AB INITIO CALCULATIONS ON THE LITHIUM AND H_3 SYSTEMS USING EXPLICITLY CORRELATED WAVE FUNCTIONS AND QUASIRANDOM INTEGRATION TECHNIQUES

By

DANIEL JAMES MICKISH

Bachelor of Science

Central State University

Edmond, Oklahoma

1966

Submitted to the Faculty of the Graduate College
of the Oklahoma State University
in partial fulfillment of the requirements
for the Degree of
DOCTOR OF PHILOSOPHY
July, 1971

AB INITIO CALCULATIONS ON THE LITHIUM AND
H_3 SYSTEMS USING EXPLICITLY CORRELATED
WAVE FUNCTIONS AND QUASIRANDOM
INTEGRATION TECHNIQUES

Thesis Approved:

Herbert A. Pohl
Thesis Adviser

[illegible]

E E Lafon

Paul Westhaus

Lionel M. Raff

J. M. Wilson

D Durham
Dean of the Graduate College

ACKNOWLEDGEMENTS

I wish to express my gratitude to Dr. H. A. Pohl, who kindly allowed me to pursue a relatively independent path of research, but who was constantly willing to give useful advice. Thanks are also given to the members of my committee, the members of the Quantum Theoretical Research Group, and fellow graduate students for many enlightening discussions and suggestions.

For fellowship support I am grateful to the National Science Foundation (1966-1969).

The use of the Oklahoma State University computing facilities was generously supported by the University. To the staff of the Computer Center I am indebted for much assistance.

I also thank Mrs. Janet Sallee for her typing excellence and advice.

Most of all, I wish to thank my wife, Charlotte, for her continual patience and encouragement throughout my graduate study.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Figure | Page

CHAPTER I

INTRODUCTION

A. Background

Except for the simplest cases, accurate solutions of molecular wave functions require the evaluation of many difficult multi-dimensional, multi-center integrals. A considerable amount of work[1-7] has been done in evaluating such integrals over Slater orbitals using sophisticated and ingenious analytical techniques. These techniques include the use of spherical, ellipsoidal, and bipolar coordinate systems, the expansion of atomic orbitals on one center in terms of functions on another, and the application of transform convolution theorems. Often the resulting "closed" expressions are long sums of terms containing auxiliary functions or infinite series which ultimately must be evaluated numerically or by means of recurrence relations.

Some researchers[8-12] have chosen to use Gaussian orbitals which lead to integrals that are relatively easy to evaluate analytically, even when many centers are involved. The disadvantage is that a much more extensive set of Gaussian orbitals is required to attain the same precision of the wave function as that attained by using a set of Slater orbitals. Using these orbitals, cusps and tails of the wave function are difficult to reproduce which in turn leads to less accurate expectation values of observables. Calculations in which large sets of Gaussian orbitals are used in order to obtain high accuracy involve sophisticated studies in data handling.

Integral evaluation can be avoided altogether, except for overlap integrals, by the use of semiempirical approximations. Sets of such approximations are the basis of the Hückel[13] scheme and the "PPP Method" developed by Pariser, Parr[14], and Pople[15] for use on π-bonded electronic systems; and the scheme developed by Pohl, Rein, and Appel[16-19] for use on σ-bonded electronic systems. Semiempirical approximations to the integrals become imperative when studying large systems such as organic molecules[13,20].

Another approach[21] which has been used to evaluate molecular integrals is to perform the simple integrations, or in the case of two-electron integrals, the integration over the coordinates of one electron analytically[22], and then perform the remaining integrations numerically by means of Gaussian quadrature.

This study is concerned with the evaluation of atomic and molecular integrals by a purely numerical means. Relatively few investigators have used this approach. Frost[23] in 1942 used a purely numerical method in which the variance of the local energy $\hat{H}\psi/\psi$ from the average of the local energy was minimized. The points at which the local energy was evaluated were selected arbitrarily and hence the method was completely independent of the concept of integration. In later studies[24] however, the points and corresponding weights were chosen to be the same as those indicated by numerical integration rules.

Boys and Rajagopal have performed SCF calculations using purely numerical methods. The systems considered ranged from H_2, with which exploratory calculations were made, to $NC + H_2$,[25] NH_3,[26] OH_3^+[27], and C_2H_4.[28] The only analytical operations that were performed resolved multi-centered distributions into a sum of single-center distributions. Numerical integration was performed around each center using Riemann sums for the radial integrations and Gauss-Legendre quadratures for the angular integrations. Special devices were introduced to handle the $1/r_{12}$ singularity which appeared in the electron-electron repulsion integrals. In a later calculation[29] involving the LiH system, the resolution of multi-centered distributions into single-center distributions was still carried out, but a form of Diophantine integration was used and, because of the nature of the correlated wave function employed, no special devices were necessary to handle the $1/r_{12}$ singularity.

Conroy[30-40] has used a purely numerical integration method of the Monte Carlo[32] and Diophantine[39] type to evaluate atomic and molecular integrals. There are several unique ideas employed in his work. The wave function is constructed[31] so that the kinetic energy operator operating upon it produces terms which cancel, in an additive manner, the nuclear attraction terms. A correlation function[34,36] is included in multi-electron wave functions which allow the electron-electron repulsion terms to be canceled in the same manner as the nuclear attraction terms. The variational principle was not used in Conroy's work since the errors occurring in the approximate integrals tended to contribute to the lowering of the energy ε, rather than canceling, "with the result that the ε obtained may be very seriously in error"[33]. However, it was found that meaningful results could be obtained using the approximate integrals when the energy variance,

$$U^2 = \int (\hat{H}\psi - E\psi)^2 \, d\tau \, / \int \psi^2 \, d\tau$$

was minimized with respect to the adjustable parameters of the trial wave function.

Since the calculation of the expectation value of the square of the Hamiltonian was required when minimizing the energy variance, little additional effort was necessary to implement lower bound formulas which require such expectation values. Conroy[33,38] developed and applied a technique using upper and lower bounds equations to predict a refined value of the energy by extrapolation to $U^2 = 0$ from the calculated wave functions.

B. This Work

This work also involves purely numerical integration of the Diophantine type, but the integrals are evaluated to such precision that the variational principle can be applied with confidence. The precision is attained by using a unique importance sampling of points technique which not only selects points from important regions of space but also removes the singularities originally appearing in the integrals.

Explicitly correlated wave functions constructed of Slater orbitals multiplied by interelectronic coordinates are employed. The total wave function is a linear combination of such products after they have been properly antisymmetrized. A combined configuration interaction - explicitly correlated wave function of this type is used in this thesis to test the numerical method by calculating the ground state energies of the lithium atom and the linear symmetric H_3 activated complex; both 3-electron systems. To make the calculations as meaningful as possible, a complete set of fully projected spin functions is employed.

The lithium calculation is performed principally as a test of techniques and programs since direct comparisons can be made with the work of Larsson[41]. To show the flexibility of the wave function employed, additional configurations which simultaneously include all possible interelectronic coordinate terms are added to the Li atom wave function. Such a calculation has never before been made on a system with more than two electrons.

The H_3 calculation is considered to be an excellent test of the usefulness of the techniques developed during the study since explicitly correlated orbitals over three centers are involved. Previous barrier height calculations on the $H + H_2 \rightleftarrows H_3 \rightleftarrows H_2 + H$ reaction have never attained "chemical accuracy" of 1 Kcal/mole. It was hoped that the adding of explicit correlation terms through interelectronic coordinates would give some insight into the poor energy convergence problem.

CHAPTER II

THEORY

A. Schrödinger Equation

The solution of the time dependent Schrödinger equation,

$$\hat{H}\psi = i\hbar \frac{\partial \Psi}{\partial t} , \qquad [1]$$

subject to initial and boundary conditions, is a wave function $\Psi(\vec{r},\sigma,t)$ which contains all the information describing the state of the physical system at time t.

If the Hamiltonian $\hat{H}$ does not explicitly depend upon the time, the energy E is a constant of the motion and Ψ has the form

$$\Psi(\vec{r},\sigma,t) = \sum_i \psi_i(\vec{r},\sigma)e^{-iE_i t/\hbar} . \qquad [2]$$

The function $\psi_i(\vec{r},\sigma)$ depends upon the coordinates of configuration and spin space but not upon the time and is a solution to the Schrödinger time independent wave equation

$$\hat{H}\psi_i = E_i\psi_i \qquad [3]$$

The description of the electronic structure of atoms and molecules requires the solutions of this equation. The Hamiltonian $\hat{H}$, in the molecular case, has the form

$$\hat{H} = \sum_{i}^{N}[-\tfrac{1}{2}\nabla_i^2 - \sum_{\gamma}^{n}\frac{Z_\gamma}{r_{i\gamma}}] + \sum_{i<j}^{N}\frac{1}{r_{ij}}, \qquad [4]$$

where the N electrons are indexed by the letters i and j, and the n nuclei are indexed by the Greek letter γ. Atomic units have been chosen such that $h = m_e = e = 1$. The linear operator $-\tfrac{1}{2}\nabla_i^2$ corresponds to the kinetic energy of electron i, Z_γ is the charge on nucleus γ, $Z_\gamma/r_{i\gamma}$ is the potential energy of interaction due to electron i and nucleus γ, and $1/r_{ij}$ is the potential energy of interaction due to electrons i and j.

The Hamiltonian is non-relativistic in form; spin-orbital interaction and various other terms have been omitted. Also employed is the Born-Oppenheimer approximation which assumes the motion of the nuclei to be negligible compared to that of the electrons and therefore allows the separation of the two motions. Thus the nuclear coordinates appear only as parameters in the electronic Hamiltonian.

B. Variational Method of Solution

Due to the terms r_{ij}^{-1} in the many-electron wave equation $\hat{H}\psi = E\psi$, a direct solution is impossible. However, there exist techniques for solving the equation which theoretically will converge to the correct solution to any desired degree of accuracy. The technique that is used most frequently, and the one used in this thesis, is the variational method[42]. It is based on the theorem that if Φ is a trial wave function satisfying the correct boundary conditions, then the normalized expectation value of the Hamiltonian operator,

$$\langle H\rangle_\Phi = \int \Phi^* H\Phi \, d\tau \;\; / \;\; \int \Phi^* \Phi \, d\tau, \qquad [5]$$

is always greater than or equal to the lowest eigenvalue of the Hamiltonian. The trial wave function normally contains several parameters which can be adjusted to give a minimum for the above energy integral. The procedure yields the closest value to the true energy subject only to the limitations of the functional form of Φ.

The way in which this theorem is used in this work is a form of the method of linear combinations: the true wave function ψ for the system under consideration is approximated by the trial function Φ which is written as a linear combination of well chosen functions:

$$\psi \approx \Phi = \sum_n C_n \Delta_n . \qquad [6]$$

The expansion functions Δ_n are linearly independent and possess all of the symmetry of the true wave function ψ.

When the Variational Principle is applied using Φ as the trial wave function with adjustable parameters C_n, a system of linear equations is obtained:

$$(\mathbb{H} - E\mathbb{S})\,\mathbb{C} = 0. \qquad [7]$$

The elements of the matrices $\mathbb{H}$ and $\mathbb{S}$ are defined by

$$H_{nm} = \int \Delta_n^* \hat{H}\, \Delta_m \, d\tau, \qquad S_{nm} = \int \Delta_n^* \, \Delta_m \, d\tau, \qquad [8]$$

and the elements of the column vector $\mathbb{C}$ are the coefficients C_n. Since only ground states are discussed here, the energy E appearing in the above secular equation is assumed to be that of the lowest eigenvalue, and the vector $\mathbb{C}$ the corresponding eigenvector.

C. Construction of Expansion Functions

1. General Structure

The purpose of this section is to discuss the construction of the configurations Δ_n used in the expansion of the trial wave function

$$\Phi = \sum_n C_n \Delta_n \; . \qquad [9]$$

For now the discussion will be confined to three-electron systems in general and later to the lithium atom and linear symmetric H_3 molecule specifically.

The total wave function and each expansion term is a function of the coordinates of each electron. These coordinates consist of three position coordinates and one spin coordinate for each electron making Φ a nine-dimensional function of position coordinates and a three-dimensional function of spin coordinates.

More explicitly, the general structure of an expansion function is chosen to be

$$\Delta_n = \hat{A}[\phi_i(1)\ \phi_j(2)\ \phi_k(3)\ r_{12}^{i'}\ r_{13}^{j'}\ r_{23}^{k'}\ \theta_q(1,2,3)]. \qquad [10]$$

The subscript n now represents the set of indices (i, j, k, i', j', k', q). The functions $\phi_i(t) \equiv \phi_i(\vec{r}_t)$ are one-electron symmetry orbitals involving only the position coordinates of electron t. Only those products of symmetry orbitals $\phi_i(1)\ \phi_j(2)\ \phi_k(3)$ that yield a term Δ_n having the symmetry of the ground state are allowed. The interelectronic distances $r_{ij}^{\nu_{ij}} \equiv |\vec{r}_j - \vec{r}_i|^{\nu_{ij}}$ are inserted directly into the wave equation to reduce correlation error. The presence of these terms allows the use of the phrase "explicitly correlated wavefunction" for describing Eq. [*10*]. The last term $\theta_q(1,2,3)$ is a 3-electron spin function which is an eigenfunction of the operators S^2 and S_z corresponding to the square of the total and z-component of the spin angular momentum respectively. The operator $\hat{A}$ is the antisymmetry operator,

$$\hat{A} = \frac{1}{\sqrt{3!}} \sum_{\hat{P}} (-1)^p \hat{P}, \qquad [11]$$

where the sum is over all 3! possible permutations $\hat{P}$ of the electronic coordinates and p is the parity of the corresponding permutation. Note that the function Δ_n can be written as a linear combination of determinants only if i', j', and k' are all zero, since only then can determinants be formed having as their elements one-electron spin functions.

2. Significance of Correlation Terms

The correlation energy is usually defined after Löwdin[43] to be the difference between the energy calculated by means of the Restricted Hartree-Fock procedure and the lowest eigenvalue of the nonrelativistic Hamiltonian:

$$E_{\text{CORR}} = E_{\text{HF}} - E_{\text{EXACT}} \; . \qquad [12]$$

The Hartree-Fock model assumes that each electron moves in an effective potential created by the nuclei and the averaged field of the other electrons. There is no provision made for the dynamical correlation among the individual motions of the electrons due to the instantaneous Coulomb repulsions.

One of the most enlightening ways of considering spatial electron correlation is by associating it with the cylindrical coordinates ρ,θ,z. "In-out" correlation can be associated with the radial coordinate ρ; that is, electron motion is correlated in such a way that when one electron is close to an internuclear axis, the others tend to be farther out radially. Angular correlation, associated with the coordinate θ, can be described as the tendency of electrons to stay on the opposite sides of an axial plane. The third type, "left-right" correlation, describes the tendency of electrons to avoid each other by staying at opposite ends of the molecule.

The first of these correlation effects can be described mathematically by assigning to different electrons occupying the same shell different orbitals which differ only in the radial parts. Angular correlation can be described by using as orbitals basis functions having strong angular dependencies. The "left-right" correlation can be taken into consideration by building molecular orbitals which have a large amplitude in one region of the molecule and a small amplitude in all other regions. An excellent example of a study describing electron correlation as has been done here is that of the H_2 molecule by McLean, Weiss, and Yoshimine[44].

It is clear that a trial wave function built of configurations, each emphasizing a certain type of correlation, would be useful in accounting for a large percentage of the total electron correlation energy. However, the convergence becomes very slow after the first few terms[45,46], even if a transformation to natural orbitals[47] is made in an attempt to obtain the maximum convergence rate[48].

The introduction of interelectronic coordinates $|\vec{r}_i - \vec{r}_j|^{\nu_{ij}} = r_{ij}^{\nu_{ij}}$ directly into the trial wave function accounts for all types of electronic correlation simultaneously. One way of observing the effect of r_{ij} terms on the correlation is by noting that the amplitude of a wave function containing these terms becomes large when r_{ij} is large and becomes small as electrons i and j approach one another. Hylleraas[49] was the first to employ internuclear coordinates and did so in calculations involving the helium atom. Convergence was significantly faster than had been attained in the past by using configuration interaction. Calculations using explicitly correlated wave functions have since been performed on lithium[41,50], beryllium[51,52], and the hydrogen molecule[53].

Two less obvious reasons have been noted for the superiority of explicitly correlated wave functions. The first is that such wave functions are much better suited for describing the cusp[54] at $r_{ij} = 0$. The term "cusp" is used to describe the discontinuity of the first derivative of the wave function with respect to r_{ij} at $r_{ij} = 0$. The "local energy" expression $\hat{H}\psi/\psi$ for an exact wave function ψ is constant and equal to the total energy of the system at every point in coordinate space. The analogous expression for a trial wave function Φ will not in general be constant and, in fact, may possess singularities at $r_{ij} = 0$ due to the electron-electron repulsion terms in $\hat{H}$. The presence of r_{ij} terms in the trial wave function tends to cancel those in the Hamiltonian and thus reduce the fluctuation of $\hat{H}\Phi/\Phi$.

The other reason for the superiority of explicitly correlated wave functions was noted by Coulson and Nielson[55]. They made a quantitative study of the "Coulomb hole" defined as the region in space in which the two electron density function,

$$f(r_{12})_{\text{EXACT}}\, dr_{12} = \int_{r_{12}=\text{Const.}} \psi^*_{\text{EXACT}}\, \psi_{\text{EXACT}}\, d\tau_1\, d\tau_2, \qquad [13]$$

is less than it would be without correlation. In the case of helium this region is spherically symmetric

$$|\vec{r}_2 - \vec{r}_1| \leq r_{\text{Coul. hole}} \ . \qquad [14]$$

The probability $[f(r_{12})\, dr_{12}]$ that $|\vec{r}_2 - \vec{r}_1| \leq r_{\text{Coul. hole}}$ calculated from an uncorrelated wave function will be greater than the same probability calculated from the true wave function.

The striking fact here is that $r_{\text{Coul. hole}}$ is large--about the same size as the atom--and not just the immediate region about the cusp. Gilbert[56] has continued this line of investigation by taking note of Coulson and Neilson's discovery that the correlation error in the energy of a trial wave function is proportional to the average electron-electron repulsion energy calculated by that wave function:

$$E_{\text{CORR}} \propto \left\langle \frac{e^2}{r_{12}} \right\rangle \ . \qquad [15]$$

The implication of Eq. [15] is that the correlation error is due mostly to electron-electron interaction with little or no contribution coming from electron-nucleus interaction. He then expresses the correlation error contribution due to the differential volume element of the Coulomb hole as

$$dE_{\text{CORR}} = e^2 \frac{[f_{\text{HF}}(r_{12}) - f_{\text{EXACT}}(r_{12})]}{r_{12}}\, dr_{12} \ . \qquad [16]$$

The results again show that the region of space in which the true wave function produces the greatest contribution to the correlation energy is about the size of the atom. Further evidence that the immediate region about the cusp does not contribute greatly to the correlation error is that the non-differential part of dE_{CORR} approaches zero as r_{12} approaches zero:

$$\lim_{r_{12}\to 0} \frac{f_{HF}(r_{12}) - f_{EXACT}(r_{12})}{r_{12}} = 0 \ . \qquad [17]$$

Gilbert summarizes his study by stating that the superiority of an explicitly correlated wave function over a configuration interaction calculation is mainly due to the fact that the Coulomb hole has a much simpler structure when viewed relative to an electron than it has when viewed relative to a fixed point.

3. Group Theoretical Considerations

Symmetry adapted expansion terms are used in the calculations because of the significant reduction in effort that comes about. The next few paragraphs will outline the group-theoretical considerations that are necessary to show the reasons for the reduction. An excellent group theory text which gives a more complete description is one by Hamermesh[57].

Consider the operator eigenvalue problem

$$\hat{H}\,\Delta^{\nu}_{n,i} = \varepsilon^{\nu}_{n}\,\Delta^{\nu}_{n,i} \ , \qquad [18]$$

where the index i is used to label the n_{ν} independent degenerate eigenfunctions belonging to the eigenvalue ε^{ν}_{n}. The index n labels the various energy levels and the associated set of degenerate eigenfunctions. All of the degenerate eigenfunctions can be considered simultaneously if they are placed in an n_ν-dimensional column vector Δ_n^ν. The eigenvalue problem becomes

$$\hat{H}\,\Delta_n^\nu = \varepsilon^\nu\,\Delta_n^\nu\,. \qquad [19]$$

After applying the operator $\hat{O}_R$ corresponding to some symmetry transformation R, one has

$$\hat{O}_R\,\hat{H}\,\Delta_n^\nu = \varepsilon_n^\nu\,\hat{O}_R\,\Delta_n^\nu\,. \qquad [20]$$

If $\hat{H}$ is invariant under the transformation R, then

$$\hat{O}_R\,\hat{H} = \hat{H}\,\hat{O}_R, \qquad [21]$$

and the eigenvalue equation becomes

$$\hat{H}(\hat{O}_R\,\Delta_n^\nu) = \varepsilon_n^\nu(\hat{O}_R\,\Delta_n^\nu)\,, \qquad [22]$$

which clearly shows that the functions $(\hat{O}_R\,\Delta_{n,i}^\nu)$ are also eigenfunctions of $\hat{H}$ belonging to the same eigenvalue ε_n^ν. Since the set of functions $\Delta_{n,i}^\nu$ completely spans the space of solutions of the eigenvalue problem with eigenvalue ε_n^ν, the eigenfunctions $(\hat{O}_R\,\Delta_{n,i}^\nu)$ must be expressible as a linear combination of these functions. This can be stated in matrix notation as

$$\hat{O}_R\,\Delta_n^\nu = \tilde{\mathbb{D}}^\nu\,(R)\,\Delta_n^\nu\,, \qquad [23]$$

where $\mathbb{D}$ is the transformation matrix and the tilde indicates that the transpose of the matrix is to be taken.

By carrying out the above procedure for all the symmetry operations under which the Hamiltonian is invariant, one obtains a set of n_ν- dimensional square matrices which constitute a representation. This can be seen by considering another transformation S belonging to the symmetry group of the Hamiltonian. The corresponding operator $\hat{O}_S$ acting upon the basis gives

$$\hat{O}_S \, \mathbb{\Delta}_n^\nu = \tilde{\mathbb{D}}^\nu(S) \, \mathbb{\Delta}_n^\nu \, . \tag{24}$$

Applying the two operators in succession leads to

$$\hat{O}_S \, \hat{O}_R \, \mathbb{\Delta}_n^\nu = \hat{O}_S \, \tilde{\mathbb{D}}^\nu(R) \, \mathbb{\Delta}_n^\nu = \tilde{\mathbb{D}}^\nu(R) \, \tilde{\mathbb{D}}^\nu(S) \, \mathbb{\Delta}_n^\nu \, . \tag{25}$$

But since the product of two symmetry operations is another symmetry operation, one also has

$$\hat{O}_S \, \hat{O}_R \, \mathbb{\Delta}_n^\nu = \hat{O}_{SR} \, \mathbb{\Delta}_n^\nu = \tilde{\mathbb{D}}^\nu(SR) \, \mathbb{\Delta}_n^\nu \, . \tag{26}$$

Comparing the last two equations the desired result is obtained:

$$\mathbb{D}^\nu(SR) = \mathbb{D}^\nu(S) \, \mathbb{D}^\nu(R) \, . \tag{27}$$

That is, the matrices transform among one another under matrix multiplication in exactly the same way as the elements of the corresponding group transform among one another, and hence form a representation with the eigenfunctions $\mathbb{\Delta}_n^\nu$ providing the basis for the representation.

If the highest level of symmetry of the Hamiltonian is considered, the representation will be irreducible and the many theorems of group theory applying to such representations will be applicable. Since for finite groups every representation is equivalent to a unitary representation, the matrices $\mathbb{D}(R)$ will henceforth be taken as unitary.

Since the symmetry of the quantum mechanical systems under investigation is known, the most general expansion of the trial wave function, Eq. [9], is one in terms of functions that transform in the same manner as the degenerate basis functions of the various irreducible representations associated with the symmetry group of the system:

$$\Phi = \sum_{n} \sum_{\nu} \sum_{i} C^{\nu}_{n,i} \, \Delta^{\nu}_{n,i} \ . \qquad [28]$$

The index n labels the occurrence of the νth irreducible representation. The application of the Variational Principle using Eq. [28] as the trial wave function will result in a secular equation with matrix elements of the form

$$\langle \Delta^{\nu}_{n,i} \mid \hat{H} \, \Delta^{\mu}_{m,j} \rangle \ , \qquad [29]$$

where the operator $\hat{H}$ possesses the full symmetry of the system. By means of a group-theoretical analysis it is possible to determine the conditions under which the matrix element [29] is zero and therefore which of the terms in the sum will contribute to the state being considered.

The unitary operators of the symmetry group do not change the scalar product, so the matrix element can be written

$$\begin{aligned} \langle \Delta^{\nu}_{n,i} \mid \hat{H} \, \Delta^{\mu}_{m,j} \rangle &= \langle \hat{O}_R \, \Delta^{\nu}_{n,i} \mid \hat{O}_R \, \hat{H} \, \Delta^{\mu}_{m,j} \rangle \\ &= \langle \hat{O}_R \, \Delta^{\nu}_{n,i} \mid \hat{H} \, \hat{O}_R \, \Delta^{\mu}_{m,j} \rangle \ . \end{aligned} \qquad [30]$$

If all of the operators of the group are considered and the terms added, then Eq. [29] can be expressed as

$$\langle \Delta^{\nu}_{n,i} \mid \hat{H}\, \Delta^{\mu}_{m,j} \rangle \;=\; \frac{1}{g} \sum_{R} \langle \hat{O}_R\, \Delta^{\nu}_{n,i} \mid \hat{H}\, \hat{O}_R\, \Delta^{\mu}_{m,j} \rangle \;, \qquad [31]$$

where g is the order of the group. It is understood that the sum is to be replaced by an integral and appropriate density function when including infinitesimal operators of a continuous group. Allowing $\hat{O}_R$ to operate on the basis functions, Eq. [31] becomes

$$\langle \Delta^{\nu}_{n,i} \mid \hat{H}\, \Delta^{\mu}_{m,j} \rangle \;=\; \frac{1}{g} \sum_{k,l} \langle \Delta^{\nu}_{n,k} \mid \hat{H}\, \Delta^{\mu}_{m,l} \rangle \sum_{R} D^{\nu *}_{ki}(R)\; D^{\mu}_{lj}(R) \;. \qquad [32]$$

According to the orthogonality relations among unitary irreducible representations, the last sum can be written as

$$\sum_{R} D^{\nu *}_{ki}(R)\; D^{\mu}_{lj}(R) \;=\; \frac{g}{n_{\nu}}\, \delta_{kl}\, \delta_{ij}\, \delta_{\nu\mu} \;. \qquad [33]$$

After inserting Eq. [33] into Eq. [32] and performing the remaining summations, the matrix element becomes

$$\begin{aligned} \langle \Delta^{\nu}_{n,i} \mid \hat{H}\, \Delta^{\mu}_{m,j} \rangle \;&=\; \frac{1}{n_{\nu}} \sum_{k} \langle \Delta^{\nu}_{n,k} \mid \hat{H}\, \Delta^{\mu}_{m,k} \rangle\, \delta_{ij}\, \delta_{\nu\mu} \\ &=\; H^{\nu}_{nm}\, \delta_{ij}\, \delta_{\nu\mu} \;, \end{aligned} \qquad [34]$$

which clearly indicates that unless $i = j$ and $\mu = \nu$ the matrix element of any operator possessing the full symmetry of the Hamiltonian is zero. Furthermore, the value H^{ν}_{nm} of the matrix element does not depend on which degenerate basis function of the irreducible representation is used to form the matrix element.

If only one state is of interest, then only those terms which transform in the same manner as one of the basis functions of the irreducible representation associated with that state need be included in the trial wave function expansion:

$$\Phi_i^{\nu} = \sum_n C_n (\Delta_{n,i}^{\nu}) . \qquad [35]$$

Terms included which do not transform in the same manner as the state under investigation cannot contribute to the energy of that state due to the orthogonality conditions that cause the subsequent factoring of the secular equation.

Since the lithium Hamiltonian has spatial symmetry of the $O(3)$ group, its eigenfunctions are a basis for the various irreducible representations of that group and therefore may be classified by the quantum numbers associated with the operators corresponding to the square of the total orbital angular momentum ($\hat{L}^2$) and one component of the total orbital angular momentum such as that along the Z axis ($\hat{L}_z$). The Hamiltonian, Eq. [4], does not include spin operators and therefore the operators associated with the square of the total spin ($\hat{S}^2$) and the components of the total spin ($\hat{S}_x$, $\hat{S}_y$, $\hat{S}_z$) commute with the Hamiltonian. The total angular momentum $\hat{\vec{J}}$ is defined as

$$\hat{\vec{J}} = \hat{\vec{L}} + \hat{\vec{S}}, \qquad [36]$$

and its square $\hat{J}^2$ and components ($\hat{J}_x$, $\hat{J}_y$, $\hat{J}_z$) also commute with the Hamiltonian. All of the operators ($\hat{H}$, $\hat{L}^2$, $\hat{L}_x$, $\hat{L}_y$, $\hat{L}_z$, $\hat{S}^2$, $\hat{S}_x$, $\hat{S}_y$, $\hat{S}_z$, $\hat{J}^2$, $\hat{J}_x$, $\hat{J}_y$, $\hat{J}_z$) do not mutually commute, but the subset ($\hat{L}^2$, $\hat{L}_z$, $\hat{S}^2$, $\hat{S}_z$) does commute and is chosen here to describe the state of the lithium atom. This mode of description is called L-S coupling and assumes there to be no interaction between total orbital and total spin angular momentum vectors. Such an approximation is usually made when working with systems involving a small number of electrons since the spin-orbit interaction is small in these systems and does not cause a coupling of spin and angular momenta. The eigenvalues belonging to the operators $\hat{L}^2$, $\hat{L}_z$, $\hat{S}^2$, and $\hat{S}_z$ will be designated $L(L+1)$, M_L, $S(S+1)$, and M_S respectively. The ground state of the lithium atom is well known to have ^2S symmetry. The symbol S implies $L = 0$ and the superscript is the multiplicity, $2S+1$. It follows that $S = \frac{1}{2}$, $M_L = 0$, and $M_S = \pm \frac{1}{2}$. The system is doubly degenerate with respect to the two possible values of M_S, so $M_S = \frac{1}{2}$ was arbitrarily chosen for the calculation.

The linear symmetric H_3 complex has $D_{\infty h}$ spatial symmetry. Its eigenfunctions are a basis for the various irreducible representations of that group and therefore may be classified by the eigenvalues of the operators associated with the component of orbital angular momentum along the internuclear axis ($\hat{L}_z$), the reflection of the electron coordinates in a plane containing the internuclear axis ($\hat{\sigma}_v$), and the inversion of the electron coordinates through the center of the molecule ($\hat{I}$). An argument which considers the electronic spin can be made for the linear symmetric H_3 complex. It is analogous to the one made for the lithium atom and results in a mode of description based on the mutually commuting set of operators $\hat{L}_z$, $\hat{\sigma}_v$, $\hat{I}$, $\hat{S}^2$, and $\hat{S}_z$. The eigenvalues belonging to these operators will be designated M_L, $\pm$, g or u, $S(S+1)$, and M_S. The symbol (-) is used when the sign of the wave function is changed upon reflection and the symbol (+) is used when no sign change occurs. Likewise the symbol (u) is used when the sign of the wave function changes upon inversion, and (g) is used when there is no change.

The lowest state of the linear symmetric H_3 complex is well known to have the symmetry of the Σ_u^+ irreducible representation of $D_{\infty h}$. The symbol Σ implies $M_L = 0$. The spin state for the ground state H_3 complex is the same as that for the ground state of Li; that is, $S = \frac{1}{2}$ and $M_S = \pm \frac{1}{2}$. The multiplicity is again 2 and $M_S = \frac{1}{2}$ is chosen for the calculations. The ground state of the linear symmetric H_3 molecule is completely described by the symbols ${}^2\Sigma_u^+$.

4. Explicit Structure of Expansion Functions

The one-electron orbitals ϕ which are used to build the expansion functions described at the beginning of this chapter,

$$\Delta_n = \hat{A}[\phi_i(1)\ \phi_j(2)\ \phi_k(3)\ r_{12}^{i'}\ r_{13}^{j'}\ r_{23}^{k'}\ \theta_q(1,2,3)], \qquad [10]$$

are either analytical Slater orbitals in the case of Li or a linear combination of such orbitals in the case of H_3. Slater orbitals are defined as

$$\chi_{n\ell m}(t) = \frac{(2\zeta)^{n+\frac{1}{2}}}{(2n!)^{\frac{1}{2}}}\, r_t^{n-1}\, e^{-\zeta r_t}\, Y_{\ell,m}\,(\theta_t,\phi_t), \qquad [37]$$

where the $Y_{\ell,m}$ are the normalized spherical harmonics. These functions are convenient to use since they have relatively simple radial dependence and are eigenfunctions of $\hat{L}_t^2$ and $\hat{L}_{z_t}$, the operators corresponding to the square of the orbital angular momentum and the z-component of the orbital angular momentum respectively of electron t.

The one-electron symmetry orbitals are classified according to an irreducible representation of the appropriate symmetry group in the same way as the total wave functions. However, lower case Latin letters

$s, p, d,$ etc., are used to identify the orbital angular momentum quantum number of orbitals belonging to the $O(3)$ rotation group and lower case Greek letters σ, π, δ, etc., are used to identify the z-component of the orbital angular momentum of the orbitals belonging to the $D_{\infty h}$ group. A principle quantum number n, labeling the occurrence of an irreducible representation, is also necessary and will be indicated by an integer preceding the symbols describing the symmetry of the one-electron atomic orbitals. A similar notation is also necessary for labeling the $D_{\infty h}$ one-electron molecular orbitals but is done by using the principle quantum number of the atomic orbitals making up the symmetry orbital and simultaneously using an integer superscript equal to the number of atomic orbitals used to build the particular symmetry orbital.

The symmetry properties of the expansion terms Δ_n considered in this work are completely independent of the explicit correlation portion $(\prod_{i<j}^{N} r_{ij}^{\nu_{ij}})$. An equivalent statement is that the commutator of the explicit correlation portion of the configurations and any operator $\hat{Q}$ associated with the $O(3)$ rotation group or the $D_{\infty h}$ group is zero. That is, the operator $\hat{Q}$ has no effect on the product $(\prod_{i<j}^{N} r_{ij}^{\nu_{ij}})$ and therefore

$$[\hat{Q}, \prod_{i<j}^{N} r_{ij}^{\nu_{ij}}] = 0 \ . \qquad [38]$$

Proofs for the cases $\hat{Q} = \hat{L}^2$ and $\hat{Q} = L_z$ are given in Appendix A. The other cases of interest are $\hat{Q} = \sigma_v$ and $\hat{Q} = \hat{I}$. In the first case the application of the operator σ_v is equivalent to changing the sign of the x components of the position vector $\vec{r} = x\vec{1}_x + y\vec{1}_y + z\vec{1}_z$ for every electron, assuming that the plane of reflection contains the x and z axes.

In the second case, $\hat{Q} = \hat{I}$, all components of the position vectors of all electrons are reversed in sign where the point of inversion is taken to be the origin of the coordinate system used to define the vectors $\vec{r}$. Hence, it is now easy to observe that the general term in the explicit correlation product

$$r_{ij}^{\nu_{ij}} = [(x_i-x_j)^2 + (y_i-y_j)^2 + (z_i-z_j)^2]^{\nu_{ij}/2} \qquad [39]$$

is unaltered by these symmetry operations. If a component of the position vector of one electron changes sign, the corresponding component of the position vector of all other electrons must simultaneously change sign. Since only the squares of the differences in components are considered, there will be no net change after application of the symmetry operators. For example, if there is a change in sign of the x-components of all the electronic coordinates, then the term $[x_i-x_j]^2$ becomes

$$[(-x_i) - (-x_j)]^2 = (-1)^2 [x_i-x_j]^2 = [x_i-x_j]^2, \qquad [40]$$

with no net change in itself or in the term $r_{ij}^{\nu_{ij}}$ containing it.

Since the antisymmetrizer $\hat{A}$ and the explicit correlation term $(\prod_{i<j}^{N} r_{ij}^{\nu_{ij}})$ commute with all of the spatial and spin operators that have been considered, the remaining product of one-electron orbitals,

$$\phi_i(1)\ \phi_j(2)\ \phi_k(3), \qquad [41]$$

completely determines the spatial symmetry, and the spin function,

$$\theta_q(1,2,3), \qquad [42]$$

completely determines the spin symmetry of the expansion term Δ_n.

