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THE APPLICATION OF PERTURBATION THEORY TOWARD THE DETERMINATION OF MOLECULAR ENERGIES AND PROPERTIES

by

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ABSTRACT

The ground state energy of the hydrogen molecule is accurately determined with the aid of Rayleigh Schroedinger perturbation theory, treating the electronic interaction as a perturbation to the remaining Hamiltonian. Techniques are developed for evaluating integrals containing zeroth order H_2^+ wave functions. A generalized Hylleraas variational method is used to determine wave functions beyond zeroth order.

The perturbation energy through fifth order at the equilibrium separation is found to be comparable in accuracy to the most accurate variational calculations.

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CHAPTER I

INTRODUCTION

In principle, the time-independent Schroedinger equation combined with the Pauli exclusion principle is capable of describing most molecular systems. In practice, mathematical difficulties associated with its solution have, until quite recently, been practically insurmountable. The changing complexion of the problem is attributable to the rapid development of high speed electronic computors.

A. Approximate Solutions to Schroedinger Equation

Various approximate methods for the solution of the Schroedinger equation have been devised. These may be divided roughly into two broad categories: the variational method and perturbation theory.

1. Variation Method

The variational method depends upon the fact that the expression

$$\tilde{E} = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \qquad \text{(I.A-1)}$$

where

$$\langle \Psi | H | \Psi \rangle = \int d\tau \, \Psi^* \Psi d\tau \qquad \text{(I.A.-2)}$$

is an upper limit to the lowest eigenvalue or ground state solution E_o. Thus, one can substitute a trial function $\Psi(\alpha,\beta - - \delta)$ into Eq. (I.A-1) and minimize $\tilde{E}$ with respect to each of the parameters $\alpha, \beta, \cdots \delta$ to get an approximation to E_o.

2. Perturbation Theory

According to the perturbation method,[1] the Hamiltonian H is regarded as consisting of an unperturbed Hamiltonian H_o, whose solution is ideally known, and a perturbation $\lambda V = H - H_o$. The energy and wavefunction are expanded in a power series in λ,

$$E = \epsilon_0 + \lambda \epsilon_1 + \lambda^2 \epsilon_2 + - - \qquad \text{(I.A-3)}$$

$$\Psi = \psi_0 + \lambda \psi_1 + \lambda^2 \psi_2 + - - - \qquad \text{(I.A-4)}$$

and substituted into the Schroedinger equation. The parameter λ may or may not have physical significance; its essential role is defining the various orders of perturbation. If physically insignificant, it is eventually replaced by unity.

Collecting in powers of λ and equating the coefficient of each individual power to zero results in the Rayleigh Schroedinger perturbation equations:

$$H_0\psi_0=\epsilon_0\psi_0 \tag{I.A-5}$$

$$(H_0-\epsilon_0)\psi_1=-(V-\epsilon_1)\psi_0 \tag{I.A-6}$$

with the general n^{th} order equation given by

$$(H_0-\epsilon_0)\psi_n=-(V-\epsilon_1)\psi_{n-1}+\sum_{K=2}^{N}\epsilon_K\psi_{n-K} \tag{I.A-7}$$

Ideally, the solutions to the zeroth order equation are known exactly.

B. Historical

Quantum mechanical perturbation theory was originally developed by Schroedinger[2] in the last of a series of three papers in 1926. Many early attempts were made to apply perturbation theory to atomic and molecular energy calculations, but these were limited by a lack of adequate computational techniques.

One of the earlier and more successful examples of its application to atomic systems was the classic work of Hylleraas[3]. Using the reciprocal of the nuclear charge, 1/Z, as an expansion parameter, he determined an energy for He through third order which was in error by less than .01eV.

Perturbation theory was first applied to molecules by Heitler and London[4] in their famous calculation on the hydrogen molecule. Their zeroth order wave function for the singlet ground state was given by

$$\psi = u_a(1)\, u_b(2) + u_a(2)\, u_b(1) \qquad \text{(I.B-1)}$$

where u_a represents a 1s orbital on nucleus a . With the aid of degenerate perturbation theory, they showed that this function was correct in the limit of infinite separation. Using the electronic repulsion as a perturbation, they determined a dissociation energy of 3.14 eV, which is in error by approximately 1.6 eV.

The Heitler-London calculation was ideally suited to describing the hydrogen molecule at large separation since the corresponding zeroth order wavefunction dissociated to the exact solution. A perturbation calculation which gave the correct solution in the limit of small R was that of Coulson[5]. His zeroth order wave function was given by

$$\chi(1)\, \chi(2) = [u_a(1) + u_b(1)][u_a(2) + u_b(2)] \qquad \text{(I.B-2)}$$

where the molecular orbital $\chi(1)$ is a good approximation to the H_2^+ eigenfunction. Using the electronic repulsion as a perturbation, he determined a dissociation energy of 2.681 eV.

In general, the results of the molecular energy calculations were not particularly encouraging. It was apparent that the perturbation treatment would have to be extended to higher orders before accurate energies could be obtained. This extension, however, was precluded by the lack of high speed computors and adequate molecular integration techniques.

On the other hand, the variation method was demonstrably capable of high accuracy. James and Coolidge[6] performed a variational calculation on H_2 using a wave function which explicitly contained the interelectronic separation r_{12}. The dissociation energy they obtained was in error by less than 0.02 eV. Thus, primary emphasis was placed on the variational method for determining molecular energies.

C. Recent Developments

A rejuvenation of interest in perturbation calculations has been sparked by recent new developments in perturbation theory.[1] Among these developments are improved methods for determining the perturbed wavefunctions. The classical method of solving for the first order wave function is to expand it in terms of a complete set of zeroth order functions. However, as shown by Dalgarno and Lewis[7], a closed form solution may often be determined by substituting

$$\psi_1 = F \psi_0 \tag{I.C-1}$$

into the first order equation, Eq. (I.A-6), leading to a new differential equation for F which is often more easily solved than the original equation. For problems in which the perturbation is not separable, such as $1/r_{12}$, there has been increased awareness of the fact that satisfactory results for high order wave function and energies can be determined using a variational technique such as that developed by Hylleraas.[3] It is also possible to combine the Dalgarno form of the wavefunction with the Hylleraas principle. These techniques are detailed in Chapter II.

The recent perturbation calculations have been primarily on atomic systems.[8] Many of these are outgrowths of Hylleraas's He calculation. Scherr and Knight[9] have extended his calculation to 15th order in the energy and obtained results comparable in accuracy to the best variational calculations. Linderberg[10] and Coulson[11] have solved the Hartree Fock equation of He through third order also using 1/Z as an expansion parameter. Hall and Rees[12] have treated diatomic hydrides using hydrogenic atomic orbitals as zeroth order wavefunctions.

D. Purpose of Present Investigation

Recent calculations on the hydrogen molecule ion have demonstrated that highly accurate values for molecular energies can be obtained using perturbation theory. See Appendix I. Motivated by these results we have determined the ground state energy of H_2, treating the electronic interaction as a perturbation to the remaining Hamiltonian. The energy expansion is extended to a high enough order to give results comparable to the most accurate variational calculations. The first order wave function is determined by using the Hylleraas variational principle which states that

$$\tilde{\epsilon}_2 \geq \epsilon_2 \qquad \text{(I.D-1)}$$

where

$$\tilde{\epsilon}_2 = \langle \tilde{\psi}_1 | (H_0 - \epsilon_0) | \tilde{\psi}_1 \rangle + 2 \langle \tilde{\psi}_1 | V - \epsilon_1 | \psi_0 \rangle \qquad \text{(I.D-2)}$$

with the trial functions $\tilde{\psi}_1$ being arbitrary. The proof of this principle and extensions to higher orders are given in Chapter II.

Two types of basis sets are used in the expansion of the trial function. One is of the Dalgarno form, Eq. (I.D-1), and the other is similar to the James and Coolidge trial function[6]. A comparison of the two basis sets is given in Chapter IV.

The unperturbed wave function is taken to be the product of two hydrogen molecule ion wavefunctions with the spin portion factored out and neglected. Since the solutions of the hydrogen molecule ion wave equation are known in analytic, but not closed, form, efficient procedures for evaluating integrals containing the H_2^+ functions are difficult to obtain. Such procedures, however, are essential to the calculation.

1. Comparison with He Isoelectronic Sequence

The present calculation is very similar to the He calculation of Hylleraas. In order to compare the two calculations, we consider the Schroedinger equation for hydrogen like molecules omitting internuclear repulsion:

$$\left\{ \sum_{i=1}^{2} \left[-\frac{\nabla_i^2}{2} - Z\left(\frac{1}{r_{a_i}} + \frac{1}{r_{b_i}} \right) \right] + \frac{1}{r_{12}} \right\} \Psi(R) = E(R)\,\Psi(R) \qquad \text{(I.D-3)}$$

Here, E is the electronic energy, r_{12} is the distance between the two electrons, r_{ai} is the distance from nucleus a to electron i , and Z is the charge on either nucleus.

Equation (I.D-3) is expressed in atomic units where the unit of length is the bohr (0.52917/Å), the unit of energy the hartree (27.20974eV), and the unit of charge, that of the electron, e^- .

Scaling the electronic coordinates by a factor Z allows us to write Eq. (I.D-3) as follows:

$$\left[\sum_{i=1}^{2}\left(-\frac{\nabla_i^2}{2}-\frac{1}{r'_{a_i}}-\frac{1}{r'_{b_i}}\right)+\frac{1}{Z r'_{12}}\right]\Psi(R') = \frac{E(R')}{Z^2}\Psi(R') \qquad \text{(I.D-4)}$$

where $R' = ZR$ with r'_{a_i} , r'_{b_i} and r'_{12} defined in an analogous manner. Expanding E/Z^2 in inverse powers of Z gives

$$\frac{E(R')}{Z^2} = \epsilon_0(R') + \frac{1}{Z}\epsilon_1(R') + \frac{1}{Z^2}\epsilon_2(R') + \cdots \qquad \text{(I.D-5)}$$

Following Hylleraas, we expand the He energy W in the form

$$\frac{W}{\bar{Z}^2} = \omega_0 + \frac{1}{\bar{Z}}\omega_1 + \frac{1}{\bar{Z}^2}\omega_2 + \cdots \qquad \text{(I.D-6)}$$

where $\bar{Z}$ is the charge on the He nucleus. The essential difference between the two expansions Eq. (I.D-5) - (I.D-6) is in the Z dependence of the energy coefficients. The ϵ_n are functions of R' and hence implicit functions of Z , while, in contrast, the ω_n are independent of Z .

In the limit of small R, the electronic energy of the hydrogen molecule becomes equal to that of helium, thus;

$$E(0) = W \qquad \text{(I.D-7)}$$

Noting that $Z = \frac{\bar{Z}}{2}$, we find

$$\epsilon_n = \frac{\omega_n}{2^{n-2}} \qquad \text{(I.D-8)}$$

2. Mathematical Justification of Perturbation Expansion

The question arises as to whether there is any mathematical justification for the energy expansion, Eq. (I.D-5). The answer is found in the important theorem by Rellich[13,1] which states that the Rayleigh-Schroedinger perturbation series converges for sufficiently small values of the expansion parameter if the unperturbed Hamiltonian is self-adjoint and if two constants, a and b can be found such that $V\psi$ and $H_0\psi$ satisfy the inequality

$$\langle V\psi, V\psi\rangle \leq a\langle H_0\psi, H_0\psi\rangle + b\langle\psi,\psi\rangle \qquad \text{(I.D-9)}$$

for all functions ψ in the domain of H_0. Kato[14] has shown that this theorem is satisfied for atoms and molecules if the perturbation V is the electron repulsion part of the total potential.

CHAPTER II

THEORY

The method used in the present investigation of determining the ground state energy of H_2 by treating the electronic repulsion energy as a perturbation to the remaining Hamiltonian is by no means original. The very first quantum mechanical calculations on this system were of a similar nature. However, none of the earlier calculations were carried out to a high enough order to actually determine the rate of convergence of the energy expansion. Unless the energy coefficients are calculated to at least third order, erroneous conclusions may be reached concerning the convergence of the series. In this chapter, the formalism required for a highly accurate determination of expansion coefficients is developed. Many of the equations are similar to those of Scherr and Knight since this problem has much in common with theirs.

A. Perturbation Formalism

In this section, the usual Rayleigh Schrodinger perturbation equations are derived and the generalized Hylleraas variational method for determining the n^{th} order perturbation wavefunctions is discussed.

1. Perturbation Equations

As shown in the introduction, the hydrogen wave equation may be put into the form

$$\left[\sum_{i=1}^{2} \left(-\frac{\nabla_i^2}{2} - \frac{1}{r'_{a_i}} - \frac{1}{r'_{b_i}} \right) + \frac{1}{Z r'_{12}} \right] \Psi(R') = \frac{E}{Z^2}(R')\,\Psi(R'). \qquad \text{(II.A-1)}$$

Now, identifying $1/r'_{12}$ as a perturbation,

$$V = \frac{1}{r'_{12}} \quad , \qquad \text{(II.A-2)}$$

to the zeroth order Hamiltonian

$$H_0 = \sum_{i=1}^{2} \left(-\frac{\nabla_i^2}{2} - \frac{1}{r'_{a_i}} - \frac{1}{r_{b_i}} \right) \qquad \text{(II.A-3)}$$

allows us to write Eq. (II.A-1) in the form

$$\left(H_0 + \frac{1}{Z} V \right) \Psi = \frac{E}{Z^2} \Psi \qquad \text{(II.A-4)}$$

Let us assume that Ψ and $\frac{E}{Z^2}$ may be expanded in inverse powers of Z :

$$\Psi = \psi_0 + \frac{1}{Z} \psi_1 + \frac{1}{Z^2} \psi_2 + \cdots \qquad \text{(II.A-5)}$$

and

$$\frac{E}{Z^2} = \epsilon_0 + \frac{1}{Z} \epsilon_1 + \frac{1}{Z^2} \epsilon_2 + \cdots \qquad \text{(II.A-6)}$$

Substituting these power series expansions into Eq. (II.A-4), and ordering in powers of 1/Z, results in the expression

$$H_0' \Psi_0 + \frac{1}{Z}(H_0' \Psi_1 + V' \Psi_0)$$

$$+ \frac{1}{Z^2}(H_0' \Psi_2 + V' \Psi_1 - \epsilon_2 \Psi_0) + \cdots \qquad \text{(II.A-7)}$$

where $H_0' = H_0 - \epsilon_0$ and $V' = V - \epsilon_1$.

