
& \int \dots \int dv(1) \dots dv(N) \sum_{j>i} \sum_{i=1}^N \frac{1}{r_{ij}} \psi_{HF}^*(1, \dots, N) \psi_{HF}(1, \dots, N) \\
&= \frac{1}{2} \sum_{j \neq i} \sum_{i=1}^N \int \dots \int dv(1) \dots dv(N) \phi_1^*(1) \dots \phi_N^*(N) r_{ij}^{-1} \sum_{t=1}^{N!} (-1)^t P_t \phi_1(1) \dots \phi_N(N) \\
&= \frac{1}{2} \sum_{j \neq i} \sum_{i=1}^N \int \dots \int dv(1) \dots dv(N) \phi_1^*(1) \dots \phi_i^*(i) \dots \phi_N^*(N) r_{ij}^{-1} \phi_1(1) \dots \\
&\quad \times [\phi_i(i) \phi_j(j) - \phi_i(j) \phi_j(i)] \dots \phi_N(N) \\
&= \frac{1}{2} \sum_{j \neq i} \sum_{i=1}^N \left[\int dv(1) \phi_1^2(1) \right] \dots \left[\int \int dv(i) dv(j) \phi_i^*(i) \phi_j^*(j) \frac{1}{r_{ij}} \phi_i(i) \phi_j(j) \right. \\
&\quad \left. - \int \int dv(i) dv(j) \phi_i^*(i) \phi_j^*(j) \frac{1}{r_{ij}} \phi_i(j) \phi_j(i) \right] \dots \\
&\quad \times \left[\int dv(N) \phi_N^2(N) \right] = \frac{1}{2} \sum_{j \neq i} \sum_{i=1}^N (J_{ij} - K_{ij}) \tag{I-11}
\end{aligned}$$

H_i , J_{ij} and K_{ij} are defined, Eqs. (2-8), (2-9), and (2-10).

Inserting these results, Eqs. (I-9), (I-10), and (I-11), into

$$E_{HF} = \frac{\int \dots \int dv(1) \dots dv(N) \psi_{HF}^*(1, \dots, N) \hat{H} \psi_{HF}(1, \dots, N)}{\int \dots \int dv(1) \dots dv(N) \psi_{HF}^*(1, \dots, N) \psi_{HF}(1, \dots, N)}$$

we obtain

$$\begin{aligned} E_{\text{HF}} &= \sum_{i=1}^N H_i + \frac{1}{2} \sum_{j \neq i} \sum_{i=1}^N (J_{ij} - K_{ij}) \\ &= \sum_{i=1}^N H_i + \sum_{j>i} \sum_{i=1}^N (J_{ij} - K_{ij}) . \end{aligned} \tag{I-12}$$

APPENDIX II

DERIVATION OF THE HARTREE-FOCK EQUATIONS

We want to minimize Eq. (2-7)

$$E_{\text{HF}} = \sum_{i=1}^N H_i + \sum_{j>i} \sum_{i=1}^N (J_{ij} - K_{ij}) \quad (\text{II-1})$$

subject to the conditions Eq. (2-6) $S_{ij} = \int dv(1) \phi_i^*(1) \phi_j(1) = \delta_{ij}$ with respect to ϕ_i . Applying Lagrange's method of undetermined multipliers we can find the minimum of the functional

$$F = E_{\text{HF}} - \sum_{j=1} \sum_{i=1} \epsilon_{ij} S_{ij} \quad (\text{II-2})$$

where the ϵ_{ij} are the constants. That is, we need

$$0 = \delta F = \sum_i \delta H_i + \frac{1}{2} \sum_{j=1} \sum_{i=1} (\delta J_{ij} - \delta K_{ij}) - \epsilon_{ij} \delta S_{ij} \quad (\text{II-3})$$

where δ 's represent virtual variations induced by virtual variations in the ϕ_i . For simplicity we can assume that all orbitals are real; then we can write

$$\delta S_{ij} = \int dv(1) \delta \phi_i(1) \phi_j(1) + \int dv(1) \phi_j(1) \delta \phi_i(1) \quad (\text{II-4})$$

$$\begin{aligned} \delta H_i(1) &= \int dv(1) \delta \phi_i(1) \hat{H}_i(1) \phi_i(1) + \int dv(1) \phi_i(1) \hat{H}_i(1) \delta \phi_i(1) \\ &= 2 \int dv(1) \delta \phi_i(1) \hat{H}_i(1) \phi_i(1) \end{aligned} \quad (\text{II-5})$$