Only atomic orbitals $\chi_{n\ell m}$ with $\ell = m = 0$ (s-type atomic orbitals) are considered in this work. It was decided that the use of Slater orbitals having angular dependence was unnecessary due to the inclusion of explicit correlation terms in the trial wave function. If only s-type atomic orbitals are used to build the expansion term, then the possible spatial symmetry properties that the expansion term may possess are s-type states ($L = 0$, $M_L = 0$) for the atomic case, and Σ^+ ($M_L = 0$, $\sigma_v \rightarrow +$) in the linear symmetric molecule case. The proof that $M_L = 0$ in both cases follows from the definition of the operator $\hat{L}_z$,

$$\hat{L}_z = \sum_t^N \hat{L}_{z_t}, \tag{43}$$

and

$$\hat{L}_z \, [\phi_i(1) \; \phi_j(2) \; \phi_k(3)] = (\sum_{t=1}^{3} m_{\ell_t}) \, [\phi_i(1) \; \phi_j(2) \; \phi_k(3)] \tag{44}$$

since

$$\hat{L}_{z_t} \, \phi(t) = m_{\ell_t} \, \phi(t). \tag{45}$$

If the orbitals $\phi(t)$ are constructed of only s-type orbitals, then by definition $m_{\ell_t} = 0$ and

$$M_L = \Sigma \, m_{\ell_t} = 0. \tag{46}$$

The proof that $L = 0$ is constructed most easily by first expressing the operator $\hat{L}^2$ in terms of the raising and lowering operators $\hat{L}_+$ and $\hat{L}_-$,

$$\hat{L}^2 = \hat{L}_+\hat{L}_- - \hat{L}_z + \hat{L}_z^2. \qquad [47]$$

All of these operators can be expressed in terms of one-electron operators:

$$\hat{L}_z^2 = (\sum_t^N L_{z_t})^2 = \sum_{t,u}^N L_{z_t} L_{z_u}, \qquad [48]$$

and

$$\hat{L}_+ = \sum_t^N L_{+_t}, \qquad \hat{L}_- = \sum_t^N \hat{L}_{-_t}, \qquad [49]$$

where

$$\hat{L}_{+_t} = L_{x_t} + i\, L_{y_t}, \qquad L_{-_t} = L_{x_t} - i\, L_{y_t}\ . \qquad [50]$$

The effect of $\hat{L}_{+_t}$ and $\hat{L}_{-_t}$ on an atomic orbital $\chi_{n\ell m}$ is to increase or decrease respectively the azimuthal quantum number m:

$$\left.\begin{array}{llll} \hat{L}_+ \chi_{n\ell m} & = N_+ \chi_{n\ell(m+1)} & \text{if} & (m<\ell), \\ \hat{L}_- \chi_{n\ell m} & = N_- \chi_{n\ell(m-1)} & \text{if} & (m>-\ell), \end{array}\right\} \qquad [51]$$

and

$$\left.\begin{array}{llll} \hat{L}_+ \chi_{n\ell\ell} & = 0 & \text{if} & (m=\ell), \\ \hat{L}_- \chi_{n\ell(-\ell)} & = 0 & \text{if} & (m=-\ell), \end{array}\right\} \qquad [52]$$

where N_+ and N_- are appropriate constants which preserve normalization. The zero results in Eq. [52] come about when the allowed range of m,

$$-\ell \le m \le \ell, \qquad [53]$$

would otherwise be exceeded.

The result of the operation $\hat{L}^2$ on the product of one-electron orbitals,

$$\hat{L}^2\, [\phi_i(1)\ \phi_j(2)\ \phi_k(3)] = 0, \qquad [54]$$

can now be shown by considering three steps corresponding to the three terms in Eq. [47]. According to Eq. [52], the operation $\hat{L}_-$ immediately produces a zero result since the orbitals $\phi(k)$ are assumed to be constructed of s-type atomic orbitals with $\ell = m = 0$. The second and third steps likewise give a zero result since

$$\hat{L}_z\, [\phi_i(1)\ \phi_j(2)\ \phi_k(3)] = 0 \qquad [55]$$

by Eqs. [44] and [46]. Since all three terms of the expansion of $\hat{L}$ produce a zero result, Eq. [54] holds.

The N-electron reflection operator σ_v can be written in terms of one-electron operators σ_{v_t}:

$$\sigma_v = \prod_{t=1}^{N} \sigma_{v_t} \,. \qquad [56]$$

Thus, applying σ_v causes all electron coordinates to be reflected simultaneously in an arbitrarily chosen plane containing the internuclear axis. Since s-type orbitals are spherically symmetric, any reflection in a plane containing the center of the orbital will have no effect on the orbital. A similar statement holds for a linear combination of s-type orbitals whose centers lie on an axis and for a reflection plane that contains that axis. The conclusion is that an N-electron reflection operator applied to a product of N one-electron orbitals constructed of s-type orbitals produces no change. In the present case of a 3-electron linear symmetric molecule, one has

$$\sigma_v \, [\phi_i(1) \; \phi_j(2) \; \phi_k(3)] \;=\; +1 \, [\phi_i(1) \; \phi_j(2) \; \phi_k(3)]. \qquad [57]$$

The remaining spatial symmetry property that must be considered is that of inversion in the case of the linear symmetric molecule. Before this is done, it is necessary to examine the symmetry properties of the individual one-electron orbitals. Tables I and II show the explicit functional form of the one-electron atomic orbitals used in the lithium calculation and the one-electron symmetry orbitals used in the linear symmetric H_3 calculation. As previously stated, the orbitals are constructed from *s*-type Slater atomic orbitals. All of the orbitals used in the lithium atom case are centered on the nucleus at the origin of the coordinate system (see Fig. 1).

The symmetry orbitals used in the linear symmetric H_3 case are constructed of linear combinations of atomic orbitals centered on the various nuclei of the molecule. These one-electron molecular orbitals are called symmetry orbitals since they possess the symmetry of one of the irreducible representations of the group $D_{\infty h}$. They are labeled accordingly, as discussed earlier in this section. The subscripts a, b, and c on the atomic orbitals making up the symmetry orbitals refer to the corresponding nuclei as indicated in Fig. 2.

As indicated, all of the symmetry orbitals are of $ns\sigma^+$ symmetry. The particular linear combinations chosen are the simplest possible leading to a linearly independent set possessing the symmetry of the point group of the molecule and they are therefore referred to as primitive symmetry orbitals. The superscript enclosed in parentheses refers to the number of atomic orbitals used in constructing the symmetry

TABLE I

ONE-ELECTRON ATOMIC ORBITALS AND EXPANSION TERMS

USED IN THE 12-TERM LITHIUM ATOM CALCULATION

Atomic Orbitals	Exponents	Integration Parameters
$\phi_1 = 1s$		
$\phi_2 = 2s$	$\zeta_{1s} = \zeta_{2s} = \zeta_{3s} = 2.76$	$s_1 = 3.0$ $s_2 = 0.3$
$\phi_3 = 3s$		
$\phi_4 = 2s'$	$\zeta_{2s'} = 0.65$	

S Expansion Terms

	Atomic Orbital			r_{ij} Exponent		
Δ_n	ϕ_i	ϕ_j	ϕ_k	$r_{12}^{i'}$	$r_{13}^{j'}$	$r_{23}^{k'}$
1	1	1	4	0	0	0
2*	1	2	4	0	0	0
3	2	2	4	0	0	0
4*	1	3	4	0	0	0
5	1	1	4	1	0	0
6	1	1	4	2	0	0
7	1	1	4	2	1	1
8*	1	2	4	1	1	1
9	2	2	4	2	1	1

*Two spin functions are possible.

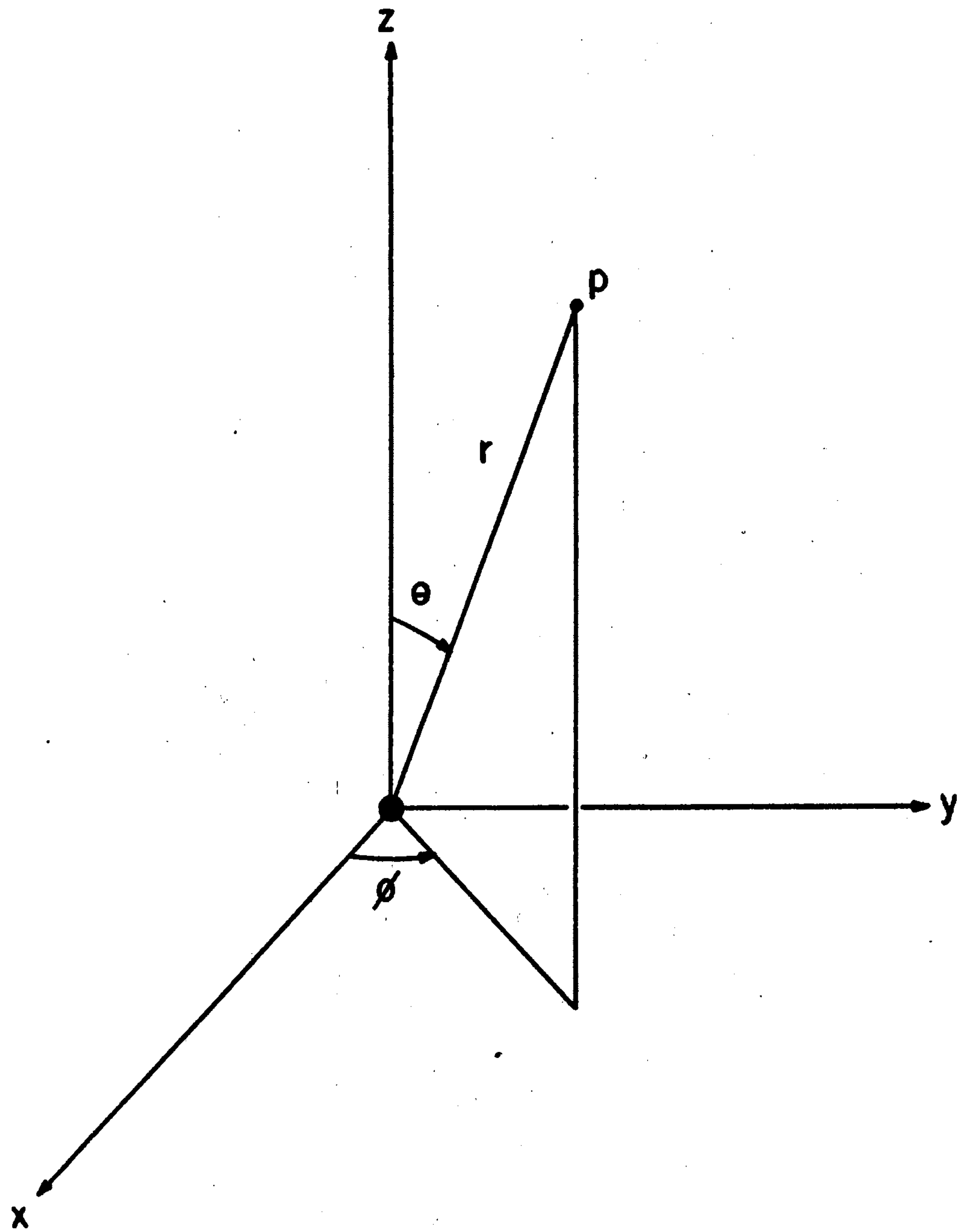

Figure 1. Spherical Coordinate System Used for Lithium Atom Calculation

TABLE II

ONE-ELECTRON PRIMITIVE SYMMETRY ORBITALS AND EXPANSION TERMS USED IN THE 21-TERM LINEAR SYMMETRIC H_3 CALCULATION ($R_{ab} = R_{bc} = 1.7924$ a.u.)

Symmetry Orbitals	Exponents	Integration Parameters
$\phi_1 = 1s\sigma_g^{+(1)} = 1s_b$	$\zeta_{1s_b} = 1.2796$	
$\phi_2 = 1s\sigma_g^{+(2)} = 1s_a + 1s_c$	$\zeta_{1s_a} = \zeta_{1s_c} = 1.1303$	$s_1 = s_2 = 1.54$
$\phi_3 = 1s\sigma_u^{+(2)} = 1s_a - 1s_c$		
$\phi_4 = 2s\sigma_u^{+(2)} = 2s_a - 2s_c$	$\zeta_{2s_a} = \zeta_{2s_c} = 1.0663$	

Σ_u^+ Expansion Terms

Δ_n	Symmetry Orbital ϕ_i	ϕ_j	ϕ_k	r_{ij} Exponent $r_{12}^{i'}$	$r_{13}^{j'}$	$r_{23}^{k'}$
1	1	1	3	0	0	0
2*	1	2	3	0	0	0
3	2	2	3	0	0	0
4	1	1	4	0	0	0
5	1	1	3	1	0	0
6*	1	1	3	0	1	0
7*	1	2	3	1	0	0
8*	1	2	3	0	1	0
9*	1	2	3	0	0	1
10	2	2	3	1	0	0
11*	2	2	3	0	1	0
12	1	1	4	1	0	0
13*	1	1	4	0	1	0
14	1	1	3	1	1	1

*Two spin functions are possible.

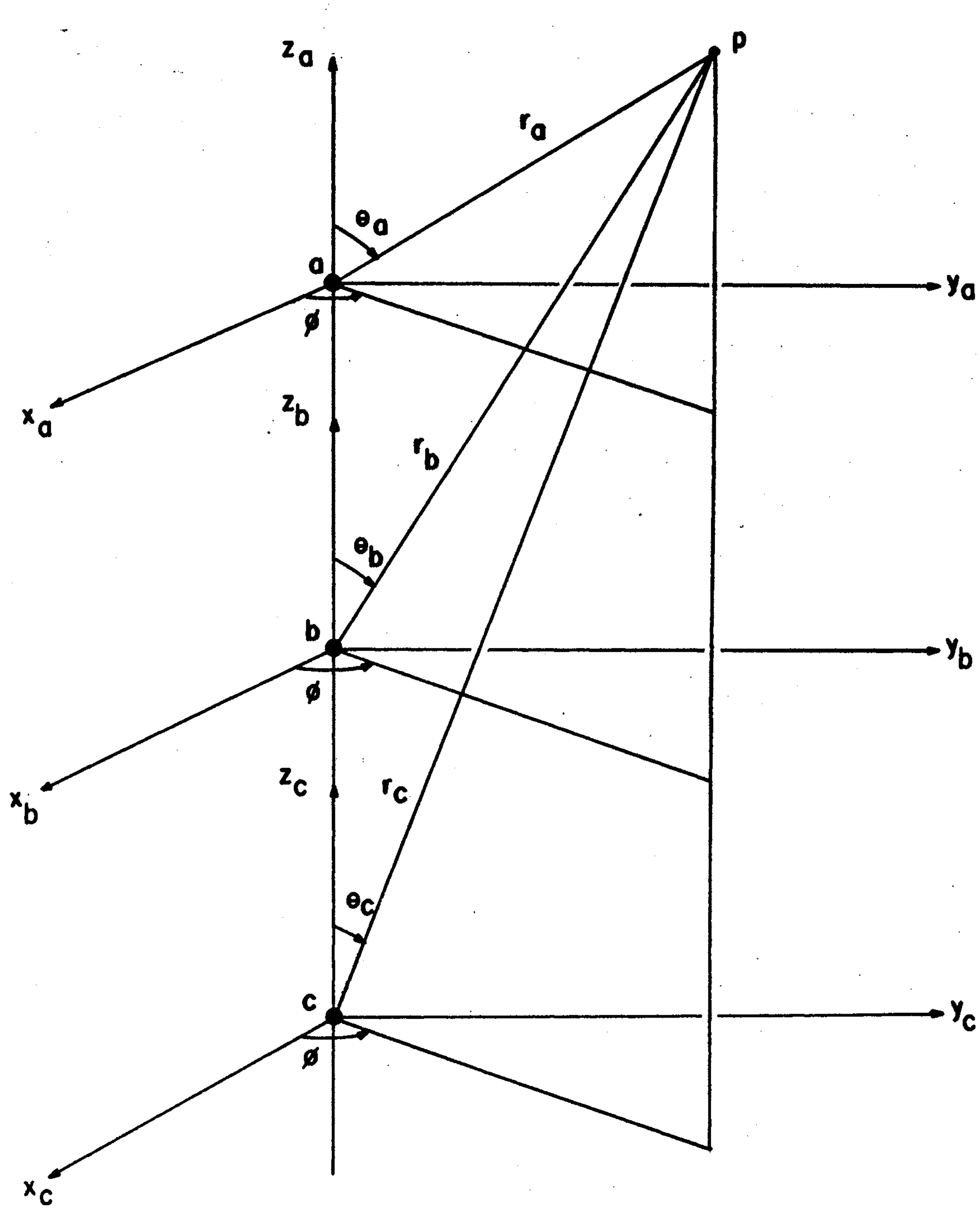

Figure 2. Spherical Coordinate Systems Centered on the Three Nuclei for the Linear Symmetric H_3 Calculation

orbital and serves to identify uniquely, along with the principle quantum number n, symmetry orbitals belonging to the same irreducible representation.

The symmetry with respect to inversion through the molecular midpoint of the symmetry orbitals is specified by the subscript g or u. The orbital $\phi_1 = 1s_b$ transforms into itself under inversion with no change and so has g-type symmetry. The orbital $\phi_2 = 1s_a + 1s_c$ also transforms into itself since the $1s$ atomic orbitals on centers a and c are simply interchanged. The orbitals $\phi_3 = 1s_a - 1s_c$ and $\phi_4 = 2s_a - 2s_c$ transform into themselves under inversion except for a sign change and therefore both have u-type symmetry.

The inversion property of an expansion term can now be determined from the symmetry orbitals used to construct it. The inversion operator written in terms of one-electron operators is

$$\hat{I} = \sum_{t=1}^{N} \hat{I}_t, \qquad [58]$$

and so the eigenvalue of the operator $\hat{I}$ is just the product of the eigenvalues of the N operators $\hat{I}_t$. For the 3-electron problem considered here, there are only two ways of obtaining an expansion term with the u-type symmetry of the ${}^2\Sigma_u^+$ ground state desired. One way is by taking a product of two g-type symmetry orbitals and a u-type symmetry orbital:

$$\hat{I}\ [\phi_{ig}(1)\ \phi_{jg}(2)\ \phi_{ku}(3)] = -1\ [\phi_{ig}(1)\ \phi_{jg}(2)\ \phi_{ku}(3)], \qquad [59]$$

or another way is by taking a product of three u-type symmetry orbitals:

$$\hat{I}\ [\phi_{iu}(1)\ \phi_{ju}(2)\ \phi_{ku}(3)] = -1\ [\phi_{iu}(1)\ \phi_{ju}(2)\ \phi_{ku}(3)]. \qquad [60]$$

A subscript u or g has been added to the symbol for a general symmetry orbital $\phi(t)$ to indicate the inversion symmetry.

Expansion terms can now be constructed for lithium and linear symmetric H_3 using the corresponding one-electron orbitals given in Tables I and II. Any product of three orbitals with the general explicit correlation terms $(r_{12}^{i'}\, r_{13}^{j'}\, r_{23}^{k'})$ is allowed, subject only to the restrictions that the resulting expansion term satisfies the symmetry conditions of the true wave function and that it is not related to another possible expansion term by a simple permutation of electronic coordinates. The first condition guarantees that no effort will be lost by including expansion terms which do not transform according to the irreducible representation of the ground state wave function. The second condition assures linear independence of each term with all others. In the work presented here the configurations are systematically constructed by requiring the indices i, j, and k of Δ_n to conform to the inequalities

$$i \le j \le k \quad i, j, k = 1,2,3 \ldots \quad i', j', k' = 0,1,2 \ldots, \qquad [61]$$

and then rejecting those terms with improper symmetry, or if one of the equalities in condition [61] holds, those terms which are linearly dependent with a term occurring earlier in the sequence.

Additional terms which did not include $\phi_4 = 2s'$ were rejected in the lithium case in order to allow direct comparison with Larsson's[41] work. Also, after the fifth term the systematic addition of terms was suspended in favor of adding appropriately chosen ones as discussed later. In the H_3 case, the systematic addition of terms was suspended only for the addition of the last one. The total number of terms considered in each case was dictated by the computer time available.

5. Construction of Spin Eigenfunctions

The ground states of both the lithium atom and the linear symmetric H_3 complex are doublets ($S = \frac{1}{2}$). The z-component of the total spin has arbitrarily been chosen as $+\frac{1}{2}$ from the two possibilities $M_S = \pm\frac{1}{2}$. There exist two 3-electron spin eigenfunctions with these properties. Construction of these spin eigenfunctions by either the genealogical construction method[4] or by the projection operator method[58] yields the same orthonormal eigenfunctions

$$G_1(1,2,3) = \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)\alpha(3) - \beta(1)\alpha(2)\alpha(3)\right],$$

$$G_2(1,2,3) = \frac{1}{\sqrt{6}}\left[\alpha(1)\beta(2)\alpha(3) + \beta(1)\alpha(2)\alpha(3) - 2\alpha(1)\alpha(2)\beta(3)\right], \qquad [62]$$

where the functions $\alpha(t)$ and $\beta(t)$ are one-electron spin eigenfunctions of the operators $\hat{S}_t^{\,2}$ and $\hat{S}_{z_t}$ such that

$$\hat{S}_t^2\,\alpha(t) = \tfrac{1}{2}(\tfrac{1}{2}+1)\,\alpha(t), \qquad \hat{S}_{z_t}\,\alpha(t) = \tfrac{1}{2}\alpha(t)$$

$$\hat{S}_t^2\,\beta(t) = \tfrac{1}{2}(\tfrac{1}{2}+1)\,\beta(t), \qquad \hat{S}_{z_t}\,\beta(t) = -\tfrac{1}{2}\,\beta(t) \qquad [63]$$

$$\langle\alpha(t)|\alpha(t)\rangle = 1, \qquad \langle\beta(t)|\beta(t)\rangle = 1, \qquad \langle\alpha(t)|\beta(t)\rangle = 0.$$

The spin functions G_1 and G_2 are not used in this work, but instead special linear combinations of these functions are used:

$$\theta_1(1,2,3) = C_{11}\,G_1 + C_{12}\,G_2,$$

$$\theta_2(1,2,3) = C_{21}\,G_1 + C_{22}\,G_2. \qquad [64]$$

The properties imposed on θ_1 and θ_2 are that they be orthonormal and that the permutation of electron spin coordinates 1 and 2 on spin function θ_1 produces θ_2. This can be written symbolically as

$$\hat{P}^{\sigma}_{12}\ \theta_1(1,2,3) = \theta_2(1,2,3), \qquad [65]$$

where the superscript σ indicates that the permutation operator $\hat{P}$ acts only on spin coordinates. The transformation from spin functions G_1 and G_2 to θ_1 and θ_2 can be thought of as a rigid rotation in spin space which maintains the orthonormality of the functions but positions them in such a way that Eq. [65] holds. Imposing these conditions requires the coefficients in Eq. [64] to be

$$C_{11} = C_{12} = C_{22} = 1/\sqrt{2}$$

$$C_{21} = -1/\sqrt{2}\ . \qquad [66]$$

The spin functions θ_1 and θ_2 become

$$\theta_1(1,2,3)=\left(\frac{1}{2\sqrt{3}}+\frac{1}{2}\right)\alpha(1)\beta(2)\alpha(3) + \left(\frac{1}{2\sqrt{3}}-\frac{1}{2}\right)\beta(1)\alpha(2)\alpha(3) - \frac{1}{\sqrt{3}}\alpha(1)\alpha(2)\beta(3),$$

$$\theta_2(1,2,3)=\left(\frac{1}{2\sqrt{3}}-\frac{1}{2}\right)\alpha(1)\beta(2)\alpha(3) + \left(\frac{1}{2\sqrt{3}}+\frac{1}{2}\right)\beta(1)\alpha(2)\alpha(2) - \frac{1}{\sqrt{3}}\alpha(1)\alpha(2)\beta(3). \qquad [67]$$

These are the spin functions employed by Gianinetti, et, al.[59] in their calculation involving the linear symmetric H_3 complex.

The reason for using spin eigenfunctions with the permutation symmetry of Eq. [65] is that only one spin function need be explicilty considered. The other spin function is included by violating the rule that no configuration be considered that differs from any other expansion term only by a permutation of coordinates in the spatial part. Such a violation would in general produce a function which is linearly dependent with all other expansion terms:

$$\hat{A}\ \hat{P}^{v}[\phi_i(1)\ \phi_j(2)\ \phi_k(3)\ r_{12}^{i'}\ r_{13}^{j'}\ r_{23}^{k'}\ \theta_q(1,2,3)] = \sum_n C_n\ \Delta_n, \qquad [68]$$

where $\hat{P}^{v}$ is some permutation operator which acts only on the spatial part of the wave function. If $\hat{P}^{v}$ is chosen to be the permutation operator $\hat{P}_{12}^{v}$ that interchanges the spatial coordinates of electrons 1 and 2, then because of the way the spin functions have been constructed, Eq. [68] becomes

$$\hat{A}\ \hat{P}_{12}^{v}[\phi_i(1)\ \phi_j(2)\ \phi_k(3)\ r_{12}^{i'}\ r_{13}^{j'}\ r_{23}^{k'}\ \theta_1(1,2,3)] = -\ \Delta_{ijk\ i'j'k'\ q=2}$$

$$\Delta_{jik\ i'k'j'\ q=1} = -\ \Delta_{ijk\ i'j'k'\ q=2}. \qquad [69]$$

These equations indicate that expansion terms containing spin function θ_2 can be constructed in two ways; either explicitly as indicated on the right side of the equations, or by interchanging the electronic coordinates 1 and 2 in the spatial part of the configuration but retaining spin function θ_1 as indicated on the left side of the equations.

In order to show that Eq. [69] holds, it is necessary to use the relations

$$[\hat{P}, \hat{A}] = 0, \qquad \hat{P}\ \hat{A} = (-1)^p\ \hat{A},$$

where $\hat{P}$ is an arbitrary permutation operator which can be written as a product of a spatial permutation $\hat{P}^{\nu}$ and a spin permutation $\hat{P}^{\sigma}$:

$$\hat{P} = \hat{P}^{\nu}\hat{P}^{\sigma} .$$

Combining the two previous equations, one obtains the relation

$$\hat{A}\ \hat{P}^{\nu} = (-1)^{p}\ \hat{A}\ (\hat{P}^{\sigma})^{-1}.$$

If $\hat{P}$ is chosen to be $\hat{P}_{12}$, then this relation becomes

$$\hat{A}\ \hat{P}^{\nu}_{12} = -\hat{A}\ \hat{P}^{\sigma}_{12},$$

since $p = 1$ and $(\hat{P}^{\sigma}_{12})^{-1} = \hat{P}^{\sigma}_{12}$. Using this operator relation on the general product wave function

$$\phi_{i}(1)\ \phi_{j}(2)\ \phi_{k}(3)\ r_{12}^{i'}\ r_{13}^{j'}\ r_{23}^{k'}\ \theta_{q}(1,2,3),$$

one obtains Eq. [*69*].

In some cases expansion terms differing only in the spin function θ_q are linearly dependent and therefore are not considered. By examining Eq. [*69*], this is seen to occur when $i = j$ and $k' = j'$. In this case the expansion terms differ only in sign.

CHAPTER III

EVALUATION OF MATRIX ELEMENTS

A. Integration Over Spin

To solve the time independent Schrödinger wave equation by the method of linear combinations, the evaluation of matrix elements of the Hamiltonian operator and the unity operator appearing in Eq. [7] is required. The symbols **H** and **S** respectively are used to represent these matrices with components

$$H_{nm} = \int \Delta_n^* \hat{H} \Delta_m \, dv \, d\sigma \equiv \langle \Delta_n | \hat{H} \Delta_m \rangle$$

and [70]

$$S_{nm} = \int \Delta_n^* \Delta_m \, dv \, d\sigma \equiv \langle \Delta_n | \Delta_m \rangle \; .$$

The symbols Δ_n and Δ_m represent general N-electron expansion terms, and the integration is over both space and spin.

The following discussion indicates the steps taken to "integrate" over the spin coordinates leaving only the spacial integration to be performed by numerical methods.

The general 3-electron expansion term considered in this work is given by Eq. [10],

$$\Delta_n = \hat{A}[\phi_i(1) \; \phi_j(2) \; \phi_k(3) \; r_{12}^{i'} \; r_{13}^{j'} \; r_{23}^{k'} \; \theta_{q=1}(1,2,3)], \qquad [71]$$

except, as explained in the last section, q can always be taken as 1 if the proper permutation of spatial coordinates is carried out. It is assumed here that any such permutations have been completed for the term under consideration. The following notation is introduced in order to keep the algebraic equations relatively simple. Only the subscripts are retained when writing the spatial part of an expansion term:

$$\Delta_n = \hat{A}[i\ j\ k\ i'\ j'\ k'\ \theta_1], \tag{72}$$

where now the order of the indices is important and corresponds to the electronic coordinates as indicated by Eq. [71]. The spin eigenfunction θ_1 given by Eq. [67] is expressed briefly as

$$\theta_1 = d_1\ \alpha\beta\alpha + d_2\ \beta\alpha\alpha + d_3\ \alpha\alpha\beta\ . \tag{73}$$

Again the sequence of symbols is important, and the constants d_i are

$$d_1 = \frac{1}{2\sqrt{3}} + \frac{1}{2},\quad d_2 = \frac{1}{2\sqrt{3}} - \frac{1}{2},\quad d_3 = -\frac{1}{\sqrt{3}}\ . \tag{74}$$

When the antisymmetrizer acts on the product wave function as in Eq. [72], new spatial products with permuted indices appear and are denoted by the following symbols:

$$\begin{aligned}
\Delta_n^{1} &= i\ j\ k\ i'\ j'\ k', \\
\Delta_n^{2} &= k\ j\ i\ k'\ j'\ i', \\
\Delta_n^{3} &= k\ i\ j\ j'\ k'\ i', \\
\Delta_n^{4} &= j\ i\ k\ i'\ k'\ j', \\
\Delta_n^{5} &= j\ k\ i\ k'\ i'\ j', \\
\Delta_n^{6} &= i\ k\ j\ j'\ i'\ k'.
\end{aligned} \tag{75}$$

Using these symbols and the definition of the antisymmetrizer given by Eq. [11], Eq. [72] can be written as

$$\Delta_n = \hat{A}[\Delta_n^1 \theta_1] = \frac{1}{\sqrt{3!}} \{[d_1(\Delta_n^1 - \Delta_n^2) + d_2(\Delta_n^3 - \Delta_n^4) + d_3(\Delta_n^5 - \Delta_n^6)] \alpha\beta\alpha$$

$$+[d_1(\Delta_n^5 - \Delta_n^4) + d_2(\Delta_n^1 - \Delta_n^6) + d_3(\Delta_n^3 - \Delta_n^2)] \beta\alpha\alpha$$

$$+[d_1(\Delta_n^3 - \Delta_n^6) + d_2(\Delta_n^5 - \Delta_n^2) + d_3(\Delta_n^1 - \Delta_n^4)] \alpha\alpha\beta\}. \qquad [76]$$

The usual technique followed in reducing the matrix element

$$O_{nm} = \langle\Delta_n|\hat{O}\,\Delta_m\rangle = \langle\hat{A}\,\Delta_n^1\,\theta_1|\hat{O}\,\hat{A}\,\Delta_m^1\,\theta_1\rangle \qquad [77]$$

of an operator $\hat{O}$ totally symmetric with respect to interchange of electronic coordinates is to eliminate one of the antisymmetrizers by making use of the following properties associated with it:

$$\hat{A}^\dagger = \hat{A}, \qquad [\hat{A},\hat{O}] = 0, \qquad \hat{A}\hat{A} = \sqrt{N!}\,\hat{A}\,. \qquad [78]$$

The dagger is used to indicate the hermitian conjugate. However, in this study it was discovered that a greater precision was attained when performing the numerical integration over the spatial coordinates if both antisymmetrizers were retained. After the substitution of Eq. [76], and the analogous equation for Δ_m, into Eq. [77] and the "integration" over spin is carried out, it is seen that all cross terms involve different products of one-electron spin functions and so drop out due to the spin function orthogonality relation given by Eq. [63]. The spin portion of the direct terms "integrate" to unity leading to the following expression for the matrix element:

$$O_{nm} = \langle\Delta_n|\hat{O}\,\Delta_m\rangle =$$

$$\frac{1}{3!}\int \{[d_1(\Delta_n^1 - \Delta_n^2) + d_2(\Delta_n^3 - \Delta_n^4) + d_3(\Delta_n^5 - \Delta_n^6)]^*$$
$$\times\ \hat{O}[d_1(\Delta_m^1 - \Delta_m^2) + d_2(\Delta_m^3 - \Delta_m^4) + d_3(\Delta_m^5 - \Delta_m^6)]$$
$$+\ [d_1(\Delta_n^5 - \Delta_n^4) + d_2(\Delta_n^1 - \Delta_n^6) + d_3(\Delta_n^3 - \Delta_n^2)]^* \qquad [79]$$
$$\times\ \hat{O}[d_1(\Delta_m^5 - \Delta_m^4) + d_2(\Delta_m^1 - \Delta_m^6) + d_3(\Delta_m^3 - \Delta_m^2)]$$
$$+\ [d_1(\Delta_n^3 - \Delta_n^6) + d_2(\Delta_n^5 - \Delta_n^2) + d_3(\Delta_n^1 - \Delta_n^4)]^*$$
$$\times\ \hat{O}[d_1(\Delta_m^3 - \Delta_m^6) + d_2(\Delta_m^5 - \Delta_m^2) + d_3(\Delta_m^1 - \Delta_m^4)]\}\ dv\ .$$

It should be noted that this matrix element is over complete 3-electron expansion terms and therefore involves an integral over 9 dimensions.

All operators $\hat{O}$, except one, that will appear in Eq. [79] are simple scalar functions representing either the unit operator or the electron-nucleus and electron-electron interaction potentials. The operator which is not a simple scalar function is the kinetic energy operator

$$\hat{O} \to \hat{T} = -\tfrac{1}{2}(\nabla_1{}^2 + \nabla_2{}^2 + \nabla_3{}^2). \qquad [80]$$

The action of this operator on the spatial product $\Delta_n{}^1$ is considered in Appendix B. The result for any other product Δ_n^i can be obtained by permuting the indices of the equations appearing in Appendix B.

Additional accuracy is obtained when performing numerical integration of the kinetic energy integrals if they are symmetrized by using the self-adjoint property of the kinetic energy operator:

$$T_{nm} = \tfrac{1}{2}[\langle\Delta_n|\hat{T}\,\Delta_m\rangle + \langle\hat{T}\,\Delta_n|\Delta_m\rangle]$$

$$= \tfrac{1}{2}\int [\Delta_n^*(\hat{T}\,\Delta_m) + (\hat{T}\,\Delta_n)^*\Delta_m]\,dv\,d\sigma \;. \qquad [81]$$

The potential energy matrices are automatically hermitian by symmetry and the kinetic energy matrix is hermitian by Eq. [*81*]. The hermiticity of these matrix elements is independent of the numerical integration procedure and the corresponding accuracy.

B. Spatial Integration

1. Inclusion of the r_{ij}^{-1} and $r_{i\gamma}^{-1}$ Singularities in the Density Function

The most troublesome problem in the use of numerical integration techniques for the direct evaluation of the Hamiltonian matrix elements of an atomic or molecular system is the presence of the r_{ij}^{-1} singularity. Numerous techniques have been developed to handle the problem, but all appear to have limitations. Examples include the moving of the singularity to the surface of the sampling volume[60] and the additive cancellation of the singularity by means of the kinetic energy term acting on an explicitly correlated wave function. Moving the singularity to a surface produces only a slight improvement and additive cancellation places a significant restriction on the flexibility of a conventional basis set[61], or requires an unconventional basis set and a non-variational approach to the solutions such as those used by Conroy[31] or Boys and Handy[62-65,29]. One other attempt to solve the singularity problem was that made by Boys and Rajagopal[25]. By an argument using approximating Gaussian functions for the electronic distributions, they found that the singularity could be removed by replacing the r_{ij}^{-1} terms by

$$r_{ij}^{-1} \rightarrow [r_{ij}^{3} + U_i^{\frac{1}{2}} U_j^{\frac{1}{2}}/3]^{-1/3}, \qquad [82]$$

where U_i represents the product of the weight w_i and the non-differential part of the volume element dv_i associated with a numerical integration point for the ith electron. Although this approach is applicable to the problems considered in this work, the use of expression [*82*] and similar devices consistently gave poorer results than if the singularity was simply ignored. Possibly the differences in success are due to the numerical integration technique that was used; Boys and Rajagopal used a Gaussian quadrature when applying expression [*82*], but a Diophantine type of numerical integration is used here.

The method used in this work to remove the singularity does not in any way restrict the flexibility of the basis set and involves no approximations to the integrals other than that resulting from using a finite number of integration points. Sobol[66] calls it the *inclusion of the singularity in the probability density function*. By means of this method it is possible to simultaneously remove the r_{ij}^{-1} and $r_{i\gamma}^{-1}$ singularities from the integrand.

The method can be expressed formally by considering a general n-dimensional integral:

$$I = \int_{\vec{x}_0}^{\vec{x}_1} f[\vec{x}]\, d\vec{x} \; . \qquad [83]$$

A transformation of variables from $\vec{x}$ to $\vec{\eta}$ may be performed with the Jacobian

$$J = \begin{vmatrix} \frac{\partial x_1}{\partial \eta_1} & \frac{\partial x_2}{\partial \eta_1} & \cdots & \frac{\partial x_n}{\partial \eta_1} \\ \frac{\partial x_1}{\partial \eta_2} & \frac{\partial x_2}{\partial \eta_2} & \cdots & \frac{\partial x_n}{\partial \eta_2} \\ \vdots & \vdots & & \vdots \\ \frac{\partial x_1}{\partial \eta_n} & \frac{\partial x_2}{\partial \eta_n} & \cdots & \frac{\partial x_n}{\partial \eta_n} \end{vmatrix},$$

so that Eq. [*83*] becomes

$$I = \int_{\vec{\eta}=(0,0,\ldots 0)}^{\vec{\eta}=(1,1,\ldots 1)} f[\vec{x}(\vec{\eta})]\, J\, d\vec{\eta}\,, \qquad [84]$$

or

$$I = \int_{\vec{\eta}=(0,0,\ldots 0)}^{\vec{\eta}=(1,1,\ldots 1)} \frac{f[\vec{x}(\vec{\eta})]}{\rho[\vec{x}(\vec{\eta})]}\, d\vec{\eta}\,, \qquad [85]$$

where $\rho \equiv J^{-1}$ is the function describing the density of points in $\vec{x}$-space that results from a mapping of a uniform distribution of points from the $\vec{\eta}$-space unit hypercube

$$0 \le \eta_i \le 1. \qquad [86]$$

The numerical approximation to the integral can now be written in general as

$$I \approx I' = \sum_i w^i \frac{f[\vec{x}(\vec{\eta}^i)]}{\rho[\vec{x}(\vec{\eta}^i)]}\,, \qquad \sum_i w^i = 1, \qquad [87]$$

where the w^i are weights depending on the integration scheme and $\vec{\eta}^i$ is the ith n-dimensional integration point. Integration points are now selected in $\vec{\eta}$-space, the corresponding vector $\vec{x}$ is determined by the transformation equations, and the transformed integrand and weights are computed and summed.