If this series is properly convergent, in order for it to equal zero for all values of 1/Z, the coefficients of powers of 1/Z must vanish separately. Equating the coefficients to zero leads to the Rayleigh Schrodinger Perturbation equations:

$$H_0' \Psi_0 = 0 \qquad \text{(II.A-8)}$$

$$H_0' \Psi_1 + V' \Psi_0 = 0 \qquad \text{(II.A-9)}$$

$$H_0' \Psi_2 + V' \Psi_1 - \epsilon_2 \Psi_0 = 0 \qquad \text{(II.A-10)}$$

and in general

$$H_0' \Psi_n + V' \Psi_{n-1} - \sum_{K=2}^{n} \epsilon_K \Psi_{n-K} = 0 \qquad \text{(II.A-11)}$$

2. Variational Solution to Perturbed Equations.

The first order wave function, ψ_1, may be determined by using the variational principle developed by Hylleraas. He pointed out that

$$\tilde{\epsilon}_2 \geqslant \epsilon_2 \qquad \text{(II.A-12)}$$

where

$$\tilde{\epsilon}_2 = \langle \tilde{\psi}_1 | (H_0 - \epsilon_0) | \tilde{\psi}_1 \rangle + 2 \langle \tilde{\psi}_1 | V' | \psi_0 \rangle \qquad \text{(II.A-13)}$$

and $\tilde{\psi}_1$ is arbitrary. We can prove this principle by substituting

$$\tilde{\psi}_1 = \psi_1 + \delta \tilde{\psi}_1 \qquad \text{(II.A-14)}$$

into Eq. (II.A-13) giving

$$\tilde{\epsilon}_2 - \epsilon_2 = 2 \langle \delta \tilde{\psi}_1 | (H_0 - \epsilon_0) \psi_1 + V' \psi_0 \rangle$$

$$+ \langle \delta \tilde{\psi}_1 | (H_0 - \epsilon_0) \delta \tilde{\psi}_1 \rangle \qquad \text{(II.A-15)}$$

The term in δ vanishes because of Eq. (II.A-9) and the term in δ^2 is positive because ϵ_0 is the lowest eigenvalue of H_0.

Variational principles for the higher order corrections may be determined conveniently using the method of Scherr and Knight. We substitute the perturbation expansions for Ψ and E into the variational expression

$$\langle \tilde{\Psi} | H | \tilde{\Psi} \rangle - E \langle \tilde{\Psi} | \tilde{\Psi} \rangle \geq 0 \qquad \text{(II.A-16)}$$

and order in inverse powers of Z resulting in

$$\begin{aligned}
&\langle \tilde{\psi}_0 | H_0' | \tilde{\psi}_0 \rangle + \frac{1}{Z} \left[2 \langle \tilde{\psi}_1 | H_0' | \tilde{\psi}_0 \rangle + 2 \langle \tilde{\psi}_0 | V' | \tilde{\psi}_0 \rangle \right] \\
&+ \frac{1}{Z^2} \left[\langle \tilde{\psi}_1 | H_0' | \tilde{\psi}_1 \rangle + 2 \langle \tilde{\psi}_1 | V' | \tilde{\psi}_0 \rangle \right. \\
&\qquad \left. - \epsilon_2 \langle \tilde{\psi}_0 | \tilde{\psi}_0 \rangle \right] \qquad \text{(II.A-17)} \\
&+ \frac{1}{Z^3} \left[2 \langle \tilde{\psi}_2 | H_0' | \tilde{\psi}_1 \rangle + 2 \langle \tilde{\psi}_2 | V' | \tilde{\psi}_0 \rangle \right. \\
&\qquad \left. + \langle \tilde{\psi}_1 | V' | \tilde{\psi}_1 \rangle - 2 \epsilon_2 \langle \tilde{\psi}_1 | \tilde{\psi}_0 \rangle - \epsilon_3 \langle \tilde{\psi}_0 | \tilde{\psi}_0 \rangle \right] \\
&+ \frac{1}{Z^4} \left[\langle \tilde{\psi}_2 | H_0 | \tilde{\psi}_2 \rangle + 2 \langle \tilde{\psi}_2 | V' | \tilde{\psi}_1 \rangle - 2 \epsilon_2 \langle \tilde{\psi}_0 | \tilde{\psi}_2 \rangle \right. \\
&\left. - \epsilon_2 \langle \tilde{\psi}_1 | \tilde{\psi}_1 \rangle - 2 \epsilon_3 \langle \tilde{\psi}_0 | \tilde{\psi}_1 \rangle - \epsilon_4 \langle \tilde{\psi}_0 | \tilde{\psi}_0 \rangle \right] + \cdots \geq 0
\end{aligned}$$

Assuming that we know the exact solution to the zeroth order equation the coefficient of Z^0 vanishes by Eq. (II.A-8) and that of $1/Z$ by Eq. (II.A-9). Now, if we let Z go to infinity, the coefficient of Z^{-2} becomes dominant leading to the variational expression

$$\tilde{\epsilon}_2\langle\psi_0|\psi_0\rangle = \langle\tilde{\psi}_1|H_0'|\tilde{\psi}_1\rangle + 2\langle\tilde{\psi}_1|V'|\psi_0\rangle \qquad \text{(II.A-18)}$$

with $\tilde{\epsilon}_2 \geqslant \epsilon_2$. Similarly, if ψ_1 is known exactly, the coefficients of Z^{-3} and Z^{-2} vanish and the coefficient of Z^{-4} becomes dominant giving

$$\begin{aligned}\tilde{\epsilon}_4\langle\psi_0|\psi_0\rangle &= \langle\tilde{\psi}_2|H_0'|\tilde{\psi}_2\rangle + 2\langle\tilde{\psi}_2|V'|\psi_1\rangle \\ &\quad - 2\epsilon_2\langle\psi_0|\tilde{\psi}_2\rangle - \epsilon_2\langle\psi_1|\psi_1\rangle - 2\epsilon_3\langle\psi_0|\psi_1\rangle \qquad \text{(II.A-19)} \\ &\quad - \epsilon_4\langle\psi_0|\psi_0\rangle\end{aligned}$$

with

$$\tilde{\epsilon}_4 \geqslant \epsilon_4 \qquad \text{(II.A-20)}$$

Minimization of $\tilde{\epsilon}_4$ results in an approximation to ψ_2 .

In general

$$\tilde{\epsilon}_{2n}\langle\psi_0|\psi_0\rangle = \langle\tilde{\Psi}_n|H_0'|\tilde{\Psi}_n\rangle + 2\langle\tilde{\Psi}_n|V'|\psi_{n-1}\rangle$$

$$-\sum_{p=2}^{2n-1}\epsilon_p\sum_{i=n-p}^{n}\langle\psi_i|\psi_{2n-p-i}\rangle \qquad \text{(II.A-21)}$$

with

$$\tilde{\epsilon}_{2n} \geqslant \epsilon_{2n} \qquad \text{(II.A-22)}$$

and

$$\tilde{\epsilon}_{2n+1}\langle\psi_0|\psi_0\rangle = \langle\tilde{\Psi}_n|V'|\tilde{\Psi}_n\rangle$$

$$-\sum_{p=2}^{2N}\epsilon_p\sum_{i=N+1-p}^{N}\langle\psi_i|\psi_{2N+1-p-i}\rangle \qquad \text{(II.A-23)}$$

where terms with negative indices are ignored. From these equations, it is clear that the energy through order can be obtained knowing the wavefunction through nth order.

3. Normalization

Normalization conditions are required to completely specify the wavefunction. We require that both the total wavefunction Ψ and the zeroth order function ψ_0 be normalized to unity. This leads to the following condition on the various orders of perturbed wave functions:

$$\sum_{K=0}^{n} \langle \psi_K | \psi_{n-K} \rangle = 0 \qquad n=1,2,\cdots \tag{II.A-24}$$

B. Solution of Zeroth Order Equation

Since the variational expressions (Eqs. (II.A-18) - (II.A-23) for determining the higher order corrections to the wave function depend upon an exact knowledge of the zeroth order function, the solution of the zeroth order equation must be determined with a high degree of accuracy. A primary source of error in the earlier calculations mentioned in the introduction was the use of inaccurate zeroth order wavefunctions. We have expended considerable time and effort in an attempt to completely eliminate this error.

Consider the zeroth order perturbation equation

$$H_0 \psi_0 = \epsilon_0 \psi_0 \tag{II.B-1}$$

where

$$H_0 = \sum_{i=1}^{2} \left(-\frac{\nabla_i^2}{2} - \frac{1}{r_{a_i}} - \frac{1}{r_{b_i}} \right) \tag{II.B-2}$$

Letting $\psi_0 = \chi(1)\chi(2)$ leads to two equations of the form

$$\left(-\frac{\nabla^2}{2} - \frac{1}{r_a} - \frac{1}{r_b}\right)\chi = W\chi \qquad \text{(II.B-3)}$$

where r_a and r_b are the distances from the two nuclei and $W = \frac{\epsilon_0}{2}$. Equation (II.B-3) is the Schrodinger equation for the hydrogen-molecule ion. Burrau[17] first pointed out that this equation is separable in confocal elliptic coordinate ξ , η and φ . The coordinates ξ and η are given by the equations

$$\xi = \frac{r_a + r_b}{R} \quad , \quad \eta = \frac{r_a - r_b}{R} \qquad \text{(II.B-4)}$$

and φ is the angle about the internuclear axis. The range of the variable ξ is from 1 to ∞ while η goes from -1 to 1 .

Inverting Eqs. (II.B-4)leads to the relationships

$$r_a = \frac{R}{2}(\xi + \eta) \; , \; r_b = \frac{R}{2}(\xi - \eta) \qquad \text{(II.B-5)}$$

Thus

$$\frac{1}{r_a} + \frac{1}{r_b} = \frac{2}{R}\left[\frac{1}{\xi + \eta} + \frac{1}{\xi - \eta}\right] \qquad \text{(II.B-6)}$$

$$= \frac{4}{R}\,\frac{\xi}{\xi + \eta^2}$$

The Laplacian in confocal elliptic coordinates is given by

$$\nabla^2 = \frac{4}{R^2(\xi^2-\eta^2)}\left\{\frac{\partial}{\partial\xi}\left[(\xi^2-1)\frac{\partial}{\partial\xi}\right]+\frac{\partial}{\partial\eta}\left[(1-\eta^2)\frac{\partial}{\partial\eta}\right]\right.$$

$$\left.+\frac{\partial}{\partial\varphi}\left[\frac{\xi^2-\eta^2}{(\xi^2-1)(1-\eta^2)}\frac{\partial}{\partial\varphi}\right]\right\} \qquad \text{(II.B-7)}$$

Substituting Eqs. (II.B-6) and (II.B-7) into Eq. (II.B-3) and multiplying by

$$\frac{R^2}{4}(\xi^2-\eta^2)$$

gives

$$\frac{\partial}{\partial\xi}\left[(\xi^2-1)\frac{\partial\chi}{\partial\xi}\right]+\frac{\partial}{\partial\eta}\left[(1-\eta^2)\frac{\partial\chi}{\partial\eta}\right]+\left(\frac{1}{\xi^2-1}+\frac{1}{1-\eta^2}\right)\frac{\partial^2\chi}{\partial\varphi^2}$$

$$+\left[\frac{R^2W(\xi^2-\eta^2)}{4}+2R\xi\right]\chi=0 \qquad \text{(II.B-8)}$$

It is seen that by replacing $\chi(\xi,\eta,\varphi)$ by the product function

$$\Psi(\xi,\eta,\varphi)=\Xi(\xi)H(\eta)\Phi(\varphi) \qquad \text{(II.B-9)}$$

Eq. (II.B-8) is separable into the three one-dimensional equations:

$$\frac{d^2\Phi}{d\varphi^2} = -m^2\Phi \qquad \text{(II.B-10)}$$

$$\frac{d}{d\eta}(1-\eta^2)\frac{dH}{d\eta} + \left[-C + \rho^2\eta^2 - \frac{m^2}{1-m^2}\right]H = 0 \qquad \text{(II.B-11)}$$

and

$$\frac{d}{d\xi}(\xi^2-1)\frac{d\Xi}{d\xi} + \left[C + 2R\xi - \rho^2\xi^2 - \frac{m^2}{\xi^2-1}\right]\Xi = 0 \qquad \text{(II.B-12)}$$

where $\rho^2 = -\frac{1}{4}R^2W$ and C is a separation constant. The solution of the familiar Φ equation is

$$\Phi(\varphi) = e^{\pm im\varphi} \qquad m = 0, 1, 2, \cdots \qquad \text{(II.B-13)}$$

To determine a solution to Eq. (II.B-11), following Hylleraas,[19] we expand the function H in terms of the associated Legendre Polynomials:

$$P_\ell^{|m|}(\eta) = (1-\eta^2)^{\frac{|m|}{2}} \frac{d^{|m|}}{d\eta^{|m|}} P_\ell(\eta) \qquad \text{(II.B-14)}$$

where the Legendre Polynomial P_ℓ is defined by

$$P_\ell(\eta) = \frac{1}{2^n n!}\frac{d^\ell}{dx_\ell}[(1-x^2)]^\ell \qquad \text{(II.B-15)}$$

The expansion of H takes the form

$$H = \sum_{\ell=|m|}^{\infty} f_\ell\, P_\ell^{|m|}(\eta) \qquad \text{(II.B-16)}$$

where the coefficients f_ℓ are constants. Substituting this expression into Eq. (II.B-11) and simplifying with the aid of the differential equation

$$(1-\eta^2)\frac{d^2P_\ell^{|m|}(\eta)}{d\eta^2} - 2\eta\frac{dP_\ell^{|m|}(\eta)}{d\eta} + \left\{\ell(\ell+1) - \frac{m^2}{1-\eta^2}\right\}P_\ell^{|m|}(\eta) = 0 \qquad \text{(II.B-17)}$$

we obtain

$$\sum_{\ell=|m|}^{\infty} f_\ell \left\{\rho^2\eta^2 - C - \ell(\ell+1)\right\} P_\ell^{|m|}(\eta) = 0 \qquad \text{(II.B-18)}$$

By successively applying the recursion formula

$$\eta P_\ell^{|m|}(\eta) = \frac{(\ell+|m|)}{2\ell+1}P_{\ell-1}^{|m|}(\eta) + \frac{(\ell-|m|+1)}{2\ell+1}P_{\ell+1}^{|m|}(\eta) \qquad \text{(II.B-19)}$$

Eq. (II.B-18) becomes a simple series in the functions whose coefficients must vanish due to the orthogonality of these functions. We thus obtain a three term recursion relation

$$u_\ell f_{\ell+2} - v_\ell f_\ell + w_\ell f_{\ell-2} = 0 \qquad \text{(II.B-20)}$$

with

$$u_\ell = \frac{(\ell-|m|+1)(\ell-|m|)}{(2\ell-3)(2\ell-1)}\rho^2 \qquad \text{(II.B-21)}$$

$$w_\ell = \frac{(\ell+|m|+2)(\ell+|m|+1)}{(2\ell+3)(2\ell+5)}\rho^2 \qquad \text{(II.B-22)}$$

and

$$v_\ell = \ell(\ell+1) + C - \rho^2\left\{\frac{(\ell-|m|+1)(\ell+|m|+1)}{(2\ell+1)(2\ell+3)} + \frac{(\ell-|m|)(\ell+|m|)}{(2\ell-1)(2\ell+1)}\right\} \qquad \text{(II.B-23)}$$

It follows from Eq. (II.B-20) that

$$O_\ell = \frac{f_\ell}{f_{\ell-2}} \qquad \text{(II.B-24)}$$

where O_ℓ is the continued fraction

$$O_\ell = \frac{w_\ell}{v_\ell - u_\ell O_{\ell+2}} = \frac{w_\ell}{v_\ell -}\;\frac{u_\ell w_{\ell+2}}{v_{\ell+2} -}\;\frac{u_{\ell+2} w_{\ell+4}}{v_{\ell+4} -}\cdots \qquad \text{(II.B-25)}$$

The roots of Eq. (II.B-24) for a given ρ and m are the eigenvalues C .