Similarly, if we recall the definitions of J_{ij} and K_{ij} from Eqs. (2-9) and (2-10)

$$J_{ij} = \iint dv(1) dv(2) \phi_i^2(1) \frac{1}{r_{12}} \phi_j(2)$$

$$= \int dv(1) \phi_i(1) J_j(1) \phi_i(1) = \int dv(2) \phi_j(2) J_i(2) \phi_j(2) \quad (\text{II-6})$$

and

$$\begin{aligned} K_{ij} &= \iint dv(1) dv(2) \phi_i(1) \phi_j(1) \frac{1}{r_{12}} \phi_i(2) \phi_j(2) \\ &= \int dv(1) \phi_i(1) K_j(1) \phi_i(1) \\ &= \int dv(2) \phi_j(2) K_i(2) \phi_j(2) \end{aligned} \quad (\text{II-7})$$

where the Coulomb and the exchange operators are as defined in Eq. (2-15)

and Eq. (2-16). Then we have

$$\begin{aligned} \delta J_{ij} &= \int dv(1) \delta \phi_i(1) J_j(1) \phi_i(1) \\ &\quad + \int dv(1) \phi_i(1) J_j(1) \delta \phi_i(1) \\ &\quad + \int dv(2) \delta \phi_j(2) J_i(2) \phi_j(2) \\ &\quad + \int dv(2) \phi_j(2) J_i(2) \delta \phi_j(2) \\ \delta J_{ij} &= 4 \int dv(1) \delta \phi_i(1) J_j(1) \phi_i(1) \end{aligned} \quad (\text{II-9})$$

and similarly

$$\begin{aligned} K_{ij} &= 2 \int dv(1) \delta \phi_i(1) K_j(1) \phi_i(1) \\ &\quad + 2 \int dv(2) \delta \phi_j(2) K_i(2) \phi_j(2) \\ \delta K_{ij} &= 4 \int dv(1) \delta \phi_i(1) K_i(1) \phi_i(1) \end{aligned} \quad (\text{II-10})$$

Thus Eq. (II-3) gives

$$\begin{aligned} 0 = \delta F &= \sum_{i=1}^N \int \delta \phi_i(1) [2H_i(1) \phi_i(1) + \frac{1}{2} \sum_{j \neq 1} (4J_j(1) \phi_i(1) \\ &\quad - 4K_j(1) \phi_i(1)) - \sum_{j=1} 2\varepsilon_{ij} \phi_j(1)] \end{aligned} \quad (\text{II-11})$$

The coefficients of each term vanish identically since $\delta \phi_i$ are arbitrary;

then we have

$$\hat{H}_i(1)\phi_i(1) + \frac{1}{2} \sum_{j \neq i} [J_j(1)\phi_i(1) - K_j(1)\phi_i(1)] = \sum_{j=1} \epsilon_{ij}\phi_j(1) \quad (\text{II-12})$$

Eqs. (II-12) are the Hartree-Fock integrodifferential equations. These equations are different from the Hartree-Fock equations Eq. (2-11) by the presence of off-diagonal multipliers ϵ_{ij} , $i \neq j$. It is possible to transform Eq. (II-12) into Eq. (2-11) as described by Blinder [21]. This transformation can be chosen so as to bring the ϵ_{ij} matrix to diagonal form:

$$\epsilon_{ij} = \delta_{ij}\epsilon_i \quad (\text{II-13})$$

Assuming that this transformation has been made, Eq. (II-12) becomes more simple:

$$\{\hat{H}_i(1) + \frac{1}{2} \sum_{j \neq i} [J_j(1) - K_j(1)]\}\phi_i(1) = \epsilon_i\phi_i(1) \quad (\text{II-14})$$

where the terms in the curled parentheses correspond to the effective Hartree-Fock Hamiltonian operator and Eqs. (II-14) are the Hartree-Fock equations.

APPENDIX III

MODIFICATIONS TO ISOIN, ISOOUT AND HSTAR SUBROUTINES

```
FUNCTION IPACK (IA,IB,N,M)
C  TRANSFER N BITS FROM ARRAY IB STARTING AT
C  LOCATION INTO ARRAY IA AT LOCATION M
IPACK = CONCAT (IA,IB,M,N-1,N)
RETURN
END
```

The CONCAT intrinsic is provided to allow partial word manipulation whereby one field of a data word may be placed into a selected field of another data word [see Burroughs -B6700/B7700 FORTRAN Reference Manual].

All changes in subroutined ISOIN, ISOOUT and HSTAR are shown as underlying. Since KSTAR is derived from HSTAR, KSTAR has the same changes as HSTAR.