Usually the transformation is chosen so that ρ will have a form as close as possible to $I^{-1}f$, where I is the value of the integral. This approach is called *importance sampling* since if $\rho \propto f$, the density of points will be greatest in the "most important regions of space"; i.e., where f is largest. The approach is also known as *minimization of variance* since, as ρ approaches $I^{-1}f$ in functional form, the variance of the transformed integrand from the value of the integral I,

$$\sigma^2 = \int \left(\frac{f}{\rho} - I\right)^2 d\vec{\eta} \approx \sum_i w^i \left(\frac{f^i}{\rho^i}\right)^2 - \left(\sum_i w^i \frac{f^i}{\rho^i}\right)^2, \qquad [88]$$

approaches zero. The concept is especially applicable to Monte Carlo numerical integration because the error in the integral approximation using random integration points is proportional to the square root of the variance.

If indeed it is possible to find a transformation such that $\rho = I^{-1}f$, which requires even more effort than simply finding I, then by Eq. [87], it can be seen that any integration rule that integrates a constant exactly will give the exact value for the integral.

It is most important to note that if the integrand $f[\vec{x}]$ in Eq. [83] exhibits singular behavior, then the transformed integrand $f[\vec{x}(\vec{\eta})]/\rho[\vec{x}(\vec{\eta})]$ in Eq. [85] can be made to exhibit no singular behavior if the transformation is chosen so that ρ will contain a singularity of the same nature as the one present in f. The singularity in the transformed integrand will then be removed through cancellation.

The above procedure can be carried out without the knowledge of the transformation equations between the coordinates $\vec{x}$ and $\vec{\eta}$ by choosing the integration points directly in $\vec{x}$-space according to the distribution $\rho[\vec{x}]$ instead of mapping a uniform distribution of points in $\vec{\eta}$-space onto $\vec{x}$-space. Or, as suggested by Ellis[67] and followed extensively in this work, several uniform distributions may be mapped onto $\vec{x}$-space in such a way that a set of points in $\vec{x}$-space is constructed according to the desired density function. In this way it is possible to construct distributions of points that "track" the atoms of a molecule or complex. The corresponding single transformation from $\vec{\eta}$-space to $\vec{x}$-space having the desired composite density function may be very complicated and expressible only after the composite density function is written in terms of products of series, each involving a single independent variable[32]. Once the points in $\vec{x}$-space are determined according to some distribution ρ, then Eq. [*87*] must be used to evaluate the integral of the function f with those points.

Including the singularity in the density function for the evaluation of quantum mechanical integrals was first done by Cowdrey and Reeves[68] to remove the nuclear attraction term $r_{i\gamma}^{-1}$. In this work a general sampling procedure is presented for the first time which will remove a singularity over a manifold, such as the electron-electron singularity r_{ij}^{-1}.

Before describing in detail the point selection technique used in this work, a simple example will be presented which shows clearly the relationships among the transformation, the Jacobian, and the density function. Consider the integral over all 2-dimensional space of some function f:

$$I = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(x_1, x_2)\, dx_1\, dx_2 \; . \qquad [89]$$

A transformation can be made to polar coordinates

$$\begin{aligned} \eta_1 &\equiv r = (x_1{}^2 + x_2{}^2)^{\frac{1}{2}} \\ \eta_2 &\equiv \theta = \tan^{-1}(x_2/x_1), \end{aligned} \qquad [90]$$

with the Jacobian

$$J = r \; . \qquad [91]$$

The integral written in terms of the new coordinates is

$$I = \int_{\theta=0}^{2\pi} \int_{r=0}^{\infty} \frac{f[x_1(r,\theta),\; x_2(r,\theta)]}{\frac{1}{r}}\, dr\, d\theta, \qquad [92]$$

where

$$\begin{aligned} x_1(r,\theta) &= r \cos\theta \\ x_2(r,\theta) &= r \sin\theta \; . \end{aligned} \qquad [93]$$

Additional independent transformations on the coordinates r and θ can be performed to normalize the range of integration to the interval 0, 1 so that Eq. [92] will correspond exactly to Eq. [85]. Neglecting the normalization of the range of integration, the density function is

$$\rho = \frac{1}{r} \; . \qquad [94]$$

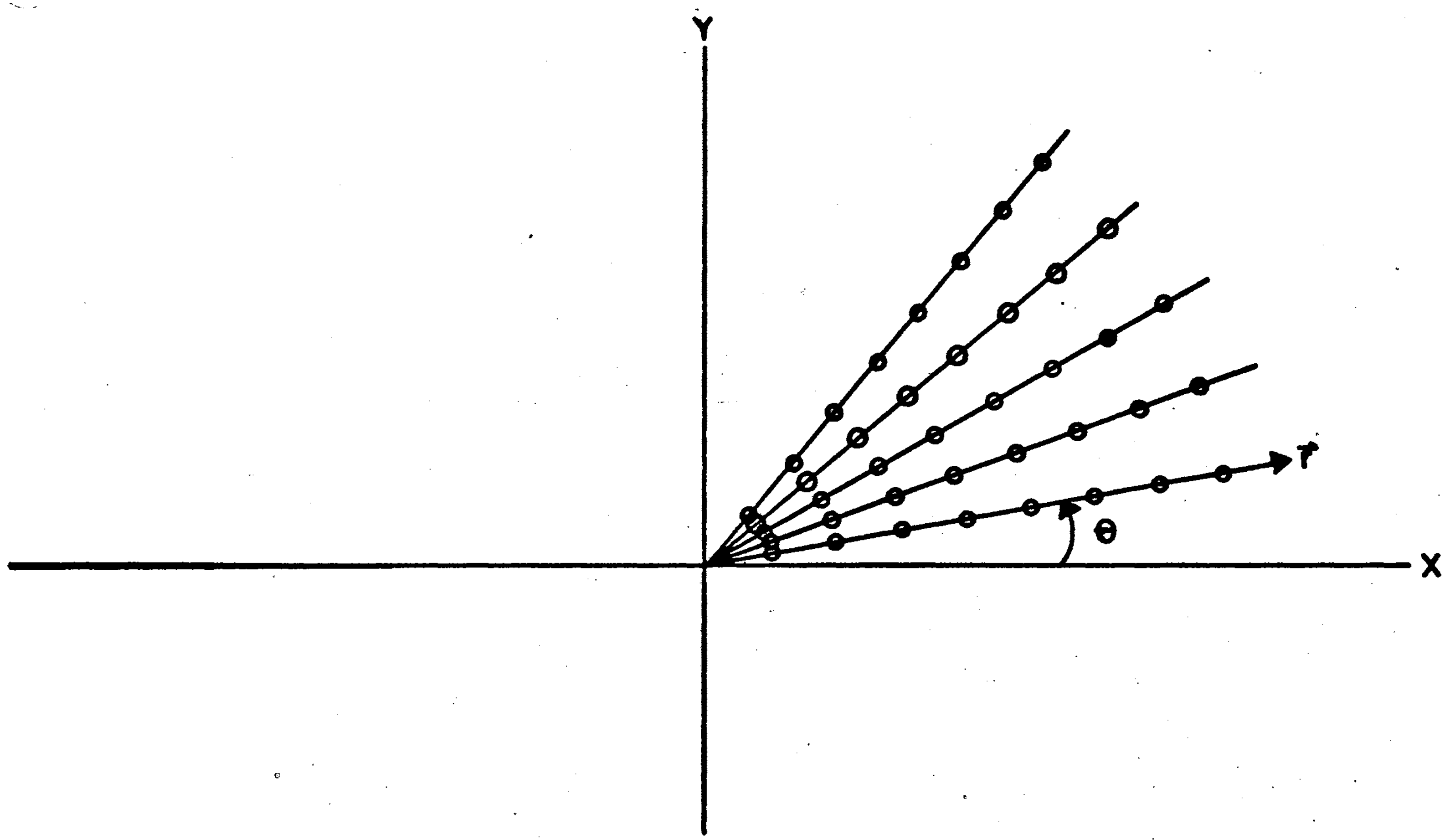

Figure 3. Distribution of Points in $\vec{x}$-Space With Density Function $\rho = 1/r$

The density of points in $\vec{x}$-space will vary as $\frac{1}{r}$ if the points are mapped from a uniform distribution in $\vec{\eta}$-space [(r,θ)-space]. The most straight forward way of selecting points uniformly in (r,θ)-space is to choose the points using equal intervals of r and θ. This has been done for a few points and the results mapped onto the $x_1 - x_2$ plane in Fig. 3. By inspection it is easily seen that the points do vary in density according to Eq. [*94*]. Using these points, the integral in Eq. [*89*] may be approximated by

$$I \approx I' = \sum_i \frac{w^i \; f[x_1(r^i,\theta^i),\; x_2(r^i,\theta^i)]}{\frac{1}{r^i}}, \qquad [95]$$

where the w^i depend on the numerical integration rule that is used. Finally, if f contains a singularity of the form $\frac{1}{r}$, then the singularity will be canceled by the density function.

In order to show the specialization of the importance sampling technique used in this work to remove a singularity over a manifold, a relatively simple case of a one-center, two-electron integral will first be considered:

$$I = \int_{\text{all}} \int_{\text{space}} e^{-\zeta_1 r_1} \frac{1}{r_{12}} \; e^{-\zeta_2 r_2} \, dv_1 \, dv_2 \; . \qquad [96]$$

The object of the transformations that follow is to select integration points with a density not only proportional to $\frac{1}{r_{12}}$ but also proportional to functions which simulate $e^{-\zeta_1 r_1}$ and $e^{-\zeta_2 r_2}$.

After transformation of the coordinates of electron 1 from rectangular to spherical coordinates, Eq. [*96*] becomes

$$I = \iint \frac{e^{-\zeta_1 r_1}}{\frac{1}{r_1^{\,2} \sin \theta_1}} dr_1 \, d\theta_1 \, d\phi_1 \; \frac{e^{-\zeta_2 r_2}}{r_{12}} dv_2 , \qquad [97]$$

where

$$o \leq r_1 < \infty, \qquad o \leq \theta \leq \pi, \qquad o \leq \phi_1 \leq 2\pi \; .$$

An additional transformation is made on the coordinates of electron 1 in order to normalize the range of integration to a unit hypercube and simultaneously simplify the density function to the desired form: a function proportional to an exponential function which is taken as $e^{-s_1 r_1}$. The transformations from the coordinates (r_1, θ_1, ϕ_1) to (η_1, η_2, η_3) are

$$\begin{aligned} \eta_1 &= 1 - e^{-s_1 r_1} (s_1 r_1 + 1) && 0 \leq \eta_1 \leq 1 \\ \eta_2 &= \tfrac{1}{2} (1 - \cos \theta_1) && 0 \leq \eta_2 \leq 1 \; . \\ \eta_3 &= \phi_1 / 2\pi && 0 \leq \eta_3 \leq 1 \end{aligned} \qquad [98]$$

The Jacobian of the transformation is diagonal:

$$\begin{aligned} J^{-1} &= \frac{d\eta_1}{dr_1} \frac{d\eta_2}{d\theta_1} \frac{d\eta_3}{d\phi_1} \\ &= (s_1^{\,2} r_1 \, e^{-s_1 r_1}) \left(\tfrac{1}{2} \sin \theta_1\right) \left(\tfrac{1}{2\pi}\right) \; . \end{aligned} \qquad [99]$$

After the transformation, Eq. [97] becomes

$$I = \iint \frac{e^{-\zeta_1 r_1}}{\frac{s_1^2}{4\pi}\frac{e^{-s_1 r_1}}{r_1}} d\eta_1 \, d\eta_2 \, d\eta_3 \, \frac{e^{-\zeta_2 r_2}}{r_{12}} \, dv_2 \; . \qquad [100]$$

The final distribution function for electron 1,

$$\rho \rightarrow D_1(r_1) = \frac{s_1^2}{4\pi}\frac{e^{-s_1 r_1}}{r_1} , \qquad [101]$$

differs from the desired density function by the factor r_1^{-1}. Another transformation for η_1, instead of the one given by Eq. [*98*], could have been considered which would have eliminated the r_1^{-1} factor. It is allowed to remain in this example since it is present in the density function used to make the actual calculations performed during the course of this study. The presence of the r_1^{-1} factor guarantees the cancellation of the nuclear attraction singularity appearing in the Hamiltonian matrix elements.

When an integration point (η_1, η_2, η_3) is selected from a uniform distribution in the 3-dimensional unit cube, the corresponding coordinates (r_1, θ_1, ϕ_1) can be determined by inverting Eq. [*98*]:

$$\begin{aligned} r_1 &= r_1(\eta_1) \\ \cos\theta_1 &= 1 - 2\eta_2 \\ \phi_1 &= 2\pi\eta_3 \; . \end{aligned} \qquad [102]$$

The transformation equation for r_1 has been written symbolically since it can only be performed numerically. To do the inversion numerically, an iterative, second order Newton-Raphson method[69] is used:

$$r_1^{(n+1)} = r_1^{(n)} + h^{(n)}, \qquad [103]$$

$$h^{(n)} = \left[\frac{s_1^2 r_1^{(n)}}{s_1 r_1^{(n)} + 1 - \exp[s_1 r_1^{(n)}](1 - \eta_1)} + \frac{1 - s_1 r_1^{(n)}}{2r_1^{(n)}}\right]^{-1},$$

where the superscripts in parentheses represent the iteration number. The method is very fast, acquiring 12 significant figures in about four iterations.

A technique will now be presented which selects the integration points of electron 2 according to a distribution function proportional to r_{12}^{-1} and $\frac{e^{-s_2 r_2}}{r_2}$. The general approach is an extension of that suggested by Sobol[70].

It is clear that any selection technique for electron 2 with a density function proportional to r_{12}^{-1} must depend on the position of electron 1. The dependence of the density function of electron 2 on the distances r_{12} and r_2 can most easily be incorporated by taking a confocal-elliptical coordinate system for electron 2 with one focus at the nucleus and the other focus at the position of electron 1 generated through Eqs. [*102*]. The coordinates are defined as usual,

$$1 \le \lambda_2 \le \infty \qquad -1 \le \mu_2 \le 1 \qquad 0 \le \phi_2' \le 2\pi, \qquad [104]$$

where these coordinates may be expressed in terms of interparticle coordinates indicated in Fig. 4:

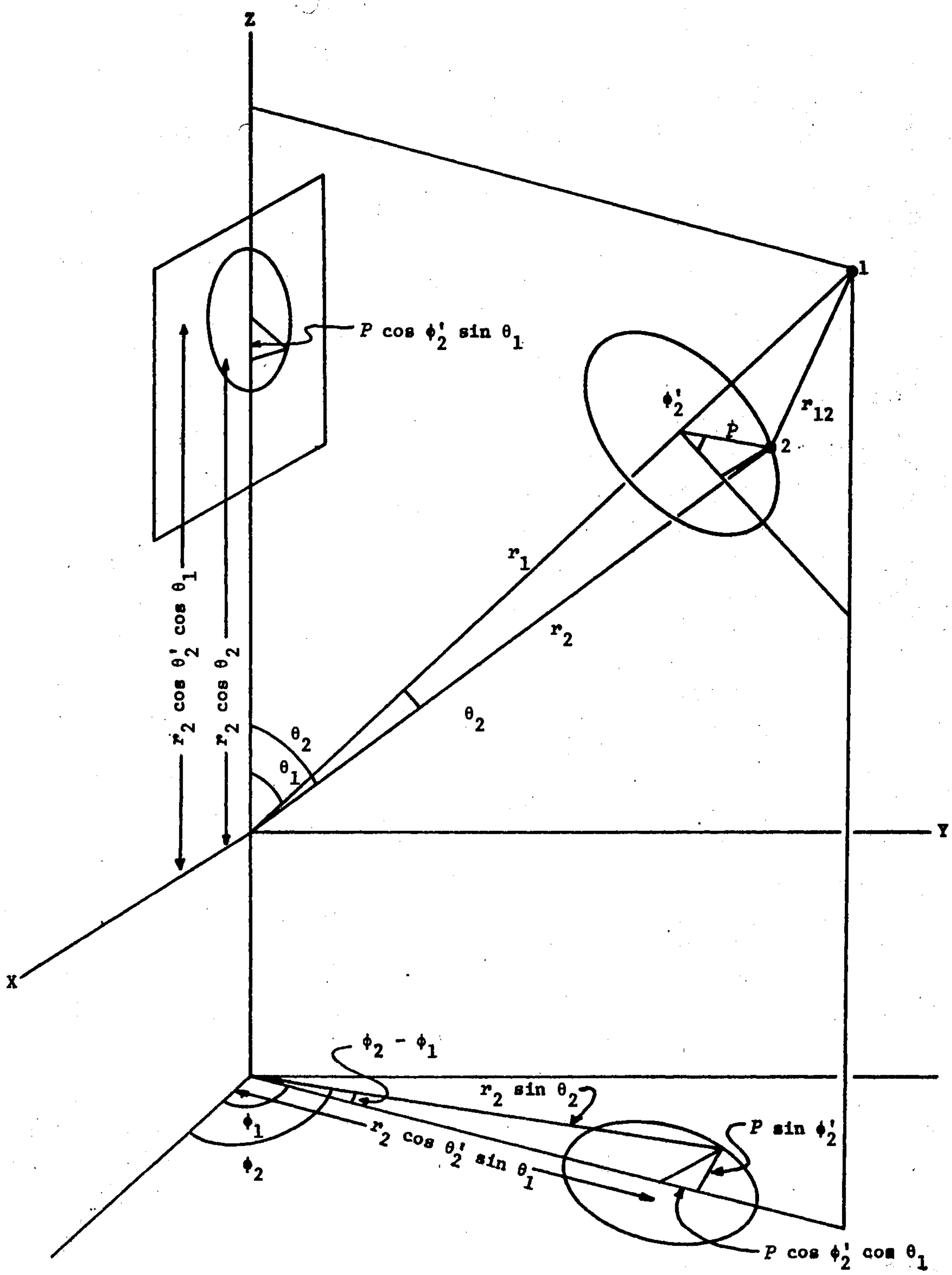

Figure 4. Confocal-Elliptical Coordinates Used to Obtain Density Function for Electron 2 of the Form $D_2(\vec{r}_1, \vec{r}_2) \propto \frac{1}{r_{12}} \frac{e^{s_2 r_2}}{r_2}$ for a Specific $\vec{r}_1$

$$\lambda_2 = (r_2 + r_{12})/r_1 \qquad \mu_2 = (r_2 - r_{12})/r_1, \tag{105}$$

and ϕ_2' is the angle of rotation about the vector $\vec{r}_1$ which is now considered to be fixed. The volume element written in terms of the interparticle coordinates is

$$dv_2 = \frac{r_1^{\,3}}{8} (\lambda_2^{\,2}-\mu_2^{\,2})d\lambda_2 d\mu_2 d\phi_2' = \frac{r_1\, r_2\, r_{12}}{2}\, d\lambda_2\, d\mu_2\, d\phi_2'. \tag{106}$$

With this transformation, Eq. [100] becomes

$$I = \int\!\!\int \frac{e^{-\zeta_1 r_1}}{\frac{s_1^{\,2}}{4\pi}\,\frac{e^{-s_1 r_1}}{r_1}}\, d\eta_1\, d\eta_2\, d\eta_3\, \frac{\frac{e^{-\zeta_2 r_2}}{2}}{r_1 r_2}\, d\lambda_2\, d\mu_2\, d\phi_2' \;. \tag{107}$$

The transformation is sufficient to cancel the r_{12} singularity; however, an additional transformation is necessary to normalize the range of integration to a unit cube and make the final distribution of points for electron 2 proportional to an exponential function ($e^{-s_2 r_2}$). This can be accomplished by the transformations

$$\begin{aligned}
\eta_4 &= 1 - \exp[s_2 r_1(\lambda_2 - 1)/2] \\
\eta_5 &= (e^{s_2 r_1/2} - e^{-s_2 r_1 \mu_2/2})/(e^{s_2 r_1/2} - e^{-s_2 r_1/2}) \\
\eta_6 &= \phi_2'/2\pi \,.
\end{aligned} \tag{108}$$

The Jacobian of the transformation is diagonal:

$$J^{-1} = \frac{d\eta_4}{d\lambda_2}\ \frac{d\eta_5}{d\mu_2}\ \frac{d\eta_6}{d\phi_2'}$$

$$= \{\frac{s_2 r_1}{2} \exp(s_2 r_1/2)\ \exp[-s_2(r_2 + r_{12})/2]\}$$

$$\times (\frac{s_2 r_1}{2}\ \frac{\exp[-s_2(r_2 - r_{12})/2]}{\exp(s_2 r_1/2) - \exp(-s_2 r_1/2)} \qquad [109]$$

$$\times (\frac{1}{2\pi})$$

$$= [\frac{r_1^2}{1-\exp(-s_2 r_1)}]\ (\frac{s_2^2}{8\pi} e^{-s_2 r_2}).$$

With the inclusion of this final transformation, Eq. [*107*] becomes

$$I = \iint \frac{e^{-\zeta_1 r_1}}{\frac{s_1^2}{4\pi}\frac{e^{-s_1 r_1}}{r_1}}\ \frac{e^{-\zeta_2 r_2}}{[\frac{r_1}{1-\exp(-s_2 r_1)}]\ \frac{s_2^2}{4\pi}\frac{e^{-s_2 r_2}}{r_2}}\ d\eta_1\ d\eta_2\ d\eta_3\ d\eta_4\ d\eta_5\ d\eta_6\ . \qquad [110]$$

The density function for electron 2, as a result of transformations [*105*] and [*108*], is

$$D_2(\vec{r}_1,\vec{r}_2) = [\frac{r_1}{1-\exp(-s_2 r_1)}]\ (\frac{s_2^2}{4\pi}\frac{e^{-s_2 r_2}}{r_2})\ \frac{1}{r_{12}}\ . \qquad [111]$$

The term in square brackets does not introduce or remove a singularity since

$$\lim_{r_1 \to 0} [\frac{r_1}{1-\exp(-s_2 r_1)}] = \frac{1}{s_2}\ . \qquad [112]$$

Once the integration point (η_4, η_5, η_6) has been selected from a uniform distribution, the corresponding spherical coordinates (r_2, θ_2, ϕ_2) can be obtained by means of three steps. First, Eq. [*108*] must be inverted giving

$$\lambda_2 = 1 - \frac{2}{s_2 r_1} \ln(1 - \eta_4)$$

$$\mu_2 = -1 - \frac{2}{s_2 r_1} \ln[1 - \eta_5(1 - e^{-s_2 r_1})] \qquad [113]$$

$$\phi_2 = 2\pi\eta_6 \; .$$

Using these coordinates, Eq. [*105*] can be inverted giving

$$r_2 = \frac{r_1}{2} (\lambda_2 + \mu_2)$$

$$\cos \theta_2' = [(1 - \lambda_2\mu_2)/(\lambda_2 + \mu_2)], \qquad [114]$$

where θ_2' is the angle between the vectors $\vec{r}_1$ and $\vec{r}_2$. The last step requires the use of simple geometry. Making use of the projections indicated in Fig. 4 and the line segment

$$P = r_2 \sin \theta_2' \; , \qquad [115]$$

the spherical coordinates θ_2 and ϕ_2 are found to be

$$\cos \theta_2 = \cos \theta_2' \; \cos \theta_1 - \sin \theta_2' \; \sin \theta_1 \cos \phi_2'$$

$$\phi_2 = \phi_1 + \tan^{-1} \left(\frac{\sin \theta_2' \sin \phi_2'}{\cos \theta_2' \; \sin \theta_1 + \sin \theta_2' \; \cos \phi_2' \; \cos \theta_1}\right). \qquad [116]$$

The extended range of the inverse tangent function,

$$-\pi \le \tan^{-1} (y/x) \le \pi, \qquad [117]$$

has been assumed in Eq. [116] which requires consideration of the signs of the numerator and denominator of the argument[71].

It is easy to show that the density functions D_1, D_2, and $D_{12} = D_1D_2$ are all properly normalized. That is, the following integrals over all space are equal to unity:

$$\int D_1(r_1)\, dv_1 = 1,$$

$$\int D_2(\vec{r}_1,\vec{r}_2)\, dv_2 = 1 \quad \text{for any } \vec{r}_1, \qquad [118]$$

$$\int D_1(r_1)\, D_2(\vec{r}_1,\vec{r}_2)\, dv_1 dv_2 = \int D_{12}(\vec{r}_1,\vec{r}_2)\, dv_1 dv_2 = 1 \; .$$

The expansion of r_{12}^{-1} in terms of the associated Legendre polynomials is required for proof in all but the first integral of Eqs. [118] (see Appendix C).

In order to construct a single density function suitable for use in all of the integral approximations, the preceding operations are symmetrized by alternately selecting the points for electrons 1 and 2 according to density functions D_1 and D_2 respectively, then selecting the points for electron 2 according to density function D_1 followed by selection of points for electron 1 from D_2. The final form of the numerical integration approximation rule [87] can be written as

$$I \approx I' = \sum_i w^i \frac{f(\vec{r}_1{}^i,\vec{r}_2{}^i)}{\left[\dfrac{D_1(r_1{}^i)\, D_2(\vec{r}_1{}^i,\vec{r}_2{}^i) + D_1(r_2{}^i)\, D_2(\vec{r}_2{}^i,\vec{r}_1{}^i)}{2}\right]} \qquad [119]$$

since, by the discussion above, the term in square brackets is the function describing the density of integration points in $\vec{x}$-space. If f contains the r_{12}^{-1} singularity as in Eq. [*96*], then it will not appear in Eq. [*119*] since the density function D_2 contains the same singularity and causes a cancellation. And if f contains exponentials of $(-r_1)$ and $(-r_2)$ then, due to the fact that D_1 and D_2 also contain similar exponentials, the variance given by Eq. [*88*], will be low, and relatively higher accuracy is expected by using the distribution indicated in Eq. [*119*] than by simply using a uniform distribution in $\vec{x}$-space.

The above technique will now be extended to a system of many electrons moving about many centers. Again, for clarity, a specific example is considered: three arbitrarily positioned nuclei and three electrons. The procedure requires the use of the density functions $D_1(r_{i\gamma})$ and $D_2(\vec{r}_{i\gamma},\vec{r}_{j\gamma})$ defined by Eqs. [*101*] and [*111*] for all electrons i and j, and for all centers γ. Using these functions, a completely symmetric point selection density function is constructed by including all possible permutations of electrons i, j, and k, and the centers γ, γ', and γ'' when sampling first from $D_1(r_{i\gamma})$, then $D_2(\vec{r}_{i\gamma'},\vec{r}_{j\gamma'})$ and finally from $D_1(r_{k\gamma''})$. The composite distribution is independent of the particular sequence (D_1, D_2, D_1) of individual density functions and can be written

$$D(\vec{r}_1,\vec{r}_2,\vec{r}_3) = \frac{1}{162} \sum_{\gamma} \sum_{\gamma'} \sum_{\gamma''} \sum_{\hat{P}} \hat{P}\, D_1(r_{i\gamma})\, D_2(\vec{r}_{i\gamma'}, \vec{r}_{j\gamma'})\, D_1(r_{k\gamma''}). \qquad [120]$$

The factor $(162)^{-1}$ is necessary for normalization of the density function

$$\int D(\vec{r}_1, \vec{r}_2, \vec{r}_3)\, dv_1\, dv_2\, dv_3 = 1, \qquad [121]$$

since there are 3 X 3 X 3 X 3! = 162 terms in the sum. The operator $\hat{P}$ permutes electronic coordinates and the sum over the permutations includes all 3! terms. Appendix C establishes the normalization of any term in the expansion [*120*] and thus verified Eq. [*121*].

If a new symbol D_2' is defined which allows the factoring of the r_{ij}^{-1} term from D_2,

$$D_2'(\vec{r}_{i\gamma'}, \vec{r}_{j\gamma'}) = D_2(\vec{r}_{i\gamma'}, \vec{r}_{j\gamma'})\, r_{ij}^{-1}, \qquad [122]$$

and the three centers are explicitly designated by a, b, and c, then Eq. [*120*] can be written

$$\begin{aligned} D(\vec{r}_1,\vec{r}_2,\vec{r}_3) = \frac{1}{162} \sum_P \hat{P}\, \{ & [D_1(r_{i\mathrm{a}}) + D_1(r_{i\mathrm{b}}) + D_1(r_{i\mathrm{c}})] \\ & \times [D_2'(\vec{r}_{i\mathrm{a}},\vec{r}_{j\mathrm{a}}) + D_2'(\vec{r}_{i\mathrm{b}},\vec{r}_{j\mathrm{b}}) + D_2'(\vec{r}_{i\mathrm{c}},\vec{r}_{j\mathrm{c}})] \qquad [123] \\ & \times [D_1(r_{k\mathrm{a}}) + D_1(r_{k\mathrm{b}}) + D_1(r_{k\mathrm{c}})] \\ & \times [r_{ik}\, r_{jk}]\}\, r_{12}^{-1}\, r_{13}^{-1}\, r_{23}^{-1} . \end{aligned}$$

It is easily seen that the density function $D(\vec{r}_1, \vec{r}_2, \vec{r}_3)$ cancels the singularities due to electron-electron potential energy terms since these terms can be written

$$\frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}} = \frac{r_{13}\, r_{23} + r_{12}\, r_{23} + r_{12}\, r_{13}}{r_{12}\, r_{13}\, r_{23}} . \qquad [124]$$

An analogous argument can be constructed to show the cancellation of the nuclear attraction singularities.

The spacial integration of all matrix elements, Eq. [*79*], appearing in the H_3 calculations is performed using the distribution of points $D(\vec{r}_1, \vec{r}_2, \vec{r}_3)$ described by Eq. [*120*] or Eq. [*123*]. The adjustable parameters s_1 and s_2 that appear in the density functions D_1 and D_2 are constrained to be equal and are determined so that the estimate of the variance, given by Eq. [*88*], is a minimum.

In the lithium case a density function is used that is completely analogous to Eq. [*120*] but which spans only a single center. The parameters s_1 and s_2, however, were adjusted independently in order to achieve minimum variance. The use of the density function $D(\vec{r}_1, \vec{r}_2, \vec{r}_3)$ in the evaluation of integrals not possessing $r_{i\gamma}^{-1}$ and r_{ij}^{-1} singularities resulted in a convergence rate not significantly slower than the rate which occurred when a density function analogous to $D(\vec{r}_1, \vec{r}_2, \vec{r}_3)$, but not possessing these singularities, was used.

2. Diophantine Numerical Integration

The Diophantine numerical integration method formulated by Richtmyer[72] and Haselgrove[73] and extended by Conroy[39] was used to evaluate the 9-dimensional integrals in this work. In one case the Monte Carlo integration technique was used for comparison purposes. Only a brief outline of the methods will be presented here; a more thorough treatment can be found in the original papers or in the texts by Hammersley and Handscomb[74], and by Davis and Rabinowitz[75].

The general form of the integral to be evaluated is

$$I = \int \frac{f(\vec{\eta})}{\rho(\vec{\eta})}\, d\vec{\eta} = \int F(\vec{\eta})\, d\vec{\eta}, \qquad [125]$$

where the region of integration is over a d-dimensional unit hypercube

$$0 \leq \eta_j \leq 1 \qquad j = 1,2,3, \ldots d. \qquad [126]$$

The integral is approximated in the simplest Diophantine method by

$$I \approx I' = \sum_{i=1}^{N} w^i \, F(\vec{\eta}^i) = \frac{1}{N} \sum_{m=1}^{N} F(|2[(m-\tfrac{1}{2})\,\vec{\alpha}]|), \qquad [127]$$

where the α_j are constants and the brackets [ ] indicate that an appropriate integer is to be subtracted from the argument so that the result lies within the interval $-\frac{1}{2}, \frac{1}{2}$. The α_j are chosen here to be a set of irrational numbers that are linearly independent over the rational numbers x_j; that is,

$$\sum_{j=1}^{N} x_j \, \alpha_j \neq 0 \quad \text{unless } \vec{x} = 0\,. \qquad [128]$$

When irrational numbers are used, the technique is called *open* Diophantine integration since the corresponding set of integration points $|2[(m-\frac{1}{2})\vec{\alpha}]|$ never repeats. The method is called *closed* Diophantine integration when rational α_j (linearly independent over the integers) are used since the set of integration points will then repeat when the number of points exceeds the common denominator of the α_j. Whether the α_j are taken to be rational or irrational numbers, it can be shown that the integration points generated in Eq. [127] are uniformly distributed within the unit hypercube.

The open form of Diophantine integration was used in this work since the number of points need not be predetermined. If the closed Diophantine integration had been used and convergence was unsatisfactory for the number of points chosen, then a new vector $\vec{\alpha}$ would had to have been selected with a common denominator equal to the number of points desired, and the integration repeated.

The analysis of the error associated with the approximation [*127*] to the integral I is somewhat detailed and therefore only the conclusions will be stated here. If the Fourier coefficients in the d-dimensional expansion of the integrand,

$$F(\vec{\eta}) = \sum_{n_1} \cdots \sum_{n_d} a(n_1, \ldots, n_d)\, e^{2\pi i \vec{n}\cdot\vec{\eta}} , \qquad [129]$$

satisfy the inequality

$$|a(n_1, \ldots, n_d)| \le M_t \, |n_1 n_2 \cdots n_d|^{-t} \qquad [130]$$

for $t > 1$, for some M_t, and with zero factors on the right removed, then the error is of "order N^{-1}":

$$\text{Error}(|I - I'|) = O(N^{-1}). \qquad [131]$$

The meaning of the last equation is that as $N \to \infty$, then $I \to I'$ at the same rate as $N^{-1} \to 0$. The inequality [*130*], with $t = 1$, may be applied to bounded functions $F(\vec{\eta})$ with a finite number of discontinuities within the unit hypercube; with $t = 2$, it may be applied to bounded continuous functions with discontinuities in their first partial derivatives; with $t = 3$, to functions with continuous first derivatives but discontinuous second derivatives; and so on. The term 'Diophantine' is used for describing the method since the theory of Diophantine approximation is used in proving that Eq. [*131*] follows from inequality [*130*].

The integrals considered in this thesis easily satisfy the inequality [*130*] since the singularities have been removed from the integrands by an appropriate choice of the point selection density function. Therefore the integrands are at least bounded and continuous.

If the integral [*125*] is approximated by

$$I \approx I' = \frac{1}{N} \sum_{i=1}^{N} F(\vec{\eta}^{\,i}),\ w^{i} = \frac{1}{N}, \qquad [132]$$

where the components of the vector $\vec{\eta}^{\,i}$ are selected at random from a uniform distribution on the interval 0 , 1, then the technique is called Monte Carlo integration. Provided the integrand is bounded, the error associated with this method is of order $N^{-\frac{1}{2}}$ and proportional to the square root of the variance σ^2 defined by Eq. [*88*].

The superiority of the Diophantine integration over the Monte Carlo integration is clear, with a convergence of $O(N^{-1})$ opposed to $O(N^{-\frac{1}{2}})$; but the superiority of closed Diophantine integration over the open type is not as apparent[76]. Because of these facts and the relative ease of application, the open form of Diophantine integration was used in this work.

The set of irrational α_j used here is not the "optimal set" capable of best integrating some "worst possible function" defined by the behavior of its Fourier coefficients. Such a set has never been determined for nine dimensions and would require an extensive amount of computer time. The set of α_j actually used in the integrations is made up of square roots of prime numbers. The prime numbers were selected so that the first integration point $\vec{\eta}^{\,1}$ has its components approximately evenly distributed on the interval 0 ,1. Shown in Table III are the prime numbers P_j such that $\alpha_j = \sqrt{P_j}$, and the corresponding components n_j^1 of the first integration point:

$$n_j^1 = |2[(m-\tfrac{1}{2})\alpha_j]| \quad m = 1. \qquad [133]$$

TABLE III

OPEN DIOPHANTINE INTEGRATION PARAMETERS

j	P_j	$\alpha_j = \sqrt{P_j}$	$\eta_j^1 = \lvert 2[(1-\frac{1}{2})\alpha_j]\rvert$
1	101	10.049...	0.049...
2	97	9.848...	0.151...
3	3	1.732...	0.267...
4	13	3.605...	0.394...
5	157	12.529...	0.529...
6	29	5.385...	0.614...
7	127	11.269...	0.730...
8	47	6.855...	0.855...
9	167	12.922...	0.922...

Relatively good results are expected with the use of the α_j given in Table III because of the lemma, proved by Haselgrove[73], that for most sets of numbers α_j, the error is not substantially worse than that which would occur using an optimal set.