The solution to the Ξ equation proceeds in a similar fashion. It has been discussed by Jaffe[20] and his derivation sketched by Bates, Ledsham. and Stewart. The solution is expressed in the form

$$\Xi(\xi) = (\xi^2-1)^{m/2}(\xi+1)^{\sigma}\exp(-\rho\xi)\sum_{\ell} g_{\ell}\left(\frac{\xi-1}{\xi+1}\right)^{\ell} \tag{II.B-26}$$

where

$$\sigma = \frac{R}{\rho} - m - 1 \tag{II.B-27}$$

Substituting this expression into Eq. (II.B-12) leads to a three-term recurrence relation for the g's :

$$\alpha_t g_{t+1} - \beta_t g_t + \gamma_t g_{t-1} = 0 \tag{II.B-28}$$

where

$$\alpha_t = (t+1)(t+m+1) \tag{II.B-29}$$

$$\beta_t = 2t^2 + (4\rho - 2\sigma)t - c - \rho^2 - 2\rho\sigma - (m+1)(m+\sigma) \tag{II.B-30}$$

and

$$\gamma_t = (t-1-\sigma)(t-1-\sigma-m) \tag{II.B-31}$$

It follows that

$$\frac{g_t}{g_{t-1}} = F_t \tag{II.B-32}$$

where F_t is the continued fraction

$$F_t = \frac{\gamma_t}{\beta_t -} \quad \frac{\alpha_t \gamma_{t+1}}{\beta_{t+1}} - \quad \frac{\alpha_{t+1} \gamma_{t+2}}{\beta_{t+2} -} \cdots \tag{II.B-33}$$

whose roots for a given ρ, m, and C are the eigenvalues The relationship, Eq. (II.B-27), is then used to determine R and hence W.

Bates, Ledsham and Stewart have tabulated ground state solutions to the H_2^+ equation for a large number of R's. Unfortunately, their calculation is accurate to only five places in the energy. We estimate a minimum of nine place accuracy is necessary to completely eliminate any errors which might result from the use of an inaccurate zeroth order wavefunction. Therefore, we have written a program which is capable of this accuracy and have used it to evaluate the H_2^+ energy for selected values of R. In Tables I, II, and III, we have listed the energy to nine significant figures along with accurate values for the parameters σ, ρ, C, h, and f. Only the ground state solution, where m = 0, has been tabulated.

C. First Order Energy

The first order energy is determined from the expression

$$\epsilon_1 = \langle \Psi_0 | V | \Psi_0 \rangle \qquad \text{(II.C-1)}$$

Substituting for Ψ_0^2 and noting that in confocal elliptic coordinates,

$$d\tau = \frac{R^3}{8}(\xi^2 - \eta^2)\, dV$$

where

$$dV = d\xi\, d\eta\, d\varphi$$

we find

$$\epsilon_1 = \frac{R^6}{64} \int_0^{2\pi} d\varphi_1 \int_0^{2\pi} d\varphi_2 \int_1^{\infty} d\xi_1 \int_1^{\infty} d\xi_2 \int_{-1}^{1} d\eta_1 \int_{-1}^{1} d\eta_2\, e^{-2\rho(\xi_1 + \xi_2)}$$

$$\times \left[\sum_{\ell, \ell' = 0}^{\infty} f_\ell f_{\ell'} P_\ell(\eta_1) P_{\ell'}(\eta_2) \right]^2$$

$$\times \left[\sum_{\ell, \ell' = 0}^{\infty} g_\ell\, g_{\ell'} \left(\frac{\xi_1 - 1}{\xi_1 + 1} \right)^{\ell} \left(\frac{\xi_2 - 1}{\xi_2 + 1} \right)^{\ell'} \right]^2 \qquad \text{(II.C-2)}$$

$$\times \frac{1}{r_{12}} (\xi_1^2 - \eta_1^2)(\xi_2^2 - \eta_2^2)$$

The evaluation of this integral is complicated by the presence of the factor $1/r_{12}$ in the integrand, which must be expanded in a complete set of orthogonal polynomials, and by the complex functional form of the zeroth order wave function.

Since methods for evaluating integrals of the form

$$G^{J,K}_{m,n} = \iint dV_1\, dV_2\, e^{-2\rho(\xi_1+\xi_2)}\, \xi_1^m\, \xi_2^n\, \eta_1^J\, \eta_2^K \frac{1}{r_{12}} \qquad \text{(II.C-3)}$$

are well-known, it was reasoned that if ψ_0 could be expanded in a power series in ξ and η without loss in accuracy, the first order energy could be expressed in terms of the G's which could then be evaluated by any of a number of methods. This approach was attempted. The function ψ_0 was first approximated by a series of Chebyshev polynomials[21] which was then ordered in powers of ξ and η resulting in:

$$\psi_0(\xi, n) = e^{-\rho\xi} \sum_{n,m} C_n C_m\, \xi^m \eta^n \qquad \text{(II.C-4)}$$

where C_n and C_m are expansion coefficients. This series was subsequently substituted into Eq. (II.C-1) leading to the expression for the first order energy

$$\epsilon_1 = \frac{R^6}{64} \sum_{n,n';m,m',j,j';k,k'} C_m C_{m'} C_n C_{n'} C_j C_{j'} C_k C_{k'} \Big[G^{j+j',k+k'}_{m+m'+2,\,n+n'+2} - G^{j+j'+2,\,k+k'}_{m+m',\,n+n'+2} - G^{j+j',\,k+k'+2}_{m+m'+2,\,n+n'} + G^{j+j'+2,\,k+k'+2}_{m+m',\,n+n'} \Big]$$

(II.C-5)

However, when this method was programmed, it was found that the sum in Eq. (II.C-5) took far too long to evaluate. This was due partly to the slow convergence of the sum and partly to the necessity of evaluating a large number of G's.

Searching for a more efficient approach, numerical integration scheme for determining ϵ_1 was devised. Part of this scheme followed closely a method which Ruedenberg used for evaluating the G's. (We will not consider this approach in detail since it is a specific case of still a more general scheme which was consequently developed.) Using this numerical integration method, it was now possible to determine ϵ_1 quickly and efficiently. However, there was dissatisfaction in the fact that a separate program was needed for its determination.

The method which was eventually used for determining the first order energy was based on the development of a generalized procedure for determining the primitive integrals

$$\begin{aligned} M_\ell^\nu(pqrs\mu) = \iint d\tau_1 d\tau_2 \, (\xi_1^2-\eta_1^2)^{-1} e^{-(2-\ell)\alpha(\xi_1+\xi_2)} \\ \times \left\{ e^{-\rho(\xi_1+\xi_2)} [(\xi_1+1)(\xi_2+1)]^\sigma \left[\sum_{nn'} g_n g_{n'} \left(\frac{\xi_1-1}{\xi_1+1}\right)^n \left(\frac{\xi_2-1}{\xi_2+1}\right) \right] \right\}^\ell \\ \times \left[\sum_{nn'} f_n f_{n'} P_n(\eta_1) P_{n'}(\eta_2) \right]^\ell \xi_1^p \, \xi_2^q \, \eta_1^r \, \eta_2^s \, r_{12}^\mu \qquad \text{(II.C-6)} \\ \times \left[(\xi_1^2-1)(\xi_2^2-1)(1-\eta_1^2)(1-\eta_2^2) \right]^{\nu/2} \cos^\nu(\varphi_1-\varphi_2) \end{aligned}$$

Note that the zeroth order wave function is incorporated into this definition. This fact is of key importance since it leads to extreme simplifications in the organization of the overall problem. One simplification is immediately obvious. The first order energy may be written trivially as

$$\epsilon_1 = M_2^0(2000,-1) - M_2^0(0020,-1) \qquad \text{(II.C-7)}$$

The details of the evaluation of the primitive integrals are given in Chapter III.

At this point, it is convenient to give the expression for the zeroth order normalization integrals in terms of primitive integrals. We have

$$\langle \psi_0 | \psi_0 \rangle = M_2^0(20000) - M_2^0(00200) \qquad \text{(II.C-8)}$$

D. Determination of Higher Order Wave Functions

In this section, generalized matrix equations for determining corrections to the zeroth order wave function are presented. Two possible choices of basis sets for substituting into these equations are considered.

1. General Formalism

The initial step in the determination of the high order corrections to the wavefunction is to expand them in terms of a complete set of basis functions $\{\varphi_i\}$:

$$\psi_n = \sum_i C_i^{(n)} \varphi_i \tag{II.D-1}$$

Substitution of this expansion into the generalized n^{th} order variational expression, Eq. (II.A-21), leads to the matrix equation:

$$\begin{aligned}\tilde{\epsilon}_{2N} &= \mathbb{C}^{(n)\dagger} \mathbb{H}' \mathbb{C}^{(n)} + 2\, \mathbb{C}^{(n)\dagger} \mathbb{V}' \mathbb{C}^{(n-1)} \\ &\quad - \sum_{p=2}^{2n-1} \epsilon_p \sum_{i=n-p}^{n} \mathbb{C}^{(i)\dagger} \mathbb{S}\, \mathbb{C}^{(2n-p-i)}\end{aligned} \tag{II.D-2}$$

where

$$\begin{aligned}(\mathbb{H}')_{ij} &= \langle \varphi_i | H_0' | \varphi_j \rangle \\ &\equiv H_{ij} - \epsilon_0 S_{ij}\end{aligned} \tag{II.D-3}$$

$$(\mathbb{S})_{ij} = \langle \varphi_i | \varphi_j \rangle \equiv S_{ij} \tag{II.D-4}$$

$$(\mathbb{V}')_{ij} = \langle \varphi_i | V' | \varphi_j \rangle \equiv V_{ij} - \epsilon_1 S_{ij} \qquad \text{(II.D-5)}$$

$$(\mathbb{S}\mathbb{C}^{(0)})_{ij} = (\mathbb{C}^{(0)+}\mathbb{S})_i$$

$$= \langle \varphi_i | \psi_0 \rangle \equiv N_{i0} \qquad \text{(II.D-6)}$$

and

$$(\mathbb{V}'\mathbb{C}^{(0)})_i = (\mathbb{C}^{(0)+}\mathbb{V})_i = \langle \varphi_i | V' | \psi_0 \rangle$$

$$\equiv V_{i0} - \epsilon_1 N_{i0} \qquad \text{(II.D-7)}$$

Partial differentiation of Eq. (II.D-2) with respect to the $C^{(n)}$'s results in the matrix equation:

$$\mathbb{H}'\mathbb{C}^{(n)} + \mathbb{V}'\mathbb{C}^{(n-1)}$$

$$- \sum_{p=2}^{n-1} \epsilon_p \mathbb{S}\mathbb{C}^{(n-p+1)} \qquad \text{(II.D-8)}$$

Assuming that $\mathbb{H}'$ is non-singular, we may solve for the n^{th} order coefficients:

$$\mathbb{C}^{(n)} = \mathbb{H}'^{-1}\mathbb{M}^{(n)} \qquad \text{(II.D-9)}$$

where

$$\mathbb{M}^{(n)} = -\mathbb{V}'\mathbb{C}^{(n-1)} + \sum_{p=2}^{n-1} \epsilon_p \mathbb{S}\mathbb{C}^{(n-p+1)} \qquad \text{(II.D-10)}$$

The energy of order 2n is determined by substituting Eq. (II.D-9) into Eq. (II.D-2). To determine the odd order energies we use the expression:

$$\epsilon_{2N+1} = \mathbb{C}^{(n)\dagger}\mathbb{V}'\mathbb{C}^{(n)} - \sum_{p=2}^{2N} \epsilon_p \sum_{i=n+1-p}^{n} \mathbb{C}^{\dagger(i)}\mathbb{S}\mathbb{C}^{(2n+1-p-i)} \qquad \text{(II.D-11)}$$

The library subroutine Matinv was used to perform the matrix inversion in Eq. (II.D-9). It uses the Jordan method to reduce the matrix $\mathbb{M}$ to the identity matrix $\mathbb{I}$. through a succession of elementary transformations. A search is made to maximize the pivot element, and rows are interchanged to put the pivot element on the diagonal. Equations (II.D-2) to (II.D-11) were programmed in general, allowing the determination of the energy coefficients to as high an order as desired.

2. Choice of Basis Set

Two types of basis sets $\{\mathbb{Q}_i\}$ have been investigated. We refer to these as the H set and the F set and to their use as the H method and the F method. Briefly, elements of the H set are composed of powers of confocal elliptic coordinates and r_{12} multiplied by an exponential factor. In the F set, the exponential is replaced by the zeroth order wave function. It is felt that the second choice has certain advantages over the first in perturbation calculations of this type. The equations relating to these particular choices are derived in the next two sections. Their relative merits are discussed in Chapter IV.

E. Evaluation of Matrix Elements

A major advance in the treatment of the hydrogen molecule was made by James and Coolidge[23] when they introduced the interelectronic separation r_{12} explicitly into the variation function. Their trial function is given by

$$\varphi_i = (p_i q_i r_i s_i \mu_i) + (q_i p_i s_i r_i \mu_i) \qquad \text{(II.E-1)}$$

$$\equiv h_i + h_i' \qquad \text{(II.E-2)}$$

with

$$(pqrs\mu) = e^{-\alpha(\xi_1+\xi_2)} \xi_1^p \xi_2^q \eta_1^r \eta_2^s r_{12}^\mu \qquad \text{(II.E-3)}$$

1. Basis Set H

These functions are used in Eq. (II.D-1) as a basis set, the H set, for expanding the nth order wave functions. The matrix elements resulting from their substitution into the variational expressions for the higher order perturbation corrections must be expressed in terms of the primitive integral M_ℓ^ν.