1982 NOV 17 16:02 (CSSCENC)BERKSOY/SCF/SOURCE/III ON PACK.

C****	CALL OVERLAY(3HTEN,10B,0,0)	00088500
	CALL JKDER	00088600
	RETURN	00088700
	END	00088800
	<u>SUBROUTINE ISOIN</u>	00088900
C*****	<u>PACK THE SYMMETRY LABLES*****</u>	00088901
	COMMON/SYMPRY/T(432),INVT(48),ISO(70,e),NT	00089000
	COMMON/ISCPAC/INDIN(48),INDCUT(8)	00089100
	IMAX=0	00089200
	I=0	00089300
10	IMIN=IMAX+1	00089400
	IMAX=IMAX+6	00089500
	IF(IMAX.GT.NT) IMAX=NT	00089600
	IF((IMAX-IMIN).EQ.5)GO TO 3219	00089601
	L=IMAX-IMIN+1	00089603
	GO TO 7658	00089606
3219	L=6	00089608
7658	IND=0	00089700
	DO 20 K=IMIN,IMAX	00089710
	IND=IPACK(IND,INDIN(IMAX+IMIN-K),7,7*(L-1))	00089801
20	L=L-1	00089803
C..20	IND=SHIFT(IND,7)+INDIN(IMAX+IMIN-K)	00089900
	I=I+1	00090000
C	WRITE(6,978) I	00090002
C978	FORMAT(1H,"I....=",I6)	00090004
	INDCUT(I)=IND	00090100
	IF(IMAX.LT.NT) GO TO 10	00090200
	RETURN	00090300
	END	00090400
	<u>SUBROUTINE ISOOUT</u>	00090500
C*****	<u>UNPACK THE SYMMETRY LABLES*****</u>	00090510
	COMMON/SYMPRY/T(432),INVT(48),ISO(70,e),NT	00090600
	COMMON/ISCPAC/INDIN(48),INDCUT(8)	00090700
C	MASK=127	00090800
CXX	MASK=63	00090801
	DO 5 IT=1,NT	00090900
5	INCIN(IT)=0	00091000
	I=0	00091100
	IMAX=0	00091200
10	IMIN=IMAX+1	00091300
	IMAX=IMAX+6	00091400
	IF(IMAX.GT.NT) IMAX=NT	00091500
	I=I+1	00091600
C	WRITE(6,987) I	00091602
C987	FORMAT(1H,"I....=",I6)	00091604
	IND=INDCUT(I)	00091700
	L=1	00091701
	DO 20 K=IMIN,IMAX	00091800
	INDIN(K)=0	00091803
	INDIN(K)=CONCAT(INDIN(K),IND,6,6+7*(L-1),7)	00091805
20	L=L+1	00091807
CXX	INDIN(K)=AND(IND,MASK)	00091900
C 20	IND=SHIFT(IND,-7)	00092000
C20	IND=SHIFT(IND,-6)	00092001
	IF(IMAX.LT.NT) GO TO 10	00092100
	RETURN	00092200
	END	00092300
	<u>SUBROUTINE TIMIT(INDEX)</u>	00092400