The pseudo-random numbers that are used for the Monte Carlo comparison were generated using the IBM-supplied subroutine RANDU[77] which has been converted for double-precision arithmetic.

Once the integrals are evaluated, the matrix eigenvalue problems are solved using the QCEP-supplied computer subroutines CEIG and NESBET[78] that have been slightly modified for use on IBM/360 computers. The main program used for the linear symmetric H_3 calculations and all subroutines are listed in Appendix D. The main program for the lithium calculation is very similar to the H_3 main program; the only differences are that it allows two integration parameters s_1 and s_2, and it is specialized to a single center. Double-precision arithmetic was used throughout all programs and subprograms.

CHAPTER IV

CALCULATIONS

A. Choice of Parameters

The choice of parameters used in the calculations on the lithium atom and the linear symmetric H_3 complex is heavily dependent on the previous large scale calculations made on these systems. The purpose in so choosing the parameters in this way was not only to use the best parameters without resorting to the variation of non-linear parameters, but to be able to allow direct comparison with these earlier studies.

For the lithium atom case, the orbital exponents and the first six expansion terms are the same as those used by Larsson[41] in his study (see Table I). The first expansion term approximates most closely the ground state with two electrons in a 1*s* inner shell and one electron in a 2*s* outer shell. Expansion terms 2 through 4 can be considered as excited state contributions of the same symmetry as the ground state. Expansion terms indicated with an asterisk are actually two terms, each with a different spin function and expansion coefficient.

The fifth and sixth expansion functions are the first to include explicit correlation factors. It is expected that these terms would contribute significantly to the lowering of the energy since the correlation factors r_{12} and r_{12}^2 will cause the two electrons occupying the same orbital to avoid each other. The remaining three expansion terms are added in order to investigate the importance of terms simultaneously containing more than one r_{ij} factor. These terms simultaneously contain all possible r_{ij} factors with a power of 2 if the factor involves electrons within the same orbital and a power of 1 if they do not. The capability of including expansion terms which simultaneously contain all possible r_{ij} factors is evidence of the nearly complete generality of the approach used in this study.

Although identically the same parameters are used for the first six expansion terms in this study and Larsson's study of the lithium atom, the spin basis functions are not the same. Both studies do, however, use the complete set of spin eigenfunctions; thus a direct comparison of results is possible, which provides a means of checking the accuracy of the computer programs.

Of the three recent and extensive *ab initio* calculations on the linear symmetric H_3 activated complex by Shavitt, et. al.;[46] Riera and Linnett[79]; and Gianinetti, et. al.;[59] the work of Gianinetti, et. al. is relied on most heavily for the selection of parameters in this work. The principle reason for this choice was that they made use of 2*s* atomic orbitals which are usually used in trial wave functions involving explicitly correlated expansion terms. Another reason for the choice was the inclusion in their work of a small scale full configuration interaction calculation which allows a simple means of checking the computer programs when multiple centers are involved.

Presented in Table IV are the parameters used in the full configuration interaction calculation performed for testing purposes. The parameters are identical to those used by Gianinetti, et. al. for the same calculation. The phrase "full configuration interaction" applies when all possible linearly independent molecular orbitals formed from a given

TABLE IV

ONE-ELECTRON SYMMETRY ORBITALS AND EXPANSION TERMS USED IN THE 4-TERM FULL CI ($1s$) LINEAR SYMMETRIC H_3 CALCULATION ($R_{ab} = R_{bc} = 1.9100$)

Symmetry Orbitals	Exponents	Integration Parameters
$\phi_1 = 1s\sigma_g^{+(1)} = 1s_b$ $\phi_2 = 1s\sigma_g^{+(2)} = 1s_a + 1s_c$ $\phi_3 = 1s\sigma_g^{+(2)} = 1s_a + 1s_c$	$\zeta_{1s_b} = 1.20$ $\zeta_{1s_a} = \zeta_{1s_c} = 1.06$	$s_1 = s_2 = 1.54$

Σ_u^+ Expansion Terms

	Symmetry Orbitals			r_{ij} Exponent		
Δ_n	ϕ_i	ϕ_j	ϕ_k	$r_{12}^{i'}$	$r_{13}^{j'}$	$r_{23}^{k'}$
1	1	1	3	0	0	0
2*	1	2	3	0	0	0
3	2	2	3	0	0	0

basis are used to construct all possible linearly independent expansion terms which do not include explicit correlation factors. In this case the given basis is a $1s$ atomic orbital on each of the three centers.

The parameters used in the linear symmetric H_3 activated complex calculation involving explicit correlation terms is given in Table II. The $1s$ and $2s$ atomic orbital exponents and internuclear distance are the same as those used by Gianinetti, et. al. in their most extensive calculation, a 200 term full configuration interaction calculation using $1s$, $2s$, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals on each center as a basis. The expansion terms 1-3 are the terms that contributed most to the 200 term wave function as indicated by the corresponding expansion coefficients. Expansion terms 5-13* are of the same form as the terms 1-3 except that they contain a single r_{ij}^{1} correlation factor included in all possible ways. Although the results from the lithium atom calculation show that the contribution due to an expansion term containing multiple correlation factors is very slight, one such term (term 14) was included in the linear symmetric H_3 calculation.

Two more linear symmetric H_3 calculations were performed which were in every way identical to the calculation just described except that the internuclear distance was changed to $R_{\mathrm{ab}} = R_{\mathrm{bc}} = 1.7650$ a.u. and 1.8198 a.u. The purpose of these calculations was to determine the force constant associated with the "symmetric stretching vibration" at the saddle point.

B. Numerical Results

Since each of the 162 distributions making up the 3-center composite distribution given by Eq. [*120*] must be sampled the same number of times, the total number of integration points must be a multiple of 162. The progress of the calculations presented here was monitored at the end of each cycle defined as the processing of 13 X 162 = 2106 9-dimensional integration points. The same 2106-point cycle was retained for the lithium calculations. Since the 1-center composite density function in the lithium case contains only 6 terms, each term is sampled 2106/6 = 351 times during each cycle.

The elements of eight matrices were tabulated at the end of each cycle. These included the kinetic energy, electron-nucleus interaction, electron-electron interaction, overlap, and the normalized variances, σ^2/I^2, of each of these elements.

As stated earlier, the integration parameters s_1 and s_2 contained in the density functions D_1 and D_2 are chosen so that the average normalized variance of all the matrix elements is a minimum. Figure 5 shows this average as a function of s_1 and s_2 for the lithium case involving only terms 1-3 of Table I when 2106 points are used to evaluate the integrals. If the two parameters are constrained to be equal, then the minimum average $\langle\sigma^2/I^2\rangle_{av}$ is equal to 3.30 when $s_1 = s_2 = 1.05$. However, if there are no constraints places on the parameters, then the minimum average variance drops to 1.28 at $s_1 = 3.0$ and $s_2 = 0.3$. Even though the integrals may be far from convergence, the change in the variance with respect to s_1 and s_2 is much greater than the change in the variance with respect to the number of integration points. For example, if $s_1 = 3.0$ and $s_2 = 0.3$, the average normalized variance changes from 1.2792 when only 2106 points are used to 1.2848 when 208,494 points are used.

In the linear symmetric H_3 case a minimum normalized average var-

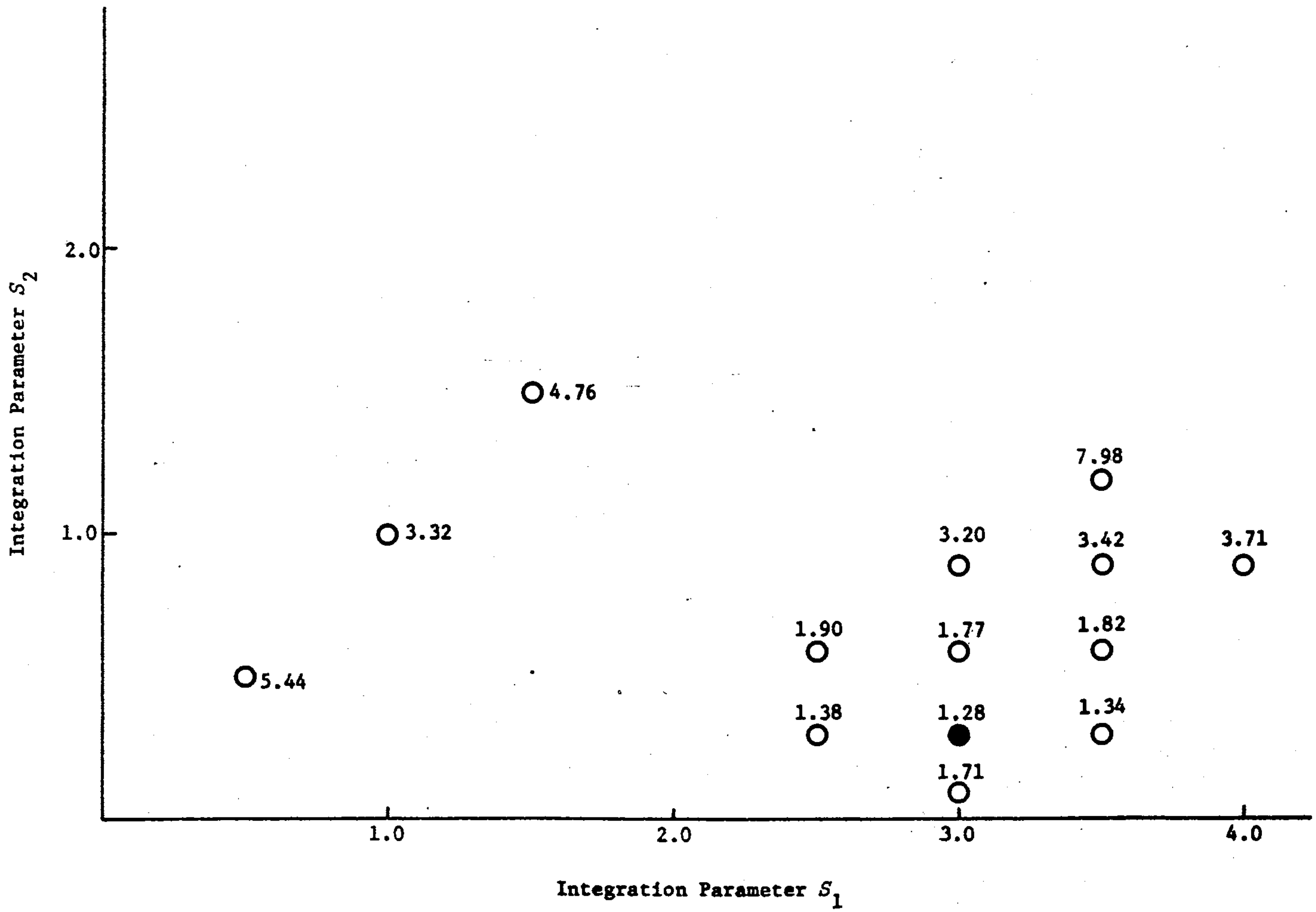

Figure 5. Average Normalized Variance as a Function of Integration Point Distribution Parameters s_1 , s_2 for the Lithium Atom Calculation Involving Only Terms 1-3 of Table I and 2106 Integration Points. The Filled Circle Indicates the Approximate Minimum.

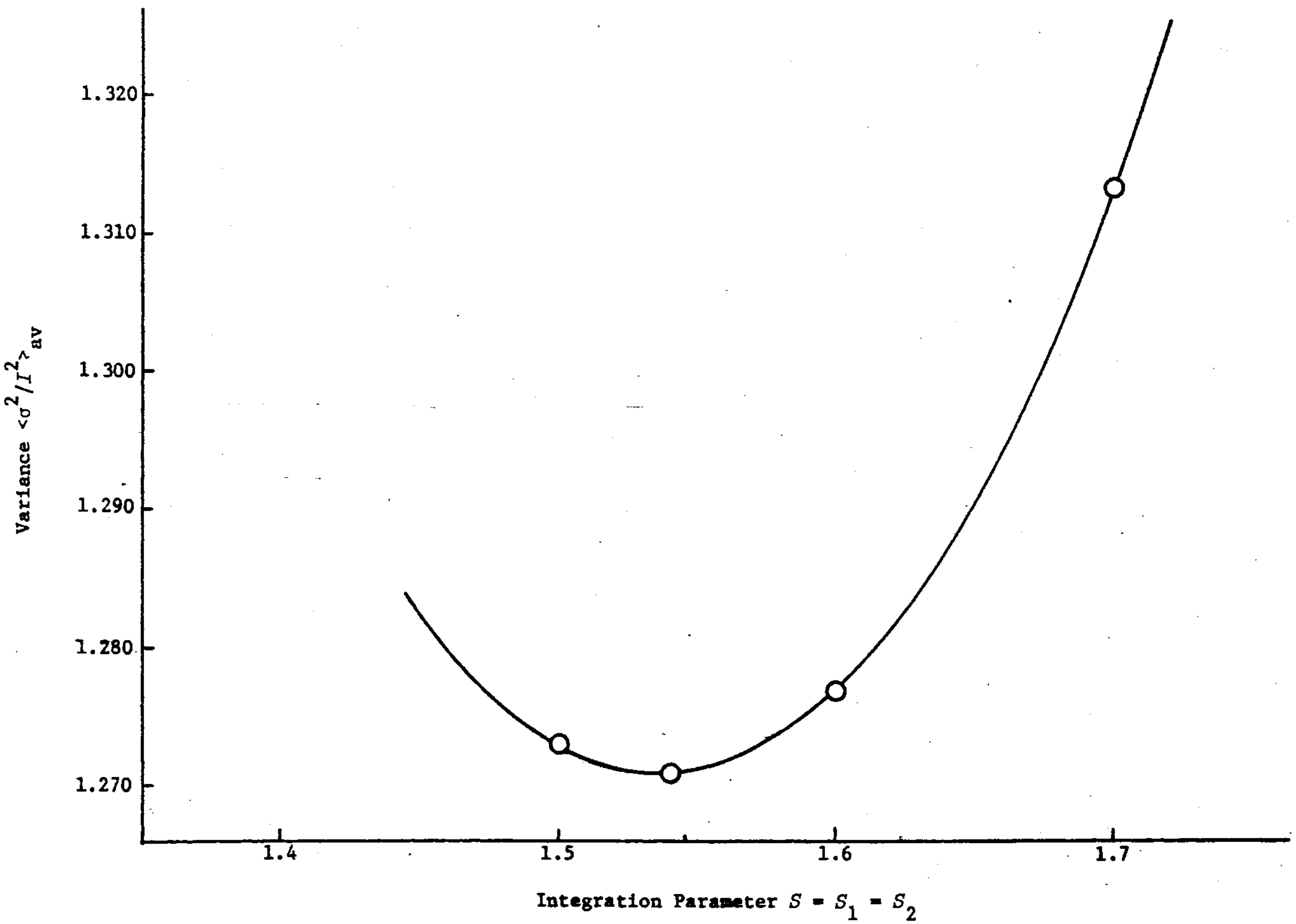

Figure 6. Average Normalized Variance as a Function of the Integration Point Distribution Parameter $s = s_1 = s_2$ for the Full CI (1s) H_3 Calculation and 6318 Integration Points

iance of 1.27 was attained when using 6318 points even with the constraint that $s_1 = s_2$; therefore it was deemed unnecessary to vary each parameter independently. Figure 6 shows $\langle \sigma^2/I^2 \rangle_{av}$ as a function of $s = s_1 = s_2$ with a minimum occurring at $s = 1.54$.

The calculated energies of the lithium atom are presented in Figure 7 for every step in the extension of the trial wave function. That is, the matrix eigenvalue problem $(\mathbb{H} - E\mathbb{S})\mathbb{C} = 0$ is transformed to $(\mathbb{H}' - E\mathbb{1})\mathbb{C}' = 0$ and the eigenvalues and eigenvectors are determined each time an expansion term is added to the trial wave function. In this way there is no contribution to the energy due to the expansion terms that are added later. The energies are plotted against the number of integration points so that the convergence properties of the wave function can be observed both with respect to the number of expansion terms and with respect to the number of integration points. The full length horizontal lines represent the analytical solution to the matrix eigenvalue problems for each step. The first analytical energy was calculated independently using standard integral formulas and the remaining analytical energies were taken from Larsson's study[41]. Since the calculations corresponding to the last three energies E_{1-7}, E_{1-8*}, and E_{1-9} have not been carried out using analytical techniques, no exact energy values are available. The horizontal line labeled E(ACCEPTED) is the energy value calculated from experiments after subtracting contributions due to relativistic and finite nuclear mass effects[80]. This energy was determined by the use of a semi-empirical scheme, based on conventional perturbation theory, by accurately extrapolating the total electronic energy and ionization potentials as a function of the nuclear charge.

The analytical, accepted, and final numerical energies are tabulated in Table V along with the potential and kinetic energy ratios (*PE*/*KE*), the eigenvector of the final numerically calculated wave function Φ^{1-9}, and the overlap of each term of Φ^{1-9}: $<\Phi^{1-9}|C_n^{1-9}\Delta_n>$. Although only three-four figures are significant when describing the final lithium atom energies calculated in this work, seven are presented to show the relative improvement in the energy with the addition of each expansion term.

Figure 8 shows the contributions to the energy of expansion terms 7, 8*, and 9 when added to the non-explicitly correlated trial wave function consisting only of terms 1-3. The analytical and numerical results for terms 1-3 are reproduced from Figure 7.

The results of a Monte Carlo calculation on the lithium atom using a trial wave function of only term 1 is shown in Figure 9 (upper curve) along with the corresponding results obtained with the open Diophantine calculation (lower curve). The analytical energy and Diophantine results for term 1 are reproduced from Figure 7.

The calculated energies for the linear symmetric H_3 test case, a full CI (1*s*), are presented in Figure 10. The value of the analytic energy, indicated by the horizontal line, is that given in the work by Gianinetti, et. al.[59] The values for the analytic and final numerical energy are given in Table VI along with the final numerical value for the potential and kinetic energy ratios (*PE*/*KE*).

Because of the large range of energies and the small energy differences, two figures are required to display the results of the linear symmetric H_3 calculation described by the parameters in Table II. Figures 11 and 12 present the energies of the H_3 complex for every step in the extension of the basis as a function of the number of integration

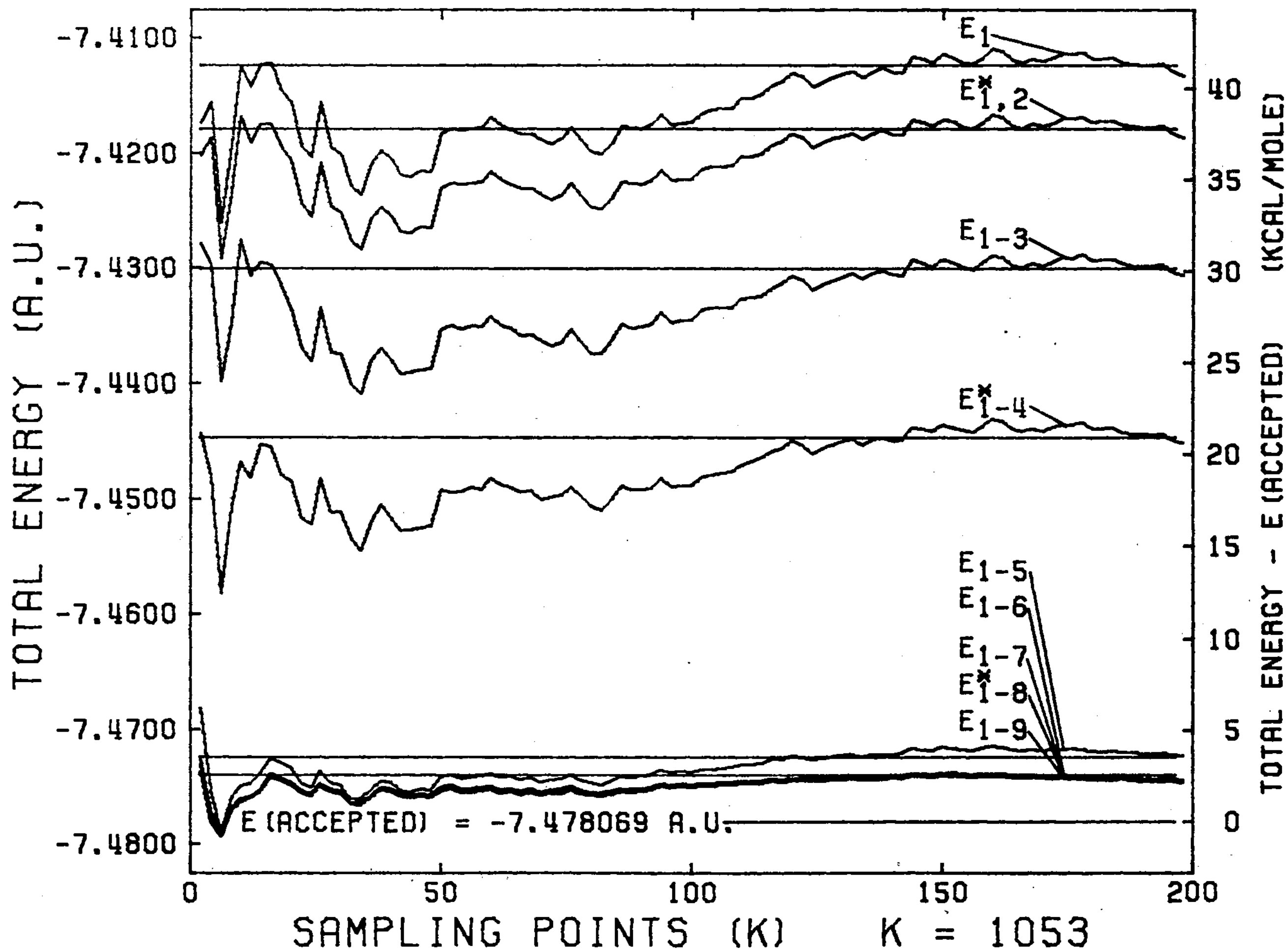

Figure 7. Convergence Properties of Lithium Atom Energies With Respect to Expansion Terms 1-9 of Table I

TABLE V

RESULTS OF LITHIUM CALCULATION FOR THE PARAMETERS AND VARIOUS NUMBERS OF EXPANSION TERMS GIVEN IN TABLE I. THE TOTAL NUMBER OF INTEGRATION POINTS IS 208,494. THE ENERGIES ARE PLOTTED IN FIG. 7.

Φ^N	Δ_n	E^N (a.u.) (Ref. 41)[a]	E^N (a.u.) (This Work)[b]	$(PE/KE)^N$	C_n^{1-9} [c]		$<\Phi^{1-9}\|C_n^{1-9}\ \Delta_n>$ [d]	
1	114 000	-7.412461	-7.413264	-1.947	0.650		0.861	
1,2*	124 000*	-7.417823	-7.418650	-1.998	-0.0966,	-0.0807	-0.0723,	-0.0568
1-3	224 000	-7.430033	-7.430632	-1.996	-0.163		-0.0640	
1-4*	134 000*	-7.444700	-7.445210	-2.001	0.126,	0.119	0.0726,	0.0572
1-5	114 100	-7.472382	-7.472356	-2.001	0.233		0.250	
1-6	114 200	-7.473999	-7.474415	-1.999	-0.0485		-0.0524	
1-7	114 211	———	-7.474425	-1.999	-0.000728		-0.0153	
1-8*	124 111*	———	-7.474592	-1.999	0.000769,	0.000596	0.00103,	0.00784
1-9	224 211	———	-7.474626	-1.999	0.000156		0.00168	
1-∞		-7.478069						

*Expansion terms with both possible spin functions have been added.

[a]Energies are from Larsson's work except for E^1 which was calculated independently and $E^{1-\infty} = E$ (accepted) which is from Ref. 80.

[b]Although only three-four figures are significant, seven figures are included to show the relative improvement in the energy with the addition of each expansion term.

[c]Expansion coefficients for the trial wave function containing all of the expansion terms listed in the second column.

[d]The overlap of each expansion term of the complete wave function with the complete wave function.

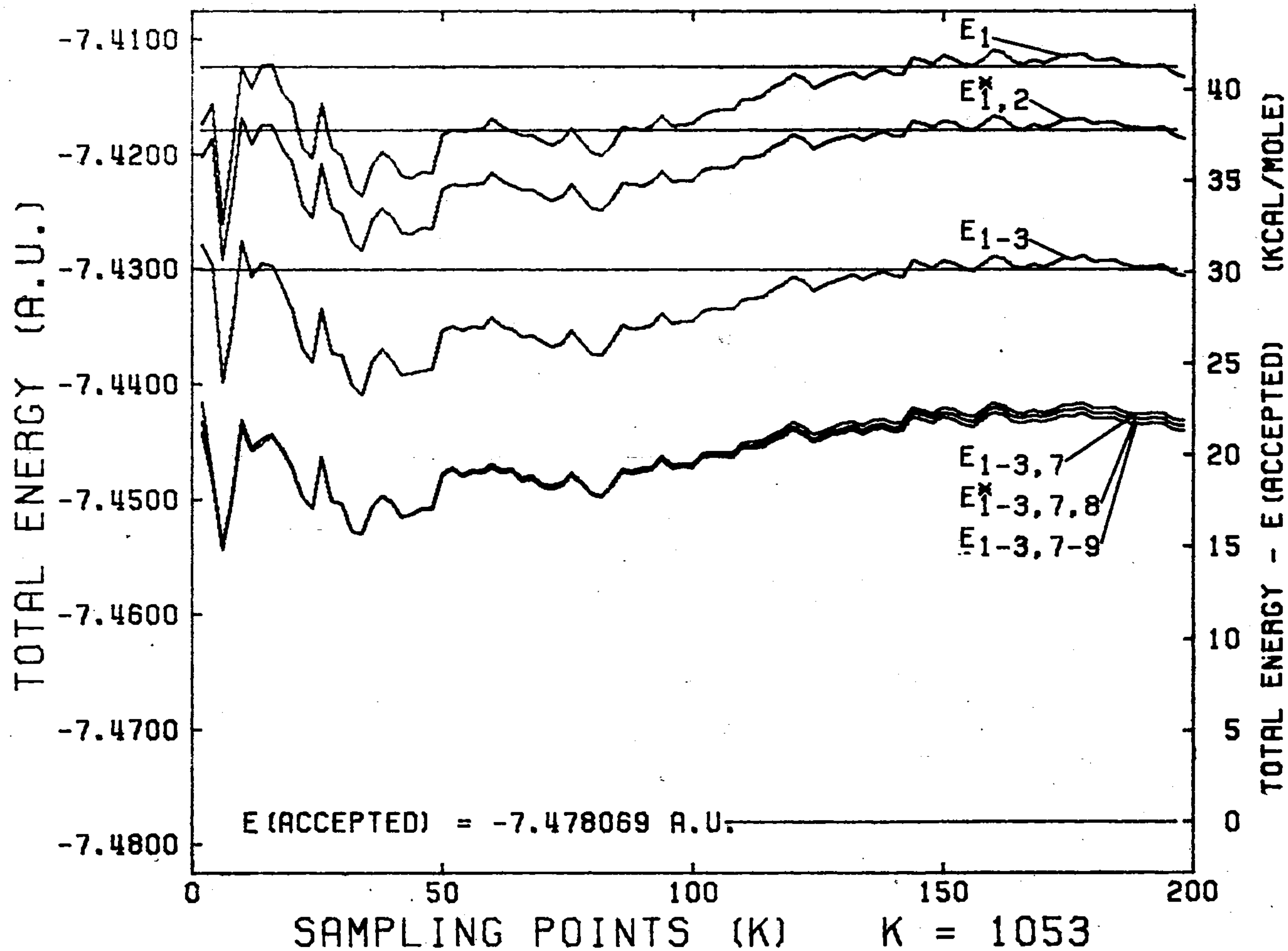

Figure 8. Convergence Properties of Lithium Atom Energies With Respect to Expansion Terms 7-9 of Table I When They Immediately Follow Terms 1-3

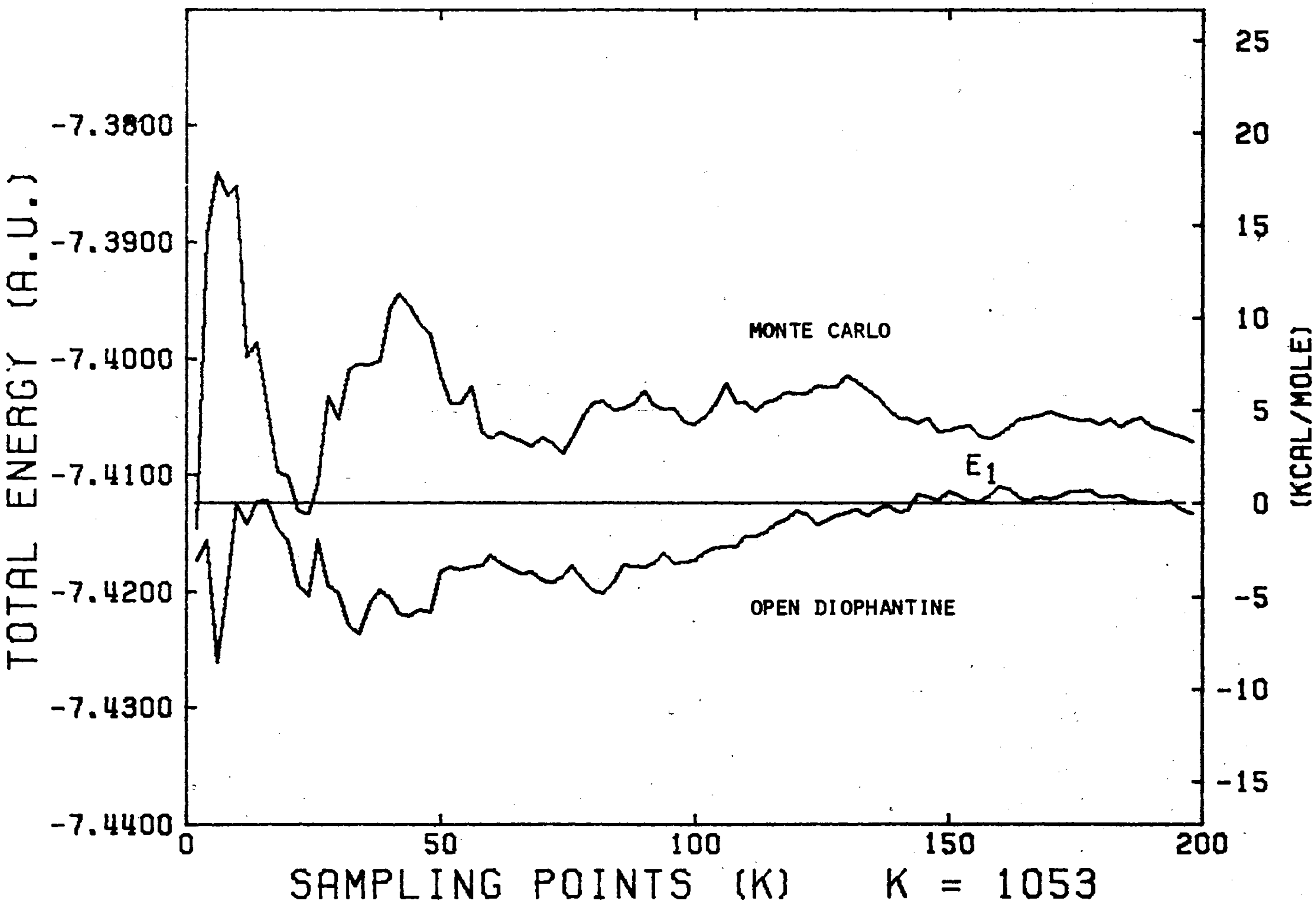

Figure 9. Comparison of Convergence Properties of Lithium Atom Energies With Respect to Expansion Term 1 of Table I When Monte Carlo and Open Diophantine Integration Techniques are Used

points. For ease of comparison the energies E_{1-4} and E_{1-5} are plotted on both figures. The range of the estimated exact energy of the H_3 system at the top of the barrier is taken to be 7-11 Kcal/mole above the energy of the H_2 + H system. The zero point of the scale on the right is taken at 9.8 Kcal/mole[81] above the energy of the H_2 + H system, the most recent estimate to date for the H_3 complex at the top of the barrier.

The final numerical energies for the linear symmetric H_3 complex are tabulated in Table VII along with the most recent exact estimate, the potential and kinetic energy ratio, the eigenvector of the final numerical calculated wave function Φ^{1-14}, and the overlap of each term of Φ^{1-14} with Φ^{1-14}: $\langle\Phi^{1-14}|C_n^{1-14}\,\Delta_n\rangle$. Although only four figures are significant when describing the final H_3 complex energies calculated in this work, seven are presented to show the relative improvement in the energy with the addition of each expansion term.

Figure 13 shows the convergence properties of the energies of the three 21-term linear symmetric H_3 calculations with parameters that differed only in the internuclear distance. The final energies and potential to kinetic energy ratios are listed in Table VIII. These three energies, along with the corresponding internuclear distances, were used to find the force constant k associated with the "symmetric stretching vibration" at the saddle point. For infinitesimal displacements, this force constant is defined by the equation $E - E_0 = \frac{1}{2}k(R - R_0)^2$, where E_0 and R_0 are the energy and internuclear distance at the saddle point and $R = R_{ab} = R_{bc}$. The calculated value of K at the end of each integration cycle is plotted in Figure 14.

The computer time required to obtain the lithium atom results pre-

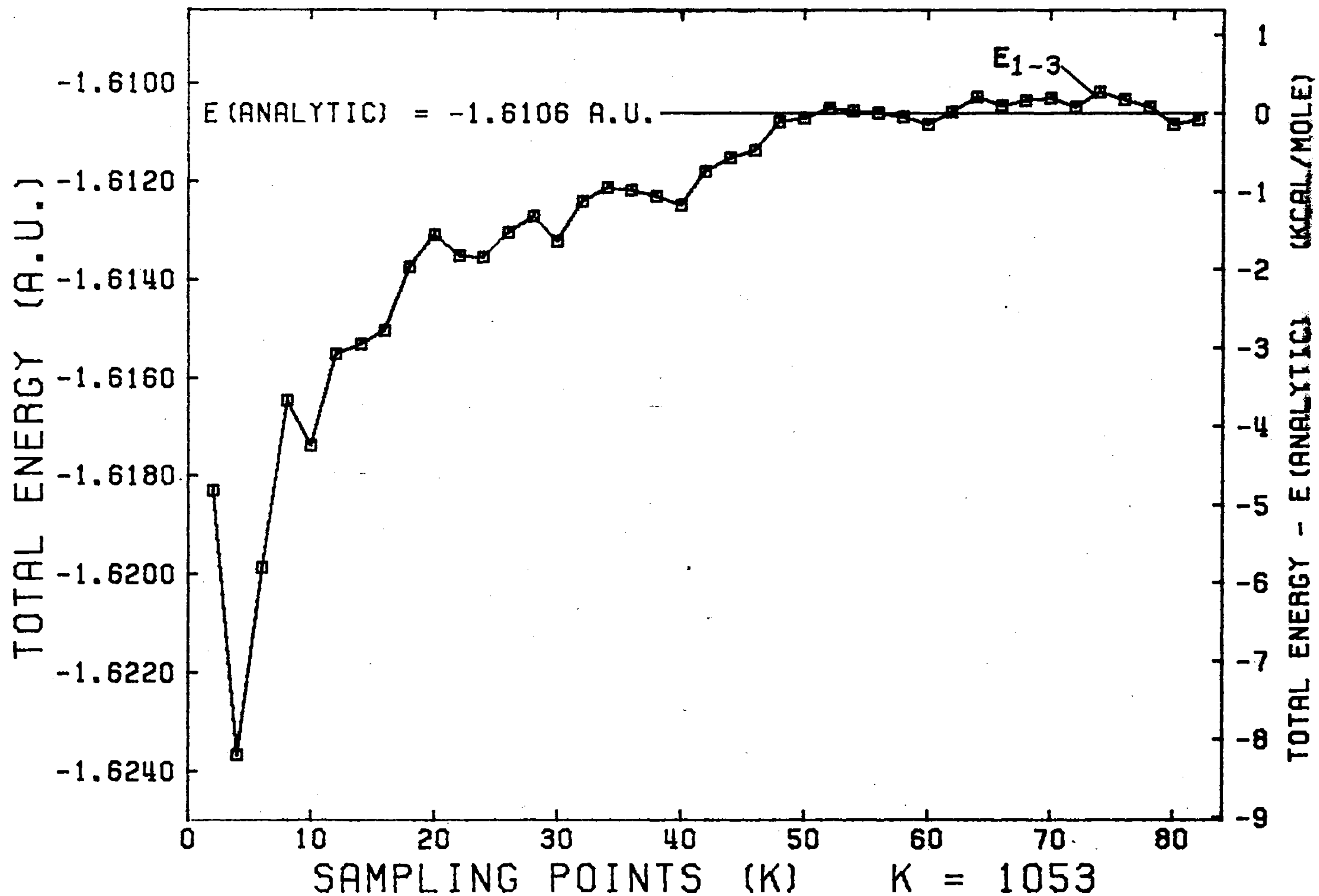

Figure 10. Convergence Properties of the H_3 Activated Complex Energy With Respect to the Full CI(1s) Wave Function

TABLE VI

RESULTS OF THE FULL CI (1*s*) CALCULATION ON THE H_3 ACTIVATED COMPLEX FOR THE PARAMETERS GIVEN IN TABLE IV. THE TOTAL NUMBER OF INTEGRATION POINTS IS 86,346. THE ENERGIES ARE PLOTTED IN FIG. 10.