The first element evaluated is H_{ij}. Expanding Eq. (II.D-3) with the use of Eq. (II.E-2) gives

$$H_{ij} = \langle h_i | H_0 | h_j \rangle + \langle h_i | H_0 | h_j' \rangle + \langle h_i' | H_0 | h_j \rangle + \langle h_i' | H_0 | h_j' \rangle \qquad \text{(II.E-4)}$$

In the evaluation of $\langle h | H_0 | h' \rangle$, the derivation of Kolos[24] and Roothaan who calculated accurate electronic wave functions for the hydrogen molecule by extending the work of James and Coolidge is followed closely. To begin with, consider the zeroth order Hamiltonian

$$H_0 = H_0^{(1)} + H_0^{(2)} \qquad \text{(II.E-5)}$$

where

$$H_0^{(i)} = -\frac{\nabla_i^2}{2} - \frac{1}{r_{a_i}} - \frac{1}{r_{b_i}} \qquad \text{(II.E-6)}$$

Since the wave function is symmetric with respect to electrons one and two, the Hamiltonian, Eq. (II.E-5), may be written as

$$H_o = 2H_o^{(1)} \tag{II.E-7}$$

Thus:

$$\langle h|H_o|h'\rangle = \langle pqrs\mu|H_o|p'q'r's'\mu'\rangle$$

$$= \langle pqrs\mu| -\nabla_1^2 - \frac{2}{r_{a_1}} - \frac{2}{r_{b_1}} |p'q'r's'\mu'\rangle \tag{II.E-8}$$

The contribution of the Laplacian to the integral is given by:

$$-\langle pqrs\mu|\nabla_1^2|p'q'r's'\mu'\rangle$$

$$= \int d\tau_2\, \varphi_{qs}(2)\, \varphi_{q's'}(2)$$

$$\times \int d\tau_1 [\nabla_1 \varphi_{pr}(1)\, r_{12}^{\mu}]\cdot[\nabla_1 \varphi_{p'r'}(1)\, r_{12}^{\mu'}] \tag{II.E-9}$$

where

$$\varphi_{pr}(i) = e^{-\alpha\xi_i}\, \xi_i^{p}\, \eta_i^{r} \tag{II.E-10}$$

Let us denote the second integral in Eq. (II.E-9) by

$$I = \int d\tau_1 \, [\vec{\nabla}_1 \varphi_{pn}(1) \Pi_{12}^{\mu}] \cdot [\vec{\nabla}_1 \varphi_{p'n'}(1) \Pi_{12}^{\mu'}] \qquad \text{(II.E-11)}$$

Following Kolos and Roothaan, the integral is transformed in the following manner:

$$\begin{aligned} I = \int d\tau_1 \, \{ & [\vec{\nabla}_1 \varphi_{pn}(1)] \cdot [\vec{\nabla}_1 \varphi_{p'n'}(1)] \Pi_{12}^{\mu+\mu'} \\ & + \varphi_{pn}(1) \varphi_{p'n'}(1) [\vec{\nabla}_1 \Pi_{12}^{\mu}] \cdot [\vec{\nabla}_1 \Pi_{12}^{\mu'}] \\ & + [\varphi_{pn}(1) \vec{\nabla}_1 \varphi_{p'n'}(1)] \cdot [\Pi_{12}^{\mu'} \vec{\nabla}_1 \Pi_{12}^{\mu}] \\ & + [\varphi_{p'n'}(1) \vec{\nabla}_1 \varphi_{pn}(1)] \cdot [\Pi_{12}^{\mu} \vec{\nabla}_1 \Pi_{12}^{\mu'}] \end{aligned} \qquad \text{(II.E-12)}$$

Continuing,

$$\begin{aligned} I = \int d\tau_1 \, \{ & [\vec{\nabla}_1 \varphi_{pn}(1)] \cdot [\vec{\nabla}_1 \varphi_{p'n'}(1)] \Pi_{12}^{\mu+\mu'} \\ & + \mu \mu' \varphi_{pn}(1) \varphi_{p'n'}(1) \Pi_{12}^{\mu+\mu'-2} \\ & + (\mu+\mu')^{-1} [\mu \varphi_{pn}(1) \vec{\nabla}_1 \varphi_{p'n'}(1) \\ & + \mu' \varphi_{p'n'}(1) \vec{\nabla}_1 \varphi_{pn}(1)] \cdot [\vec{\nabla}_1 \Pi_{12}^{\mu+\mu'}] \} \end{aligned} \qquad \text{(II.E-13)}$$

By Green's theorem,

$$\int d\tau_1 \, \varphi_{pn}(1) \, \Pi_{12}^{\mu+\mu'} \, \nabla_1^{\,2} \varphi_{p'n'}(1) =$$

$$- \int d\tau_1 \, \vec{\nabla}_1 \varphi_{p'n'}(1) \cdot \vec{\nabla} \left(\varphi_{pn}(1) \, \Pi_{12}^{\mu+\mu'} \right) \qquad \text{(II.E-14)}$$

where the surface integral of $\varphi_{pq}(1) \, \Pi_{12}^{\mu+\mu'} \vec{\nabla} \varphi_{p'q'}(1)$ vanishes. Application of this equation to I results in, after some manipulation,

$$I = \int d\tau_1 \; \{ \mu\mu' \varphi_{pn}(1) \, \varphi_{p'n'}(1) \, \Pi_{12}^{\mu+\mu'-2}$$

$$-(\mu+\mu')^{-1} [\mu \varphi_{pn}(1) \, \nabla_1^{\,2} \varphi_{p'n'}(1)$$

$$+\mu' \varphi_{p'n'}(1) \, \nabla_1^{\,2} \varphi_{pn}(1)] \, \Pi_{12}^{\mu+\mu'} \qquad \text{(II.E-15)}$$

This expression is valid for the cases where either μ on μ' equals zero. Where both parameters vanish the interpretation

$$\frac{\mu}{\mu+\mu'} = \frac{\mu'}{\mu+\mu'} = \frac{1}{2} \qquad \text{(II.E-16)}$$

is made. The other contribution to $\langle h \,|\, H_0 \,|\, h' \rangle$ is simply evaluated. By Eq. (II.B-6),

$$\langle h| -\frac{2}{r_{a_1}} - \frac{2}{r_{b_1}} |h'\rangle = -\frac{8}{R}\langle h| \frac{\xi_1}{\xi_1^2-\eta_1^2}|h'\rangle \qquad \text{(II.E-17)}$$

Combining Eqs. (II.E-17) and (II.E-15)and applying the formula for the Laplacian in confocal elliptic coordinates given in Eq. (II.B-7) results in the final expression:

$$\begin{aligned}
\langle h| H_0 |h'\rangle = -4R^{-2}\Big[& \alpha^2 [M_0^\circ(\bar{p}+2, \bar{q}\bar{n}\bar{s}\bar{\mu}) \\
& - M_0^\circ(\bar{p}\bar{q}\bar{n}\bar{s}\bar{\mu})] - 2\alpha\Big\{ \frac{(\mu' p + \mu p')}{\bar{\mu}} [M_0^\circ(\bar{p}+1, \bar{q}\bar{n}\bar{s}\bar{\mu}) \\
& - M_0^\circ(\bar{p}-1, \bar{q}\bar{n}\bar{s}\bar{\mu})] + 2M_0^\circ(\bar{p}+1, \bar{q}\bar{n}\bar{s}\bar{\mu})\Big\} \\
& + \Big[\frac{(\mu' p + \mu p')}{\bar{\mu}}(\bar{p}+1) - pp'\Big][M_0^\circ(\bar{p}\bar{q}\bar{n}\bar{s}\bar{\mu}) \\
& - M_0^\circ(\bar{p}-2, \bar{q}\bar{n}\bar{s}\bar{\mu})] - \Big[\frac{(\mu' q + \mu q')}{\bar{\mu}}(\bar{q}+1) - qq'\Big] \\
& \times [M_0^\circ(\bar{p}\bar{q}\bar{n}\bar{s}\bar{\mu}) - M_0^\circ(\bar{p}\bar{q}, \bar{n}-2, \bar{s}\bar{\mu})] \\
& + 2\frac{(\mu' p + \mu p')}{\bar{\mu}} M_0^\circ(\bar{p}-2, \bar{q}\bar{n}\bar{s}\bar{\mu}) \\
& - 2\frac{(\mu' q + q'\mu)}{\bar{\mu}} M_0^\circ(\bar{p}\bar{q}, \bar{n}-2, \bar{s}\bar{\mu})\Big] \\
& + \mu\mu' [M_0^\circ(\bar{p}+2, \bar{q}\bar{n}\bar{s}, \bar{\mu}-2) - M_0^\circ(\bar{p}\bar{q}, \bar{n}-2, \bar{s}, \bar{\mu}-2)] \\
& - 8R^{-1} M_0^\circ(\bar{p}+1, \bar{q}\bar{n}\bar{s}\bar{\mu}) \qquad \text{(II.E-18)}
\end{aligned}$$

with $\bar{\mu} = \mu + \mu'$, $\bar{p} = p + p'$, $\bar{n} = n + n'$, $\bar{q} = q + q'$
and $\bar{s} = s + s'$.

The evaluation of the remaining matrix elements is straightforward. Substituting Eq. (II.E-2) into Eqs. (II.D-3) - (II.D-7) leads to

$$S_{ij} = \langle h_i | h_j \rangle + \langle h_i | h_j' \rangle + \langle h_i' | h_j \rangle + \langle h_i' | h_j' \rangle \tag{II.E-19}$$

$$V_{ij} = \langle h_i | V | h_j \rangle + \langle h_i | V | h_j' \rangle + \langle h_i' | V | h_j \rangle + \langle h_i' | V | h_j' \rangle \tag{II.E-20}$$

$$V_{io} = \langle h_i | V | \psi_o \rangle + \langle h_i' | V | \psi_o \rangle \tag{II.E-21}$$

and

$$N_{io} = \langle h_i | \psi_o \rangle + \langle h_i' | \psi_o \rangle \tag{II.E-22}$$

The elements on the right hand side of these equations may be written immediately in terms of the primitive integrals:

$$\langle h | h' \rangle = M_o^o(\bar{p}+2, \bar{q}\, \bar{n}\, \bar{s}\, \bar{\mu}) - M_o^o(\bar{p}\, \bar{q}, \bar{n}+2, \bar{s}\, \bar{\mu}) \tag{II.E-23}$$

$$\langle h|V|h'\rangle = M_0^0(\bar{p}+2, \bar{q}\,\bar{n}\,\bar{s}\,\bar{\mu}) - M_0^0(\bar{p}\,\bar{q}, \bar{n}+2, \bar{s}\,\bar{\mu}) \qquad \text{(II.E-24)}$$

$$\langle h|\psi_0\rangle = M_1^0(p+2, q\,n\,s\,\mu) - M_1^0(p\,q, n+2, s\,\mu) \qquad \text{(II.E-25)}$$

and

$$\langle h|V|\psi_0\rangle = M_1^0(p+2, q\,n\,s, \mu-1) - M_1^0(p\,q, n+2, s, \mu-1) \qquad \text{(II.E.26)}$$

2. Basis Set F

A popular method, generally associated with Dalgarno and Lewis[8], for facilitating the analytical determination of the first order wave function is to write ψ_1 in the form:

$$\psi_1 = F\psi_0 \qquad \text{(II.E.27)}$$

The substitution of this expression into the first order perturbation equation, Eq. (II.A-9), produces a differential equation for F which is often more susceptible to solution than the equation for ψ_1. The question arises: are there any advantages to be gained by incorporating the zeroth order wavefunction in the higher order corrections when using a variational principle to solve the perturbation equations. In order to find out, the nth order wave function is written in the form

$$\psi_n = F_n \psi_0 = \sum_i C_i^{(n)} [f_i + f_i'] \psi_0 \qquad \text{(II.E-28)}$$

where

$$f = \xi_1^{p} \xi_2^{q} \eta_1^{r} \eta_2^{s} r_{12}^{\mu} \qquad \text{(II.E-29)}$$

and

$$f' = \xi_1^{q} \xi_2^{p} \eta_1^{s} \eta_2^{r} r_{12}^{\mu} \qquad \text{(II.E-30)}$$

The wavefunction expansion is then substituted into the variation expression, Eq. (II.D-2),and the corresponding matrix elements are evaluated.

The first matrix element considered is

$$H_{ij} = \langle \psi_0 | f_i H_0' f_j | \psi_0 \rangle + \langle \psi_0 | f_i' H_0' f_j | \psi_0 \rangle$$

$$+ \langle \psi_0 | f_i H_0' f_j | \psi_0 \rangle + \langle \psi_0 | f_i' H_0' f_j' | \psi_0 \rangle \qquad \text{(II.E-31)}$$

The integrals on the right of Eq. (II.E-31) may be reduced in the following manner:

$$\langle \psi_0 | f H_0' f | \psi_0 \rangle = \langle \psi_0 | f H_0 f' - f f' H_0 | \psi_0 \rangle$$

$$= - \langle \psi_0 | f \vec{\nabla}_1 \cdot \vec{\nabla}_1 f' + 2 f \vec{\nabla}_1 f' \cdot \vec{\nabla}_1 | \psi_0 \rangle \tag{II.E-32}$$

The integrand is now written in the form

$$\psi_0^2 f \vec{\nabla}_1 \cdot \vec{\nabla}_1 f' + 2 \psi_0^2 f \vec{\nabla}_1 f' \cdot \vec{\nabla}_1 \psi_0$$

$$= - \psi_0^2 \vec{\nabla}_1 f \cdot \vec{\nabla}_1 f' - \vec{\nabla}_1 \cdot (f \psi_0^2 \vec{\nabla}_1 f') \tag{II.E-33}$$

Integrating Eq. (II.E-33), applying Green's theorem, and noting that the surface integral of $f \psi_0^2 \cdot \vec{\nabla}_1 f'$ vanishes, leads to

$$\langle \psi_0 | f H_0' f' | \psi_0 \rangle = \langle \psi_0 | \vec{\nabla}_1 f \cdot \vec{\nabla}_1 f' | \psi_0 \rangle \tag{II.E-34}$$

In order to evaluate Eq. (II.E-34), an expression for the del operator in confocal elliptic coordinates is required:

$$\vec{\nabla} = \frac{2}{R}\sqrt{\frac{\xi^2-1}{\xi^2-\eta^2}}\;\hat{\xi}\,\frac{\partial}{\partial\xi} + \frac{2}{R}\sqrt{\frac{1-\eta^2}{\xi^2-\eta^2}}\;\hat{\eta}\,\frac{\partial}{\partial\eta} + \frac{2}{R}\,\frac{1}{\sqrt{(\xi^2-1)(1-\eta^2)}}\;\hat{\phi}\,\frac{\partial}{\partial\phi} \tag{II.E-35}$$

It is convenient to define

$$f = \xi_1^{p}\,\xi_2^{q}\,\eta_1^{n}\,\eta_2^{s}\,\Pi_{12}^{\mu} \equiv \alpha(1)_{pn}\,\alpha(2)_{qs}\,\Pi_{12}^{\mu} \equiv \varphi\,\Pi_{12}^{\mu} \tag{II.E-36}$$

Substituting Eq. (II.E-36) into Eq. (II.E-34) gives

$$\langle\psi_0|fH_0'f'|\psi_0\rangle = \langle\psi_0|\Pi_{12}^{\mu+\mu'}\vec{\nabla}_1\varphi\cdot\vec{\nabla}_1\varphi' + \varphi\varphi'\vec{\nabla}_1\Pi_{12}^{\mu}\cdot\vec{\nabla}_1\Pi_{12}^{\mu'} + \varphi\nabla_1\varphi'\cdot\left(\Pi_{12}^{\mu'}\vec{\nabla}_1\Pi_{12}^{\mu}\right) + \varphi'\vec{\nabla}_1\varphi\cdot\left(\Pi_{12}^{\mu}\vec{\nabla}_1\Pi_{12}^{\mu'}\right)|\psi_0\rangle \tag{II.E-37}$$

It is thus necessary to evaluate the four integrals

$$I_1 = \langle\psi_0|\Pi_{12}^{\mu+\mu'}\vec{\nabla}_1\varphi\cdot\vec{\nabla}_1\varphi'|\psi_0\rangle \tag{II.E-38}$$

$$I_2 = \langle\psi_0|\varphi\varphi'\vec{\nabla}_1\Pi_{12}^{\mu}\cdot\vec{\nabla}_1\Pi_{12}^{\mu'}|\psi_0\rangle \tag{II.E-39}$$

$$I_3 = \langle \Psi_0 | \varphi \vec{\nabla}_1 \varphi' \cdot (\Pi_{12}^{\mu'} \vec{\nabla}_1 \Pi_{12}^{\mu}) | \Psi_0 \rangle \qquad \text{(II.E-40)}$$

and

$$I_4 = \langle \Psi_0 | \varphi' \vec{\nabla}_1 \varphi \cdot (\Pi_{12}^{\mu} \vec{\nabla}_1 \Pi_{12}^{\mu'}) | \Psi_0 \rangle \qquad \text{(II.E-41)}$$