1982 NOV 17 16:02 (CSSCENC)BERKSOY/SCF/SOURCE/III ON PACK.

	ETOT=ZERO	01514200
	EHF=-EN	01514300
1500	CONTINUE	01514400
C		01514500
C	----- PRINT ACTUAL VALUE OF ENERGY -----	01514600
C		01514700
	WRITE(IW,9979) ETOT,EHF	01514800
	IF(NPRINT.EQ.5.OR.NPRINT.EQ.-5) GO TO 1600	01514900
C**	CALL READMS(IDAF,V,L2,5)	01515000
	READ(IDAF=5)((V(I,J),J=1,86),I=1,86)	01515100
C**	CALL READMS(IDAF,DA,NX,6)	01515200
	READ(IDAF=6)(DA(I22),I22=1,NX)	01515300
C**	CALL READMS(IDAF,E,NUMSCF,7)	01515400
	READ(IDAF=7)(E(I22),I22=1,NUMSCF)	01515500
	WRITE(IW,9996)	01515600
	DO 1550 I=1,NCOORD	01515700
1550	WRITE(IW,9995) I,E(I)	01515800
	WRITE(IW,9994)	01515900
	CALL VOLT(V,E,NCOORD,NUMSCF)	01516000
	WRITE(IW,9993)	01516100
	CALL COUT(DA,NUMSCF)	01516200
1600	CONTINUE	01516300
	IF(PPUNCH.EQ.0) GO TO 1800	01516400
C		01516500
C	----- PUNCH THE OCCUPIED ORBITALS	01516600
C		01516700
C**	CALL READMS(IDAF,V,L2,5)	01516800
	READ(IDAF=5)((V(I,J),J=1,86),I=1,86)	01516900
	DO 1750 J=1,NA	01517000
	IC=0	01517100
	MAX=0	01517200
1700	MIN=MAX+1	01517300
	MAX=MAX+5	01517400
	IC=IC+1	01517500
	IF(MAX.GT.NUMSCF) MAX=NUMSCF	01517600
	WRITE(IP,9988) J,IC,(V(I,J),I=MIN,MAX)	01517700
	IF(MAX.LT.NUMSCF) GO TO 1700	01517800
1750	CONTINUE	01517900
1800	CONTINUE	01518000
	CALL TIMIT(1)	01518100
	WRITE(IP,9986)TIMLIM,NPRINT,ITOL,ICUT,NORMF,NORMP,NCPK,IREST,	01518200
	1 IST,JST,KST,LST,NREC,INTLOC,IHES	01518300
C***	CALL WRITMS(IDAF,IREST,7,20,-1)	01518400
	WRITE(ICAF=20)IREST,NREC,INTLOC,IST,JST,KST,LST	01518500
	RETURN	01518600
	END	01518700
	----- SUBROUTINE HSTAR(D,F,XX,IX,NINTPX,IA,NPK) -----	01518800
C		01518900
C	----- SUBROUTINE HSTAR FORMS THE SKELETON MATRIX	01519000
C	F=(H'+H)/2	01519100
C		01519200
C	F(I,J)=(H**(I,J)+H**(J,I))/2	01519300
C		01519400
C	INDICES IN LABELS ARE IN STANDARD ORDER:	01519500
C	I.GE.J , K.GE.L , (IJ).GE.(KL)	01519600
C		01519700
C	ALL CONTRIBUTIONS ARE MADE INTO LOWER HALF OF	01519800
C	SKELETON MATRIX.	01519900

```

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C ONLY OFF-DIAGONAL ELEMENTS NEED BE DIVIDED BY TWO, 015200CC
C TO OBTAIN THE CORRECT F MATRIX. 01520100
C 01520200
COMMON/IOFILE/IR,IW,IP,IS,IPK,IDAF,IOCA(21) 01520300
DIMENSION D(2),F(2),IA(2) 01520400
DIMENSION XX(NINTMX),IX(NINTMX) 01520500
COMMON/INFOA/NAT,ICH,MUL,NUMSCF,NCOORE,NX,NE,NA,NE,ZAN(10), 01520600
IC(3,10) 01520700
DATA ZERO,TWO/0.0E+00,2.0E+00/ 01520800
C DATA MASK15,MASK30/77777B,77777777B/ 01520900
C# DATA MASK9,MASK18/511,262143/ 01520910
DO 50 M=1,NX 01521000
50 F(M)=ZERO 01521100
I=0 01521200
J=0 01521300
K=0 01521400
L=0 01521500
IF(NOPK.NE.1) GO TO 100C 01521600
C 01521700
C ----- INTEGRALS ARE NOT IN SUPERMATRIX FORM (NOPK=.TRUE.) ----- 015218CC
C 01521900
100 CALL PREAD(IS,XX,IX,NXX,NINTMX) 01522000
IDX=IABS(NXX) 01522003
IF(NXX.EQ.0) GO TO 350 01522100
NINT=IABS(NXX) 01522200
IF(NINT.GT.NINTMX) CALL CLOSDA(5) 01522300
DO 300 M=1,NINT 01522400
LABEL=IX(M) 01522500
I=0 01522501
I=CCNCAT(I,LABEL,9,39,10) 01522505
C L=LABEL.AND.PASK15 01522600
C LABEL=SHIFT(LABEL,-15) 01522700
J=0 01522702
J=CCNCAT(J,LABEL,9,29,10) 01522703
C K=LABEL.AND.PASK15 01522800
C LABEL=SHIFT(LABEL,-15) 01522900
K=0 01522905
K=CCNCAT(K,LABEL,9,19,10) 01522908
C J=LABEL.AND.PASK15 01523000
C I=SHIFT(LABEL,-15) 01523100
L=0 01523101
L=CCNCAT(L,LABEL,9,9,10) 01523103
VAL=XX(M) 01523200
VAL4=(VAL+VAL)+(VAL+VAL) 01523300
NIJ=IA(I)+J 01523400
NKL=IA(K)+L 01523500