Φ^N	E^N (a.u.) (Ref. 59)	E^N (a.u.) (This Work)	$(PE/KE)^N$
1-3	-1.6106	-1.6107	-2.005

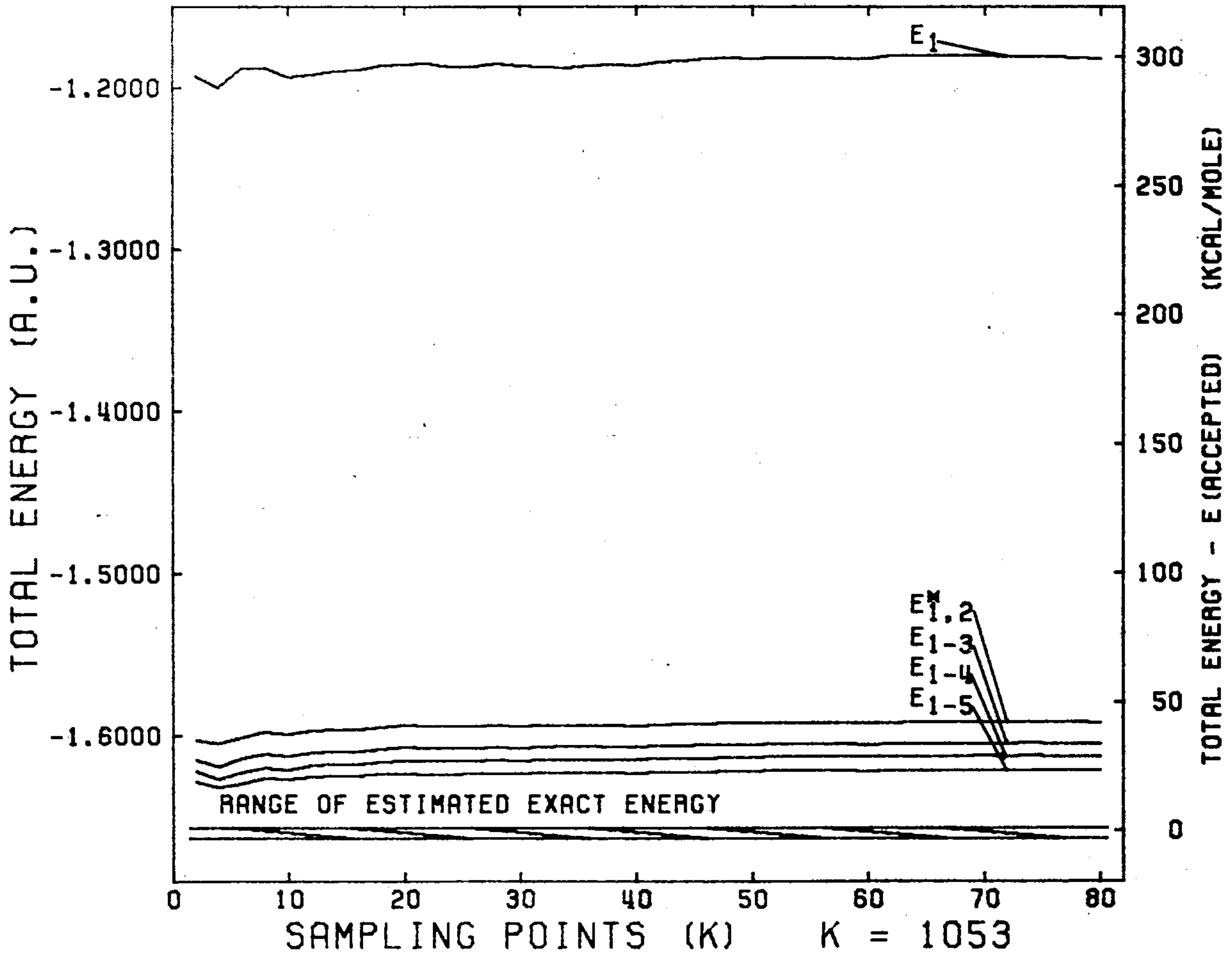

Figure 11. Convergence Properties of H_3 Activated Complex Energies With Respect to Expansion Terms 1-5 of Table II

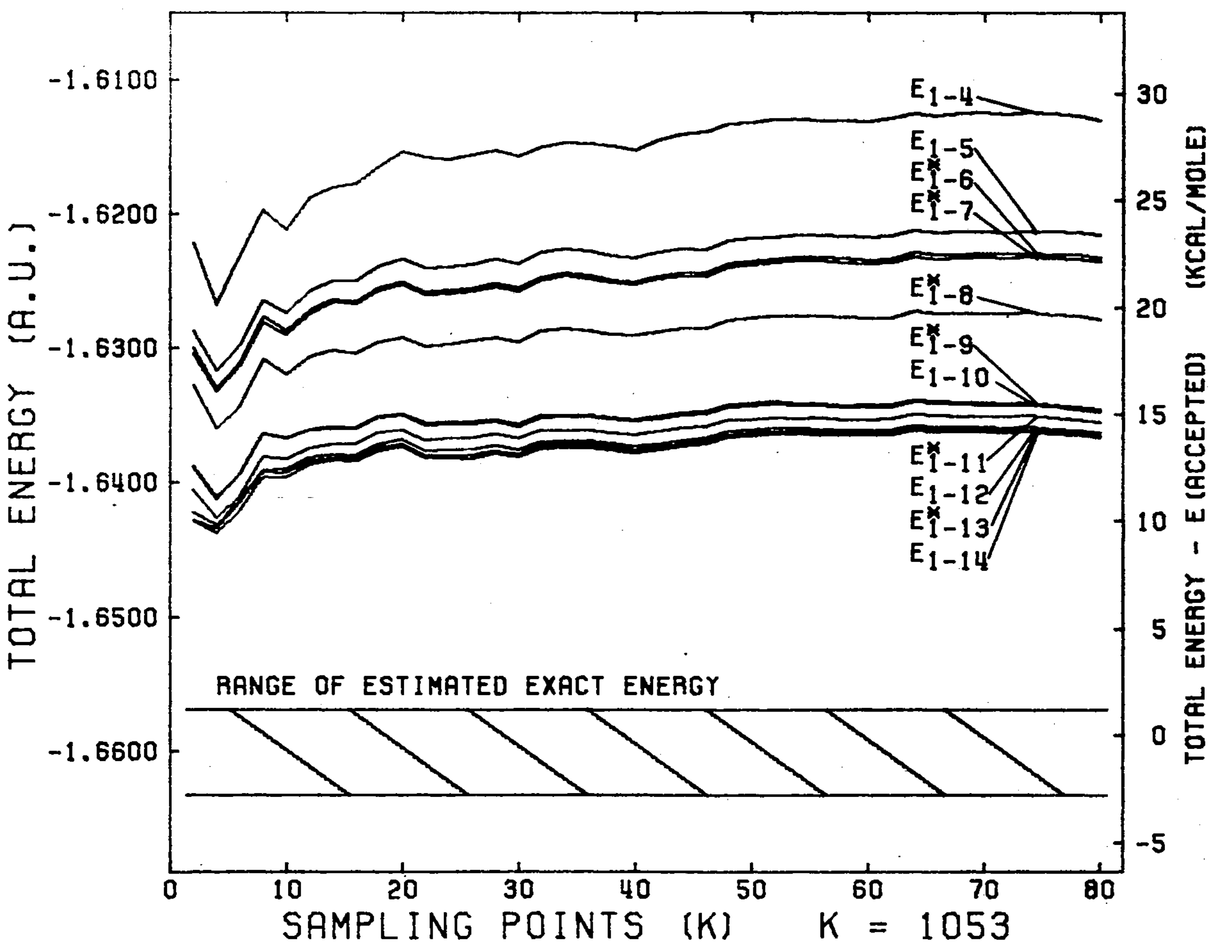

Figure 12. Convergence Properties of H_3 Activated Complex Energies With Respect to Expansion Terms 4-14 of Table II.

TABLE VII

RESULTS OF THE H_3 ACTIVATED COMPLEX CALCULATION FOR THE PARAMETERS AND VARIOUS NUMBERS OF EXPANSION TERMS GIVEN IN TABLE II. THE TOTAL NUMBER OF INTEGRATION POINTS IS 86,346. THE ENERGIES ARE PLOTTED IN FIGURES 11 AND 12.

ϕ^N	Δ_n	E^N (a.u.) (This Work)[a,b]	$(PE/KE)^N$	C_n^{1-14} [c]	$\langle\phi^{1-14}\|C_n^{1-14}\Delta_n\rangle$ [d]
1	113 000	-1.182417	-1.488	-0.00985	-0.0102
1,2*	123 000*	-1.591908	-1.845	0.0585, 0.209	0.0901, 0.371
1-3	223 000	-1.605270	-1.888	0.0822	0.208
1-4	114 000	-1.613066	-1.938	0.00301	0.00219
1-5	113 100	-1.621626	-1.974	0.0403	0.0873
1-6*	113 010*	-1.623268	-1.978	0.0304, -0.0266	0.104, -0.0740
1-7*	123 100*	-1.623553	-1.977	-0.00420, 0.0196	-0.0159, 0.0865
1-8*	123 010*	-1.627838	-2.012	0.0242, 0.0385	0.123, 0.181
1-9*	123 001*	-1.634601	-2.028	0.0171, -0.0305	0.0742, -0.226
1-10	223 100	-1.634757	-2.028	-0.00103	-0.00718
1-11*	223 010*	-1.635524	-2.027	-0.0105, 0.00944	-0.110, 0.0651
1-12	114 100	-1.636335	-2.037	0.0496	0.0754
1-13*	114 010*	-1.636534	-2.036	-0.0138, 0.0224	-0.0375, 0.0514
1-14	113 111	-1.636646	-2.036	-0.00178	-0.0382
1-∞		-1.65884			

[a] $E^{1-\infty}$ corresponds to the estimate of the exact energy given in Ref. 81.

*,b,c, and [d] See corresponding footnotes in Table V.

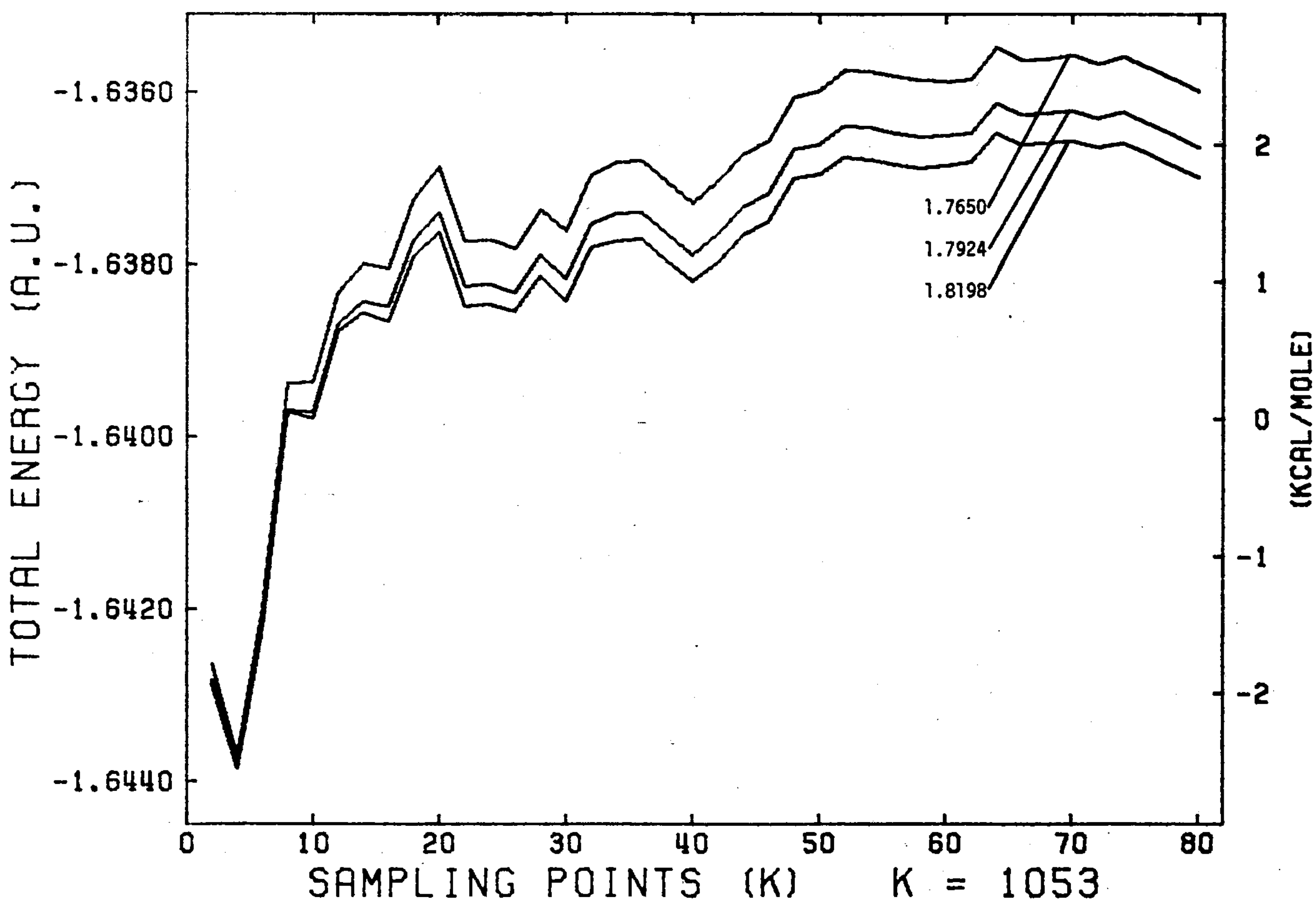

Figure 13. Convergence Properties of Linear Symmetric H_3 Energies With Respect to 21-Term Explicitly Correlated Wave Functions Describing Different Internuclear Distances

TABLE VIII

RESULTS OF 21-TERM EXPLICITLY CORRELATED WAVE FUNCTION CALCULATIONS ON THE LINEAR SYMMETRIC H_3 SYSTEM WITH DIFFERENT INTERNUCLEAR DISTANCES. THE TOTAL NUMBER OF INTEGRATION POINTS IS 86,346. THE ENERGIES ARE PLOTTED IN FIG. 13.

$R = R_{ab} = R_{bc}$ (a.u.)	E (a.u.)	(PE/KE)
1.7650	-1.636006	-2.031
1.7924	-1.636646	-2.036
1.8198	-1.636997	-2.041

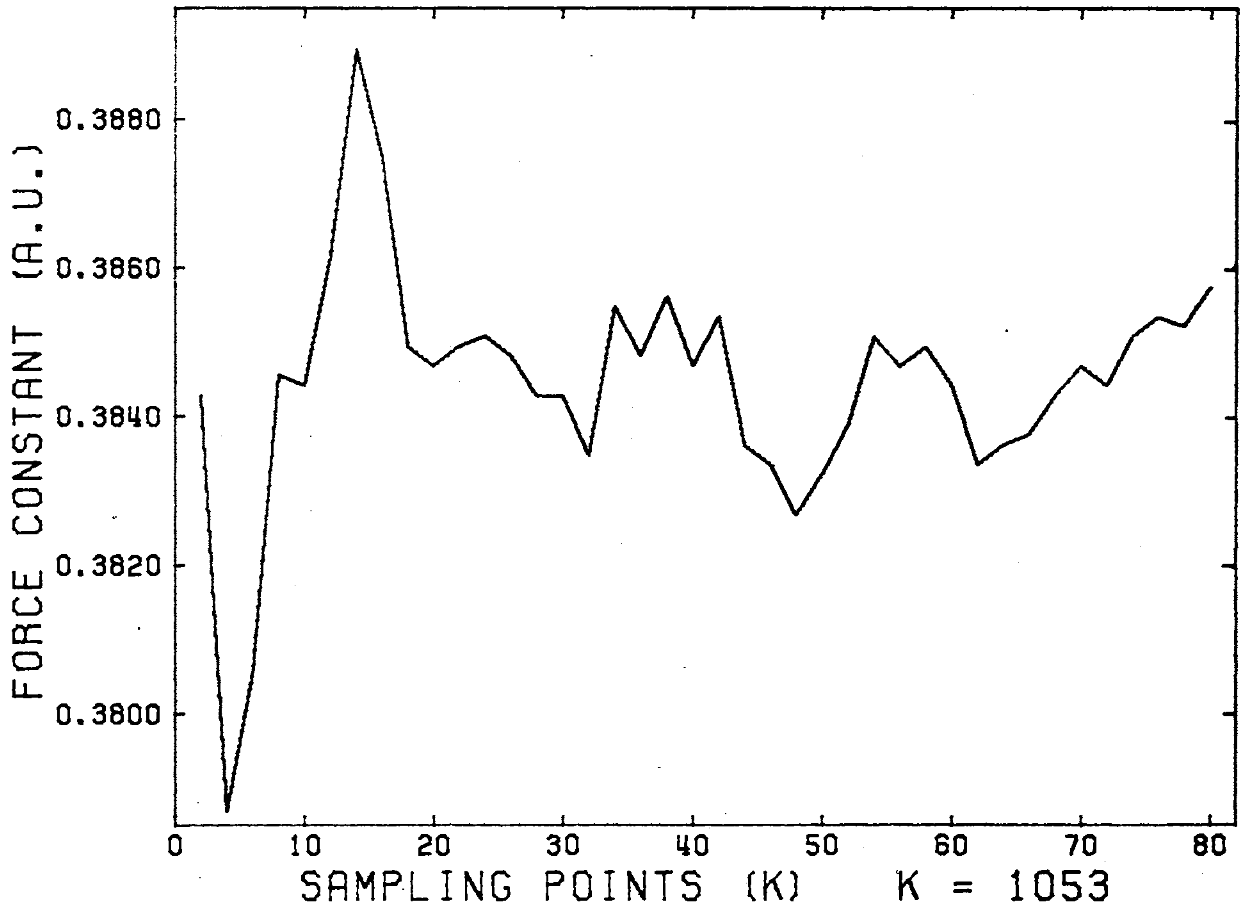

Figure 14. Convergence Properties of the Force Constant Associated With the "Symmetric Stretching Vibration" at the Saddle Point of the H_3 Energy Surface

sented in Figure 7 and Table V is about 4.5 hr. and that required to obtain the linear symmetric H_3 results presented in Figures 11 and 12 and Table VII is about 3.5 hr. using the IBM 360/65. The time varies approximately linearly with the number of expansion terms in the trial wave function.

C. Discussion

The integration point distribution functions $D(\vec{r}_1,\vec{r}_2,\vec{r}_3)$ given by Eq. [*120*] for the H_3 case and the analogous distribution function involving only one center for the lithium case appear to have been well chosen when the average normalized variance $\langle\sigma^2/I^2\rangle_{av}$ is considered. When the parameters $s_1 = 3.0$ and $s_2 = 0.3$ (determined as shown in Figure 5 by minimizing the variance $\langle\sigma^2/I^2\rangle_{av}$ using only terms 1-3 of the lithium trial wave function) are used in the calculation involving all of the terms listed in Table I, the variance $\langle\sigma^2/I^2\rangle_{av}$ is found to be equal to 1.91. And when the parameters $s = s_1 = s_2 = 1.54$ (determined as shown in Figure 6 by minimizing the variance $\langle\sigma^2/I^2\rangle_{av}$ using only the H_3 full CI (1*s*) wave function of Table IV) are used in the calculation involving all of the terms listed in Table II, the variance $\langle\sigma^2/I^2\rangle_{av}$ is found to be 1.67. These values for the normalized variance are very good considering that the smallest value Cowdrey and Reeves[68] obtained was 2.56 for a 3-dimensional 2-center integral using an integration point density function specially constructed for that integral.

The convergence rate of the energies failed to be as rapid as the inverse of the number of points N^{-1} as predicted by the error analysis associated with open Diophantine integration. However, the rate of convergence was somewhat faster than $N^{-\frac{1}{2}}$ in the lithium case and significantly faster than $N^{-\frac{1}{2}}$ in the H_3 case. The correctness of the stated convergence rates can be verified by considering the most ill-conditioned case; the lithium atom calculation involving only the first expansion term. The greatest deviation of the energy E^1 from the exact value beyond 150,000 integration points is $E^1 = 7.411008$ when $N = 168{,}480$. The inequality

$$\frac{1}{N} < \left| \frac{E^1_{\text{analytic}} - E^1}{E^1_{\text{analytic}}} \right| < \frac{1}{N^{\frac{1}{2}}} \qquad [134]$$

indeed holds with the substitution of E^1_{analytic} from Table V as seen by the resulting numerical values,

$$0.000006 < 0.000196 < 0.002436, \qquad [135]$$

and thus verifies the above statements.

The complexity of the calculation appears to have an effect on the rate of convergence. The presence of both antisymmetrizers in Eq. [*77*], the use of symmetry orbitals in the H_3 case as opposed to atomic orbitals in the lithium case, and the use of a large number of expansion terms all contribute to the complexity of the calculations and also result in an increase in the rate of convergence of the energies. Indeed, 200,000 nine-dimensional integration points were required in the lithium calculations to achieve the same accuracy (1 Kcal/mole) as obtained using 80,000 integration points in the H_3 calculations.

The results of the Monte Carlo calculation on the lithium atom using only term 1 of Table I is presented in Figure 9. Although the rate of convergence is slightly more rapid than $N^{-\frac{1}{2}}$ predicted by the associated error analysis, it is clearly slower than the rate of convergence of the analogous calculation using open Diophantine integration.

As shown in Figure 7, the lithium atom energies plotted for each step in the extension of the trial wave function converges to the analytical energy to within .1 Kcal/mole, but only after 200,000 nine-dimensional integration points have been used to evaluate the integrals.

The expansion terms 7-9 defined in Table I which simultaneously contain all possible interelectronic distances are found to contribute little to the reduction in the energy of the lithium atom. Referring to Table V, it can be seen that the contribution to the energy of these terms is about 0.0002 a.u. or 0.13 Kcal/mole. The contribution of these terms to the total wave function, as measured by the amount of overlap with the total wave function (listed in the last column of Table V), is seen to be the smallest of all the terms making up the wave function. Even when these terms are added to a trial wave function containing only terms 1-3 with no explicit correlation, their contribution is still relatively small as can be seen in Figure 8. The reduction in energy is not as great as that which originally resulted when the uncorrelated term 4* of Table I was added.

The ratio of potential and kinetic energies, referred to as (*PE*/*KE*) in Table V, is consistently close to -2.0 which indicates, according to the virial theorem, that the atomic orbital exponents are nearly optimum even for this relatively small basis.

Before discussing the linear symmetric H_3 results, an example of a rather recent study will be described which was made in order to determine the barrier height of the reaction

$$H + H_2 \rightleftarrows H_3 \rightleftarrows H_2 + H. \qquad [136]$$

The barrier height is defined as the energy difference between the H_3 activated complex and the reactants $H + H_2$,

$$E_b = E(H_3^{\ddagger}) - E(H + H_2), \qquad [137]$$

and is the lowest relative translational energy at which reaction can occur. The "activated complex" is the name given to the intermediate state when it possesses maximum energy with respect to the reaction path and minimum energy with respect to motions at right angles to the reaction path, and is usually designated by the symbol $\ddagger$.

The experimental study described here was made by LeRoy, Ridley, and Quickert[82] who used the spin states of the hydrogen nuclei to trace the progress of the chemical reaction. The term 'para-hydrogen' is used to describe the H_2 molecule when the spins of the nuclei are anti-parallel; the term 'ortho-hydrogen' is used when the spins are parallel. Equation [*137*] can be written as

$$H + p\text{-}H_2 = o\text{-}H_2 + H \qquad [138]$$

to indicate the reaction describing the conversion of para-hydrogen to ortho-hydrogen. The rate of the above reaction is found to be directly proportional to the concentrations of the reactants:

$$Rate = k[H][p\text{-}H_2], \qquad [139]$$

where k is the proportionality constant called the rate constant. The hydrogen atom concentration was found experimentally be measuring the temperature rise (increase in resistance) brought about by H-atom combination on a current-carrying wire. The para- and ortho-hydrogen molecule concentrations were determined by measuring the area under the peaks produced by a gas chromatograph which had recieved injection samples from the reaction vessel.

The rate constant k was determined experimentally by means of the equation

$$\ln \frac{[\text{p-H}_2]_0}{[\text{p-H}_2]_{x_0}} = \frac{k}{f} \int_0^{x_0} [\text{H}]\, dx \,. \qquad [140]$$

The positions 0 and x_0 refer to the ends of the chromatograph column and f is the linear flow rate of the carrier gas. The ratio on the left is related to the areas A under the chromatograph peaks by the equation

$$\frac{[\text{p-H}_2]_0}{[\text{p-H}_2]_{x_0}} = (A_{\text{p-H}_2}/A_{\text{He}})_0 / (A_{\text{p-H}_2}/A_{\text{He}})_{x_0} \,. \qquad [141]$$

where helium is used as the carrier gas.

The experimental rate constants $k(T)$, determined at various temperatures and multiplied by 4/3 to convert from experimental net rates to theoretical rates, were then used in an absolute transition-state theory analysis to find the barrier height E_b. According to this theory, the rate constant can be expressed as

$$k(T) = \frac{\text{k}T}{h} \frac{Q_{\text{H}_3^{\ddagger}}}{Q_{\text{p-H}_2} Q_{\text{H}}} e^{-E_b/RT} , \qquad [142]$$

where $Q_{\text{p-H}_2}$ and Q_{H} are the complete partition functions for the reagents and $Q_{\text{H}_3^{\ddagger}}$ is the analogous partition function for the complex except for the contribution from motion along the reaction coordinate. After the appropriate substitutions are made for the partition functions and tunneling is considered, Eq. [*142*] can be written as

$$k(T) = A \frac{\Omega(T)\ \Gamma(T, \nu_a, E_b)}{T^{\frac{1}{2}}} e^{-E_o/RT} \qquad [143]$$

where A is a constant, $\Omega(T)$ is the harmonic oscillator partition function ratio, $\Gamma(T, \nu_a, E_b)$ is a tunneling factor, and E_o is the energy difference between complex and reagents measured from the zero-point-energy levels. By iterating E_o and the parameters in Γ, the best least squares fit of Eq. [*143*] to the experimental $k(T)$ was obtained with a resulting value for E_b of 9.2 Kcal/mole. This value is approximately the average of the 7-11 Kcal/mole range of energies usually obtained by experiment.

Shavitt[81] has recently made a careful study of the experimental data in light of results obtained from an extensive CI calculation[46]. He found that best agreement with the experimental data resulted when the theoretical energy surface was scaled down to a point where the barrier height is 9.8 Kcal/mole, corresponding to a total energy of the H_3 activated complex of -1.65884 a.u.

The results of the full CI (1*s*) preliminary test calculation on the H_3 activated complex presented in Figure 10 and Table VI are good evidence of the correctness of the computer programs when three centers are involved. The convergence of the calculated energy to the analytically obtained energy is well within 1 Kcal/mole using 80,000 integration points. The ratio of the potential energy to kinetic energy is near -2.0 which indicates, according to the virial theorem, that the atomic orbital exponents and internuclear distance are nearly optimum for describing the H_3 system while in the quasi-equilibrium--activated complex state.

As shown in Figures 11 and 12 and tabulated in Table VII, the energies for the H_3 activated complex fall far short of the estimated exact energy range. However, the energy from the 21-term explicitly correlated calculation used here was superior to the energies of the 27-term CI calculation of Michels and Harris[83], the 34-term CI calculation of Shavitt, et. al.[46], and the 100-term CI calculation of Gianinetti, et. al.[59] The energies of these calculations as well as those from superior CI calculations are presented in Table IX. The atomic orbital basis functions used in these various calculations are also indicated.

The trend that appears among the energies calculated here and those calculated by CI methods is that explicitly correlated wave functions require about 1/3 as many terms as do CI wave functions for attaining equivalent accuracy in the energy. This can be seen by noting the closeness of the energies of Φ^{1-8*} of Table VII containing 12 terms and the first two CI calculations of Table IX containing 34 and 27 terms. Likewise, the energy of Φ^{1-14} containing 21 terms is near the energy of the 62-term CI calculation. It appears that a 100- to 200-term explicitly correlated wave function (equivalent to a 300- to 600-term CI wave function) would be capable of describing the true energy of the H_3 complex to within 1 Kcal/mole. It is important to note that because of the complexity of such a wave function, the number of integration points required for convergence of the integrals would be substantially reduced from the 80,000 points used here.

Terms that simultaneously contain all possible interelectronic coordinates such as term 14 of Table II appear to contribute more to the H_3

TABLE IX

TOTAL ENERGIES AND FORCE CONSTANTS OF THE H_3 ACTIVATED COMPLEX

Reference	Basis	Number of Terms	E (a.u.)	K (a.u.)
83	$1s$, $2p_z$	27	-1.6302	10.0
46	$1s$, $1s'$	34	-1.6305	0.30
59	$1s$, $2s$, $2p_z$	100	-1.6343	------
This Work	Correlated	21	-1.6366	0.385
79	$1s$, $2p_{x,y,z}$	62	-1.6387	0.296
59	$1s$, $2s$, $2p_{x,y,z}$	200	-1.6473	------
46	$1s$, $1s$, $2p_{x,y,z}$	200	-1.6521	0.31
81		∞	-1.6588	

wave function than to the lithium wave function. As can be seen by examining the overlap of each term with the total wave function, term 14 contributes more to the wave function than the same term with no explicit correlation factor (term 1), but less than term 5 containing only the factor r_{12}.

The ratio of the potential energy to the kinetic energy is seen in Table VII to deviate more from -2.0 for the 21-term H_3 calculation than in the other calculations reported here. The deviation indicates that either the atomic orbital exponents or the internuclear distance (or both) are not optimum for describing the H_3 activated complex using the expansion terms in Table II.

The convergence properties shown in Figure 13, of the linear symmetric H_3 energies associated with different internuclear distances indicate that convergence is not necessary in order to determine the optimum internuclear distance since the energies are well separated and do not cross prior to convergence.

The convergence properties of the "symmetric stretching vibration" force constant are shown in Figure 14. Although convergence has not been achieved, the value of K is approximately 0.385 a.u. This is somewhat larger than 0.30 a.u. usually obtained using CI wave functions as indicated in Table IX. The cause of this difference is probably due to the use of non-optimum atomic orbital exponents. This is indicated since the potential to kinetic energy ratio (PE/KE) diverges from -2.0 as the internuclear distances $R = R_{ab} = R_{bc}$ approaches the optimum value (see Table VIII).

CHAPTER V

CONCLUSION

Trial wave functions containing explicit correlation due to the presence of interelectronic distance coordinates r_{ij} are used to make calculations on the ^2S ground state of the lithium atom and the linear symmetric $^2\Sigma_u^+$ state of the activated H_3 complex. A type of quasirandom integration--open Diophantine integration--is used to evaluate the 9-dimensional Hamiltonian matrix elements. A technique is developed which removes the r_{ij}^{-1} singularities over a manifold by including the singularities in the integration point density function.

The rate of convergence of the variationally found energies was found to be more rapid than $N^{-\frac{1}{2}}$, where N is the number of integration points, but not as rapid as N^{-1} which is usually associated with open Diophantine integration. The convergence rate was found to increase as the complexity of the calculation increased.

When expansion terms simultaneously containing all possible interelectronic distances were added to the trial wave function for the lithium atom, the reduction in energy was relatively small, indicating that there is little or no advantage in being able to include this type of term in the calculation.

A 21-term explicitly correlated trial wave function used in the H_3 calculation resulted in a barrier height of 0.0378 a.u. for the $H_2 + H \rightleftarrows H + H_2$ exchange reaction which was superior to an earlier 100-

term configuration interaction (CI) calculation, but inferior to the 200-term CI calculations that have been reported. It appears that a 100- to 200-term explicitly correlated wave function (equivalent to a 300- to 600-term CI wave function) would be capable of describing the true energy of the H_3 complex to within 1 Kcal/mole. Because of the complexity of such a wave function, the required number of integration points should be significantly less than the 80,000 points needed for the 21-term wave function considered in this study.

There are three significant features associated with the approach used to solve atomic and molecular problems in this thesis. The first is that a minimum amount of computer storage is required since only two hermitian matrices, which are calculated directly, must be stored. These are the Hamiltonian and overlap matrices over the many-electron expansion terms of the trial wave function. Another feature is that the computation time increases only slightly faster than the number of expansion terms since it is unnecessary to reduce the matrix elements to one- and two-electron integrals over atomic orbitals. The third feature, due to the purely numerical methods used to evaluate the integrals, is that any reasonable type of basis functions may be used such as the new integral transform functions of Somorgai[84]. Likewise any reasonable type of potentials may be considered such as those that appear in nuclear physics.

REFERENCES

1. Roothaan, C. C. J., "A Study of Two-Center Integrals Useful in Calculations on Molecular Structure. I", J. Chem. Phys., 19, 1445 (1951).

2. Rudenberg, K., "A Study of Two-Center Integrals Useful in Calculations on Molecular Structure. II. The Two-Center Exchange Integrals", J. Chem. Phys., 19, 1459 (1951).

3. Rudenberg, K., Roothaan, C. C. J., and Jaunzemis, W., "Study of Two-Center Integrals Useful in Calculations on Molecular Structure. III. A Unified Treatment of the Hybrid, Coulomb, and One-Electron Integrals", J. Chem. Phys., 24, 201 (1956).

4. Kotani, A. A., Ishiguro, E., and Kimura, T., Table of Molecular Integrals, Maruzen Company, Ltd., Tokyo, Japan, 1955.

5. Barnett, M. P., "The Evaluation of Molecular Integrals by the Zeta Function Expansion", Methods in Computational Physics, B. J. Adler, S. Fernbach, and M. Rotenberg, eds., Vol. 2, p. 95, Academic Press, New York (1963).

6. Harris, F. E., and Michels, H. H., "The Evaluation of Molecular Integrals for Slater-Type Orbitals", Advan. Chem. Phys., 13, 205 (1967).

7. Christoffersen, R. E., and Ruedenberg, K., "Hybrid Integrals over Slater-Type Atomic Orbitals, J. Chem. Phys., 49, 4285 (1968).

8. Boys, S. F., "Electronic Wave Functions I, A General Method of Calculation for the Stationary States of Any Molecular System", Proc. Roy. Soc. (London), Ser. A. 200, 542 (1950).

9. Boys, S. F., "The Integral Formulae for the Variational Solution of the Molecular Many-Electron Wave Equation in Terms of Gaussian Functions With Direct Electronic Correlation", Proc. Roy. Soc. (London), Ser. A. 258, 402 (1960).

10. Schwartz, M. E., and Schaad, L. J., "*Ab initio* Studies of Small Molecules Using 1s Gaussian Basis Functions. I. Exploratory Calculations", J. Chem. Phys. 46, 4112 (1967). Also see Ph.D. dissertation, Vanderbilt University, 1966.

11. Schwartz, M. E., and Schaad, L. J., "*Ab initio* Studies of Small Molecules Using 1s Gaussian Basis Functions. II. H_3^+", J. Chem. Phys. 48, 5325 (1967).

12. Schwartz, M. E., and Schaad, L. J., "*Ab initio* Studies of Small Molecules Using 1s Gaussian Basis Functions. III. LCGTO SCF MO Wavefunctions of the Three- and Four-Electron Systems He_2^+, He_2, and Linear H_3, H_4^+, H_4", J. Chem. Phys. 48, 4709 (1968).

13. Streitwieser, Jr., A., Molecular Orbital Theory for Organic Chemists, John Wiley, New York (1961).

14. Pariser, R., and Parr, R. G., "Semi-Empirical Theory of the Electronic Spectra and Electronic Structure of Complex Unsaturated Molecules: I, II.", J. Chem. Phys. 21, 466, 767 (1953).

15. Pople, J. A., "Electron Interaction in Unsaturated Hydrocarbons" Trans. Faraday Soc., 49, 1375 (1953).

16. Pohl, H. A., Rein, R., and Appel, K., "Simplified SCF Method for Sigma-Bonded Systems. I. Physical Properties of Hydrogen Halides", J. Chem. Physics, 41, 3385 (1964).

17. Harris, F. E., and Pohl, H. A., "Split-Shell Molecular Orbitals for Sigma-Bonded Systems: Hydrogen Halides", J. Chem. Phys., 42, 3648 (1965).

18. Pohl, H. A., and Raff, L. M., "Simplified SCF Calculations for Sigma-Bonded Systems. II. The Interhalogens", Int. J. Quant. Chem., 1, 577 (1967).

19. Mickish, D. J., and Pohl, H. A., "Simplified SCF Calculations for Sigma-Bonded Systems: Extension to Hydrogen Bonding", Sigma Molecular Orbital Theory, ed. O. Sinanoğlu and K. Wiberg, Yale University Press, New Haven, Connecticut (1970), p. 105.

20. Rein, R., and Harris, F. E., "Studies of Hydrogen-Bonded Systems I. The Electronic Structure and the Double Well Potential of the N-H···N Hydrogen Bond of the Guanine-Cytosine Base Pair", J. Chem. Phys., 41, 3393 (1964).

21. Goodisman, J., "Numerical Calculation of H_2^+ and H_2 Wavefunctions", J. Chem. Phys., 41, 3889 (1964).

22. Magnusson, E. A., and Zauli, C., "Evaluation of Molecular Integrals by a Numerical Method", Proc. Phys. Soc. (London), 78, 53 (1961).