The first of these integrals, upon application of Eq. (II.E-35), becomes

$$I_1 = \frac{4}{R^2} \langle \Psi_0 | f f' [\xi_1^2 - \eta_1^2]^{-1} [pp' - nn' - pp'\xi_1^{-2} + nn'\eta_1^{-2}] | \Psi_0 \rangle \qquad \text{(II.E-42)}$$

The integral I_2 is easily evaluated. Application of the del operator to Π_{12}^{μ} results in the expression

$$I_2 = \langle \Psi_0 | \mu\mu' \Pi_{12}^{\mu+\mu'-2} | \Psi_0 \rangle \qquad \text{(II.E-43)}$$

The integrals I_3 and I_4 are evaluated together. Combining Eq. (II.E-40) and (II.E-41) gives

$$I_3 + I_4 = \int d\tau_1 d\tau_2 \, (\mu+\mu')^{-1} (\mu \varphi \vec{\nabla}_1 \varphi' + \mu' \varphi' \vec{\nabla}_1 \varphi) \cdot \vec{\nabla}_1 \Pi_{12}^{\mu+\mu'} \qquad \text{(II.E-44)}$$

Introducing the relationship

$$\Pi_{12} = \frac{R}{2}\left\{ \xi_1^2 + \xi_2^2 + \eta_1^2 + \eta_2^2 - 2 - 2\xi_1\xi_2\eta_1\eta_2 - \left[(\xi_1^2-1)(\xi_2^2-1)(1-\eta_1^2)(1-\eta_2^2)\right]^{1/2}\cos(\varphi_1-\varphi_2)\right\}^{1/2} \quad \text{(II.E-45)}$$

and applying the Laplacian.Eq. (II.E-35), leads to

$$I_3 + I_4 = \frac{2}{R^2}\int d\tau_1 d\tau_2\, \Pi_{12}^{\mu+\mu'-2}(\xi_1^2-\eta_1^2)^{-1}$$

$$\times\left\{ \frac{\xi_1^2-1}{\xi_1}(\mu p'\varphi\varphi' + \mu' p\varphi\varphi')\left(2\xi_1 - 2\xi_2\eta_1\eta_2 - \frac{2T\xi_1}{(\xi_1^2-1)}\right)\right.$$

$$\left. + \frac{(1-\eta_1^2)}{\eta_1}(\mu\pi'\varphi\varphi' + \mu'\pi\varphi\varphi')\left(2\eta_1 - 2\xi_1\xi_2\eta_2 + \frac{2T\eta_1}{(1-\eta_1^2)}\right)\right\}$$

where (II.E-46)

$$T = \left[(\xi_1^2-1)(\xi_2^2-1)(1-\eta_1^2)(1-\eta_2^2)\right]^{1/2}\cos(\varphi_1-\varphi_2) \quad \text{(II.E-47)}$$

Substituting the integrals I_1, I_2, I_3, and I_4 into Eq. (II.E-37) and expressing the results in terms of the primitive integrals M_l^{ν} results in the final expression:

$$\langle \Psi_0 | f H_0' f' | \Psi_0 \rangle = 2R^{-2}[(2\rho\rho' - \eta\eta' - \beta - \gamma)$$

$$\times M_2^0(\bar{\rho}\bar{q}\bar{\eta}\bar{s}\bar{\mu}) - 2\rho\rho' M_2^0(\bar{\rho}-2, \bar{q}\bar{\eta}\bar{s}\bar{\mu})$$

$$2\eta\eta' M_2^0(\bar{\rho}\bar{q}, \bar{\eta}-2, \bar{s}\bar{\mu})]$$

$$+\frac{1}{2}(2\mu\mu' + \beta + \gamma)[M_2^0(\bar{\rho}+2, \bar{q}\bar{\eta}\bar{s}, \bar{\mu}-2)$$

$$- M_2^0(\bar{\rho}\bar{q}, \bar{\eta}+2, \bar{s}, \bar{\mu}-2)]$$

$$+\frac{1}{2}(\beta - \gamma)[M_2^0(\bar{\rho}+2, \bar{q}\bar{\eta}\bar{s}, \bar{\mu}-2)$$

$$- M_2^0(\bar{\rho}\bar{q}, \bar{\eta}+2, \bar{s}, \bar{\mu}-2)]$$

$$+\gamma M_2^0(\bar{\rho}-1, \bar{q}+1, \bar{\eta}+1, \bar{s}+1, \bar{\mu}-2)$$

$$-\beta M_2^0(\bar{\rho}+1, \bar{q}+1, \bar{\eta}-1, \bar{s}+1, \bar{\mu}-2) \qquad \text{(II.E-48)}$$

where

$$\beta = \mu\rho' + \mu'\rho \qquad \gamma = \mu\eta' + \mu'\eta \qquad \text{(II.E-49)}$$

The remaining matrix elements, determined by substituting $\varphi_i = f_i + f_i'$ into Eqs. (II.D-2) - (II.D-7), are:

$$S_{ij} = \langle \psi_0 | f_i f_j | \psi_0 \rangle + \langle \psi_0 | f_i f_j' | \psi_0 \rangle + \langle \psi_0 | f_i' f_j | \psi_0 \rangle + \langle \psi_0 | f_i' f_j' | \psi_0 \rangle \qquad \text{(II.E-50)}$$

$$V_{ij} = \langle \psi_0 | f_i V f_j | \psi_0 \rangle + \langle \psi_0 | f_i V f_j' | \psi_0 \rangle + \langle \psi_0 | f_i' V f_j | \psi_0 \rangle + \langle \psi_0 | f_i' V f_j' | \psi_0 \rangle \qquad \text{(II.E-51)}$$

$$V_{io} = \langle \psi_0 | f_i V | \psi_0 \rangle + \langle \psi_0 | f_i' V | \psi_0 \rangle \qquad \text{(II.E-52)}$$

and

$$N_{io} = \langle \psi_0 | f_i | \psi_0 \rangle + \langle \psi_0 | f_i' | \psi_0 \rangle \qquad \text{(II.E-53)}$$

Comparison of the integrals on the right of these equations with Eq. (II.C-6) leads to the final expressions,

$$\langle \psi_0 | f f' | \psi_0 \rangle = M_2^0(\bar{p}+2, \bar{q}\, \bar{n}\, \bar{s}\, \bar{\mu}) - M_2^0(\bar{p}\, \bar{q}, \bar{n}+2, \bar{s}\, \bar{\mu}) \qquad \text{(II.E-54)}$$

$$\langle \psi_0 | f V f' | \psi_0 \rangle = M_2^0(\bar{p}+2, \bar{q}\,\bar{n}\bar{s}, \bar{\mu}-1) - M_2^0(\bar{p}\bar{q}, \bar{n}+2, \bar{s}, \bar{\mu}-1) \qquad \text{(II.E-55)}$$

$$\langle \psi_0 | f | \psi_0 \rangle = M_2^0(p+2, q n s \mu) - M_2^0(p q, n+2, s \mu) \qquad \text{(II.E-56)}$$

and

$$\langle \psi_0 | f V | \psi_0 \rangle = M_2^0(p+2, q n s, \mu-1) - M_2^0(p q, n+2, s, \mu-1) \qquad \text{(II.E-57)}$$

Notice that all matrix elements are expressible as combinations of $M_2^0(p q n s \mu)$. In contrast, the matrix elements corresponding to the H Set required the additional sets of integrals $M_1^0(p q n s \mu)$ and $M_0^0(p q n s \mu)$.

CHAPTER III

COMPUTATIONAL

In this chapter, the primitive integrals M_ℓ^ν are evaluated. Because of the complex functional form of the hydrogen molecular ion eigenfunctions, this evaluation is quite difficult. Although the theory of two center integrals is highly developed, it is rather specialized in that most investigators have been primarily interested in the problems associated with integrations over atomic Slater orbitals. Unfortunately, the integrands in the present problem contain functions of a more complex nature.

Our first thought was to expand the eigenfunction in terms of Chebyshev polynomials, and to order the resulting expansion in powers of ξ and η. The advantage of such an approach is that it allows the primitive integrals to be expressed in terms of well known integrals which have been thoroughly investigated. Unfortunately, this method turned out to be so inefficient and time consuming that it was impossible to obtain high accuracy using a reasonable amount of computing time.

In search of a better approach, existing methods available for evaluating the usual two center exchange integrals were analyzed. It was discovered that a formalism developed by Ruedenberg could be extended to allow efficient evaluation of $1/r_{12}$ integrals over arbitrary well behaved functions, provided they were separable in confocal elliptic coordinates. This method was consequently adopted.

The general procedure for evaluating the primitive integrals is to first reduce the power of r_{12} to either zero or minus one depending on whether it was initially even or odd. These two cases are then treated separately.

The integrals which contain no power of r_{12} in the integrand are immediately separable into six one dimensional integrals. The integrations over the φ and η coordinates are performed analytically. The remaining integrations are accomplished, except for special cases, by numerical techniques.

It is in the second case - where the integrands contain $1/r_{12}$ - that difficulties are encountered. The preliminary step in the evaluation of these integrals is to expand $1/r_{12}$ in terms of infinite sets of orthogonal polynomials. The integrals over the φ and η coordinates may be evaluated analytically. The integration over the ξ coordinate is accomplished by a generalized Ruedenberg technique.

A. Evaluation of Primitive Integrals

For convenience, we rewrite the primitive integrals Eq. (II.C-6) in the form

$$M_\ell^\nu(pqrs\mu) = \iint d\tau_1 d\tau_2 (\xi_1^2-\eta_1^2)^{-1}$$

$$\times e^{-\delta_\ell(\xi_1+\xi_2)} f^\ell g^\ell [(\xi_1^2-1)(\xi_2^2-1)(1-\eta_1^2)(1-\eta_2^2)]^{\nu/2}$$

$$\times \cos^\nu(\varphi_1-\varphi_2)\, \xi_1^p \xi_2^q \eta_1^r \eta_2^s r_{12}^\mu \qquad \text{(III.A-1)}$$

where the quantities f, g, and δ_ℓ are defined in the following manner:

$$f = [(\xi_1+1)(\xi_2+1)]^\sigma$$

$$\times \sum_{k,k'=0}^{\infty} g_k g_{k'} \left(\frac{\xi_1-1}{\xi_1+1}\right)^k \left(\frac{\xi_2-1}{\xi_2+1}\right)^{k'} \qquad \text{(III.A-2)}$$

$$g = \sum_{j,j'=0}^{\infty} f_j f_{j'} P_j(\eta_1) P_{j'}(\eta_2) \qquad \text{(III.A-3)}$$

and

$$\delta_\ell = \ell\rho - \alpha(\ell-2) \qquad \text{(III.A-4)}$$

As a preliminary step in the evaluation of M_ℓ^ν , odd powers of r_{12} are reduced to minus one and even powers to zero. This is accomplished by substituting the expression for r_{12} in confocal elliptic coordinates, Eq. (III.A-1), into Eq. (II.E-45) resulting in the relationship:

$$M_\ell^\nu(pqns,\mu+2) = M_\ell^\nu(p+2,qns\mu) + M_\ell^\nu(p,q+2,ns\mu)$$

$$+ M_\ell^\nu(pq,n+2,s\mu) + M_\ell^\nu(pqn,s+2,\mu) - 2M_\ell^\nu(pqns\mu)$$

$$-2M_\ell^\nu(p+1,q+1,n+1,s+1,\mu) - 2M_\ell^{\nu+1}(pqns\mu) \qquad \text{(III.A-5)}$$

Thus it is only necessary to consider the two sets of integrals $M_\ell^\nu(pqns,0)$ and $M_\ell^\nu(pqns,-1)$. These integrals are evaluated in the next two sections.

1. Reduction of $M_\ell^\nu(pqns,0)$

As shown in the last section, all integrals containing even powers of r_{12} may be reduced to the set of integrals

$$M_\ell^\nu(pqns,0) = \frac{R^6}{64}\int_0^{2\pi}\int_0^{2\pi} d\varphi_1\, d\varphi_2 \cos\nu(\varphi_1-\varphi_2)$$

$$\times \int_1^\infty d\xi_1 \int_1^\infty d\xi_2 \int_{-1}^{1} d\eta_1 \int_{-1}^{1} d\eta_2\, e^{-\delta_\ell(\xi_1+\xi_2)} f^\ell g^\ell$$

$$\times [(\xi_1^2-1)(\xi_2^2-1)(1-\eta_1^2)(1-\eta_2^2)]^{\nu/2} \xi_1^p \xi_2^q \eta_1^n \eta_2^s (\xi_2^2-\eta_2^2) \qquad \text{(III.A-6)}$$

Since these integrals do not contain the coordinate, r_{12}, they are relatively easy to evaluate. The integration over the coordinates φ_1 and φ_2 is accomplished analytically.

For even values of ν ,

$$\int_0^{2\pi}\int_0^{2\pi} d\varphi_1\, d\varphi_2 \cos^{\nu}(\varphi_1-\varphi_2) = \frac{4\pi^2}{2^{\nu}}\binom{\nu}{\nu/2} \tag{III.A-7}$$

For odd values of ν the integral vanishes. Here, the binomial expansion $\binom{n}{K}$ is defined by the relationship:

$$\binom{n}{K} = \frac{n!}{(n-K)!\,K!} \tag{III.A-8}$$

Let us define the integral,

$$W_\ell^{\nu}(pqns) = \int_1^{\infty} d\xi_1 \int_1^{\infty} d\xi_2 \int_{-1}^{1} d\eta_1 \int_{-1}^{1} d\eta_2\, e^{-\delta_\ell(\xi_1+\xi_2)} f^{\ell} g^{\ell}$$

$$[(\xi_1^2-1)(\xi_2^2-1)(1-\eta_1^2)(1-\eta_2^2)]^{\nu/2}\, \xi_1^{p}\, \xi_2^{q}\, \eta_1^{n}\, \eta_2^{s} \tag{III.A-9}$$

The substitution of Eq. (III.A-7) and Eq. (III.A-9) into Eq. (III.A-6) results, for even values of ν , in the expression

$$M_\ell^{\nu}(pqns,0) = \frac{\pi^2 R^6}{2^{(\nu+4)}}\binom{\nu}{\nu/2}\left[W_\ell^{\nu}(p+2,qns) - W_\ell^{\nu}(pq,n+2,s)\right] \tag{III.A-10}$$

For odd values of ν , the integral vanishes.