NIK=IA(I)+K 01523600
NIL=IA(I)+L 01523700
IF(J.LT.K) GO TO 150C 01523800
NJK=IA(J)+K 01523900
NJL=IA(J)+L 01524000
GO TO 250 01524100
150 NJK=IA(K)+J 01524200
IF(J.LT.L) GO TO 200C 01524300
NJL=IA(J)+L 01524400
GO TO 250 01524500
200 NJL=IA(L)+J 01524600
250 F(NIJ)=F(NIJ)+VAL4*D(NKL) 01524700

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	F(NKL)=F(NKL)+VAL4*D(NIJ)	01524800
	F(NIK)=F(NIK)-VAL*D(NJL)	01524900
	F(NIL)=F(NIL)-VAL*D(NJK)	01525000
	F(NJK)=F(NJK)-VAL*D(NIL)	01525100
	F(NJL)=F(NJL)-VAL*D(NIK)	01525200
300	CONTINUE	01525300
	IF(NXX.GT.0) GO TO 100	01525400
350	CONTINUE	01525500
	IF(NUMSCF.EQ.1) GO TO 500	01525600
	CG 400 M=2,NUMSCF	01525700
	MAX=M-1	01525800
	DO 400 N=1,MAX	01525900
	NIJ=IAC(M)+N	01526000
400	F(NIJ)=F(NIJ)/TWO	01526100
500	CONTINUE	01526200
	REWIND (IS)	01526300
	RETURN	01526400
1000	CONTINUE	01526500
C		01526600
C	----- INTEGRALS ARE IN SUPERMATRIX FORM (NOPK=.FALSE.) -----	01526700
C		01526800
	DO 1050 M=1,NUMSCF	01526900
	NIJ=IAC(M)+M	01527000
1050	D(NIJ)=D(NIJ)/TWO	01527100
1100	CALL PREAD(IS,XX,IX,NXX,NINTMX)	01527200
	IF(NXX.EQ.0) GO TO 1350	01527300
	NINT=IABS(NXX)	01527400
	IF(NINT.GT.NINTMX) CALL CLOSDA(5)	01527500
	DC 1300 M=1,NINT	01527600
	LABEL=IX(M)	01527700
C	NKL=LABEL.AND.MASK30	01527800
	NKL=0	01527810
	NKL=CONCAT(NKL,LABEL,19,19,20)	01527812
C	NIJ=SHIFT(LABEL,-30)	01527900
	NIJ=0	01527901
	NIJ=CONCAT(NIJ,LABEL,19,39,20)	01527902
	VAL=XX(M)	01528000
	F(NIJ)=F(NIJ)+VAL*D(NKL)	01528100
	F(NKL)=F(NKL)+VAL*D(NIJ)	01528200
1300	CONTINUE	01528300
	IF(NXX.GT.0) GO TO 1100	01528400
1350	CONTINUE	01528500
	DO 1400 M=1,NUMSCF	01528600
	NIJ=IAC(M)+M	01528700
1400	D(NIJ)=D(NIJ)+D(NIJ)	01528800
	DO 1500 M=1,NX	01528900
1500	F(M)=F(M)/TWO	01529000
	REWIND (IS)	01529100
	RETURN	01529200
	END	01529300
C***	OVERLAY(FIV,5,3)	01529400
C##	PROGRAM SCFOP	01529500
	SUBROUTINE SCFOP	01529600
	COMMON/SCFOP/SZ,S2	01529700
C	----- UNRESTRICTED HF-SCF CALCULATION -----	01529800
C	J.A. POPE AND R.K. NESBET,	01529900
C	J.CHEM.PHYS. 22, 571 (1954)	01530000
C		01530100

APPENDIX IV

ONE-DETERMINANT APPROXIMATION

The density functions, $\rho_1(1;1')$ and $\rho_2(1,2;1',2')$, are special cases of the reduced density matrices. For a one-particle system, with a probability, w_i , say, of being found in state ϕ_i , the "pure state" density matrix $\rho(1;1') = \phi(1)\phi^*(1')$ for the definite state Ψ is replaced by the "statistical" density matrix [32]

$$\rho(1;1') = \sum_i w_i \phi_i(1)\phi_i^*(1') \quad (\text{IV-1})$$

The density matrix for the whole system is given as follows:

$$\rho(1,2,\dots,N;1',2',\dots,N') = \Psi(1,2,\dots,N)\Psi^*(1',2',\dots,N') \quad (\text{IV-2})$$

It is common in statistical mechanics to use the term "reduced" density matrix when referring to $\rho_1(1;1')$, $\rho_2(1,2;1',2')$, etc.

The total energy expression which is already obtained in terms of spin orbitals in Appendix I can be rewritten as

$$\begin{aligned} E_{\text{HF}} = & \sum_{i=1}^N \int dv(1) \phi_i^*(1) \hat{H}_i \phi_i(1) + \frac{1}{2} \sum' \left(\iint dv(1)dv(2) \right. \\ & \times \phi_i^*(1)\phi_j^*(2) \frac{1}{r_{12}} \phi_j(2)\phi_i(1) - \iint dv(1)dv(2) \phi_i^*(1)\phi_j^*(2) \\ & \left. \times \frac{1}{r_{12}} \phi_j(1)\phi_i(2) \right) \end{aligned} \quad (\text{IV-3})$$

The one-matrix $\rho_1(1;1')$ may be expanded in the spin orbital form