23. Frost, A. A., "The Approximate Solution of Schrödinger Equations by a Least Squares Method", J. Chem. Phys. 10, 240 (1942).

24. Gimarc, B. M., and Frost, A. A., "Energy of the Lithium Atom by the Least-Squares Local Energy Method", J. Chem. Phys., 39, 1698 (1963).

25. Boys, S. F., and Rajagopal, P., "Quantum Calculations Which Are Accumulative in Accuracy, Unrestricted in Expansion Functions, and Economical in Computation", Adv. Quant. Chem., 2, 1 (1965).

26. Rajagopal, P., "Convergent S. C. F. Wave Function and Properties of the Ammonia Molecule", Z. Naturforschg. 20a, 1557 (1965).

27. Rajagopal, P., "S.C.F. Study of the OH_3^+ Ion", Z. Naturforschg., 21a, 1211 (1966).

28. Rajagopal, P., "Ethylene Wave Functions in the S.C.F. Approximation", Z. Naturforschg., 22a, 295 (1967).

29. Boys, S. F., and Handy, N. C., "A First Solution, for LiH, of a Molecular Transcorrelated Wave Equation by Means of Restricted Numerical Integration", Proc. Roy. Soc. A., 311, 309 (1969).

30. Conroy, H., "Potential Energy Surfaces for the H_3^+ Molecule-Ion", J. Chem. Phys., 40, 603 (1964).

31. Conroy, H., "Molecular Schrödinger Equation. I. One-Electron Solutions", J. Chem. Phys., 41, 1327 (1964).

32. Conroy, H., "Molecular Schrödinger Equation. II. Monte Carlo Evaluation of Integrals", J. Chem. Phys., 41, 1331 (1964).

33. Conroy, H., "Molecular Schrödinger Equation. III. Calculation of Ground-State Energies by Extrapolation", J. Chem. Phys., 41, 1336 (1964).

34. Conroy, H., "Molecular Schrödinger Equation. IV. Results for One- and Two-Electron Systems", J. Chem. Phys., 41, 1341 (1964).

35. Conroy, H., "Energy Surface for the Linear H_3 System ", J. Chem. Phys., 42, 4047 (1965).

36. Conroy, H., "Molecular Schrödinger Equation. V. A Correlated Polyelectronic Wavefunction", J. Chem. Phys., 47, 912 (1967).

37. Conroy, H., and Bruner, B. L., "Molecular Schrödinger Equation. VI. Results for H_3 and Other Simple Systems", J. Chem. Phys., 47, 921 (1967).

38. Conroy, H., "Molecular Schrödinger Equation. VII. Properties of the Energy Variance Function: The Estimation of Energy Eigenvalues", J. Chem. Phys., 47, 930 (1967).

39. Conroy, H., "Molecular Schrödinger Equation. VIII. A New Method for the Evaluation of Multidimensional Integrals", J. Chem. Phys., 47, 5307 (1967).

40. Conroy, H., and Malli, G., "Molecular Schrödinger Equation. IX. Square and Rectangular States of H_4 and the Molecular Ions H_4^{3+} and H_4^{2+}", J. Chem. Phys., 50, 5049 (1969).

41. Larsson, S., "Calculations on the ^2S Ground State of the Lithium Atom Using Wave Functions of Hylleraas Type", Physical Review, 169, 49 (1968).

42. Eckart, C., "The Theory and Calculation of Screening Constants", Phys. Rev., 36, 878 (1930); Hylleraas, E. A., and Undheim, B., "Numerische Berechnung der 2 *S*-Terme von Ortho- und Par-Helium", Z. Physik, 65, 759 (1930).

43. Löwdin, P. O., "Correlation in Quantum Mechanics. I.", Advances in Chemical Physics, Vol. II, Prigogine, I., edit., Interscience Publishers, Inc., New York (1959).

44. McLean, A. D., Weiss, A., and Yoshimine, M., "Configuration Interaction in the Hydrogen Molecule--The Ground State", Revs. Mod. Phys., 32, 211 (1960).

45. Weiss, A. W., "Configuration Interaction in Simple Atomic Systems", Phys. Rev., 122, 1826 (1961).

46. Shavitt, I., et. al., "Potential-Energy Surface for H_3", J. Chem. Phys., 48, 2700 (1968).

47. Löwdin, P. O., "Quantum Theory of Many-Particle Systems. I. Physical Interpretations by Means of Density Matrices, Natural Spin-Orbitals, and Convergence Problems in the Method of Configurational Interaction", Phys. Rev., 97, 1474 (1955).

48. Gimarc, B. M., Cooney, W. A., and Parr, R. G., "Range of Electron Correlation in the Helium Atom", J. Chem. Phys., 42, 21 (1965).

49. Hylleraas, E., "Neue Berechnung der Energie des Heliums im Grundzustande, sowie des tiefsten Terms von Ortho-helium", Z. Physik, 54, 347 (1929).

50. James, H. M., and Coolidge, A. S., "On the Ground State of Lithium", Phys. Rev., 49, 688 (1936).

51. Gentner, R. F., and Burke, E. A., "Calculation of the ^1S State of the Beryllium Atom in Hylleraas Coordinates", Phys. Rev., 176, 63 (1968).

52. Sims, J., "A Combined Configuration Interaction-Hylleraas Type Wave Function Study of the Ground State of the Beryllium Atom", Ph.D. Thesis, Dept. Chemical Physics, Indiana Univ., Bloomington, Indiana (1969).

53. Kolos, W., and Roothaan, C. C. J., "Correlated Orbitals for the Ground State of the Hydrogen Molecule", Revs. Mod. Phys., 32, 205 (1960).

54. Roothaan, C. C. J., and Weiss, A. W., "Correlated Orbitals for the Ground State of Helium Like Systems", Revs. Mod. Phys., 32, 194 (1960).

55. Coulson, C. A., and Neilson, A. H., "Electron Correlation in the Ground State of Helium", Proc. Phys. Soc., 78, 831, (1961).

56. Gilbert, T. L., "Interpretation of the Rapid Convergence of Correlated Wave Functions", Revs. Mod. Phys., 35, 491 (1963).

57. Hamermesh, M., Group Theory and its Application to Physical Problems, Addison-Wesley Pub. Co., Inc., Reading, Massachusetts (1962).

58. Löwdin, P. O., "Angular Momentum Wavefunctions Constructed by Projection Operators", Rev. Mod. Phys., 36, 966 (1964).

59. Gianinetti, E., et. al., "Configuration Interaction Study of H_2 and H_3 Systems", Intern. J. Quant. Chem., 3, 45 (1969).

60. Goodisman, J., "Numerical Calculation of H_2 and HeH^+ Wavefunctions", J. Chem. Phys., 43, 3037 (1965).

61. Goodisman, J, and Secrest, D., "Use of Numerical Integration in the Computation of the Expectation Value of $\hat{H}^2$ with Applications to H_2", J. Chem. Phys., 45, 1515 (1966).

62. Boys, S. F., "Some Bilinear Convergence Characteristics of the Solutions of Dissymmetric Secular Equations", Proc. Roy. Soc. A., 309, 195 (1969).

63. Boys, S. F., and Handy, N. C., "A Condition to Remove the Indeterminancy in Interelectronic Correlation Functions", Proc. Roy. Soc. A., 309, 209 (1969).

64. Boys, S. F., and Handy, N. C., "The Determination of Energies and Wavefunctions with Full Electronic Correlation", Proc. Roy. Soc. A., 310, 43 (1969).

65. Boys, S. F., and Handy, N. C., "A Calculation for the Energies and Wavefunctions for States of Neon with Full Electronic Correlation Accuracy", Proc. Roy. Soc. A., 310, 63 (1969).

66. Sobol, I. M., "Computation of Definite Integrals", Chapter II, The Monte Carlo Method, Yu. A. Shreider, ed., p. 115, Pergamon Press, Oxford (1966).

67. Ellis, D. E., "Application of Diophantine Integration to Hartree-Fock and Configuration Interaction Calculations", Int. J. Quant. Chem., II S, 35 (1968).

68. Cowdrey, D. R., and Reeves, C. M., "An Application of the Monte Carlo Method to the Evaluation of Some Molecular Integrals", Computer J., 6, 277 (1963).

69. Salvadori, M. G., and Baron, M. L., Numerical Methods in Engineering, p. 6, Prentice-Hall, Inc., Englewood Cliffs, N. J., (1961).

70. Sobol, I. M., Ref. 66, p. 116.

71. IBM System/360 Operating System, FORTRAN IV Library--Mathematical and Service Subprograms, Form GC28-0589, Subroutine DATAN2, IBM Corporation, New York (1969).

72. Richtmeyer, R. D., "On the Evaluation of Definite Integrals and a Quasi-Monte Carlo Method Based on Properties of Algebraic Numbers", Report LA-1342, Los Alamos Scientific Laboratory, Los Alamos, N. M. (1952).

73. Haselgrove, C. B., "A Method for Numerical Integration", Math. Comp., 15, 323 (1961).

74. Hammersley, J. M., and Handscomb, D. C., Monte Carlo Methods, Methuen & Co., Ltd., London (1964).

75. Davis, P. J., and Rabinowitz, P., Numerical Integration, Blaisdell Publishing Co., Waltham, Mass. (1967).

76. Lyness, J. N., and Gabriel, J. R., "Comment on a New Method for the Evaluation of Multidimensional Integrals", J. Chem. Phys., 50, 565 (1969).

77. IBM System/360 Scientific Subroutine Package, Programmer's Manual, Form H20-0205, Subroutine RANDU, IBM Corporation, New York (1966).

78. Michels, H. H., VanDine, C. P., and Elliott, P., "CEIG - Eigenvalues and Eigenvectors for $(\mathbb{H} - \lambda\mathbb{S})\mathbb{C} = 0$", Quantum Chemistry Program Exchange, No. 97, Department of Chemistry, Indiana University, Bloomington, Indiana; Michels, H. H., and Elliott, P., "Eigenvalues and Eigenvectors of Large Matrices", ibid., No. 93.

79. Riera, A., and Linnett, J. W., "*Ab initio* Calculations on the H_3 Activated Complex", Theoret. chim. Acta (Berl.), 15, 181 (1969).

80. Scherr, C. W., Silverman, J. N., and Matsen, F. A., "Perturbation Energy Coefficients and Ionization Potentials of the Ground State of Three- to Ten-Electron Isoelectronic Atomic Series.", Phys. Rev., 127, 830 (1962).

81. Shavitt, I., "Correlation of Experimental Rate Constants of the Hydrogen Exchange Reactions with a Theoretical H_3 Potential Surface, Using Transition-State Theory", J. Chem. Phys., 49, 4048 (1968).

82. Le Roy, D. J., Ridley, B. A., and Quickert, K. A., "Kinetics of the Four Basic Thermal Three-Centre Exchange Reactions of the Hydrogen Isotopes", Discussions Faraday Soc., 44, 92 (1967).

83. Michels, H. H., and Harris, F. E., "Configuration-Interaction Study of the Linear H_3 System", J. Chem. Phys., 48, 2371 (1968).

84. Somarjai, R. L., "Integral Transform Functions. A New Class of Approximate Wave Functions", Chem. Phys. Letters, 2, 399 (1968).

APPENDIX A

THE COMMUTATORS $[\hat{L}_z, \prod_{i<j} r_{ij}^{\nu_{ij}}]$ AND $[\hat{L}^2, \prod_{i<j} r_{ij}^{\nu_{ij}}]$

In this appendix a proof is presented that shows that the commutation relations

$$[\hat{L}_z, \prod_{i<j}^{N} r_{ij}^{\nu_{ij}}] = 0 \text{ and } [\hat{L}^2, \prod_{i<j}^{N} r_{ij}^{\nu_{ij}}] = 0, \qquad [A.1]$$

hold for any number of electrons. By definition the total angular momentum operator $\hat{\mathbf{L}}$ is the sum of the one-electron angular momentum operators of all N electrons:

$$\hat{\mathbf{L}} = \sum_{t=1}^{N} \hat{\mathbf{L}}_t . \qquad [A.2]$$

The z-component of $\hat{\mathbf{L}}$ is

$$\hat{L}_z = \sum_t \hat{L}_{z_t}, \qquad [A.3]$$

with analogous relations for $\hat{L}_x$ and $\hat{L}_y$. The square of the total angular momentum operator is

$$\begin{aligned} \hat{L}^2 &= \hat{L}_x^{\,2} + \hat{L}_y^{\,2} + \hat{L}_z^{\,2} \\ &= (\sum_t \hat{L}_{x_t})^2 + (\sum_t \hat{L}_{y_t})^2 + (\sum_t \hat{L}_{z_t})^2 . \end{aligned} \qquad [A.4]$$

The proof begins with the use of the commutation relation,

$$[\hat{L}_{z_t}, F]\, G = G\, \hat{L}_{z_t}\, F, \qquad [A.5]$$

where F and G can be any function and the operator $\hat{L}_{x_t}$ in Cartesian coordinates is

$$\hat{L}_{z_t} = \frac{1}{i}\left(x_t \frac{\partial}{\partial y_t} - y_t \frac{\partial}{\partial x_t}\right) . \qquad [A.6]$$

Again, analogous relations hold for the operators $\hat{L}_{x_t}$ and $\hat{L}_{y_t}$. Taking $F = \prod_{i<j} r_{ij}^{\nu_{ij}}$ and G to be the remaining portion of a product wave function, it will first be shown that

$$\sum_t [\hat{L}_{z_t}, F]\, G = [\hat{L}_z, F]\, G = 0. \qquad [A.7]$$

It is convenient to factor from F parts which depend on the coordinate r_t:

$$F = F_{i,j\neq t}\, F_t = F_{i,j\neq t} \prod_{i=1}^{i=t-1} r_{it}^{\nu_{it}} \prod_{j=t+1}^{N} r_{tj}^{\nu_{tj}} . \qquad [A.8]$$

The two product terms in Eq. [A.8] will be referred to as F_{t1} and F_{t2}, respectively allowing F to be written as the product

$$F = F_{i,j\neq t}\, F_{t1}\, F_{t2} . \qquad [A.9]$$

Using this notation, the commutator involving $\hat{L}_{z_t}$ is

$$[\hat{L}_{z_t}, F]\, G = G\, \hat{L}_{z_t}\, F$$

$$= \frac{1}{i} F_{i,j\neq t}\, G[x_t(F_{t1} \frac{\partial F_{t2}}{\partial y_t} + \frac{\partial F_{t1}}{\partial y_t} F_{t2}) \qquad [A.10]$$

$$- y_t(F_{t1} \frac{\partial F_{t2}}{\partial x_t} + \frac{\partial F_{t1}}{\partial x_t} F_{t2})].$$

The required partial derivatives of F_{t1} and F_{t2} are found to be

$$\frac{\partial F_{t1}}{\partial x_t} = F_{t1} \sum_{u=1}^{t-1} \nu_{ut}\, r_{ut}^{\nu_{ut}-3} (x_t - x_u)$$

$$\frac{\partial F_{t1}}{\partial y_t} = F_{t1} \sum_{u=1}^{t-1} \nu_{ut}\, r_{ut}^{\nu_{ut}-3} (y_t - y_u)$$

$$\frac{\partial F_{t2}}{\partial x_t} = F_{t2} \sum_{u=t+1}^{N} \nu_{tu}\, r_{tu}^{\nu_{tu}-3} (x_t - x_u) \qquad [A.11]$$

$$\frac{\partial F_{t2}}{\partial y_t} = F_{t2} \sum_{u=t+1}^{N} \nu_{tu}\, r_{tu}^{\nu_{tu}-3} (y_t - y_u) .$$

After substitution of these derivatives into the expression for the commutator and summing over all electrons, the result is

$$\sum_t [\hat{L}_{z_t}, F]\, G = [\hat{L}_z, F] G$$

$$[A.12]$$

$$= \frac{1}{i} F_{i,j\neq t}\, G\, F_{t1}\, F_{t2} [\sum_{t=1}^{N} \sum_{u=t+1}^{N} \nu_{tu}\, r_{tu}^{\nu_{tu}-3} (y_t\, x_u - y_u\, x_t)$$

$$+ \sum_{t=1}^{N} \sum_{u=1}^{t-1} \nu_{ut}\, r_{ut}^{\nu_{ut}-3} (y_t\, x_u - y_u x_t)].$$

Rewriting the second sum so that it has the same structure as the first sum, one has

$$- \sum_{t=1}^{N} \sum_{u=1}^{t-1} \nu_{ut}\, r_{ut}^{\nu_{ut}-3}\, (y_u\, x_t - y_t\, x_u) \ . \qquad [A.13]$$

By interchanging subscript names in the second sum and noticing that both sums are over all possible subscripts, the two sums are seen to cancel giving

$$[\hat{L}_z, F]\, G = 0, \qquad [A.14]$$

which concludes the first part of the proof. By the use of the definition of a commutator, the commutator involving $\hat{L}_z^{\,2}$ can be written in terms of commutators involving $\hat{L}_z$:

$$[\hat{L}_z^{\,2}, F]\, G = \hat{L}_z\, [\hat{L}_z, F]\, G + [\hat{L}_z, F]\, \hat{L}_z\, G \ . \qquad [A.15]$$

The first term on the right is clearly zero from the discussion above and the second term is also seen to be zero if a new function $G' = \hat{L}_z G$ is used in the place of G. The arguments above can be repeated with the angular momentum components $\hat{L}_x$ and $\hat{L}_y$ leading to analogous relationships. The commutator involving the square of the total angular momentum operator can now be written

$$[\hat{L}^2, F]\, G = [\hat{L}_x^{\,2}, F]\, G + [\hat{L}_y^{\,2}, F]\, G + [\hat{L}_z^{\,2}, F]\, G = 0 \qquad [A.16]$$

and is zero since the commutator involving each component is zero.

APPENDIX B

ACTION OF THE KINETIC ENERGY OPERATOR ON THE

GENERAL PRODUCT WAVE FUNCTION

The explicit evaluation of the kinetic energy operator acting on a general product wave function of the type used in this study is carried out in this appendix. Using the notation of Chapter III, Section A, the term under consideration can be written symbolically as:

$$\begin{aligned} T &= -\tfrac{1}{2}(\nabla_1^{\,2} + \nabla_2^{\,2} + \nabla_3^{\,2})(i\ j\ k\ i'\ j'\ k') \\ &= -\tfrac{1}{2}(\nabla_1^{\,2} + \nabla_2^{\,2} + \nabla_3^{\,2})(i\ j\ k\ g), \end{aligned} \qquad [B.1]$$

where, for simplicity, the symbol g is used for the explicit correlation product:

$$g \;=\; r_{12}^{i'}\, r_{13}^{j'}\, r_{23}^{k'} \;\equiv\; i'\ j'\ k'. \qquad [B.2]$$

According to the theorems of vector calculus, Eq. [B.1] can be expanded as follows:

$$\begin{aligned} T = -\tfrac{1}{2}\{&[(\nabla_1^{\,2} i)\ j\ k + i(\nabla_2^{\,2} j)\ k + i\ j(\nabla_3^{\,2} k)]g \\ &+2[(\vec{\nabla}_1 i\cdot\vec{\nabla}_1 g) j\ k + i(\vec{\nabla}_2 j\cdot\vec{\nabla}_2 g)k + i\ j(\vec{\nabla}_3 k\cdot\vec{\nabla}_3 g)] \\ &+i\ j\ k\ (\nabla_1^{\,2} + \nabla_2^{\,2} + \nabla_3^{\,2})g\}\ . \end{aligned} \qquad [B.3]$$

The orbitals i, j, and k are assumed to be Slater s-type atomic orbitals (defined by Eq. [37] with $\ell = m = o$) or a linear combination of such orbitals. The gradient of a Slater s-type atomic orbital is easily found to be

$$\vec{\nabla}_t\, \chi_{n00}(t) = \vec{\nabla}_t (N r_t^{n-1}\, e^{-\zeta r_t}) = \left(\frac{n-1}{r_t^{\,2}} - \frac{\zeta}{r_t}\right) \vec{r}_t\, \chi_{n00}(t), \qquad [B.4]$$

and the Laplacian is found to be

$$\nabla_t^{\,2}\, \chi_{n00}(t) = (\zeta^2 - 2\zeta\, n/r_t + n(n-1)/r_t^{\,2})\, \chi_{n00}(t)\ . \qquad [B.5]$$

The remaining terms in Eq. [B.3] involve the gradient and Laplacian of the function g. These are easily determined by again applying the theorems of vector calculus and are found to be:

$$\vec{\nabla}_1 g = [\ (\vec{\nabla}_1 r_{12}^{i'})\, r_{13}^{j'} + r_{12}^{i'}\, (\vec{\nabla}_1 r_{13}^{j'})]\, r_{23}^{k'},$$

$$\vec{\nabla}_2 g = [-(\vec{\nabla}_1 r_{12}^{i'})\, r_{23}^{k'} + r_{12}^{i'}\, (\vec{\nabla}_2 r_{23}^{k'})]\, r_{13}^{j'}.$$

$$\vec{\nabla}_3 g = [-(\vec{\nabla}_1 r_{13}^{j'})\, r_{23}^{k'} - r_{13}^{j'}\, (\vec{\nabla}_2 r_{23}^{k'})]\, r_{12}^{k'},$$

$$\nabla_1^{\,2} g = [(\nabla_1^{\,2} r_{12}^{i'})\, r_{13}^{j'} + 2(\vec{\nabla}_1 r_{12}^{i'}) \cdot (\vec{\nabla}_1 r_{13}^{j'}) + r_{12}^{i'}\, (\nabla_1^{\,2} r_{13}^{j'})]\, r_{23}^{k'}, \qquad [B.6]$$

$$\nabla_2^{\,2} g = [(\nabla_1^{\,2} r_{12}^{i'})\, r_{23}^{k'} - 2(\vec{\nabla}_1 r_{12}^{i'}) \cdot (\vec{\nabla}_2 r_{23}^{k'}) + r_{12}^{i'}\, (\nabla_2^{\,2} r_{23}^{k'})]\, r_{13}^{j'},$$

$$\nabla_3^{\,2} g = [(\nabla_k^{\,2} r_{13}^{i'})\, r_{23}^{k'} + 2(\vec{\nabla}_1 r_{13}^{j'}) \cdot (\vec{\nabla}_2 r_{23}^{k'}) + r_{13}^{j'}\, (\nabla_2^{\,2} r_{23}^{k'})]\, r_{12}^{i'}.$$

The gradient and Laplacian of the general interelectronic term $r_{ij}^{\nu_{ij}}$ remain to be determined. These are most easily calculated using rectangular coordinates and are given by

$$\vec{\nabla}_i r_{ij}^{\nu_{ij}} = -\vec{\nabla}_j r_{ij}^{\nu_{ij}} = \nu_{ij}(\vec{r}_i - \vec{r}_j)\, r_{ij}^{\nu_{ij}-2}, \qquad [B.7]$$

and

$$\nabla_i^2 r_{ij}^{\nu_{ij}} = \nabla_j^2 r_{ij}^{\nu_{ij}} = \nu_{ij}(\nu_{ij} + 1)\, r_{ij}^{\nu_{ij}-2} \qquad [B.8]$$

Equation [*B.7*] shows that the gradients with respect to the coordinates of electrons i and j of the term $r_{ij}^{\nu_{ij}}$ differ only in sign. This is the source of the negative signs appearing in Eq. [*B.6*], since a change of sign is made when some of the individual terms are rewritten so that the gradient is always with respect to the ith electron's coordinates of the $r_{ij}^{\nu_{ij}}$ term.

APPENDIX C

NORMALIZATION OF DENSITY FUNCTION $D(\vec{r}_1, \vec{r}_2, \vec{r}_3)$

In this appendix the normalization of the general 3-center, 3-electron point selection density function $D(\vec{r}_1, \vec{r}_2, \vec{r}_3)$, given by Eq. [*120*], is established. Thus, it is to be shown that

$$\int D(\vec{r}_1, \vec{r}_2, \vec{r}_3)\, dv_1\, dv_2\, dv_3 = 1 \qquad [C.1]$$

Factoring a term of the density function into three separate density functions as indicated by Eq. [*120*], the general term of the normalization integral becomes

$$I = \int D_1(r_{1\gamma})\, D_2(\vec{r}_{1\gamma'}, \vec{r}_{2\gamma'})\, D_1(r_{3\gamma''})\, dv_1\, dv_2\, dv_3 \ . \qquad [C.2]$$

The integration over the coordinates of electron 3 can be performed independently. It is easily shown that the density function D_1 is normalized:

$$D_1(r_{3\gamma''})\, dv_3 = 1.$$

The normalization integral term can now be written

$$I = \int D_1(r_{1\gamma})\, D_2(\vec{r}_{1\gamma'}, \vec{r}_{2\gamma'})\, dv_1\, dv_2,$$

and explicitly

$$I = \int \frac{s_1^{\,2}}{4\pi}\ \frac{e^{-s_1 r_{1\gamma}}}{r_{1\gamma}}\ \frac{r_{2\gamma'}}{1 - \exp(s_2\ r_{2\gamma'})}\ \frac{s_2^{\,2}}{4\pi}\ \left(\int \frac{e^{-s_2 r_{2\gamma'}}}{r_{2\gamma'}}\ \frac{1}{r_{12}}\ dv_2 \right) dv_1 . \qquad [C.3]$$

The integral

$$K(\vec{r}_{1\gamma}) = \int \frac{e^{-s_2 r_{2\gamma'}}}{r_{2\gamma'}}\ \frac{1}{r_{12}}\ dv_2 \qquad [C.4]$$

over the coordinates of electron 2 will be considered first. The inter-electronic distance r_{12} is conveniently defined in terms of vectors originating from center γ':

$$r_{12} = |\vec{r}_{1\gamma'} - \vec{r}_{2\gamma'}| . \qquad [C.5]$$

The term r_{12} can be expanded in terms of the associated Lengendre polynomials

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \sum_{m=-k}^{k} \frac{(k-|m|)!}{(k+|m|)!}\ \frac{r_<^{\,k}}{r_>^{\,k+1}}\ P_k^{|m|}(\cos\theta_1)\ P_k^{|m|}(\cos\theta_2)\ e^{im(\phi_1-\phi_2)} , \qquad [C.6]$$

where r_1, θ_1, ϕ_1 and r_2, θ_2, ϕ_2 are the spherical coordinates of the vectors $\vec{r}_{1\gamma'}$ and $\vec{r}_{2\gamma'}$ respectively, and $r_>$, $r_<$ are the larger and smaller of the quantities r_1 and r_2. Since the remaining portion of the integrand in Eq. [C.4] is independent of angles, and

$$\int_0^{2\pi} e^{im\phi}\ d\phi = 2\pi\ \delta_{m0}$$

$$\int_0^{\pi} P_k^{\,0}\ (\cos\theta)\ \sin\theta\ d\theta = 2\delta_{k0} . \qquad [C.7]$$

the substitution of the expansion for r_{12}^{-1} into Eq. [C.4] and subsequent integration over angles yields

$$K = 4\pi\left(\frac{1}{r_{1\gamma'}} \int_0^{r_{1\gamma'}} r_{2\gamma'}\, e^{-s_2 r_{2\gamma'}}\, dr_{2\gamma'} + \int_{r_{1\gamma'}}^{\infty} e^{-s_2 r_{2\gamma'}}\, dr_{2\gamma'}\right)$$

$$= \frac{4\pi}{s_2^{\,2} r_{1\gamma'}} \left(1 - e^{-s_2 r_{1\gamma'}}\right). \qquad [C.8]$$

Inserting this expression for K into the normalization integral [*C.3*], the result is simply

$$I = \int \frac{s_1^{\,2}}{4\pi} \frac{e^{-s_1 r_{1\gamma}}}{r_{1\gamma}}\, dv_1 = \int D_1(r_{1\gamma})\, dv_1 = 1, \qquad [C.9]$$

since the density function D_1 is normalized.

The normalization of a general term of the point selection density function $D(\vec{r}_1, \vec{r}_2, \vec{r}_3)$ has been established and is completely independent of the location of the various centers. Since there are 162 terms, the factor $(162)^{-1}$ is required to normalize the complete density function, and Eq. [*120*] follows.

APPENDIX D

PROGRAM LISTINGS AND DESCRIPTIONS

The computer programs (main and subroutines) used to make the H_3 calculations are listed in this appendix. The function of each routine is described in detail. Sample input and output are also given.

MAIN The main program supervises input and output, generates the integration points, calculates the integrals, and supervised the solution of the eigenvalue problem. All arrays are singly subscripted except those used as input to the routines acquired from the Quantum Chemistry Program Exchange. The equations and appendices referred to in the programs are those appearing in this thesis. The description of the input deck follows:

Parameter	Description	Columns
	I/O Card	
DTAIL	(Logical) TRUE--all matrices are printed, FALSE--Hamiltonian matrix is printed	10-14
PUNCH	(Logical) TRUE--reproduce parameter cards and write matrices, eigenvector, and energy in 1P4D20.12 format using FORTRAN logical output file 7.	50-54
	Expansion Term Cards	
CDNO	(Integer) Expansion term number ≤ 26: Δ_n	1-3
SOINDX	(Integer) Symmetry orbital indices ≤ 4: ϕ_i	11-20
	ϕ_j	21-30

	ϕ_k	31-40
EEXP	(Integer) Interelectronic distance exponent	
	≤ 2: $r_{12}^{i'}$,	51-55
	$r_{13}^{j'}$	56-60
	$r_{23}^{k'}$	61-65

Separation Card

999	Indicates end of expansion terms	1-3

Atomic Orbital Exponents

J	(Integer) Sequence number ≤ 3	1-3
FILL	(Alphabetic) Description or label	4-8
ZZ	(Real) Exponent	21-30

Separation Card

999	Indicates end of exponents	1-3

Integration Parameters

SETN9	(Integer) Closed Diophantine integration point set ≤ 7	5-6
IEND	(Integer) Number of last cycle to be processed	13-14
PTSELT	(Integer) Point selection technique 1--closed Diophantine integration 2--Monte Carlo integration 3--open Diophantine integration	17-18
SCHEME	(Integer) Integration point distribution 1--single distribution (Eq. [*120*]) used for all integrals 2--Eq. [*120*] used for r_{ij}^{-1} integrals; same distribution, but with D_2 replaced by D_1, used for all other integrals	19-20
RAIDS	(Real) Rejects points that lie closer than this distance from a nucleus	21-30

NOPTS9	(Integer) Number of integration points (N) NOPTS9 $< 0 \rightarrow N = \|\text{NOPTS9}\|$ NOPTS9 $= 0 \rightarrow N$ = smallest multiple of 162 greater than the number of points implied by the closed Diophantine integration set requested NOPTS9 $> 0 \rightarrow N$ = smallest multiple of 162 greater than NOPTS9	41-45
IBEGIN	(Integer) Number of first cycle to be processed, may be omitted if IBEGIN = 1 is desired. If IBEGIN $\neq$ 1, then data from last cycle must follow next card (see I/O card 'PUNCH' parameter).	52-53
R12IDS	(Real) Rejects points that lie closer than this distance from another electron	61-70
ROOTS	(Integer) Number of eigenvalues desired (N) ROOTS $= 0 \rightarrow N = 5$ ROOTS $\geq 5 \rightarrow N = 5$ Otherwise N = ROOTS	77-78
NROUT	(Integer) Eigenvalue routine desired NROUT = 1 $\rightarrow$ GIVENS (Listed here as dummy) NROUT = 2 $\rightarrow$ NESBET	79-80

Internuclear Distance and
Distribution Function Parameter

RR23	(Real) Internuclear separation	1-10
SSS	(Real) Distribution function parameter $s = s_1 = s_2$	11-20

LAPSI This subroutine calculates the numerical value of

$$T = -\tfrac{1}{2}(\nabla_1^2 + \nabla_2^2 + \nabla_3^2)\ (i\ j\ k\ i'\ j'\ k')$$

as indicated in Appendix B.

DRANDU This subroutine is a double precision version of RANDU distributed by IBM[77].

CEIG This subroutine, slightly modified for use on the IBM/360, was obtained from the QCPE[78]. It transforms the original eigenvalue problem from the form $(\mathbb{H} - E\mathbb{S})\mathbb{C} = 0$ to the form $(\mathbb{H}' - E\mathbb{1})\mathbb{C}' = 0$.

NESBET This routine is also from the QCPE[78], and is slightly modified from the original version for use on the IBM/360. It solves the eigenvalue problem after transformation by CEIG.

GIVENS This routine is a dummy form of the subroutine by the same name available from the QCPE.

DTRMNT This routine calculates the determinant of a matrix and is used to check the relation $\det|\mathbb{H} - E\mathbb{S}| = 0$.

OUT1 This routine writes out a linear array using an alphabetic literal to label the elements.

OUT2 This routine writes out a two-dimensional array using an alphabetic literal to label the elements. The number of rows and columns to be written can be specified and whether the matrix is to be written in transpose form.

OUT2S1 This routine is similar to OUT2 except that it handles two-dimensional matrices that have been stored using a single subscript. The matrix may be stored by rows or columns.

ELAPSE This assembler language routine determines the time that has elapsed since it was last called. It is distributed by the Oklahoma State University Computer Center.