For convenience, let us define the two integrals:

$$E_\ell^\nu(p) = \int_1^\infty e^{-\delta_\ell \xi} \xi^p (\xi^2-1)^{\nu/2} (\xi+1)^{\ell\sigma}$$

$$\times\left[\sum_n g_n \left(\frac{\xi-1}{\xi+1}\right)^n\right]^\ell d\xi \qquad \text{(III.A-11)}$$

and

$$G_\ell^\nu(n) = \int_{-1}^1 (1-\eta^2)^{\nu/2} \eta^n$$

$$\times\left[\sum_n f_n P_n(\eta)\right]^\ell d\eta \qquad \text{(III.A-12)}$$

These integrals may be reduced by expanding $(\xi^2-1)^{\nu/2}$ and $(1-\eta^2)^{\nu/2}$ with the aid of the binomial theorem, leading to

$$E_\ell^\nu(n) = \sum_{K=0}^{\nu/2} (-1)^K \binom{\nu/2}{K} A_\ell(p+\nu-K) \qquad \text{(III.A-13)}$$

and

$$G_\ell^\nu(s) = \sum_{K=0}^{\nu/2} (-1)^K \binom{\nu/2}{K} B_\ell(s+2K) \qquad \text{(III.A-14)}$$

where the basic integrals A_ℓ and B_ℓ are defined by

$$A_\ell(m) = \int_1^\infty e^{-\delta_\ell \xi} \xi^m \left[(\xi+1)^\sigma \sum_j g_j \left(\frac{\xi-1}{\xi+1}\right)^j\right]^\ell d\xi \qquad \text{(III.A-15)}$$

and

$$B_\ell(s) = \int_{-1}^{1} \left[\sum_m f_m P_m(\eta)\right]^\ell \eta^s d\eta \qquad \text{(III.A-16)}$$

Since the H_2^+ eigenfunction is even in η, the integral $B_\ell(s)$ vanishes for odd values of s . Combining results leads to an expression for $M_\ell^\nu(pqnso)$ of the form

$$M_\ell^\nu(pqnso) = \frac{\pi^2 R^6}{2^{\nu+4}} \frac{\nu!}{[(\nu/2)!]^2} \sum_{ijkm=0}^{\nu/2} D_{ij}^{km}$$

$$\times \left[A_\ell(p+\nu+2-i) A_\ell(q+\nu-j) B_\ell(n+2k) B_\ell(s+2m)\right.$$

$$\left. - A_\ell(p+\nu-i) A_\ell(q+\nu-i) B_\ell(n+2k+2) B_\ell(j+2m)\right] \qquad \text{(III.A-17)}$$

where

$$D_{ij}^{km} = \frac{(-1)^{i+j+k+m} \, [(\nu/2)!]^4}{i!\, j!\, k!\, m!\, (i-\nu/2)!\, (j-\nu/2)!\, (k-\nu/2)!\, (m-\nu/2)!} \qquad \text{(III.A-18)}$$

a. Calculation of $B_\ell(j)$

The integrals B (j) are evaluated for three separate values of ℓ . Consider the case where $\ell = 0$. Here, for even values of j :

$$B_0(j) = \int_{-1}^{1} \eta^j \, d\eta$$

$$= \frac{2}{j+1} \qquad \text{(III.A-19)}$$

For odd values of j, the integral vanishes.

The second case considered is $\ell = 1$. Here

$$B_1(j) = \int_{-1}^{1} \Big[\sum_m f_m P_m(\eta)\Big] \eta^j \, d\eta \qquad \text{(III.A-20)}$$

Interchanging the summation and integration gives

$$B_1(j) = \sum_m g_m R_m(j) \qquad \text{(III.A-21)}$$

where

$$R_m(j) = \int_{-1}^{1} P_m(\eta) \, \eta^j \, d\eta \qquad \text{(III.A-22)}$$

The R_m's exist only for even values of m + j. They are reduced by making use of the recursion formula (Eq. II.B-19) which, when substituted into Eq. (III.A-22) leads to the recursion relation

$$(m+1) R_{m+1}(j) = (2m+1) R_m(j+1) - m R_{m-1}(j) \qquad \text{(III.A-23)}$$

All integrals are subsequently expressed in terms of

$$\mathcal{R}_0(j) = \mathcal{B}_0(j) = \frac{2}{j+1} \qquad \text{(III.A-24)}$$

and

$$\mathcal{R}_1(j) = \mathcal{B}_0(j+1) \qquad \text{(III.A-25)}$$

Finally, we consider the remaining value, $\ell = 2$. For this case

$$\mathcal{B}_2(j) = \int_{-1}^{1} d\eta \, \eta^{j} \left[\sum_m f_m P_m(\eta)\right]^2 \qquad \text{(III.A-26)}$$

Performing the multiplication and interchanging the summation and integration gives

$$\mathcal{B}_2(j) = \sum_{m,n} g_m g_n F_{mn}(j) \qquad \text{(III.A-27)}$$

where the integral F_{mn} is defined by

$$F_{mn}(j) = \int_{-1}^{1} P_m(\eta) P_n(\eta) \eta^{j} d\eta \qquad \text{(III.A-28)}$$

Substituting Eq. (II.B-19) into Eq. (III.A-28) leads to the recursion relation

$$(n+1)F_{m,n+1}(j)=(2n+1)F_{m,n}(j+1)-nF_{m,n-1}(j) \qquad \text{(III.A-29)}$$

which is used to reduce the $F_{m,n}'s$ to either

$$F_{m,0}(j)=R_m(j) \qquad \text{(III.A-30)}$$

or

$$F_{m,1}(j)=R_m(j+1) \qquad \text{(III.A-31)}$$

An alternate method of determining the K's when ℓ is not equal to zero, is to perform the integration numerically using the method of Gaussian quadrature. Again, this would be slightly more inefficient than the analytical approach but would allow for greater generality in the application of the computor programs.

b. Calculation of $A_\ell(j)$

The integral A_ℓ is treated separately for three different values of ℓ. For the case $\ell = 0$

$$A_0(j)=\int_1^\infty e^{-2\alpha\xi}\,\xi^j\,d\xi \qquad \text{(III.A-32)}$$

The integrals $A_o(j)$ are often encountered in molecular calculations. They are usually denoted by $A_j(2\alpha)$. Their evaluation is accomplished by the reduction to

$$A_o(o) = \frac{e^{-2\alpha}}{2\alpha} \qquad \text{(III.A-33)}$$

using the recursion formula

$$A_o(j) = \frac{1}{2\alpha}\left[e^{-2\alpha} + m A_o(j-1)\right] \qquad \text{(III.A-34)}$$

When ℓ is not equal to zero, the complicated form of the integrands in Eq. (III.A-15) makes the analytical integration of the A_ℓ's impractical but not impossible. They may be evaluated analytically by expanding the integrands using the binomial expansion and the expressing the results in terms of the incomplete Gamma Function.[21] However, a superior approach from the standpoint of both accuracy and generality is numerical quadrature, using Laguerre Gauss formalism.

2. Reduction of $M_\ell^\nu(pq\,ns,-1)$

The only integrals remaining to be calculated are

$$M_\ell^\nu(pq\,ns,-1) = J_\ell^\nu(p,q+2,ns) - J_\ell^\nu(pq\,n,s+2)$$

(III.A-35)

where

$$J_\ell^\nu(pqns) = \frac{R^6}{64}\int_1^\infty d\xi_1 \int_1^\infty d\xi_2 \int_{-1}^1 d\eta_1 \int_{-1}^1 d\eta_2 \int_0^{2\pi} d\varphi_1 \int_0^{2\pi} d\varphi_2$$

$$\times\, e^{-\delta_\ell(\xi_1+\xi_2)}\, \xi_1^{p}\, \xi_2^{q}\, \eta_1^{n}\, \eta_2^{s}\, [(\xi_1^2-1)(\xi_2^2-1)]^{\nu/2}$$

$$[(1-\eta_1^2)(1-\eta_2^2)]^{\nu/2} \cos^\nu(\varphi_1-\varphi_2) \left(\frac{1}{r_{12}}\right)$$

$$\left[\sum_{m,n} g_m g_n \left(\frac{\xi_1-1}{\xi_1+1}\right)^n \left(\frac{\xi_2-1}{\xi_2+1}\right)\right]^\ell$$

$$\left[\sum_{m,n} f_m f_n P_m(\eta_1) P_n(\eta_2)\right]^\ell \qquad \text{(III.A-36)}$$

Reduction of Eq. (III.A-36) is accomplished by the introduction of the Neumann expansion

$$\frac{1}{r_{12}} = \frac{4}{R}\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell} (-1)^m \frac{(\ell-|m|)!}{(\ell+|m|)!} P_\ell^{|m|}(\xi_>) Q_\ell^{|m|}(\xi_<)$$

$$\times\, \mathcal{P}_\ell^{|m|}(\eta_1)\, \mathcal{P}_\ell^{|m|}(\eta_2) \exp[im(\varphi_1-\varphi_2)] \qquad \text{(III.A-37)}$$

where $P_\ell^{|m|}$ and $Q_\ell^{|m|}$, the unnormalized associated Legendre function of the first and second kind, respectively, are defined by the relationships:

$$P_\ell^{|m|}(x) = |(1-x^2)|^{m/2} \frac{d^m}{dx^m} P_\ell(x) \qquad \text{(III.A-38)}$$

and

$$Q_\ell^{|m|}(x) = |(x^2-1)|^{m/2}\frac{d^m}{dx^m}Q_\ell(x) \qquad \text{(III.A-39)}$$

where

$$P_\ell(x) = \frac{1}{2^n n!}\frac{d^\ell}{dx^\ell}((1-x^2)|^\ell \qquad \text{(III.A-40)}$$

and

$$Q_\ell(x) = \frac{P_\ell(x)}{2}\ln\left|\frac{x+1}{1-x}\right| - \sum_{m=1}^{\ell}\frac{1}{m}P_{m-1}(x)\,P_{\ell-m}(x) \qquad \text{(III.A-41)}$$

The normalized associated Legendre function is given by

$$\mathcal{P}_\ell^{|m|}(x) = \left[\frac{(2\ell+1)(\ell-m)!}{2(\ell+m)!}\right]^{1/2} \times P_\ell^{|m|}(x) \qquad \text{(III.A-42)}$$

Substituting the Neumann expansion into Eq. (III.A-36) and regrouping terms leads to the expression

$$J_\ell^\nu(pqns) = \frac{R^5}{8}\sum_{\lambda=0}^{\infty}\sum_{m=-\lambda}^{\lambda}(-1)^m\frac{(\lambda-|m|)!}{(\lambda+|m|)!}$$

$$\times\int_0^{2\pi}d\varphi_1\int_0^{2\pi}d\varphi_2\; e^{im(\varphi_1-\varphi_2)}\cos^\nu(\varphi_1-\varphi_2)$$

$$\times\int_{-1}^{1}d\eta_1\left[\sum_n f_n P_n(\eta_1)\right]^\ell \mathcal{P}_\lambda^{|m|}(\eta_1)\,\eta_1^{\,n}$$

$$\times\int_{-1}^{1}d\eta_2\left[\sum_n f_n P_n(\eta_2)\right]^\ell \mathcal{P}_\lambda^{|m|}(\eta_2)\,\eta_2^{\,s}$$

$$\int_1^\infty\int_1^\infty d\xi_1\,d\xi_2\; e^{-\delta_\ell(\xi_1+\xi_2)}\,\xi_1^{\,p}\,\xi_2^{\,q}$$

$$\times\left[(\xi_1^2-1)(\xi_2^2-1)\right]^{\frac{\nu+m}{2}} h^\ell\, P_\lambda^{|m|}(\xi_<)\,Q_\lambda^{|m|}(\xi_>)$$

(III.A-43)

The integrations over the φ coordinates are accomplished readily. For values of m and ν satisfying the conditions $m \leq \nu$, with m even,

$$\int_0^{2\pi}\int_0^{2\pi}d\varphi_1\,d\varphi_2\,\exp[im(\varphi_1-\varphi_2)]\cos^\nu(\varphi_1-\varphi_2)$$

$$= \frac{4\pi^2}{2^\nu}\binom{\nu}{\frac{m+\nu}{2}}$$ (III.A-44)

For all other values of m and ν the integral vanishes.

Defining the auxiliary functions

$$\mathcal{Q}_{\ell,\lambda}^{m,n}(r) = \int_{-1}^{1} d\eta \, (1-\eta^2)^{\frac{m+n}{2}} \, \eta^n \, \mathcal{P}_\lambda^{|m|}(\eta)$$

$$\times \Big[\sum_i f_i \, P_i(\eta) \Big]^\ell \tag{III.A-45}$$

$$\Phi_{\ell\lambda}^{m,n}(pq) = (-1)^m \frac{(\lambda-|m|)!}{(\lambda+|m|)!} \int_1^\infty \int_1^\infty d\xi_1 \, d\xi_2 \, e^{-\delta_\ell(\xi_1+\xi_2)}$$

$$\xi_1^p \, \xi_2^q \, [(\xi_1^2-1)(\xi_2^2-1)]^{\frac{n+m}{2}} \, h^\ell \, P_\lambda^{|m|}(\xi_<) \, Q_\lambda^{|m|}(\xi_>) \tag{III.A-46}$$

and

$$\sigma(\nu,m) = \begin{cases} \dfrac{4\pi^2}{2^{\nu+3}} \dbinom{\nu}{\frac{m+\nu}{2}} R^6 & m+\nu \text{ even} \\ 0 & \text{otherwise} \end{cases} \tag{III.A-47}$$

and making use of Eq. (III.A-44) results in the expression

$$J_\ell^\nu(pqrs) = \sum_{m=-\nu}^{\nu} \sum_{\lambda=|m|}^{\infty} \sigma(\nu,m)$$

$$\times \mathcal{Q}_{\ell,\lambda}^{m,\nu-|m|}(r) \, \mathcal{Q}_{\ell,\lambda}^{m,\nu-|m|}(s) \, \Phi_{\ell,\lambda}^{m,\nu-|m|}(pq) \tag{III.A-48}$$

Methods for the evaluation of the integrals $\mathcal{Q}_{\ell,\lambda}^{m,n}$ and $\Phi_{\ell,\lambda}^{m,n}$ are presented in the next two sections.

a. Calculation of $\mathcal{Q}_{\ell,\lambda}^{m,n}(n)$

The preliminary step in the determination of the integrals $\mathcal{Q}_{\ell,\lambda}^{m,n}$ is to reduce them to

$$\mathcal{Q}_{\ell,\lambda}^{m,n}(n) = \int_{-1}^{1} (1-\eta^2)^{m/2}\, \eta^n\, \mathcal{P}_\lambda^{|m|}(\eta) \times \Big[\sum_i f_i\, P_i(\eta)\Big]^\ell d\eta$$

using the recursion relation,

$$\mathcal{Q}_{\ell,\lambda}^{m,n}(n) = \mathcal{Q}_{\ell,\lambda}^{m,n-2}(n) - \mathcal{Q}_{\ell,\lambda}^{m,n-2}(n+2) \qquad \text{(III.A-50)}$$

The $\mathcal{Q}_{\ell,\lambda}^{m,n}$ are considered separately for three different values of ℓ.

Case 1: $\ell=0$

This is the simplest of the three cases in that the H_2^+ function is absent from the integrand:

$$\mathcal{Q}_{0,\lambda}^{m,m}(n) = \int_{-1}^{1} (1-\eta^2)^{m/2}\, \eta^n\, \mathcal{P}_\lambda^{|m|}(\eta)\, d\eta \qquad \text{(III.A-51)}$$

Introducing the expression for the normalized associated Legendre Function, Eq. (III.A-42), leads to

$$\mathcal{Q}_{0,\lambda}^{m,m}(n) = \left[\frac{(2\lambda+1)(\lambda-m)!}{2(\lambda+m)!}\right]^{1/2} R_\lambda^m(n) \qquad \text{(III.A-52)}$$

where

$$R_\lambda^m(n) = \int_{-1}^{1} \eta^n (1-\eta^2)^{m/2} P_\lambda(\eta) \qquad \text{(III.A-53)}$$

These integrals are often encountered in atomic and molecular calculations. Kotani's[27] solution is given by:

$$R_\lambda^m(n) = 2\cdot \frac{n!(\lambda+m)(\lambda+m-1)\cdots(\lambda-m+1)}{2\cdot 4\cdot\cdots(m+n-\lambda)\cdot 1\cdot 3\cdots(\lambda+m+\nu+1)} \qquad \lambda+m+n=\text{even} \qquad \text{(III.A-54)}$$

$$= 0 \qquad \text{otherwise}$$

This form for the R_λ^{m}'s is convenient if only a few particular integrals are desired. However, an approach which is better suited for use with high speed computors depends upon the recursion relation,

$$R_\lambda^{m+1}(n) = (\lambda-m)\, R_\lambda^m(n+1) - (\lambda+m)\, R_{\lambda-1}^m(n) \qquad \text{(III.A-55)}$$

which is derived by substituting into Eq. (III.A-53) the relationship for varying the order of associated Legendre polynomials[26]

$$P_{\nu}^{\mu+1}(z) = (z^2-1)^{-1/2}\left[(\nu-\mu)\, z\, P_{\nu}^{\mu}(z) - (\nu+\mu)\, P_{\nu-1}^{\mu}(z)\right] \qquad \text{(III.A-56)}$$

The $R_{\lambda}^{m}(n)$ are reduced to the integrals, $R_{\lambda}(n)$ which are then calculated using the methods of Section III.A-1a.