$$\rho_1(1;1') = \sum_{i,j} \rho_{1ij} \phi_i(1)\phi_j^*(1') \quad (\text{IV-4})$$

where the ρ_{1ij} is the numerical coefficient and the factors ϕ_i and ϕ_j^* arise

from Ψ and Ψ^* , respectively. Thus the general one-electron energy term has the spin orbital form Eq. (3-4)

$$\begin{aligned} \int_{1'=1} dv(1) \hat{H}_1 \rho_1(1;1') &= \sum_{i,j} \rho_{1ij} \int dv(1) \phi_j^*(1) \hat{H}_1 \phi_i(1) \\ &= \sum_{i,j} \rho_{1ij} \langle \phi_j | \hat{H}_1 | \phi_i \rangle \end{aligned} \quad (\text{IV-5})$$

In Eq. (IV-5), the coefficient ρ_{1ij} is simply the coefficient of usual orbital one-electron energy in Eq. (IV-3). If we compare Eq. (IV-5) with Eq. (IV-3) we can see that if ϕ_i is occupied $\rho_{1ij} = 1$; otherwise $\rho_{1ij} = 0$. Thus, the one-determinant approximation to $\rho_1(1;1')$ takes the special form

$$\rho(1;1') = \sum_{i(\text{occ})} \phi_i(1) \phi_i^*(1') \quad (\text{IV-6})$$

In a similar way, by comparing the two-electron energy part in Eq. (3-8) with Eq. (IV-3), the expression for $\rho_2(1;2)$ can be represented as follows:

$$\begin{aligned} \rho_2(1,2;1',2') &= \sum_{i,j} [\phi_i(1) \phi_j(2) \phi_i^*(1') \phi_j^*(2') \\ &\quad - \phi_i(2) \phi_j(1) \phi_i^*(1') \phi_j^*(2')] \end{aligned} \quad (\text{IV-7})$$

Considering Eq. (IV-6), Eq. (IV-7) can be rewritten in terms of ρ_1

$$\rho_2(1,2;1',2') = \rho_1(1;1') \rho_1(2;2') - \rho_1(2;1') \rho_1(1;2') \quad (\text{IV-8})$$

The factorization of the two-matrix in terms of the one-matrix $\rho_1(1;1')$ is peculiar to the one-determinant approximation; it means that in this approximation everything can be determined by the one-matrix $\rho_1(1;1')$ which is also known as the Dirac density matrix [43].

The energy expression for a "closed shell" system in which the orbitals

are doubly occupied can be expressed in terms of spatial orbitals [44] as follows:

$$\begin{aligned}
 E_{\text{HF}} = & 2 \sum_{\mu}^n \int dr(1) X_{\mu} \hat{H}_i X_{\mu} + \sum_{\mu, \nu}^n \sum [2 \iint dr(1) dr(2) \\
 & \times X_{\mu}^*(1) X_{\nu}(2)^* \frac{1}{r_{12}} \phi_{\nu}(2) \phi_{\mu}(1) - \iint dr(1) dr(2) \\
 & \times X_{\mu}^*(1) X_{\nu}^*(2) \frac{1}{r_{12}} X_{\nu}(1) X_{\mu}(2)] \quad (\text{IV-9})
 \end{aligned}$$

where n is the number of orbitals and μ and ν stand for the spatial orbitals.

The exchange integral in Eq. (IV-9) has reduced weight if we compare it to the exchange integral in Eq. (IV-3), because spin integration gives

$$\langle \phi_i(1) \phi_j(2) \frac{1}{r_{12}} \phi_j(1) \phi_i(2) \rangle = \langle X_{\mu}(1) X_{\nu}(2) \frac{1}{r_{12}} X_{\nu}(1) X_{\mu}(2) \rangle$$

or zero, according as ϕ_i and ϕ_j have parallel spins or not. Eq. (IV-9) can be rewritten as

$$\begin{aligned}
 E_{\text{HF}} = & 2 \sum_{\mu} \int_{1'=1} dr(1) \hat{H}_i X_{\mu}(1) X_{\mu}^*(1') \\
 & + \sum_{\mu, \nu} \int_{1'=1} \int_{2'=2} dr(1) dr(2) \frac{1}{r_{12}} [2 X_{\mu}(1) X_{\nu}(2) X_{\mu}^*(1') X_{\nu}^*(2') \\
 & - X_{\nu}(1) X_{\mu}(2) X_{\mu}^*(1') X_{\nu}^*(2')] \quad (\text{IV-10})
 \end{aligned}$$

If we compare Eq. (IV-10) with spinless energy expression Eq. (3-11), the spinless analogues of Eqs. (IV-6) and (IV-7) can be found

$$P_1(1;1') = 2 \sum_{\text{occ}} X(1) X^*(1') \quad (\text{IV-11})$$

and

$$P_2(1,2;1',2') = P_1(1;1') P_1(2;2') - \frac{1}{2} P_1(2;1') P_1(1;2') \quad (\text{IV-12})$$

APPENDIX V

INVERSION OF THE MATRIX