Sample input data to the programs is given in Table X. The resulting output immediately follows the program listings. The meaning of the symbols used in the output is indicated in the following list:

GG -- $<\Delta_n|r_{12}^{-1} + r_{13}^{-1} + r_{23}^{-1}|\Delta_m>$

SS -- $<\Delta_n|\Delta_m>$

KEKE -- $<\Delta_n|-\frac{1}{2}(\nabla_1^2 + \nabla_2^2 + \nabla_3^2)|\Delta_m>$

NUCNUC -- $<\Delta_n|\sum_i^3 \sum_\gamma^3 r_{i\gamma}|\Delta_m>$

The suffix 'V' applied to the above symbols indicate the normalized variances of these integrals, σ^2/I^2 (see Eq. [88]). Additional symbols have the meanings:

AVE -- Average of variances

VV -- GG + NUCNUC + nucleus-nucleus repulsion energy

HH -- KEKE + GG + NUCNUC or $<\Delta_n|\hat{H}\Delta_m>$

COET -- Eigenvectors C_i

E -- Eigenvalues

CCH -- $<\Phi|\hat{H}\Phi> = \sum_i \sum_j C_i C_j (\mathrm{HH})_{ij}$

CCKE -- $<\Phi|\hat{T}\Phi> = \sum_i \sum_j C_i C_j (\mathrm{KEKE})_{ij}$

CCV -- $<\Phi|\hat{V}\Phi> = \sum_i \sum_j C_i C_j (\mathrm{VV})_{ij}$

VRATIO -- CCV/CCKE

OVRMAX -- Maximum of the $<\Phi|C_n\Delta_n>$

OVER -- $<\Phi|C_n\Delta_n>$

CCS -- $<\Phi|\Phi> = \sum_i \sum_j C_i C_j (\mathrm{SS})_{ij}$

HESC -- $(\mathbf{H} - E\mathbf{S})\mathbf{C}$

DET -- $\det|\mathbb{H} - E\mathbb{S}|$

ETOTAL -- Eigenvalue + nucleus-nucleus repulsion energy.

```
OPTIONS - NAME= MAIN,OPT=02,LINECNT=60,SOURCE,EBCDIC,NOLIST,NODECK
      IMPLICIT REAL*8(A-H,L,O-Z)
      DIMENSION A9(63),OVER(27,27),SUMR(3),A9SAVE(9),AA9(9),
     1          XX(9),ZZZ(10),SS( 378),GG( 378),VV( 378),
     2          HH( 378),HMAT( 378),SMAT( 378),COET(29,29),VEC(29,5),
     3          E(27),CCKE(27),CCV(27),CCH(27),CCS(0378),OVRMAX(27),
     4          VRATIO(27),HESC(27),DET(27),ETOTAL(27),HES(27,27),
     5          XXXX(3),YYYY(3),ZZZZ(3),RO(10),DT1(3),DT2(3),DT3(3),
     6          DT4(3),DT5(3),SSV( 378),GGV( 378),CA(3),DB(3),DC(3),
     7          ABUFF(10)
      REAL*8 KEKE( 378),NUCNUC( 378),MU,LAMBDA,KBRA1,KBRA2,KBRA3,
     1       LAMBMU,NUCNUV( 378),KEKEV( 378),NDA1,NDAG,KET1(27),
     2       KET2(27),KET3(27),KEBRA1(27),KEBRA2(27),KEBRA3(27),
     3       KET1JJ,KET2JJ,KET3JJ,NDAS
      REAL*4 TIM9DS,TIMEVS,TIMTS
      REAL*4 FLOAT
      INTEGER COND(27),SOINDX(81),SETN9,ROOTS,P9(7,9),L,LP,TSUB,
     1        SUB,TIMEV,ROWSW,TIM9D,EEXP(81),SEQIX3,SEQINX,ELSEQ(18),
     2        ELN,ELNTH,ELN1,REJG,REJ1,SCHEME,PTSELT
      DIMENSICN M9(7),KPP(29)
      LOGICAL NDTAIL,DTAIL,NPUNCH,PUNCH,LLINIT
      COMMON /KEGRUP/SO(45),LSO(45),DSOX(45),DSOY(45),DSOZ(45),
     2               DR12X(4),DR13X(4),DR23X(4),R12E(4),LR12(4),
     3               DR12Y(4),DR13Y(4),DR23Y(4),R13E(4),LR13(4),
     4               DR12Z(4),DR13Z(4),DR23Z(4),R23E(4),LR23(4),
     5               MAXSO,MAXSO2,HALF
      DATA ZNUCNU/'NUCNUC'/,ZKEKE/'  KEKE'/,ZGG/'    GG'/,ZVV/'    VV'/,
     2     ZHH/'    HH'/,ZCOET/'  COET'/,ZE/'     E'/,ZCCH/'   CCH'/,
     3     ZCCKE/'  CCKE'/,ZCCV/'   CCV'/,ZVRAT/'VRATIO'/,
     4     ZHESC/'  HESC'/,ZDET/'   DET'/,ZETOT/'ETOTAL'/,
     5     ZCCS/'   CCS'/,ZOVER/'  OVER'/,
     6     ZOVMAX/'OVRMAX'/,ZSS/'    SS'/,ZNUCNV/'NUCNUV'/,
     7     ZKEKEV/' KEKEV'/,ZGGV/'   GGV'/,ZSSV/'   SSV'/
CCCCCC     CONSTANTS FOR CONROY'S CLOSED DIOPHANTINE INTEGRATION
CCCCCC             -- ONLY REFERRED TO -- NOT USED IN THESIS
      DATA M9/   20,3722,6044,9644,15014,20018,30026/,
     1     P9/    1, 119,  43, 457,  823, 1003, 1639,
     2            2, 339,  87, 509, 1633, 2047, 3207,
     3            3, 437, 179,1677, 2443, 3029, 4821,
     4            4, 773,1421,1723, 3215, 4043, 6443,
     5            5, 937,1479,2173, 4039, 5035, 8015,
     6            6,1219,1589,2423, 4827, 6031, 9671,
     7            7,1503,2189,2489, 5671, 7067,11249,
     8            8,1697,2191,3431, 6485, 8135,12989,
     9            9,1747,2783,3719, 7277, 9071,14531/
CCCCCC     ELECTRON PERMUTATIONS IN EQ. (120)
      DATA ELSEQ/ 1,2,3,
     1            1,3,2,
     2            2,1,3,
     3            2,3,1,
     4            3,1,2,
     5            3,2,1/
CCCCCC     STARTING VALUES FOR EQ. (103)
      DATA RO/ 3.6D-1,6.8D-1,9.6D-1,1.2D+0,1.5D+0,
     1         1.8D+0,2.2D+0,2.7D+0,3.4D+0,4.7D+0/
CCCCCC     ATOMIC ORBITAL NORMALIZATICN -- EQ. (37)
      ZZNOR(NN,ZZ)=DSQRT(ZZ**(2*NN+1))
CCCCCC     OPEN DIOPHANTINE INTEGRATION CONSTANTS GIVEN IN TABLE III
      AA9(1)=DSQRT(101.0D+0)
      AA9(2)=DSQRT(97.0D+0)
      AA9(3)=DSQRT(3.0D+0)
      AA9(4)=DSQRT(13.0D+0)
      AA9(5)=DSQRT(157.0D+0)
      AA9(6)=DSQRT(29.0D+0)
      AA9(7)=DSQRT(127.0D+0)
      AA9(8)=DSQRT(47.0D+0)
      AA9(9)=DSQRT(167.0D+0)
      MAXSO=15
      MAXSO2=2*MAXSO
      MAXCON=27
      MXCON2=MAXCON+2
C     MAXSS=MAXCON*(MAXCON+1)/2
C     MAXSS=378
      MAXEXP=10
      NOCNTR=3
      PI=3.141592653589793
      RTPII=1.0D+0/DSQRT(PI)
      TWOPI=2.0D+0*PI
      RT32=DSQRT(3.0D+0)/2.0D+0
      RT3I=1.0D+0/DSQRT(3.0D+0)
      SIXTH=1.0D+0/6.0D+0
      HALF=1.0D+0/2.0D+0
      NODENS=162
CCCCCC      EQ. (73)
      D1=HALF*(RT3I+1.0D+0)
      D2=HALF*(RT3I-1.0D+0)
      D3=0.0D+0-RT3I
      READ(5,909) DTAIL,PUNCH
      NDTAIL=.NOT.DTAIL
      NPUNCH=.NOT.PUNCH
  909 FORMAT(9X,L5,T50,L5)
      WRITE(6,924) DTAIL,PUNCH
  924 FORMAT(' DETAIL = ',L1,20X'PUNCH = ',L1)
C     CONVERT INTEGRATION POINT SETS FROM INTEGER TO DOUBLE PRECISION
 1999 DO 37 I=1,7
      ISUB=(I-1)*9
      DO 37 J=1,9
   37 A9(ISUB+J)=DFLOAT(P9(I,J))/DFLOAT(M9(I))
C     ****************************************************************
C     ****************************************************************
C     ****************************************************************
C      CONFIGURATION INPUT
C     ****************************************************************
      DO 30 J=1,MAXCON
      JSUB=(J-1)*3
      READ(5,900,END=9000) COND(J),(SOINDX(JSUB+I),I=1,3),
     1                     (EEXP(JSUB+I),I=1,3),ABUFF
  900 FORMAT(I3,7X,3I10,T51,3I5,T1,10A8)
      IF (PUNCH) WRITE(7,927) ABUFF
  927 FORMAT(10A8)
      IF (COND(J).EQ.999) GO TO 32
   30 CONTINUE
   32 NNN=J-1
      NOSS=NNN*(NNN+1)/2
      WRITE(6,901) (J,COND(J),(SOINDX((J-1)*3+I),I=1,3),
     1 (EEXP((J-1)*3+I),I=1,3),J=1,NNN)
  901 FORMAT ('1 CD.NO.',T20,'CONF.',T44,'SO.1',T57,'SO.2',T70,'SO.3',
```

```
     1 T89,'R12',T102,'R13',T115,'R23',
     2 /(' ',I5,T20,I3,11X3I13,5X3I13))
      NOELEC=3
      IF (SOINDX(3).EQ.0) NOELEC=2
      WRITE(6,925) NOELEC
  925 FORMAT('0',I2,' ELECTRON SYSTEM')
C     EXPONENTS
      WRITE(6,906)
  906 FORMAT(/'1',T16,'EXPONENT(S)',T37,'VALUE'/)
C     READ INITIAL ORBITAL EXPONENTS
      DO 33 I=1,998
      READ(5,905) J,FILL,ZZ,ABUFF
  905 FORMAT(I3,A8,T21,-4PD10.4,T1,10A8)
      IF (PUNCH) WRITE(7,927) ABUFF
      IF (J.EQ.999) GO TO 34
      ZZZ(J)=ZZ*1.0D-4
   33 WRITE(6,908) I,J,FILL,ZZZ(J)
  908 FORMAT(' ',I5,T16,I2,A8,T33,1PD12.5)
   34 CONTINUE
      ZZ1=ZZZ(1)
      ZZ2=ZZZ(2)
      ZZ3=ZZZ(3)
      ZZ1M=0.0D+0-ZZ1
      ZZ2M=0.0D+0-ZZ2
      ZZ3M=0.0D+0-ZZ3
      TOZZ1N=2.0D+0*ZZ1
      TOZZ2N=2.0D+0*ZZ2
      TOZZ3N=4.0D+0*ZZ3
      ZZ12=ZZ1*ZZ1
      ZZ22=ZZ2*ZZ2
      ZZ32=ZZ3*ZZ3
      XNOR1=RTPII*ZZNOR(1,ZZ1)
      XNOR2=RTPII*ZZNOR(1,ZZ2)
      XNOR3=ZZNOR(2,ZZ3)/CSQRT(3.0D+0*PI)
C     SET NUMBERS
      READ(5,904) SETN9,IEND,PTSELT,SCHEME,RAIDS,NOPTS9,IBEGIN,
     1                                         R12IDS,ROOTS,NROUT,ABUFF
  904 FORMAT(4XI2,6XI2,2X2I2,T21,D10.0,T41,I5,T52,I2,
     1       T61,D10.0,T77,2I2,T1,10A8)
      IF (PUNCH) WRITE(7,927) ABUFF
C     R23
      READ(5,902) RR23,SSS,ABUFF
  902 FORMAT(-4PD10.4,-2PD10.2,T1,10A8)
      IF (PUNCH) WRITE(7,927) ABUFF
      RR23=RR23*1.0D-4
      SSS=SSS*1.0D-2
      RR232=RR23*RR23
      TORR23=2.0D+0*RR23
      SSSM=0.0D+0-SSS
      S24PI=SSS*SSS/(4.0D+0*PI)
      WRITE(6,903) RR23,SSS
  903 FORMAT(/'0',T7,'R23',T29,'SSS',
     1       /' ',1PD12.5,T24,D12.5)
CCCCCC       REFINE STARTING VALUES FOR EQ. (103)
      LLINIT=.TRUE.
      I=0
    1 I=I+1
      ETA=(DFLOAT(I-1)+HALF)*1.0D-1
      GO TO 136
    3 RO(I)=R
      IF (I.LT.10) GO TO 1
      LLINIT=.FALSE.
      IF (NOPTS9) 26,27,28
   26 NOPTS9=0-NOPTS9
      GO TO 29
   27 NOPTS9=(M9(SETN9)/2/NODENS+1)*NODENS
      GO TO 29
   28 NOPTS9=(NOPTS9/NODENS+1)*NODENS
   29 CALL ELAPSE(TIM9D)
C     ******************************************************************
C     ******************************************************************
C     ******************************************************************
C     9-D INTEGRATION OVER CONFIGURATIONS
C     ******************************************************************
CCCCCC       EQS. (B.7) AND (B.8)
      LR12(1)=0.0D+0
      LR12(3)=6.0D+0
      LR13(1)=0.0D+0
      LR13(3)=6.0D+0
      LR23(1)=0.0D+0
      LR23(3)=6.0D+0
      DR12X(1)=0.0D+0
      DR13X(1)=0.0D+0
      DR23X(1)=0.0D+0
      DR12Y(1)=0.0D+0
      DR13Y(1)=0.0D+0
      DR23Y(1)=0.0D+0
      DR12Z(1)=0.0D+0
      DR13Z(1)=0.0D+0
      DR23Z(1)=0.0D+0
      R12E(1)=1.0D+0
      R13E(1)=1.0D+0
      R23E(1)=1.0D+0
      REJ1=0
      REJG=0
      TSUB=(SETN9-1)*9
      IF (IBEGIN.LE.1) GO TO 89
CCCCCC       RESTART PROGRAM WITH CYCLE IBEGIN IF IBEGIN .GT. 1
      IREPTX=IBEGIN-1
      NXT=IREPTX*NOPTS9
      READ(5,2006) (GG(I),I=1,NOSS)
      READ(5,2006) (SS(I),I=1,NOSS)
      READ(5,2006) (KEKE(I),I=1,NOSS)
      READ(5,2006) (NUCNUC(I),I=1,NOSS)
      READ(5,2006) (GGV(I),I=1,NOSS)
      READ(5,2006) (SSV(I),I=1,NOSS)
      READ(5,2006) (KEKEV(I),I=1,NOSS)
      READ(5,2006) (NUCNUV(I),I=1,NOSS)
      READ(5,2006) (COET(I,1),I=1,NNN)
      READ(5,2007) E(1),IX
      NDA1=1.0D+0/DFLOAT(NXT)
      NDAS=NDA1
      NDAG=NDA1
      GO TO 25
   89 DO 90 I=1,NOSS
      SSV(I)=0.0D+0
```

```
      KEKEV(I)=0.0D+0
      NUCNUV(I)=0.0D+0
      GGV(I)=0.0D+0
      SS(I)=0.0D+0
      KEKE(I)=0.0D+0
      NUCNUC(I)=0.0D+0
   90 GG(I)=0.0D+0
      IREPTX=0
      IX=65549
      NXT=0
  160 IREPTX=IREPTX+1
      NTPTS=IREPTX*NOPTS9
      WRITE(6,912) NOPTS9,IEND,IREPTX,NTPTS,PTSELT,SCHEME,RAIDS,R12IDS
  912 FORMAT('1',I6,' 9-D POINTS',I4,' TIMES',5X'CYCLE #',I2,
     1       5X'TOTAL OF',I7,' POINTS'/
     2       5X'#',I2,' PCINT SELECTION TECHNIQUE',
     3       5XI2,' DISTRIBUTION SCHEME(S)'/
     4 8X'MINIMUM R DISPLACEMENT =',1PD10.3,
     5 8X'MINIMUM R12 DISPLACEMENT =',D10.3)
      NX=0
      SEQINX=1
      INTGNO=1
      NC1=1
      NC2=1
      NC3=1
   72 NX=NX+1
      NXT=NXT+1
      IF (PTSELT-2) 48,50,52
CCCCCC      GENERATE CONROY POINTS -- CLOSED DIOPHANTINE INTEGRATION
   48 XM=DFLOAT(NX)-0.5D+0
      DO 49 J=1,9
      XXX=XM*A9(TSUB+J)
      XXX=XXX-DFLOAT(IDINT(XXX))
      IF (XXX.GT.0.5D+0) XXX=XXX-1.0D+0
   49 XX(J)=2.0D+0*DABS(XXX)
      GO TO 151
CCCCCC      GENERATE PSEUDO RANDOM NUMBERS
   50 DO 51 J=1,9
      CALL DRANDU(IX,IY,YFL)
      IX=IY
   51 XX(J)=YFL
      GO TO 151
CCCCCC      GENERATE OPEN DIOPHANTINE INTEGRATION POINTS -- EQ. (127)
   52 XM=DFLOAT(NXT)-0.5D+0
      DO 53 J=1,9
      XXX=XM*AA9(J)
      XXX=XXX-DFLOAT(IDINT(XXX))
      IF (XXX.GT.0.5D+0) XXX=XXX-1.0D+0
   53 XX(J)=2.0D+0*DABS(XXX)
CCCCCC      SELECT CENTER AND ELECTRON FOR EQ. (120)
CCCCCC      IF INTGO=2, REPLACE INTEGRATION POINT GENERATED BY D2 WITH
CCCCCC            POINT GENERATED BY D1 AND USE TO INTEGRATE REMAINING
CCCCCC            INTEGRALS (ALL INTEGRALS EXCEPT ELECT.-ELECT.
CCCCCC            REPULSICN  REMAIN)
CCCCCC      INTGO=2 POSSIBLE ONLY IF SCHEME=2
CCCCCC            -- ONLY REFERRED TO -- NOT USED IN THESIS
  151 IF (INTGNO.EQ.2) GO TO 57
      SEQIX3=3*SEQINX
      ELNTH=1
      NC=NC1
      ELN=ELSEQ(SEQIX3-2)
      GO TO 42
   57 ELNTH=2
      NC=NC2
      ELN=ELSEQ(SEQIX3-1)
      GO TO 42
   58 IF (INTGNO.EQ.2) GO TO 60
      ELNTH=3
      NC=NC3
      ELN=ELSEQ(SEQIX3)
      GO TO 42
   60 X1MX2=XXXX(1)-XXXX(2)
      X1MX3=XXXX(1)-XXXX(3)
      X2MX3=XXXX(2)-XXXX(3)
      Y1MY2=YYYY(1)-YYYY(2)
      Y1MY3=YYYY(1)-YYYY(3)
      Y2MY3=YYYY(2)-YYYY(3)
      Z1MZ2=ZZZZ(1)-ZZZZ(2)
      Z1MZ3=ZZZZ(1)-ZZZZ(3)
      Z2MZ3=ZZZZ(2)-ZZZZ(3)
      R122=(X1MX2)**2+(Y1MY2)**2+(Z1MZ2)**2
      R132=(X1MX3)**2+(Y1MY3)**2+(Z1MZ3)**2
      R232=(X2MX3)**2+(Y2MY3)**2+(Z2MZ3)**2
      R12=DSQRT(R122)
      R13=DSQRT(R132)
      R23=DSQRT(R232)
      IF (R12.GT.R12IDS.AND.R13.GT.R12IDS.AND.R23.GT.R12IDS) GO TO 93
      IF (DTAIL) WRITE(6,1015) R12,R13,R23,NX,ZGG,NC,INTGNO
 1015 FORMAT (' NOTE  ',1P3D20.10,I10,4XA6,3I10)
      IF (INTGNO.EQ.2) GO TO 157
  140 REJG=REJG+1
      GO TO 154
   93 R12E(2)=R12
      R12E(3)=R122
      R13E(2)=R13
      R13E(3)=R132
      R23E(2)=R23
      R23E(3)=R232
      IF (INTGNO.EQ.2) GO TO 152
CCCCCC      DENSITY FUNCTION EQ. (120)
      TEMP=162.0D+0
     1      /(((DT2(1)*DA(2)+DT3(1)*DB(2)+DT4(1)*DC(2)
     2          +DT2(2)*DA(1)+DT3(2)*DB(1)+DT4(2)*DC(1))*DT1(3)*R13
     3         +(DT2(1)*DA(3)+DT3(1)*DB(3)+DT4(1)*DC(3)
     4          +DT2(3)*DA(1)+DT3(3)*DB(1)+DT4(3)*DC(1))*DT1(2)*R12)*R23
     5         +(DT2(2)*DA(3)+DT3(2)*DB(3)+DT4(2)*DC(3)
     6          +DT2(3)*DA(2)+DT3(3)*DB(2)+DT4(3)*DC(2))*DT1(1)*R12*R13)
      SRIJDT=((R13+R12)*R23+R12*R13)*DT5(1)*DT5(2)*DT5(3)*TEMP
      DTT=R12*R13*R23*TEMP
      GO TO 159
CCCCCC      DENSITY FUNCTION EQ. (120) WITH D2 REPLACED BY D1
CCCCCC            -- ONLY REFERRED TO IN THESIS, NOT USED
  152 DTT=27.0D+0/(DT1(1)*DT1(2)*DT1(3))
  159 DT=DT5(1)*DT5(2)*DT5(3)*DTT
      IF (SCHEME.NE.1.AND.INTGNO.EQ.1) GO TO 153
      SRIDT=((SUMR(1)*DT5(2)+DT5(1)*SUMR(2))*DT5(3)
```

```
     1          +DT5(1)*DT5(2)*SUMR(3))*DTT
      R12I=1.0D+0/R12
      R13I=1.0D+0/R13
      R23I=1.0D+0/R23
CCCCCC      EQ. (B.8)
      LR12(2)=2.0D+0*R12I
      LR13(2)=2.0D+0*R13I
      LR23(2)=2.0D+0*R23I
CCCCCC      EQ. (B.7)
      DR12X(2)=X1MX2*R12I
      DR12X(3)=2.0D+0*X1MX2
      DR13X(2)=X1MX3*R13I
      DR13X(3)=2.0D+0*X1MX3
      DR23X(2)=X2MX3*R23I
      DR23X(3)=2.0D+0*X2MX3
      DR12Y(2)=Y1MY2*R12I
      DR12Y(3)=2.0D+0*Y1MY2
      DR13Y(2)=Y1MY3*R13I
      DR13Y(3)=2.0D+0*Y1MY3
      DR23Y(2)=Y2MY3*R23I
      DR23Y(3)=2.0D+0*Y2MY3
      DR12Z(2)=Z1MZ2*R12I
      DR12Z(3)=2.0D+0*Z1MZ2
      DR13Z(2)=Z1MZ3*R13I
      DR13Z(3)=2.0D+0*Z1MZ3
      DR23Z(2)=Z2MZ3*R23I
      DR23Z(3)=2.0D+0*Z2MZ3
  153 DO 134 JJ=1,NNN
      JJSUB=(JJ-1)*3
      L=SOINDX(JJSUB+1)
      LP=EEXP(JJSUB+1)
      M=SOINDX(JJSUB+2)
      MP=EEXP(JJSUB+2)
      N=SOINDX(JJSUB+3)
      NP=EEXP(JJSUB+3)
      SOL1=SO(L)
      SOL2=SO(MAXSO+L)
      SOL3=SO(MAXSO2+L)
      SOM1=SO(M)
      SOM2=SO(MAXSO+M)
      SOM3=SO(MAXSO2+M)
      SON1=SO(N)
      SON2=SO(MAXSO+N)
      SON3=SO(MAXSO2+N)
      R12LP=R12E(LP+1)
      R12MP=R12E(MP+1)
      R12NP=R12E(NP+1)
      R13LP=R13E(LP+1)
      R13MP=R13E(MP+1)
      R13NP=R13E(NP+1)
      R23LP=R23E(LP+1)
      R23MP=R23E(MP+1)
      R23NP=R23E(NP+1)
CCCCCC      EQ. (75)
      PSI1=SOL1*SOM2*SON3*R12LP*R13MP*R23NP
      PSI2=SON1*SOM2*SOL3*R12NP*R13MP*R23LP
      PSI3=SON1*SOL2*SOM3*R12MP*R13NP*R23LP
      PSI4=SOM1*SOL2*SON3*R12LP*R13NP*R23MP
      PSI5=SOM1*SON2*SOL3*R12NP*R13LP*R23MP
      PSI6=SOL1*SON2*SOM3*R12MP*R13LP*R23NP
CCCCCC      EQ. (76)
      KET1(JJ)=D1*(PSI1-PSI2)+D2*(PSI3-PSI4)+D3*(PSI5-PSI6)
      KET2(JJ)=D1*(PSI5-PSI4)+D2*(PSI1-PSI6)+D3*(PSI3-PSI2)
      KET3(JJ)=D1*(PSI3-PSI6)+D2*(PSI5-PSI2)+D3*(PSI1-PSI4)
      IF (SCHEME.NE.1.AND.INTGNO.EQ.1) GO TO 134
CCCCCC      SEE APPENDIX B
      LAPSI1=LAPSI(L,M,N,LP,MP,NP)
      LAPSI2=LAPSI(N,M,L,NP,MP,LP)
      LAPSI3=LAPSI(N,L,M,NP,NP,LP)
      LAPSI4=LAPSI(M,L,N,LP,NP,MP)
      LAPSI5=LAPSI(M,N,L,NP,LP,MP)
      LAPSI6=LAPSI(L,N,M,MP,LP,NP)
      KEBRA1(JJ)=D1*(LAPSI1-LAPSI2)+D2*(LAPSI3-LAPSI4)
     1                              +D3*(LAPSI5-LAPSI6)
      KEBRA2(JJ)=D1*(LAPSI5-LAPSI4)+D2*(LAPSI1-LAPSI6)
     1                              +D3*(LAPSI3-LAPSI2)
      KEBRA3(JJ)=D1*(LAPSI3-LAPSI6)+D2*(LAPSI5-LAPSI2)
     1                              +D3*(LAPSI1-LAPSI4)
  134 CONTINUE
      DO 135 II=1,NNN
      BRA1=KET1(II)
      BRA2=KET2(II)
      BRA3=KET3(II)
      IF (SCHEME.NE.1.AND.INTGNO.EQ.1) GO TO 149
      KBRA1=KEBRA1(II)
      KBRA2=KEBRA2(II)
      KBRA3=KEBRA3(II)
  149 DO 148 JJ=II,NNN
      INDEX=JJ*(JJ-1)/2+II
      KET1JJ=KET1(JJ)
      KET2JJ=KET2(JJ)
      KET3JJ=KET3(JJ)
CCCCCC      EQ. (79)
      TEMP=(BRA1*KET1JJ+BRA2*KET2JJ+BRA3*KET3JJ)*SIXTH
      BSKJ=TEMP*DT
      SS(INDEX)=SS(INDEX)+BSKJ
      SSV(INDEX)=SSV(INDEX)+BSKJ*BSKJ
      IF (INTGNO.NE.1) GO TO 150
      BEKJ=TEMP*SRIJDT
      GG(INDEX)=GG(INDEX)+BEKJ
      GGV(INDEX)=GGV(INDEX)+BEKJ*BEKJ
      IF (SCHEME.NE.1) GO TO 148
CCCCCC      EQ. (81)
  150 BKEKJ=(KBRA1*KET1JJ+KBRA2*KET2JJ+KBRA3*KET3JJ
     1      +BRA1*KEBRA1(JJ)+BRA2*KEBRA2(JJ)+BRA3*KEBRA3(JJ))
     2      *SIXTH*HALF*DT
      KEKE(INDEX)=KEKE(INDEX)+BKEKJ
      KEKEV(INDEX)=KEKEV(INDEX)+BKEKJ*BKEKJ
      BRIKJ=TEMP*SRIDT
      NUCNUC(INDEX)=NUCNUC(INDEX)+BRIKJ
      NUCNUV(INDEX)=NUCNUV(INDEX)+BRIKJ*BRIKJ
  148 CONTINUE
  135 CONTINUE
  154 CONTINUE
      INTGNO=INTGNO+1
      IF (INTGNO.LE.SCHEME) GO TO 151
```

```
      INTGNO=1
      IF (NX.GE.NOPTS9) GO TO 145
CCCCCC      PERMUTE CENTERS
      NC3=NC3+1
      IF (NC3.LE.NOCNTR) GO TO 72
      NC3=1
      NC2=NC2+1
      IF (NC2.LE.NOCNTR) GO TO 72
      NC2=1
      NC1=NC1+1
      IF (NC1.LE.NOCNTR) GO TO 72
      NC1=1
      SEQINX=SEQINX+1
      IF (SEQINX.LE.6) GO TO 72
      SEQINX=1
      GO TO 72
  145 IF (SCHEME.EQ.1) REJ1=REJG
      NDA1=1.0D+0/DFLOAT(NXT-REJ1)
      NDAS=NDA1
      IF (SCHEME.EQ.2) NDAS=1.0D+0/DFLOAT(2*NXT-REJ1-REJG)
      NDAG=1.0D+0/DFLOAT(NXT-REJG)
      IF (DTAIL) WRITE(6,1014) REJ1,NDA1,REJG,NDAG
 1014 FORMAT('0',I5,'    R POINTS REJECTED',5X'1-EL NORMALIZATION =',
     1              1PD14.7/
     2        ' ',I5,' RIJ POINTS REJECTED',5X'2-EL NORMALIZATION =',
     4                 D14.7/)
      AGGV=0.0D+0
      ASSV=0.0D+0
      AKEKEV=0.0D+0
      ANUCNV=0.0D+0
CCCCCC      EQS. (87) AND (88)
      DO 137 I=1,NOSS
      GG(I)=GG(I)*NDAG
      GGV(I)=DSQRT(GGV(I)*NDAG/GG(I)**2-1.0D+0)
      AGGV=AGGV+GGV(I)
      SS(I)=SS(I)*NDAS
      SSV(I)=DSQRT(SSV(I)*NDAS/SS(I)**2-1.0D+0)
      ASSV=ASSV+SSV(I)
      KEKE(I)=KEKE(I)*NDA1
      KEKEV(I)=DSQRT(KEKEV(I)*NDA1/KEKE(I)**2-1.0D+D)
      AKEKEV=AKEKEV+KEKEV(I)
      NUCNUC(I)=NUCNUC(I)*NDA1
      NUCNUV(I)=DSQRT(NUCNUV(I)*NDA1/NUCNUC(I)**2-1.0D+0)
  137 ANUCNV=ANUCNV+NUCNUV(I)
      RNOSSI=1.0D+0/DFLOAT(NOSS)
      AGGV=AGGV*RNOSSI
      ASSV=ASSV*RNOSSI
      AKEKEV=AKEKEV*RNOSSI
      ANUCNV=ANUCNV*RNOSSI
      IF (NPUNCH) GO TO 138
      WRITE(7,2006) (GG(I),I=1,NOSS)
      WRITE(7,2006) (SS(I),I=1,NOSS)
      WRITE(7,2006) (KEKE(I),I=1,NOSS)
      WRITE(7,2006) (NUCNUC(I),I=1,NOSS)
      WRITE(7,2006) (GGV(I),I=1,NOSS)
      WRITE(7,2006) (SSV(I),I=1,NOSS)
      WRITE(7,2006) (KEKEV(I),I=1,NOSS)
      WRITE(7,2006) (NUCNUV(I),I=1,NOSS)
  138 CONTINUE
      IF (NDTAIL) GO TO 139
      CALL OUT2S1(GG,NNN,.TRUE.,ZGG)
      CALL OUT2S1(SS,NNN,.TRUE.,ZSS)
      CALL OUT2S1(KEKE,NNN,.TRUE.,ZKEKE)
      CALL OUT2S1(NUCNUC,NNN,.TRUE.,ZNUCNU)
      CALL OUT2S1(GGV,NNN,.TRUE.,ZGGV)
      WRITE(6,926) AGGV
      CALL OUT2S1(SSV,NNN,.TRUE.,ZSSV)
      WRITE(6,926) ASSV
      CALL OUT2S1(KEKEV,NNN,.TRUE.,ZKEKEV)
      WRITE(6,926) AKEKEV
      CALL OUT2S1(NUCNUV,NNN,.TRUE.,ZNUCNV)
      WRITE(6,926) ANUCNV
      ASUMV=(AGGV+ASSV+AKEKEV+ANUCNV)*0.25D+0
      WRITE(6,926) ASUMV
  926 FORMAT(' ',109X'AVE =',1PD17.10)
  139 CONTINUE
      CALL ELAPSE(TIM9D)
      TIM9DS=FLOAT(TIM9D)/1000.0/60.0
      WRITE(6,919) TIM9DS
  919 FORMAT('0',F7.2,' MINUTES REQUIRED FOR 9-D INTEGRATION')
C     ****************************************************************
C     ****************************************************************
C     ****************************************************************
C     EIGEN-VALUES, -VECTORS AND CHECKING
C     ****************************************************************
      DO 62 I=1,NOSS
      VV(I)=-NUCNUC(I)+GG(I)
   62 HH(I)=KEKE(I)+VV(I)
      CALL OUT2S1(VV,NNN,.TRUE.,ZVV)
      CALL OUT2S1(HH,NNN,.TRUE.,ZHH)
      CALL OUT2S1(SS,NNN,.TRUE.,ZSS)
      L=0
      DO 76 I=1,NOSS
      HMAT(I)=HH(I)
   76 SMAT(I)=SS(I)
      DO 83 I=1,MXCON2
      KPP(I)=0
      DO 83 L=1,5
      COET(I,L)=0.0D+0
   83 VEC(I,L)=0.0D+0
      IF (ROOTS.EQ.0) ROOTS=5
      IF (ROOTS.GT.5) ROOTS=5
      IF (NROUT.EQ.2) ROOTS=1
      WRITE (6,917) ROOTS,NROUT
  917 FORMAT(/'0FIND ',I2,' ROOT(S) USING ROUTINE',I2)
      CALL CEIG(NNN,ROOTS,MXCON2,HMAT,SMAT,E,COET,VEC,KPP,NROUT)
      CALL OUT2(COET,MXCON2,ROOTS,MXCON2,NNN,.TRUE.,ZCOET)
      CALL OUT1(E,ROOTS,ZE)
      IF (PUNCH) WRITE(7,2006) (COET(I,1),I=1,NNN)
      IF (PUNCH) WRITE(7,2007) E(1),IX
 2006 FORMAT(1P4D20.12)
 2007 FORMAT(1PD20.12,I20)
      IF (NOELEC-3) 122,123,123
  122 REPNUC=HALF/RR23
      GO TO 125
  123 REPNUC=5.0D+0*HALF/RR23
```

```
125 KLSUB=0
    DO 77 L=1,ROOTS
    CCKE(L)=0.0D+0
    CCV(L)=REPNUC
    CCH(L)=0.0D+0
    DO 77 K=1,L
    KLSUB=KLSUB+1
 77 CCS(KLSUB)=0.0D+0
    DO 78 L=1,ROOTS
    IJSUB=0
    DO 78 J=1,NNN
    DO 78 I=1,J
    IJSUB=IJSUB+1
    CICJ=COET(I,L)*COET(J,L)
    IF (I.NE.J) CICJ=CICJ*2.0D+0
    CCKE(L)=CCKE(L)+CICJ*KEKE(IJSUB)
    CCV(L)=CCV(L)+CICJ*VV(IJSUB)
 78 CCH(L)=CCH(L)+CICJ*HH(IJSUB)
    CALL OUT1(CCH,ROOTS,ZCCH)
    CALL OUT1(CCKE,ROOTS,ZCCKE)
    CALL OUT1(CCV,ROOTS,ZCCV)
    DO 103 L=1,ROOTS
103 VRATIO(L)=CCV(L)/CCKE(L)
    CALL OUT1(VRATIO,ROOTS,ZVRAT)
    DO 128 L=1,ROOTS
    DO 128 J=1,NNN
128 OVER(J,L)=0.0D+0
    DO 133 L=1,ROOTS
    DO 130 J=1,NNN
    JSUB=J*(J-1)/2
    DO 127 I=1,NNN
    IF (J.LT.I) GO TO 129
    SSIJ=SS(JSUB+I)
    GO TO 127
129 SSIJ=SS(I*(I-1)/2+J)
127 OVER(J,L)=OVER(J,L)+COET(I,L)*SSIJ
130 OVER(J,L)=COET(J,L)*OVER(J,L)
    OVMAX=DABS(OVER(1,L))
    IF (NNN.LE.1) GO TO 132
    DO 131 J=2,NNN
    IF (DABS(OVER(J,L)).GT.OVMAX) OVMAX=DABS(OVER(J,L))
131 CONTINUE
132 OVRMAX(L)=OVMAX
133 CONTINUE
    CALL OUT1(OVRMAX,ROOTS,ZOVMAX)
    CALL OUT2(OVER,MXCON,ROOTS,MXCON,NNN,.TRUE.,ZOVER)
    KLSUB=0
    DO 79 L=1,ROOTS
    DO 79 K=1,L
    KLSUB=KLSUB+1
    DO 79 J=1,NNN
    JSUB=J*(J-1)/2
    COETJL=COET(J,L)
    DO 79 I=1,NNN
    IF (J.LT.I) GO TO 101
    SSIJ=SS(JSUB+I)
    GO TO 79
101 SSIJ=SS(I*(I-1)/2+J)
 79 CCS(KLSUB)=CCS(KLSUB)+COET(I,K)*COETJL*SSIJ
    CALL OUT2S1(CCS,ROOTS,.TRUE.,ZCCS)
    DO 100 L=1,ROOTS
    IJSUB=0
    DO 104 J=1,NNN
    DO 104 I=1,J
    IJSUB=IJSUB+1
    HES(I,J)=HH(IJSUB)-E(L)*SS(IJSUB)
104 IF (I.NE.J) HES(J,I)=HES(I,J)
    DO 102 I=1,NNN
    HESC(I)=0.0D+0
    DO 102 J=1,NNN
102 HESC(I)=HESC(I)+HES(I,J)*COET(J,L)
    WRITE(6,916) L
916 FORMAT(/'ORESUBSTITUTION OF EIGEN VALUE AND VECTOR ',I2)
    CALL OUT1(HESC,NNN,ZHESC)
    DET(L)=DTRMNT(HES,MAXCON,NNN)
100 CONTINUE
    CALL OUT1(DET,ROOTS,ZDET)
    WRITE(6,910) REPNUC
910 FORMAT(//'ONUCLEAR REPULSION ENERGY ='1PD14.7)
    DO 80 L=1,ROOTS
 80 ETOTAL(L)=E(L)+REPNUC
    CALL OUT1(ETOTAL,ROOTS,ZETOT)
    CALL ELAPSE(TIMEV)
    TIMEVS=FLOAT(TIMEV)/1000.0/60.0
    WRITE(6,920) TIMEVS
920 FORMAT('0',F7.2,' MINUTES REQUIRED FOR FINDING EIGEN VALUES + VECT
   1ORS, AND FOR CHECKING')
    TIMTS=TIM9DS+TIMEVS
    WRITE(6,923) TIMTS
923 FORMAT(/'0',F7.2,' MINUTES REQUIRED FOR CALCULATION')
    IF (IREPTX.GE.IEND) GO TO 1999
    IF (PTSELT.NE.1) GO TO 25
    SAVE=A9(TSUB+1)
    DO 158 J=1,8
158 A9(TSUB+J)=A9(TSUB+J+1)
    A9(TSUB+9)=SAVE
 25 DO 161 I=1,NOSS
    GGV(I)=(GGV(I)**2+1.0D+0)*GG(I)**2/NDAG
    GG(I)=GG(I)/NDAG
    SSV(I)=(SSV(I)**2+1.0D+0)*SS(I)**2/NDAS
    SS(I)=SS(I)/NDAS
    KEKEV(I)=(KEKEV(I)**2+1.0D+0)*KEKE(I)**2/NDA1
    KEKE(I)=KEKE(I)/NDA1
    NUCNUV(I)=(NUCNUV(I)**2+1.0D+0)*NUCNUC(I)**2/NDA1
161 NUCNUC(I)=NUCNUC(I)/NDA1
    GO TO 160
C     ****************************************************************
C     ****************************************************************
C     ****************************************************************
C     CALCULATE COORDINATES AND EVALUATE ORBITALS
C     ****************************************************************
C     CENTERS ARE IN ORDER A, B, C.
C     NC=1 INDICATES CENTER A, NC=2 INDICATES CENTER B,
C          AND NC=3 INDICATES CENTER C.
C     THE Z AXES OF THE COORDINATE SYSTEMS CENTERED ON A, B, AND C,
C          ARE ALL ORIENTED IN THE SAME DIRECTION.
```

```
   42 ELN1=ELN-1
      ROWSW=ELN1*MAXSO
      SUB=3*ELN-2
      IF (ELNTH.EQ.2.AND.INTGNO.EQ.1) GO TO 200
      ETA=XX(SUB)
CCCCCC        EQ. (103)
  136 R=RO(10.0D+0*ETA+1.0D+0)
      DO 146 J=1,20
      SSSR=SSS*R
      EXPSR=DEXP(SSSR)
      DENOM=SSSR+1.0D+0-(1.0D+0-ETA)*EXPSR
      IF (DABS(DENOM).LT.1.0D-40) DENOM=1.0D-40
      DELTR=1.0D+0/(SSS*SSSR/DENCM+HALF*(1.0D+0-SSSR)/R)
      R=R+DELTR
      IF (DABS(ETA-(1.0D+0-(SSSR+1.0D+0)/EXPSR)).LT.1.0D-14) GO TO 147
  146 CONTINUE
  147 IF (LLINIT) GO TO 3
CCCCCC        EQ. (102)
      MU=XX(SUB+1)
      COST=1.0D+0-2.0D+0*MU
      PHI=TWOPI*XX(SUB+2)
      GO TO 41
  200 IF (NC-2) 201,202,203
  201 RI=RA
      COSTI=ZA/RA
      GO TO 204
  202 RI=RB
      COSTI=ZB/RB
      GO TO 204
  203 RI=RC
      COSTI=ZC/RC
  204 SINTI=DSQRT(1.0D+0-COSTI*COSTI)
      ZETA=XX(SUB)
      XI=XX(SUB+1)
      PHIP=TWOPI*XX(SUB+2)
      CPHIP=DCOS(PHIP)
      SPHIP=DSIN(PHIP)
      SRI2M=SSSM*RI/2.0D+0
CCCCCC        EQ. (113)
      LAMBDA=1.0D+0+DLOG(1.0D+0-ZETA)/SRI2M
      MU=DLOG(1.0D+0-(1.0D+0-DEXP(2.0D+0*SRI2M))*XI)/SRI2M-1.0D+0
      LAMBMU=LAMBDA+MU
CCCCCC        EQ. (114)
      R=LAMBMU*RI/2.0D+0
      COSTP=(1.0D+0+LAMBDA*MU)/LAMBMU
      SINTP=DSQRT(1.0D+0-COSTP*COSTP)
CCCCCC        EQ. (116)
      COST=COSTP*COSTI-SINTP*SINTI*CPHIP
      PHI=PHI+DATAN2(SINTP*SPHIP,COSTP*SINTI+SINTP*CPHIP*COSTI)
   41 RSINT=R*DSQRT(1.0D+0-COST*COST)
      Z=R*COST
      R2=R*R
      TEMP1=R2+RR232
CCCCCC        CALCULATE COORDINATES WITH RESPECT TO ALL OTHER CENTERS
CCCCCC                  (SEE FIG. 2)
      TEMP2=TORR23*Z
      IF (NC-2) 141,142,143
  141 RA=R
      RA2=R2
      ZA=Z
      ZB=Z-RR23
      ZC=Z-TORR23
      RB2=TEMP1-TEMP2
      RB=DSQRT(RB2)
      RC2=4.0D+0*RR232+R2-2.0D+0*TEMP2
      RC=DSQRT(RC2)
      GO TO 144
  142 RB=R
      RB2=R2
      ZA=Z+RR23
      ZB=Z
      ZC=Z-RR23
      RA2=TEMP1+TEMP2
      RA=DSQRT(RA2)
      RC2=TEMP1-TEMP2
      RC=DSQRT(RC2)
      GO TO 144
  143 RC=R
      RC2=R2
      ZA=Z+TORR23
      ZB=Z+RR23
      ZC=Z
      RA2=4.0D+0*RR232+R2+2.0D+0*TEMP2
      RA=DSQRT(RA2)
      RB2=TEMP1+TEMP2
      RB=DSQRT(RB2)
  144 IF (RA.GT.RAIDS.AND.RB.GT.RAIDS.AND.RC.GT.RAIDS) GO TO 47
      IF (DTAIL) WRITE(6,1015) RA,RB,RC,NX,ZNUCNU,NC,SUB,INTGNO
      IF (INTGNO.EQ.1) GO TO 140
  157 REJ1=REJ1+1
      GO TO 154
CCCCCC        CALCULATE COMPONENTS OF INTEGRATION POINT DENSITY FUNCTION
   47 ESMRA=DEXP(SSSM*RA)
      ESMRB=DEXP(SSSM*RB)
      ESMRC=DEXP(SSSM*RC)
      RARB=RA*RB
      ESMRAP=RB*RC*ESMRA*S24PI
      ESMRBP=RA*RC*ESMRB*S24PI
      ESMRCP=RARB*ESMRC*S24PI
      TEMP=ESMRAP+ESMRBP+ESMRCP
      DT1(ELN)=TEMP
      IF (INTGNO.EQ.2) GO TO 156
      DT2(ELN)=TEMP*RA/(1.0D+0-ESMRA)
      DT3(ELN)=TEMP*RB/(1.0D+0-ESMRB)
      DT4(ELN)=TEMP*RC/(1.0D+0-ESMRC)
      DA(ELN)=ESMRAP
      DB(ELN)=ESMRBP
      DC(ELN)=ESMRCP
  156 DT5(ELN)=RARB*RC
      SUMR(ELN)=(RB+RA)*RC+RARB
      X=RSINT*DCOS(PHI)
      Y=RSINT*DSIN(PHI)
      XXXX(ELN)=X
      YYYY(ELN)=Y
      ZZZZ(ELN)=ZB
CCCCCC        EQ. (37) AND TABLE II
```

```
      AO1A=XNOR1*DEXP(ZZ1M*RA)
      AO1B=XNOR2*DEXP(ZZ2M*RB)
      AO1C=XNOR1*DEXP(ZZ1M*RC)
      AO2A=XNOR3*RA*DEXP(ZZ3M*RA)
      AO2C=XNOR3*RC*DEXP(ZZ3M*RC)
      SO(ROWSW+1)=AO1B
      SO(ROWSW+2)=AO1A+AO1C
      SO(ROWSW+3)=AO1A-AO1C
      SO(ROWSW+4)=AO2A-AO2C
      IF (SCHEME.NE.1.AND.ELNTH.EQ.2.AND.INTGNO.EQ.1) GO TO 155
      RAI=1.0D+0/RA
      RBI=1.0D+0/RB
      RCI=1.0D+0/RC
CCCCCC      EQ. (B.4)
      Z1RA1=ZZ1M*RAI*AO1A
      DAO1AX=X*Z1RA1
      DAO1AY=Y*Z1RA1
      DAO1AZ=ZA*Z1RA1
      Z2RB1=ZZ2M*RBI*AO1B
      DAO1BX=X*Z2RB1
      DAO1BY=Y*Z2RB1
      DAO1BZ=ZB*Z2RB1
      Z1RC1=ZZ1M*RCI*AO1C
      DAO1CX=X*Z1RC1
      DAO1CY=Y*Z1RC1
      DAO1CZ=ZC*Z1RC1
      RAI2=RAI*RAI
      RCI2=RCI*RCI
      Z3RA2=(RAI2-ZZ3*RAI)*AO2A
      DAO2AX=X*Z3RA2
      DAO2AY=Y*Z3RA2
      DAO2AZ=ZA*Z3RA2
      Z3RC2=(RCI2-ZZ3*RCI)*AO2C
      DAO2CX=X*Z3RC2
      DAO2CY=Y*Z3RC2
      DAO2CZ=ZC*Z3RC2
CCCCCC      EQ. (B.8)
      LAO1A=(ZZ12-TOZZ1N*RAI)*AO1A
      LAO1B=(ZZ22-TOZZ2N*RBI)*AO1B
      LAO1C=(ZZ12-TOZZ1N*RCI)*AO1C
      LAO2A=(ZZ32-4.0D+0*ZZ3*RAI+2.0D+0*RAI2)*AO2A
      LAO2C=(ZZ32-4.0D+0*ZZ3*RCI+2.0D+0*RCI2)*AO2C
      INDEX=ROWSW+1
      DSOX(INDEX)=DAO1BX
      DSOY(INDEX)=DAO1BY
      DSOZ(INDEX)=DAO1BZ
      LSO(INDEX)=LAO1B
      INDEX=ROWSW+2
      DSOX(INDEX)=DAO1AX+DAO1CX
      DSOY(INDEX)=DAO1AY+DAO1CY
      DSOZ(INDEX)=DAO1AZ+DAO1CZ
      LSO(INDEX)=LAO1A+LAO1C
      INDEX=ROWSW+3
      DSOX(INDEX)=DAO1AX-DAO1CX
      DSOY(INDEX)=DAO1AY-DAO1CY
      DSOZ(INDEX)=DAO1AZ-DAO1CZ
      LSO(INDEX)=LAO1A-LAO1C
      INDEX=ROWSW+4
      DSOX(INDEX)=DAO2AX-DAO2CX
      DSOY(INDEX)=DAO2AY-DAO2CY
      DSOZ(INDEX)=DAO2AZ-DAO2CZ
      LSO(INDEX)=LAO2A-LAO2C
  155 IF (ELNTH-2) 57,58,60
 9000 STOP
      END
```

```
                                  OS/360  FORTRAN H

    OPTIONS - NAME=  MAIN,OPT=02,LINECNT=60,SOURCE,EBCDIC,NOLIST,NODECK
      FUNCTION LAPSI(I,J,K,IP,JP,KP)
CCCCCC      SEE APPENDIX B
      IMPLICIT REAL*8(A-H,L,O-Z)
      COMMON /KEGRUP/SO(45),LSO(45),DSOX(45),DSOY(45),DSOZ(45),
     2               DR12X(4),DR13X(4),DR23X(4),R12E(4),LR12(4),
     3               DR12Y(4),DR13Y(4),DR23Y(4),R13E(4),LR13(4),
     4               DR12Z(4),DR13Z(4),DR23Z(4),R23E(4),LR23(4),
     5               MAXSO,MAXSO2,HALF
      R12IP=R12E(IP+1)
      R13JP=R13E(JP+1)
      R23KP=R23E(KP+1)
      SOI=SO(I)
      SOJ=SO(MAXSO+J)
      SOK=SO(MAXSO2+K)
      SOIJK=SOI*SOJ*SOK
      DR12IX=DR12X(IP+1)
      DR12IY=DR12Y(IP+1)
      DR12IZ=DR12Z(IP+1)
      DR13JX=DR13X(JP+1)
      DR13JY=DR13Y(JP+1)
      DR13JZ=DR13Z(JP+1)
      DR23KX=DR23X(KP+1)
      DR23KY=DR23Y(KP+I)
      DR23KZ=DR23Z(KP+I)
      DSOIX=DSOX(I)
      DSOIY=DSOY(I)
      DSOIZ=DSOZ(I)
      INDEX=MAXSO+J
      DSOJX=DSOX(INDEX)
      DSOJY=DSOY(INDEX)
      DSOJZ=DSOZ(INDEX)
      INDEX=MAXSO2+K
      DSOKX=DSOX(INDEX)
      DSOKY=DSOY(INDEX)
      DSOKZ=DSOZ(INDEX)
      LAPSI=((LR12(IP+1)*R13JP+R12IP*LR13(JP+1))*R23KP
     1       +R12IP*R13JP*LR23(KP+1)
     2     +(DR12IX*DR13JX+DR12IY*DR13JY+DR12IZ*DR13JZ)*R23KP
     3     -(DR12IX*DR23KX+DR12IY*DR23KY+DR12IZ*DR23KZ)*R13JP
     4     +(DR13JX*DR23KX+DR13JY*DR23KY+DR13JZ*DR23KZ)*R12IP)*SOIJK
     5    +((DSOIX*DR13JX+DSOIY*DR13JY+DSOIZ*DR13JZ)*R12IP
     6     +(DSOIX*DR12IX+DSOIY*DR12IY+DSOIZ*DR12IZ)*R13JP)
     7       *R23KP*SOJ*SOK
      LAPSI=0.D+0-(LAPSI+((DSOJX*DR23KX+DSOJY*DR23KY+DSOJZ*DR23KZ)*R12IP
     1     -(DSOJX*DR12IX+DSOJY*DR12IY+DSOJZ*DR12IZ)*R23KP)
     2       *R13JP*SOI*SOK
     3    -((DSOKX*DR23KX+DSOKY*DR23KY+DSOKZ*DR23KZ)*R13JP
     4     +(DSOKX*DR13JX+DSOKY*DR13JY+DSOKZ*DR13JZ)*R23KP)
     5       *R12IP*SOI*SOJ
     6     +HALF*((LSO(I)*SOJ+SOI*LSO(MAXSO+J))*SOK
     7       +SOI*SOJ*LSO(MAXSO2+K))*R12IP*R13JP*R23KP)
      RETURN
      END
```

```
                                  OS/360  FORTRAN H

    OPTIONS - NAME=  MAIN,OPT=02,LINECNT=60,SOURCE,EBCDIC,NOLIST,NODECK
      SUBROUTINE DRANDU(IX,IY,YFL)
      REAL*8 YFL
      IY=IX*65539
      IF (IY.GE.0) GO TO 6
      IY=IY+2147483647+1
    6 YFL=IY
      YFL=YFL*0.4656612873077393D-9
      RETURN
      END
```