Case 2: $\ell = 1$

The substitution of Eq. (III.A-42) into Eq. (III.A-49) gives

$$\mathcal{Q}_{1,\lambda}^{m,m}(n) = \left[\frac{(2\lambda+1)(\lambda-m)!}{2(\lambda+m)!}\right]^{1/2} B_{1,\lambda}^{m}(n) \qquad \text{(III.A-57)}$$

where

$$B_{\ell,\lambda}^{m}(n) = \int_{-1}^{1} (1-\eta^2)^{m/2}\, \eta^{n}\, P_{\lambda}^{|m|}(n) \times \left[\sum_{n} f_n P_n(\eta)\right]^{\ell} d\eta \qquad \text{(III.A-58)}$$

The $B^{m}_{l,\lambda}$'s are reduced to the B_l's, which were considered in Section III.A-1a, by the use of the two recursion formulas:

$$B^{m+1}_{l,\lambda}(n) = (\lambda - m)\, B^{m}_{l,\lambda}(n+1) - (\lambda+m)\, B^{m}_{l,\lambda-1}(n) \qquad \text{(III.A-59)}$$

and

$$(\lambda+1)\, B^{0}_{l,\lambda+1}(n) = (2\lambda+1)\, B^{0}_{l,\lambda}(n+1) - \lambda\, B^{0}_{l,\lambda-1}(n) \qquad \text{(III.A-60)}$$

Case 3: $l = 2$

The $Q^{m,m}_{l,\lambda}$ for this value of l are written in the form:

$$Q^{m,m}_{2,\lambda}(n) = \left[\frac{(2\lambda+1)(\lambda-m)!}{2(\lambda+m)!}\right]^{1/2} B^{m}_{2,\lambda}(n) \qquad \text{(III.A-61)}$$

The most straightforward way of evaluating these integrals is to reduce them to the integrals $B_2(n)$, Eq. (III.A-26), by applying the recursion formulas, Eq. (III.A-59) and (III.A-60). An alternate approach based on the following composition[28] for spherical harmonics could also be used:

$$\int Y_{\ell_1}^{m_1}(\Omega)\, Y_{\ell_2}^{m_2}(\Omega)\, Y_{\ell_3}^{m_3}(\Omega)\, d\Omega$$

$$= \left[\frac{(2\ell_1+1)(2\ell_2+1)(2\ell_3+1)}{4\pi}\right]^{1/2} \begin{pmatrix} \ell_1 & \ell_2 & \ell_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_1 & \ell_2 & \ell_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$$

(III.A-62)

Here $\begin{pmatrix} \ell_1 & \ell_2 & \ell_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$ is the Wigner 3j symbol. As an example, we consider the integrals $B^{0}_{2,\lambda}(0)$. Expanding the zeroth order wave function gives:

$$B^{0}_{2,\lambda}(0) = \sum_{jK} f_j f_K \int_{-1}^{1} P_\lambda(\eta) P_j(\eta) P_K(\eta)\, d\eta$$

$$= \sum_{j,K} f_j f_K \begin{pmatrix} \lambda & j & K \\ 0 & 0 & 0 \end{pmatrix}^2 \qquad \text{(III.A-63)}$$

The 3j symbol for[28] the case $m_1 = m_2 = m_3 = 0$ has the following value:

$$\begin{pmatrix} \ell & j & K \\ 0 & 0 & 0 \end{pmatrix} = \begin{cases} 0 & \ell+j+K \text{ odd} \\ (-1)^p \sqrt{\Delta(\ell j K)}\, \dfrac{p!}{(p-\ell)!(p-j)!(p-K)!} & 2p \equiv \ell+j+K \text{ even} \end{cases}$$

(III.A-64)

with

$$\sqrt{\Delta(\ell j k)} = \frac{(\ell+j-k)!\,(j+k-\ell)!\,(k+\ell-j)!}{(\ell+j+k+1)!}$$

(III.A-65)

b. Calculation of $\Phi^{m,n}_{\ell,\lambda}(pq)$

Of the integrals which have been considered thus far, the remaining integrals

$$\begin{aligned}\Phi^{m,n}_{\ell,\lambda}(pq) = {} & (-1)^m \frac{(\lambda-|m|)!}{(\lambda+|m|)!}\int_1^\infty\int_1^\infty d\xi_1\, d\xi_2\, \xi_1^{p}\, \xi_2^{q} \\ & \times [(\xi_1^2-1)(\xi_2^2-1)]^{\frac{n+m}{2}}\, e^{-\delta_\ell(\xi_1+\xi_2)}\, P_\lambda^{|m|}(\xi_<)\, Q_\lambda^{|m|}(\xi_>) \\ & \times \Big[\sum_{i,j} g_i g_j \Big(\frac{\xi_1-1}{\xi_1+1}\Big)^{i} \Big(\frac{\xi_2-1}{\xi_2+1}\Big)^{j}\Big]^{\lambda} [(\xi_1+1)(\xi_2+1)]^{\lambda\sigma}\end{aligned}$$

(III.A-66)

are the most difficult to evaluate. The complex nature of the Jaffe form of the zeroth order eigenfunctions in the integrands precludes an analytical evaluation. Thus, it is necessary to rely solely on numerical integration procedures.

Unfortunately, the integrands contain associated Legendre polynomials of the second kind. Considerable loss in accuracy generally results from the use of recursion relations involving these functions. It is important then, to somehow get rid of the Q's before attempting numerical integration.

Ruedenberg, in the evaluation of two center exchange integrals, has devised an ingenious method of accomplishing this. The fact that this method can be extended to include the evaluation of the $\Phi_{\ell,\lambda}^{m,n}$ is indeed fortunate.

As a preliminary step in the determination of the $\Phi_{\ell,\lambda}^{m,n}$ the recursion relation

$$\Phi_{\ell,\lambda}^{m,n}(pq) = \Phi_{\ell,\lambda}^{m,n-2}(p+2,q+2) - \Phi_{\ell,\lambda}^{m,n-2}(p+2,q) - \Phi_{\ell,\lambda}^{m,n-2}(p,q+2) + \Phi_{\ell,\lambda}^{m,n-2}(p,q) \qquad \text{(III.A-67)}$$

is used to reduce them to $\Phi_{\ell,\lambda}^{m,0} \equiv \Phi_{\ell,\lambda}^{m}$. Next, the recursion relation[29]

$$\Phi_{\ell,\lambda}^{m}(pq) = \Phi_{\ell,\lambda}^{m-1}(p+1,q+1) - \frac{(\ell+m-1)}{(2\ell+1)}\Phi_{\ell,\lambda+1}^{m-1}(pq) - \frac{(\ell-m)}{2\ell+1}\Phi_{\ell,\lambda+1}^{m-1}(pq) \qquad \text{(III.A-68)}$$

is used to further reduce the $\Phi_{\ell,\lambda}^{m}$ to the form

$$\Phi_{\ell,\lambda}^{0} \equiv \Phi_{\ell,\lambda} ,$$

where

$$\Phi_{\ell,\lambda}(pq) = \int_1^\infty \int_1^\infty d\xi_1 d\xi_2 \, e^{-\delta_\lambda(\xi_1+\xi_2)}$$

$$\times \xi_1^{p} \xi_2^{q} \, (\xi_1+1)^{\lambda\sigma} \, (\xi_2+1)^{\lambda\sigma}$$

$$\times \left[\sum_{i,j=0}^{\infty} g_i \, g_j \left(\frac{\xi_1-1}{\xi_1+1}\right)^{i} \left(\frac{\xi_2-1}{\xi_2+1}\right)^{j} \right]^{\lambda} \qquad \text{(III.A-69)}$$

let us define

$$\alpha_{\ell,\lambda}^{p}(\xi) = e^{-\delta_\lambda \xi} \, (\xi+1)^{\lambda\sigma}$$

$$\times \sum_{n} g_n \left(\frac{\xi-1}{\xi+1}\right)^{n} \xi^{p} \qquad \text{(III.A-70)}$$

Using this definition, Eq. (III.A-69) is written in the form

$$\Phi_{\ell,\lambda}(pq) = \int_1^\infty d\xi_1\, Q_\lambda(\xi_1)\,\alpha^{p}_{\ell,\lambda}(\xi_1) \int_1^{\xi_1} d\xi_2\, \alpha^{q}_{\ell,\lambda}(\xi_2)\, P_\lambda(\xi_2)$$

$$+ \int_1^\infty d\xi_1\, P_\lambda(\xi_1)\,\alpha^{p}_{\ell,\lambda}(\xi_1) \int_{\xi_1}^\infty d\xi_2\, \alpha^{q}_{\ell,\lambda}(\xi_2)\, Q_\lambda(\xi_2)$$

(III.A-71)

Following Ruedenberg, the second term on the right hand side of Eq. (III.A-71) is integrated by parts giving

$$\int_1^\infty d\xi_1\, P_\lambda(\xi_1)\,\alpha^{p}_{\ell,\lambda}(\xi_1) \int_{\xi_1}^\infty d\xi_2\, \alpha^{q}_{\ell,\lambda}(\xi_2)\, Q_\lambda(\xi_2)$$

$$= \int_1^{\xi_1} d\xi_2\, Q_\ell(\xi_2)\,\alpha^{q}_{\ell,\lambda}(\xi_2) \int_{\xi_1}^\infty d\xi_2\, P_\ell(\xi_2)\,\alpha^{p}_{\ell,\lambda}(\xi_2) \Bigg|_{\xi_1=1}^{\xi_1=\infty}$$

$$+ \int_1^\infty d\xi_1\, Q_\ell(\xi_1)\,\alpha^{q}_{\ell,\lambda}(\xi_1) \int_1^{\xi_1} d\xi_2\, P_\ell(\xi_2)\,\alpha^{p}_{\ell,\lambda}(\xi_2)$$

(III.A-72)

The first term on the right of the equal sign vanishes, since the range of one or the other of the integrals is zero at the limit points. Equation (III.A-71) may therefore be written in the form

$$\Phi_{\ell,\lambda}(pq) = \int_1^\infty d\xi_1\, Q_{\ell,\lambda}(\xi_1)\Big[\alpha^{p}_{\ell,\lambda}(\xi_1) \int_1^{\xi_1} d\xi_2\, \alpha^{q}_{\ell,\lambda}(\xi_2)\, P_\ell(\xi_2)$$

$$+ \alpha^{q}_{\ell,\lambda}(\xi_1) \int_1^{\xi_1} d\xi_2\, \alpha^{p}_{\ell,\lambda}(\xi_2)\, P_\ell(\xi_2)\Big]$$

(III.A-73)

This is then expressed as

$$\Phi_{\ell,\lambda}(pq) = \int_1^{\infty} d\xi \; \frac{Q_\ell(\xi)}{P_\ell(\xi)} \frac{d}{d\xi}$$

$$\times \left[\int_1^{\xi} dx \, \alpha^{p}_{\ell,\lambda}(x) \, P_\ell(x) \int_1^{\xi} dy \, \alpha^{q}_{\ell}(y) \, P_\ell(y) \right]$$

(III.A-74)

If we now perform a partial integration we find:

$$\Phi_{\ell,\lambda}(pq) = \frac{Q_\ell(\xi)}{P_\ell(\xi)} \int_1^{\xi} dx \, \alpha^{p}_{\ell,\lambda}(x) \, P_\ell(x) \int_1^{\xi} dy \, \alpha^{q}_{\ell,\lambda}(y) \, P_\ell(y) \Big|_1^{\infty}$$

$$- \int_1^{\infty} \frac{d}{d\xi} \left[\frac{Q_\ell(\xi)}{P_\ell(\xi)} \right] \int_1^{\xi} dx \, \alpha^{p}_{\ell,\lambda}(x) \, P_\ell(x) \int_1^{\xi} dy \, \alpha^{q}_{\ell,\lambda}(y) \, P_\ell(y)$$

(III.A-75)

Consider the first term on the right hand side of Eq. (III.A-75). At the lower limit, Q_ℓ / P_ℓ approaches a constant value while the range of the two integrals approaches zero. At the upper limit, assuming the functions $\alpha^{p}_{\ell,\lambda}$ are well behaved, which is the present case, the integrals remain finite while Q_ℓ / P_ℓ approaches zero. Thus the term vanishes. Continuing the Ruedenberg derivation, we introduce the Wronskian

$$[P_\ell, Q_\ell] = \frac{1}{(1-x^2)} \qquad \text{(III.A-76)}$$

resulting in the expression

$$\Phi_{\ell,\lambda}(pq) = \int_1^\infty d\xi\, [(\xi^2-1)^{1/2} P_\ell(\xi)]^{-1/2}$$

$$\times\, \mathcal{J}^{p}_{\ell,\lambda}(\xi)\; \mathcal{J}^{q}_{\ell,\lambda}(\xi) \qquad \text{(III.A-77)}$$

where

$$\mathcal{J}^{p}_{\ell,\lambda}(\xi) = \int_1^\xi dx\, \alpha^{p}_{\ell,\lambda}(x)\, P_\ell(x) \qquad \text{(III.A-78)}$$

The integrals, Eq. (III.A-77), are now in a form convenient for numerical quadrature.

The important aspect of the preceding development is the fact that the Ruedenberg method does not require a particular functional form for the integrands. This implies that the rapid evaluation of diatomic electron repulsion integrals of the form $\langle \Phi(1)\Phi(2)|\frac{1}{r_{12}}|\Phi(1)\Phi(2)\rangle$ depends far more on the separability of Φ's than upon their complexity. This result is important for the adaptation of perturbation techniques to molecular problems since perturbation wave functions are often quite complex.[30,31]

B. Numerical Details

1. General Integration Procedure

Throughout the last section, continual emphasis was placed on the fact that, if integrals were evaluated using numerical quadrature methods exclusively, generalized programs could be developed which would be readily adaptable to other molecular perturbation calculations. This is an important result in that the development of molecular integral programs is a difficult, expensive and time consuming task.

Perturbation functions tend to be quite complex. If integrals containing these functions are evaluated analytically, each calculation requires individual treatment. It would thus seem reasonable to evaluate all such integrals numerically using a program sufficiently generalized that very few changes would have to be made for each individual calculation.