Δ is the overlap matrix and S is the intermolecular overlap matrix.

The matrix Δ can be separated into two parts:

$$\Delta = 1 + S \quad (V-1)$$

where the elements of Δ are given as

$$\Delta_{\mu\nu} = \int dr (1) X_{\mu} X_{\nu} = \langle \mu | \nu \rangle \quad (V-2)$$

If $\mu = \nu$, $\langle \mu | \nu \rangle$ is 1; otherwise, 0. For two orbital systems:

$$\begin{pmatrix} \Delta_{11} & \Delta_{12} \\ \Delta_{21} & \Delta_{22} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \quad (V-3)$$

then the elements of S matrix can be written in terms of the elements of Δ matrix.

$$S = \begin{pmatrix} \Delta_{11} - 1 & \Delta_{12} - 0 \\ \Delta_{21} - 0 & \Delta_{22} - 1 \end{pmatrix} \quad (V-4)$$

From Eq. (V-4) the equality of S_{12} to Δ_{12} is seen.

It is convenient to express the matrix Δ^{-1} in the following form:

$$\Delta^{-1} = 1 + D \quad (V-5)$$

where

$$D = -S \Delta^{-1} = -\left(S \cdot \frac{1}{(1 + S)}\right) \quad (V-6)$$

The inverse of the matrix can be found from the following formula [45]:

$$\Delta^{-1} = \text{transpose of } \left(\frac{(-1)^{i+j} \det(\Delta_{ij})}{\det(\Delta)} \right) \quad (V-7)$$

Applying the above formula, Eq. (V-7), to $(1 + S)$ matrix, one can get the

inverse of the matrix $(1 + S)$ as in the following form

$$(1 + S)^{-1} = \frac{1}{1 - \Delta_{12}^2} \begin{pmatrix} 1 & -\Delta_{12} \\ -\Delta_{12} & 1 \end{pmatrix} \quad (\text{V-8})$$

Then the matrix D can be calculated as

$$D = -S(1 + S)^{-1} \quad (\text{V-9})$$

$$= \frac{-\Delta_{12}}{1 - \Delta_{12}^2} \begin{pmatrix} -\Delta_{12} & 1 \\ 1 & -\Delta_{12} \end{pmatrix} \quad (\text{V-10})$$

Thus the matrix elements of D can be found:

$$D_{11} = D_{22} = \frac{\Delta_{12}^2}{1 - \Delta_{12}^2} \quad (\text{V-11})$$

$$D_{12} = D_{21} = -\frac{\Delta_{12}}{1 - \Delta_{12}^2} \quad (\text{V-12})$$

As has been seen to invert the matrix Δ is easy when the matrix dimension is 2×2 . As the matrix dimension increases, finding the inverse of the matrix becomes more difficult. In these cases the IMSL subroutines can be used to invert the matrix.

APPENDIX VI

VERIFICATION OF A AND C COEFFICIENTS

Considering Eq. (3-26), $P_1(1;3)$ can be expressed as follows:

$$P_1(1;3) = A^2[a(1)a(3) + b(1)b(3)] + C^2[a(1)b(3) + b(1)a(3)] \quad (\text{VI-1})$$

From the idempotency condition which is given in Eq. (3-31) as

$$\int dr(3)P_1(1;3)P_1(3;2) = 2P_1(1;2) \quad (\text{VI-2})$$

the following equation can be obtained by

$$\begin{aligned} 4[A^2a(1)a(2) + A^2a(1)b(2)\Delta_{12} + ACa(1)b(2) \\ + ACa(1)a(2)\Delta_{12} + A^2b(1)a(2)\Delta_{12} + A^2b(1)b(2) \\ + ACb(1)b(2)\Delta_{12} + ACb(1)a(2) + ACa(1)a(2)\Delta_{12} \\ + ACb(1)a(2) + ACa(1)b(2) + ACb(1)b(2)\Delta_{12} \\ + C^2a(1)b(2)\Delta_{12} + C^2a(1)a(2) + C^2b(1)b(2) \\ + C^2b(1)a(2)\Delta_{12}] = 4[Aa(1)a(2) + Ab(1)b(2) \\ + Ca(1)b(2) + Cb(1)a(2)] \end{aligned} \quad (\text{VI-3})$$

where

$$\Delta_{12} = \int dr(3)a(3)b(3) \quad (\text{VI-4})$$

Since the atomic orbitals a and b are normalized the following relation has been considered in Eq. (VI-3).

Equating the coefficients of the same functions of both sides of Eq. (VI-3) the following equations are obtained:

$$4(A^2 + 2AC\Delta_{12} + C^2) = 4A \quad (\text{VI-6})$$

and

$$4(A^2\Delta_{12} + 2AC + C^2\Delta_{12}) = 4C \quad (\text{VI-7})$$

Recalling Eqs. (3-30), (V-11) and (V-12), the values of A and C can be found as