OS/360 FORTRAN H

```
OPTIONS - NAME=  MAIN,OPT=02,LINECNT=60,SOURCE,EBCDIC,NOLIST,NODECK
      SUBROUTINE CEIG (N,N1,NN,HMAT,SMAT,E,COET,VEC,KP,NROUT)
      IMPLICIT REAL*8(A-H,O-Z)
CCEIG
C
C     SUBROUTINE SOLVES SECULAR EQUATIONS OF FORM (H-LS)X=0, WHERE L
C     IS A SCALAR. THIS ROUTINE BEGINS BY TRIANGULARIZATION OF  S
C     FOLLOWED BY A SINGLE DIAGONALIZATION. CMAT (WHICH CAN OCCUPY THE
C     SAME LOCATION AS THE ORIGINAL OVERLAP MATRIX, SMAT) * CMAT TRANS-
C     POSE = SMAT. THE TRANSFORMED HMAT IS STORED BACK OVER THE ORIGINAL
C     HMAT BEFORE THE DIAGONALIZATION ROUTINE GIVENS IS CALLED AND THUS
C     DESTROYS THE ORIGINAL HAMILTONIAN MATRIX. THE PARAMETERS ARE...
C     N     SIZE OF MATRIX BEING DIAGONALIZED
C     N1    NUMBER OF ROOTS WANTED.
C     NN    FORTRAN DIMENSION OF THE MATRIX IN THE CALLING PROGRAM.
C     HMAT HAMILTONIAN MATRIX - INPUT
C     SMAT OVERLAP MATRIX - INPUT
C     E     EIGENVALUE - OUTPUT
C     COET EIGENVECTOR - OUTPUT
C     VEC  TEMPORARY STORAGE
C     KP   TEMPORARY STORAGE
      DIMENSION E(1), HMAT(1), SMAT(1), VEC(NN,5), COET(NN,NN), KP(1)
      DO 30 I=1,N
 30   KP(I) = (I*(I-1))/2
      COET(1,1) =DSQRT(SMAT(1))
C     CMAT(1) = 1.0/ COET(1,1)
      SMAT(1) = 1.0/ COET(1,1)
C     CMAT HAS BEEN REPLACED HERE BY SMAT BECAUSE FORTRAN RULES SPECIFY
C     THAT A VARIABLE APPEARING IN THE CALLING SEQUENCE CANNOT BE EQUI-
C     VALENCED TO ANOTHER VARIABLE. ALL ORIGINAL STATEMENTS USING CMAT
C     ARE SAVED ON COMMENT CARDS SO THAT THE USER CAN FOLLOW THE LOGIC
C     MORE READILY.
      IF(N-1)  2,2,3
 3    DO 10 J = 2,N
      III = KP(J) +1
 10   COET(1,J) = SMAT(III)/COET(1,1)
      DO 11 I = 2,N
      SUM = 0.0
      III=KP(I)+I
      IM1 = I-1
      IP1 = I+1
      DO 12 K = 1,IM1
 12   SUM = SUM + COET(K,I)**2
      COET(I,I) =DSQRT(SMAT(III) - SUM)
C     CMAT(III) = 1.0/ COET(I,I)
      SMAT(III) = 1.0/ COET(I,I)
      IF(IP1-N)  6,6,4
 6    DO 13 J = IP1,N
      SUM = 0.0
      DO 14 K = 1,IM1
 14   SUM = SUM +COET(K,I)*COET(K,J)
      III = KP(J) +I
 13   COET(I,J) =(SMAT(III) - SUM)/COET(I,I)
 4    II = I-1
      DO 16 I1 = 1,IM1
      IJW = II  +  KP(I)
      SUM = 0.0
      IIP = II+1
      DO 15 K = IIP,I
      KJW = K +  KP(I)
C 15  SUM = SUM +  COET(II,K) * CMAT(KJW)
  15  SUM = SUM +  COET(II,K) * SMAT(KJW)
C     CMAT(IJW) =  - SUM/ COET(II,II)
      SMAT(IJW) =  - SUM/ COET(II,II)
  16  II = II-1
  11  CONTINUE
  2   DO 40  J1=1,N
      DO 40  L=1,J1
      COET (L,J1)=0.0
      DO 41  K=1,J1
      KJ1 = K + KP(J1)
      IF(L-K)  42,42,43
 43   III=K+KP(L)
      GO TO 41
 42   III=L+KP(K)
C 41  COET(L,J1) = COET(L,J1) + HMAT(III) * CMAT(KJ1)
  41  COET(L,J1) = COET(L,J1) + HMAT(III) * SMAT(KJ1)
 40   CONTINUE
      DO 44  J1=1,N
      DO 44  I1=1,J1
      KKK = I1 + KP(J1)
C     W(KKK) = 0.0
      HMAT(KKK) = 0.0
C     HMAT REPLACES W FOR THE SAME REASON THAT SMAT REPLACES CMAT.
      DO 44  L=1,I1
      LI1 = L + KP(I1)
C 44  W(KKK) = W(KKK) + CMAT(LI1)*COET(L,J1)
 44   HMAT(KKK) = HMAT(KKK) + SMAT(LI1)*COET(L,J1)
      GO TO (64,65),NROUT
   64 CALL GIVENS (N,N1,NN,HMAT,VEC,E,COET)
      GO TO 66
   65 CALL NESBET (N,N1,NN,HMAT,KP,E,COET)
   66 N1ABS=IABS(N1)
  63  DO 61 J = 1,N1ABS
      DO 60  I=1,N
      VEC(I,1) = 0.
      DO 60 JJ = I ,N
      IJJ = I + KP(JJ)
C 60  VEC(I,1) = VEC(I,1) +CMAT(IJJ)*COET(JJ,J)
  60  VEC(I,1) = VEC(I,1) +SMAT(IJJ)*COET(JJ,J)
      DO 50 I = 1,N
  50  COET(I,J) = VEC(I,1)
  61  CONTINUE
      RETURN
      END
```

OS/360 FORTRAN H

```
OPTIONS - NAME=  MAIN,OPT=02,LINECNT=60,SOURCE,EBCDIC,NOLIST,NODECK
      SUBROUTINE NESBET(N,NROOTX,NN,H,KP,E,C)
      IMPLICIT REAL*8(A-H,C-Z)
      DIMENSION H(1),KP(1),E(1),C(NN,NN)
      TOL=1.D-14
      DO 30 I=1,N
   30 KP(I)=(I*(I-1))/2
      NROOTX=1
      CA=2.0D+0
      CTEST=0.0999D+0
      DO 5 I=1,N
    5 C(I,1)=0.0D+0
   48 E(1)=10.0D+0
      DO 50 J=1,N
      JJJ=J+KP(J)
      IF(E(1)-H(JJJ))50,50,52
   52 E(1)=H(JJJ)
      JS=J
   50 CONTINUE
      JJS=JS+KP(JS)
      C(JS,1)=1.0D+0
      IF(N-1)43,43,55
   55 JS2=0
      DO 70 J=1,N
      IF(J.EQ.JS)GO TO 70
      JJJ=J+KP(J)
      IF(E(1).LT.H(JJJ))GO TO 70
   71 J12=JS+KP(J)
      IF(H(J12).EQ.0.0D+0) GO TO 70
      JS2=J
      GO TO 72
   70 CONTINUE
   72 IF(JS2.EQ.0) GO TO 73
      H12=H(J12)
      E(1)=H(JJS)-DABS(H12)
      C(JS2,1)=DSIGN(1.D+0,-H12)
   73 CONTINUE
    8 CMAX=0.0D+0
      DO 3 J=1,N
      IF(J-JS)9,3,9
    9 SIG=-E(1)*C(J,1)
      JJJ=J+KP(J)
      DO 4 I=1,N
      IF(I-J)1,1,2
    2 IJJ=J+KP(I)
      GO TO 4
    1 IJJ=I+KP(J)
    4 SIG=SIG+H(IJJ)*C(I,1)
   21 DELC=SIG/(E(1)-H(JJJ))
    7 DELD=(C(J,1)+C(J,1)+DELC)*DELC
      D=0.0D+0
      DO 6 K=1,N
    6 D=D+C(K,1)**2
   22 DELE=SIG*DELC/(D+DELD)
   24 C(J,1)=C(J,1)+DELC
      CMAX=DMAX1(CMAX,DABS(DELC))
   25 E(1)=E(1)+DELE
   26 IF(DABS(DELC)-CA)3,3,8
    3 CONTINUE
      CA=CA/2.0D+0
   31 IF(CMAX-CTEST)13,13,8
   13 CTEST=.01D+0*CTEST
      E1=0.D+0
      D=0.D+0
      DO 36 KI=1,N
      D=D+C(KI,1)**2
      DO 36 KJ=KI,N
      KKK=KI+KP(KJ)
      TERM=C(KI,1)*C(KJ,1)*H(KKK)
      IF(KI-KJ)35,34,35
   34 E1=E1+TERM
      GO TO 36
   35 E1=E1+TERM+TERM
   36 CONTINUE
      E(1)=E1/D
      IF(CMAX-TOL)59,59,8
   59 BRAFN=H(JJS)-E(1)
      DO 60 I=1,N
      IF(I-JS)61,60,62
   61 KI=I+KP(JS)
      GO TO 63
   62 KI=JS+KP(I)
   63 BRAFN=BRAFN+H(KI)*C(I,1)
   60 CONTINUE
      E(1)=E(1)+BRAFN/D
   32 D=DSQRT(D)
      DO 16 I=1,N
   16 C(I,1)=C(I,1)/D
   43 RETURN
      END
```

```
                        OS/360  FORTRAN H

OPTIONS - NAME=  MAIN,OPT=02,LINECNT=60,SOURCE,EBCDIC,NOLIST,NODECK
  SUBROUTINE GIVENS(NX,NROOTX,NJX,A,B,ROOT,VECT)
  IMPLICIT REAL*8(A-H,O-Z)
   DIMENSION B(NX,5),A(1),ROOT(NROOTX),VECT(NJX,NROOTX)
   EQUIVALENCE (TEMP,ITEMP), (TM,ITM)
  RETURN
  END
```

```
                        OS/360  FORTRAN H

OPTIONS - NAME=  MAIN,OPT=02,LINECNT=60,SOURCE,EBCDIC,NOLIST,NODECK
  FUNCTION DTRMNT(A,NN,N)
  IMPLICIT REAL*8 (A-H,O-Z)
  DIMENSION A(NN,NN)
  DTRMNT=A(1,1)
  IF (N.EQ.1) RETURN
  DTRMNT=1.0D+0
  N1=N-1
  DO 8 L=1,N1
  AIJMAX=DABS(A(L,L))
  MAXROW=L
  MAXCOL=L
  DO 1 I=L,N
  DO 1 J=L,N
  IF (DABS(A(I,J)).LE.AIJMAX) GO TO 1
  AIJMAX=DABS(A(I,J))
  MAXROW=I
  MAXCOL=J
1 CONTINUE
  IF (MAXCOL.EQ.L) GO TO 3
  DO 2 I=L,N
  SAVE=A(I,L)
  A(I,L)=A(I,MAXCOL)
2 A(I,MAXCOL)=SAVE
  DTRMNT=DTRMNT*(-1.0D+0)
3 IF (MAXROW.EQ.L) GO TO 5
  DO 4 J=L,N
  SAVE=A(L,J)
  A(L,J)=A(MAXROW,J)
4 A(MAXROW,J)=SAVE
  DTRMNT=DTRMNT*(-1.0D+0)
5 L1=L+1
  DO 6 I=L1,N
  RATIO=A(I,L)/A(L,L)
  DO 6 J=L1,N
6 A(I,J)=A(I,J)-RATIO*A(L,J)
8 CONTINUE
  DO 7 I=1,N
7 DTRMNT=DTRMNT*A(I,I)
  RETURN
  END
```

```
                        OS/360  FORTRAN H

OPTIONS - NAME=  MAIN,OPT=02,LINECNT=60,SOURCE,EBCDIC,NOLIST,NODECK
  SUBROUTINE OUT1(XXXXXX,N,ZZZZ)
  IMPLICIT REAL*8 (A-H,O-Z)
  DIMENSION XXXXXX(N)
  WRITE(6,1)
1 FORMAT(1H0)
  WRITE(6,2) (ZZZZ,J,XXXXXX(J),J=1,N)
2 FORMAT(1P4(1XA6,1H(,I2,3H) =,D20.13))
  RETURN
  END
```

```
                        OS/360  FORTRAN H

OPTIONS - NAME=  MAIN,OPT=02,LINECNT=60,SOURCE,EBCDIC,NOLIST,NODECK
  SUBROUTINE OUT2(XXXXXX,N,NMAX,M,MAX,TRANS,ZZZZ)
  IMPLICIT REAL*8 (A-H,O-Z)
  LOGICAL TRANS
  DIMENSION XXXXXX(N,N)
  WRITE(6,1)
1 FORMAT(///)
  JMAX=MAX
  DO 3 I=1,NMAX
  IF (MAX.EQ.0) JMAX=I
  IF (.NOT.TRANS) GO TO 2
  WRITE(6,4) (ZZZZ,J,I,XXXXXX(J,I),J=1,JMAX)
  GO TO 3
2 WRITE(6,4) (ZZZZ,I,J,XXXXXX(I,J),J=1,JMAX)
3 CONTINUE
4 FORMAT(1P4(1XA6,'(',I2,',',I2,') =',D17.10))
  RETURN
  END
```

```
                        OS/360  FORTRAN H

OPTIONS - NAME=  MAIN,OPT=02,LINECNT=60,SOURCE,EBCDIC,NOLIST,NODECK
  SUBROUTINE OUT2S1(A,N,UP,Z)
  IMPLICIT REAL*8 (A-H,O-Z)
  LOGICAL UP
  DIMENSION A(1)
  WRITE(6,5)
5 FORMAT(/)
  IF (.NOT.UP) GO TO 3
  DO 1 J=1,N
  JSUB=J*(J-1)/2
1 WRITE(6,2) (Z,I,J,A(JSUB+I),I=1,J)
2 FORMAT(1P4(' ',A6,'(',I2,',',I2,') =',D17.10))
  RETURN
3 NM1=N-1
  MAXAL=N*(N-1)/2
  DO 4 J=1,NM1
  JP1=J+1
  NMJ=N-J
  JSUB=MAXAL-NMJ*(NMJ+1)/2-J
4 WRITE(6,2) (Z,I,J,A(JSUB+I),I=JP1,N)
  RETURN
  END
```

```
  LOC  OBJECT CODE    ADDR1 ADDR2  STMT   SOURCE STATEMENT

000000                               1 ELAPSE   START 0
000000 47FF 000C            0000C    2          BC    15,12(15) BRANCH AROUND CONSTANTS
000004 07                            3          DC    X'7'
000005 C5D3C1D7E2C540                4          DC    CL7'ELAPSE '
00000C 90E5 D00C            0000C    5          STM   14,5,12(13)
000010 0540                          6          BALR  4,0
000012                               7          USING *,4        ESTABLISH 4 AS BASE REG.
000012 5851 0000            00000    8          L     5,0(1)   PLACE ADDRESS OF ARG IN REG. 5
                                     9          TTIMER CANCEL  PLACE DECREMENTD TIMER IN REG 0
000016 4110 0001            00001   10+         LA    1,1(0,0) INDICATE CANCEL
00001A 0A2E                         11+         SVC   46 ISSUE TTIMER SVC
00001C 5830 402E            00040   12          L     3,GO     LOAD ORIGINAL VALUE OF TIMER
000020 1B30                         13          SR    3,0      SUBTRACT PRESENT VALUE
000022 5C20 4036            00048   14          M     2,=F'26' MULTIPLY TIMER UNITS BY 26 GIVING MICROSEC.
000026 5D20 403A            0004C   15          D     2,=F'1000'       DIVIDE BY 1000 GIVING MILLISEC
00002A 5035 0000            00000   16          ST    3,0(5)   STORE ELAPSED TIME IN ARG
                                    17          STIMER TASK,,TUINTVL=GO  START TIMER FOR NEXT CALL
00002E 4110 402E            00040   18+         LA    1,GO LOAD PARAMETER REG 1
000032 1B00                         19+         SR    0,0 INDICATE TASK,TUINTVL=
000034 0A2F                         20+         SVC   47 ISSUE STIMER SVC
000036 9825 D01C            0001C   21          LM    2,5,28(13)  RESTORE REGISTERS
00003A 92FF D00C      0000C         22          MVI   12(13),X'FF' INDICATE CONTROL TO FORTRAN
00003E 07FE                         23          BCR   15,14
000040                              24          DS    0F
000040 7FFFFFFF                     25 GO       DC    X'7FFFFFFF'    DEFINE INITIAL VALUE OF TIMER
                                    26          END
000048 0000001A                     27                =F'26'
00004C 000003E8                     28                =F'1000'
```

TABLE X

SAMPLE INPUT DATA FOR H_3 PROGRAM

Column Number

```
         11111111112222222222333333333344444444445555555555666666666677777777778
12345678901234567890123456789012345678901234567890123456789012345678901234567890
         TRUE                                    FALSE
  1                1         1         3              0    0    0
  2                1         2         3              1    0    0
  3                1         1         3              1    1    1
999
  1                     1.1303
  2                     1.2796
  3                     1.0663
999
            1    3 1  1.00D-03          2000                  1.00D-03       1 2
   1.7924      1.540
```

DETAIL = T PUNCH = F

CD.NO.	CONF.	SO.1	SO.2	SO.3	R12	R13	R23
1	1	1	1	3	0	0	0
2	2	1	2	3	1	0	0
3	3	1	1	3	1	1	1

3 ELECTRON SYSTEM

	EXPONENT(S)	VALUE
1	1	1.13030D 00
2	2	1.27960D 00
3	3	1.06630D 00

R23	SSS
1.79240D 00	1.54000D 00

```
2106 9-D POINTS   1 TIMES     CYCLE # 1     TOTAL OF   2106 POINTS
  # 3 POINT SELECTION TECHNIQUE       1 DISTRIBUTION SCHEME(S)
     MINIMUM R DISPLACEMENT = 1.000D-03         MINIMUM R12 DISPLACEMENT = 1.000D-03

  0   R POINTS REJECTED     1-EL NORMALIZATION = 4.7483381D-04
  0 RIJ POINTS REJECTED     2-EL NORMALIZATION = 4.7483381D-04


  GG( 1, 1) = 2.7602531504D 00
  GG( 1, 2) = 5.1487519440D 00     GG( 2, 2) = 3.5448609162D 01
  GG( 1, 3) = 2.8002606747D 01     GG( 2, 3) = 8.1600166994D 01     GG( 3, 3) = 6.1709777979D 02


  SS( 1, 1) = 1.6465786139D 00
  SS( 1, 2) = 3.6764862198D 00     SS( 2, 2) = 2.6692337821D 01
  SS( 1, 3) = 2.2560823061D 01     SS( 2, 3) = 7.6600291702D 01     SS( 3, 3) = 6.2852517816D 02


KEKE( 1, 1) = 3.9254492477D 00
KEKE( 1, 2) = 5.6806720791D 00   KEKE( 2, 2) = 5.0771155330D 01
KEKE( 1, 3) = 3.4335485228D 01   KEKE( 2, 3) = 9.0716605892D 01   KEKE( 3, 3) = 8.6265309242D 02


NUCNUC( 1, 1) = 1.0946105091D 01
NUCNUC( 1, 2) = 2.2212660651D 01 NUCNUC( 2, 2) = 1.5406381632D 02
NUCNUC( 1, 3) = 1.3072613374D 02 NUCNUC( 2, 3) = 4.0585807165D 02 NUCNUC( 3, 3) = 3.1965721934D 03


  GGV( 1, 1) = 1.4315826944D 00
  GGV( 1, 2) = 8.8139533851D-01    GGV( 2, 2) = 1.2920353487D 00
  GGV( 1, 3) = 1.3831724880D 00    GGV( 2, 3) = 1.2141063919D 00    GGV( 3, 3) = 2.1904773940D 00
                                                                                                  AVE = 1.3987949426D 00


  SSV( 1, 1) = 1.3085531947D 00
  SSV( 1, 2) = 9.3775858521D-01    SSV( 2, 2) = 1.3432275926D 00
  SSV( 1, 3) = 1.5556338963D 00    SSV( 2, 3) = 1.5185099897D 00    SSV( 3, 3) = 2.6884762441D 00
                                                                                                  AVE = 1.5586932504D 00


 KEKEV( 1, 1) = 1.7437705273D 00
 KEKEV( 1, 2) = 1.2120131711D 00  KEKEV( 2, 2) = 1.6352582145D 00
 KEKEV( 1, 3) = 2.0262241003D 00  KEKEV( 2, 3) = 1.6770693754D 00  KEKEV( 3, 3) = 2.8329710836D 00
                                                                                                  AVE = 1.8545510787D 00


NUCNUV( 1, 1) = 1.3289504909D 00
NUCNUV( 1, 2) = 8.4653171104D-01 NUCNUV( 2, 2) = 1.2344156405D 00
NUCNUV( 1, 3) = 1.3944524619D 00 NUCNUV( 2, 3) = 1.2505602483D 00 NUCNUV( 3, 3) = 2.2544486867D 00
                                                                                                  AVE = 1.3848932066D 00
                                                                                                  AVE = 1.5492331196D 00

  1.08 MINUTES REQUIRED FOR 9-D INTEGRATION


  VV( 1, 1) =-8.1858519405D 00
  VV( 1, 2) =-1.7063908707D 01     VV( 2, 2) =-1.1861520716D 02
  VV( 1, 3) =-1.0272352700D 02     VV( 2, 3) =-3.2425790465D 02     VV( 3, 3) =-2.5794744136D 03


  HH( 1, 1) =-4.2604026928D 00
  HH( 1, 2) =-1.1383236628D 01     HH( 2, 2) =-6.7844051832D 01
  HH( 1, 3) =-6.8388041770D 01     HH( 2, 3) =-2.3354129876D 02     HH( 3, 3) =-1.7168213212D 03
```

```
   SS( 1, 1) = 1.64657861390 00
   SS( 1, 2) = 3.67648621980 00      SS( 2, 2) = 2.66923378210 01
   SS( 1, 3) = 2.25608230610 01      SS( 2, 3) = 7.66002917020 01      SS( 3, 3) = 6.28525178160 02

FIND  1 ROOT(S) USING ROUTINE 2


  COET( 1, 1) = 2.64718952890-01   COET( 2, 1) = 5.74882080980-02   COET( 3, 1) = 2.03912971780-02

     E( 1) =-2.86895201937250 00

   CCH( 1) =-2.86895201937250 00

  CCKE( 1) = 1.55783852968400 00

   CCV( 1) =-3.03201259770630 00

VRATIO( 1) =-1.94629452278430 00

OVRMAX( 1) = 4.72921788275640-01


  OVER( 1, 1) = 2.93117901310-01   OVER( 2, 1) = 2.33960310420-01   OVER( 3, 1) = 4.72921788280-01

   CCS( 1, 1) = 1.00000000000 00

RESUBSTITUTION OF EIGEN VALUE AND VECTOR  1

  HESC( 1) =-1.38777878078140-16   HESC( 2) =-5.55111512312580-17   HESC( 3) = 3.33066907387550-15

   DET( 1) = 2.74305884837300-13

NUCLEAR REPULSION ENERGY = 1.39477800 00

ETOTAL( 1) =-1.47417406802230 00
   0.00 MINUTES REQUIRED FOR FINDING EIGEN VALUES + VECTORS, AND FOR CHECKING

   1.09 MINUTES REQUIRED FOR CALCULATION
```

VITA

Daniel James Mickish

Candidate for the Degree of

Doctor of Philosophy

Thesis: *AB INITIO* CALCULATIONS ON THE LITHIUM AND H_3 SYSTEMS USING EXPLICITLY CORRELATED WAVE FUNCTIONS AND QUASIRANDOM INTEGRATION TECHNIQUES

Major Field: Physics

Biographical:

Personal Data: Born in Geneva, Nebraska, July 11, 1944, the son of Albert and Mildred Mickish.

Education: Graduated from Senior High School, Edmond, Oklahoma, in May 1962; received the Bachelor of Science degree with a major in mathematics and physics from Central State University, Edmond, Oklahoma, in May, 1966; awarded National Science Foundation Traineeship, 1966-1969; attended the University of Uppsala, Sweden, Summer of 1968; completed requirements for the Doctor of Philosophy degree at Oklahoma State University in July, 1971.

Professional Experience: Programmer, Central State University, 1962-1966; Instructor, Central State University Mathematics Department, 1966; Operations Supervisor, Oklahoma State University Computer Center, Summer 1966; Graduate Teaching Assistant, Oklahoma State University Physics Department, 1969-1971.

Professional Organizations: American Institute of Physics Student Section, Sigma Pi Sigma National Physics Honor Society, Sigma Xi Honorary Research Society.

Publications: "Simplified Self Consistent Field Calculations for Sigma-Bonded Systems III: Extension to Hydrogen Bonding", with H. A. Pohl, SIGMA MOLECULAR ORBITAL THEORY, ed. by O. Sinanoğlu and K. Wiberg.