$$\left(1 + \frac{\Delta_{12}^2}{1 - \Delta_{12}^2}\right) \quad \text{and} \quad \left(-\frac{\Delta_{12}}{1 - \Delta_{12}^2}\right),$$

respectively. Inserting the values of A and C into Eqs. (VI-6) and (VI-7), the correctness of A and C coefficients are verified.

APPENDIX VII

THE RULE OF "THREE SIGMAS" AND THE CENTRAL LIMIT THEOREM

Let say S_N be the sum of the identically distributed random variables X_1, X_2, \dots, X_N for sufficiently large N . Since the probability densities of these variables coincide, and hence their mathematical expectations and variances also coincide, we can write

$$E(X_1) = E(X_2) = \dots = E(X_N) = m \quad (\text{VII-1})$$

$$\text{Var}(X_1) = \text{Var}(X_2) = \dots = \text{Var}(X_N) = v^2 \quad (\text{VII-2})$$

and

$$E(S_N) = Nm \quad (\text{VII-3})$$

$$\text{Var}(S_N) = Nv^2 \quad (\text{VII-4})$$

The rule of "three sigmas" for a normal density $p_Z(x)$ [38]

$$\int_{Nm - 3\sigma}^{Nm + 3\sigma} p_Z(x) dx = 0.997 \quad (\text{VII-5})$$

where σ is the standard deviation. The probability of a normal random variable Z in the interval $(Nm - 3\sigma, Nm + 3\sigma)$ is equal to Eq. (VII-5).

$$\text{Prob}(Nm - 3\sigma < Z < Nm + 3\sigma) = 0.997 \quad (\text{VII-6})$$

From Eq. (VII-6) we conclude that for a single trial the value of Z can not differ from $E(Z)$ by more than 3σ .

The Central Limit Theorem states that the density of the sum S_N approaches the density of the normal variable Z_N in such a way that for every x , $p\left(\frac{S_N - Nm}{v\sqrt{N}} < x\right) \approx p\left(\frac{Z_N - Nm}{v\sqrt{N}} < x\right)$ for all large N . From this theorem we conclude that the sum S_N of a large number of identical random variables has an approximately normal distribution ($p_{S_N}(x) \approx p_{Z_N}(x)$) with parameters

Nm and $\sigma^2 = Nv^2$. From Eq. (VII-5) the following relation can be written for

S_N :

$$\text{prob}(Nm - 3v\sqrt{N} < S_N < Nm + 3v\sqrt{N}) \approx 0.997 .$$

If we divide by N the probability remains the same:

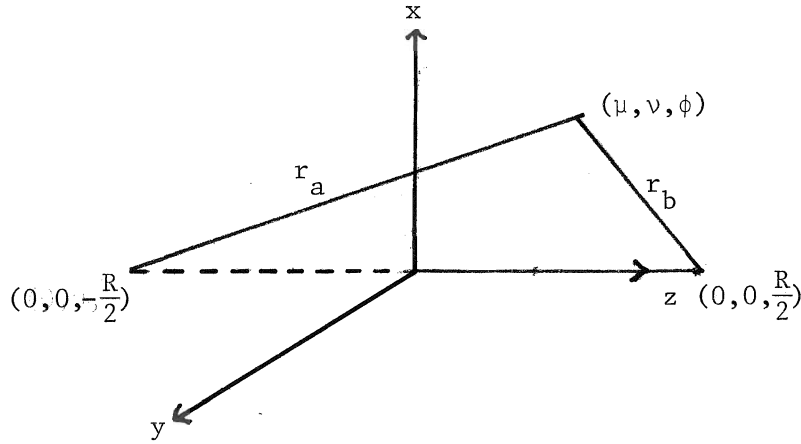
$$\text{prob}\left(m - \frac{3v}{\sqrt{N}} < \frac{S_N}{N} < m + \frac{3v}{\sqrt{N}}\right) = 0.997 .$$

This relation gives the uncertainty of our estimation.

APPENDIX VIII

PROLATE SPHEROIDAL COORDINATES

The prolate spheroidal coordinates can be generated as a three-dimensional system by rotating about the major axes of the elliptical coordinates and introducing ϕ as an azimuth angle [41]. The two centres will correspond to the two focal points $(0,0,\frac{R}{2})$ and $(0,0,-\frac{R}{2})$, of ellipsoids and hyperboloids of revolution. As long as rotating about the major axes of the elliptical coordinates is considered, the prolate spheroidal coordinates can be called simply as the elliptical coordinates [46].



$$\mu = (r_a + r_b)/R \quad (1 < \mu < \infty) \quad (\text{VII-1})$$

$$\nu = (r_a - r_b)/R \quad (-1 < \nu < 1) \quad (\text{VII-2})$$

$$\phi \quad (0 < \phi < 2\pi) \quad (\text{VII-3})$$

$$x = \frac{R}{2} [(\mu^2 - 1)(1 - \nu^2)]^{1/2} \cos\phi \quad (\text{VII-4})$$

$$y = \frac{R}{2} [(\mu^2 - 1)(1 - \nu^2)]^{1/2} \sin\phi \quad (\text{VII-5})$$

$$z = \frac{R}{2} \mu\nu \quad (\text{VII-6})$$

The volume element

$$d\tau = \left(\frac{R}{2}\right)^3 (\mu^2 - \nu^2) d\mu d\nu d\phi \quad (\text{VII-7})$$

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