In order to demonstrate how such a program could be written and to emphasize the simplification in organization resulting from a completely numerical approach, the results of the last section are rederived from a slightly different point of view with the function ψ_0 replaced by an arbitrary function φ .

Consider the primitive integrals

$$\bar{M}_\ell^\nu(pqns\mu) = \iint d\tau_1 d\tau_2 \, (\xi_1^2-\eta_1^2)^{-1}$$

$$\times\, e^{-\ell\alpha(\xi_1+\xi_2)} \varphi_1^\ell(\xi_1)\varphi_2^\ell(\xi_2)\varphi_3^\ell(\eta_1)\varphi_4^\ell(\eta_2)$$

$$\times\, [(\xi_1^2-1)(\xi_2^2-1)(1-\eta_1^2)(1-\eta_2^2)]^{1/2}\cos^\nu(\varphi_1-\varphi_2)\, \xi_1^p \xi_2^q \eta_1^n \eta_2^s r_{12}^\mu$$

(III.B-1)

where φ_1, φ_2, φ_3 and φ_4 are arbitrary functions of the coordinates ξ_1, ξ_2, η_1, and η_2 respectively. As before, the preliminary step in the evaluation of these integrals is the reduction to $M_\ell^\nu(pqns,0)$ and $M_\ell^\nu(pqns,-1)$ using the relationship Eq. (III.A-5).

The integrals $M_\ell^\nu(pqns,0)$ are immediately separable into products of one electron integrals. Integrating out the dependence, we find that for even values of the parameters ν, r, and s:

$$M_\ell^\nu(pqns,0) = \frac{R^6\pi^2}{2^{\nu+4}}\binom{\nu}{\frac{\nu}{2}}\left[\bar{B}_\ell^\nu(p+2,qns) - \bar{B}_\ell^\nu(pq,n+2,s)\right]$$

(III.B-2)

where

$$\bar{B}_\ell^\nu(pqns) = F_\ell^\nu(p,1)F_\ell^\nu(q,2)G_\ell^\nu(n,3)G_\ell^\nu(s,4)$$

(III.B-3)

with the basic integrals G_ℓ^ν and F_ℓ^ν defined by

$$F_\ell^\nu(p,j) = \int_1^\infty e^{-\ell\alpha\xi}\,\xi^p\,\varphi_j^\ell(\xi)(\xi^2-1)^{\nu/2}\,d\xi \qquad \text{(III.B-4)}$$

and

$$G_\ell^\nu(n,j) = \int_{-1}^{1}(1-\eta^2)^{\nu/2}\,\eta^n\,\varphi_j^\ell(\eta)\,d\eta \qquad \text{(III.B-5)}$$

For all other combinations of ν, r, and s, the integrals are equal to zero. The integrations of $F_\ell^\nu(p,j)$ and $G_\ell^\nu(n,s)$ are now accomplished by applying the numerical quadrature procedures which are detailed in the next section.

The remaining integrals $\bar{M}_\ell^\nu(pqns,-1)$ are evaluated by introducing the Neumann expansion for $1/r_{12}$ and integrating out the φ dependence leading to

$$\bar{M}_\ell^\nu(pqns,-1) = \bar{J}_\ell^\nu(p,q+2,ns) - \bar{J}_\ell^\nu(pqn,s+2) \qquad \text{(III.B-6)}$$

where

$$\bar{J}_\ell^\nu(pqns) = \sum_{m=-\nu}^{\nu}\sum_{\ell=|m|}^{\infty}\sigma(\nu,m)\,\mathcal{Q}_{\ell,\lambda}^{m,\nu-|m|}(n,3) \times \mathcal{Q}_{\ell,\lambda}^{m,\nu-|m|}(s,4)\,\Phi_{\ell,\lambda}^{m,\nu-|m|}(pq,1,2) \qquad \text{(III.B-7)}$$

with $\sigma(\nu,m)$ given by Eq. (III.A-47) while the two basic integrals $\mathcal{Q}^{m,n}_{\ell,\lambda}$ and $\Phi^{m,n}_{\ell,\lambda}$ are defined by

$$\mathcal{Q}^{m,n}_{\ell,\lambda}(n,j) = \int_{-1}^{1} d\eta\,(1-\eta^2)^{\frac{n+m}{2}}\,\eta^n\,\mathcal{P}^{|m|}_{\lambda}(\eta)\,\varphi^{\ell}_{j}(\eta) \tag{III.B-8}$$

and

$$\Phi^{m,n}_{\ell,\lambda}(pq,i,j) = (-1)^m \frac{(\lambda-|m|)!}{(\lambda+|m|)!}\int_1^\infty\int_1^\infty d\xi_1\,d\xi_2\,e^{-\ell\alpha(\xi_1+\xi_2)}$$

$$\xi_1^p\,\xi_2^q\,[(\xi_1^2-1)(\xi_2^2-1)]^{\frac{n+m}{2}}\,\varphi_1^{\ell}(\xi_1)\,\varphi_2^{\ell}(\xi_2)\,P_\lambda^{|m|}(\xi_<)\,Q_\lambda^{|m|}(\xi_>) \tag{III.B-9}$$

Using the relationship

$$\mathcal{Q}^{m,n}_{\ell,\lambda}(n,j) = \mathcal{Q}^{m,n-2}_{\ell,\lambda}(n,j) - \mathcal{Q}^{m,n-2}_{\ell,\lambda}(n+2,j) \tag{III.B-10}$$

the $\mathcal{Q}^{m,n}_{\ell,\lambda}$ are reduced to the integrals

$$\mathcal{Q}^{m,m}_{\ell,\lambda}(n,j) = \int_{-1}^{1} \eta^n (1-\eta^2)^{m/2}\,\mathcal{P}^{|m|}_{\lambda}(\eta)\,\varphi^{\ell}_{j}(\eta) \tag{III.B-11}$$

which are evaluated numerically.

The preliminary step in the evaluation of the $\Phi^{m,n}_{\ell,\lambda}(pqij)$ is their reduction to $\Phi_{\ell\lambda}(pqij)$ using the two relationships

$$\Phi_{\ell,\lambda}^{m,n}(pqij)=\Phi_{\ell,\lambda}^{m,n-2}(p+2,q+2,ij)-\Phi_{\ell,\lambda}^{m,n-2}(p+2,qij)$$

$$-\Phi_{\ell,\lambda}^{m,n-2}(p,q+2,ij)+\Phi_{\ell,\lambda}^{m,n-2}(pqij) \qquad \text{(III.B-12)}$$

and

$$\Phi_{\ell,\lambda}^{m}(pqij)=\Phi_{\ell,\lambda}^{m-1}(p+1,q+1,ij)-\frac{(\ell+m-1)}{(2\ell+1)}\Phi_{\ell-1,\lambda}^{m-1}(pqij)$$

$$-\frac{(\ell-m)}{(2\ell+1)}\Phi_{\ell+1,\lambda}^{m-1}(pqij) \qquad \text{(III.B-13)}$$

The $\Phi_{\ell,\lambda}$ are transformed using the method of Ruedenberg to the form

$$\Phi_{\ell,\lambda}(pqij)=\int_1^\infty d\xi\,[(\xi^2-1)^{1/2}P_\ell(\xi)]^{-2}$$

$$\times\,\mathcal{J}_{\ell,\lambda}^{p,i}\,\mathcal{J}_{\ell,\lambda}^{q,j} \qquad \text{(III.B-14)}$$

where

$$\mathcal{J}_{\ell,\lambda}^{p,i}=\int_1^\xi dx\,P_\lambda(x)\,e^{-\ell\alpha x}\,\varphi_j^{\ell}(x)\,x^{p} \qquad \text{(III.B-15)}$$

Equation (III.B-15) is then integrated numerically.

As an application of these results, consider the recent perturbation calculation on the hydrogen molecular ion by Lyon, Matcha, Sanders, Meath, and Hirschfelder,[30] in which the energy is determined through third order. The details of this calculation and a definition of symbols are given in Appendix I.

In order to define a perturbation problem, the H_2^+ Hamiltonian is written in the form

$$H = -\frac{\nabla^2}{2} - \frac{1}{r_a} - \frac{1}{r_b} = H_0 + V \qquad \text{(III.B-16)}$$

where

$$H_0 = -\frac{\nabla^2}{2} - \left(\frac{2a}{R}\right)\left(\frac{\xi}{\xi^2-\eta^2}\right)$$

$$-\frac{(a^2-b^2)}{2}\left(\frac{1-\eta^2}{\xi^2-\eta^2}\right) - \frac{2b\eta}{R(\xi^2-\eta^2)} \tanh(Rb\eta/2) \qquad \text{(III.B-17)}$$

with the perturbation determined from the equation

$$V = H - H_0 \qquad \text{(III.B-18)}$$

The exact solution to the zeroth order equation is given by

$$\psi_0 = e^{-\frac{Ra\xi}{2}} \cosh\left(\frac{Rb}{2}\eta\right) \qquad \text{(III.B-19)}$$

The analytical expression for the first order wave function is found to be:

$$\psi_1 = \psi_0 \left(F_\eta + F_\xi \right) \tag{III.B-20}$$

where

$$
\begin{aligned}
F_\eta = \Bigg[& \left[\frac{a^2-b^2-2\epsilon_1}{3b^2}\right]\ln\cosh\left(\frac{Rb\eta}{2}\right) + \left[\frac{3(a^2-b^2)-2R\epsilon_1}{12b}\right]\eta\tanh\left(\frac{Rb\eta}{2}\right) \\
& + \sum_{n=0}^{\infty} \frac{\ln\left[1-\frac{(1-\eta^2)R^2b^2}{\sigma_n^2+R^2b^2}\right]}{\sigma_n^2+R^2b^2} \left[\begin{gathered} -\frac{2\epsilon_1}{a} - \frac{4}{a} - \frac{2R\epsilon_1}{a} - 4R \\ +2Ra + \frac{2\epsilon_1}{b^2} - (a^2-b^2)/b^2 \end{gathered}\right] \\
& \qquad\qquad + \frac{\sigma_n^2-R^2b^2}{\sigma_n^2+R^2b^2}\left[\begin{gathered} -\frac{2\epsilon_1}{a^2} - \frac{4}{a} + 2Ra - 4R \\ -\frac{2R\epsilon_1}{a} - \frac{2R^2\epsilon_1}{3} + \frac{2\epsilon_1}{b^2} \\ -\frac{(a^2-b^2)}{b^2} + \frac{R^2(a^2-b^2)}{3} \end{gathered}\right] \\
& \left[\begin{gathered} -\frac{2\epsilon_1}{a^2} - \frac{4}{a} + 2Ra - 4R \\ -\frac{2R\epsilon_1}{a} - \frac{2R^2\epsilon_1}{3} + \frac{2\epsilon_1}{b^2} \\ -\frac{(a^2-b^2)}{b^2} + \frac{R^2(a^2-b^2)}{3} \end{gathered}\right] \frac{[\eta\tanh\left(\frac{Rb}{2}\eta\right) - \tanh\left(\frac{Rb}{2}\right)}{2Rb(1-\eta^2)} \\
& + F_2^0 \Bigg]
\end{aligned}
$$

(III.B-21)

and

$$F_\eta = \left(\frac{\epsilon_1}{a^2} + \frac{2Z-a}{a}\right)\ln(\xi+1) + \frac{R\epsilon_1\xi}{2a} + F_1^0 \qquad \text{(III.B-22)}$$

In order to normalize the total wavefunction, the integral $\langle\psi_0|\psi_1\rangle$ must be evaluated. An analytical evaluation required a month to complete. Let us consider its evaluation in terms of the $\overline{M}_\ell^{\nu}$'s . Writing

$$\frac{\langle\psi_0|\psi_1\rangle}{\langle\psi_0|\psi_0\rangle} = \frac{\langle\psi_0|F_\eta + F_\xi|\psi_0\rangle}{\langle\psi_0|\psi_0\rangle} \qquad \text{(III.B-23)}$$

we find it is necessary to evaluate the integrals $\langle\psi_0|\psi_0\rangle$, $\langle\psi_0|F_\eta|\psi_0\rangle$, and $\langle\psi_0|F_\xi|\psi_0\rangle$.

The first is given by

$$\langle\psi_0|\psi_0\rangle = \overline{M}_2^0(20000) - \overline{M}_2^0(00200) \qquad \text{(III.B-24)}$$

with $\alpha = \frac{Ra}{2}$, $\varphi_1 = \varphi_2 = \varphi_4 = 1$, and $\varphi_3 = \left[\cosh\frac{Rb}{2}\eta\right]^{1/2}$.

Similarly the second integral is given by

$$\langle\psi_0|F_\eta|\psi_0\rangle = \overline{M}_2^0(20000) - \overline{M}_2^0(00200) \qquad \text{(III.B-25)}$$

with $\alpha = \frac{Ra}{2}$, $\varphi_1 = \varphi_2 = \varphi_4 = 1$, and $\varphi_3 = \left[F_\eta \left(\cosh \frac{Rb}{2}\eta\right)\right]^{1/2}$.

The remaining integral has exactly the same form:

$$\langle \psi_0 | F_\xi | \psi_0 \rangle = \overline{M}_2^0(20000) - \overline{M}_2^0(00200)$$

with $\alpha = \frac{Ra}{2}$, $\varphi_2 = \varphi_4 = 1$, $\varphi_1 = F_\xi^{1/2}$ and $\varphi_3 = \left[\cosh\left(\frac{Rb}{2}\right)\right]^{1/2}$

(III.B-26)

2. Mechanical Quadrature

In this section, we consider numerical schemes for evaluating integrals with both finite and infinite limits.[32] A numerical quadrature procedure is one which approximates an integral, with limits (a,b) over a function $f(x)$ in the following manner:

$$\int_a^b f(x)\,dx = \sum_{i=1}^{N} W_i\, f(a_i) \qquad \text{(III.B-27)}$$

Here, the a_i are discrete points on the interval (a,b) and W_i are corresponding weights. Since the a_i and W_i form a set of 2N constants, the sum is capable of uniquely specifying a polynomial of degree 2N-1.

The distinguishing characteristic of various quadrature formulae is the manner in which the constants are chosen. Of interest to us are the two families of quadrature formulae discussed below.

a. Gauss Quadrature

Gauss quadrature formulas are characterized by the fact that no restrictions are placed on the 2N constants. Thus these formulae are capable of specifying uniquely a polynomial of order 2N-1. Two important members of this group are the Legendre-Gauss and Laguerre Gauss formulae.

The Legendre-Gauss quadrature formula for approximately evaluating a definite integral with limits (-1,1) is given by

$$\int_{-1}^{1} dx\, g(x) = \sum_{i=1}^{N} L_i\, g(a_i) \qquad \text{(III.B-28)}$$

where

$$L_i = \frac{2}{(1-a_i)\left[P_n'(a_i)\right]^2} \qquad \text{(III.B-29)}$$

and the abscissae a_i are the roots of the Legendre polynomials $P_n(x)$.

The Laguerre-Gauss formula for approximating the integral with limit $(0, \infty)$ and containing a weighting factor $e^{-\alpha x}$ is given by

$$\int_{0}^{\infty} e^{-x} f(x)\, dx = \sum_{i=1}^{N} H_i \cdot f(a_i) \qquad \text{(III.B-30)}$$

where

$$H_i = \frac{(n!)^2}{a_i\,[L_n'(a_i)]^2} \qquad \text{(III.B-31)}$$

The abscissae a_i are roots of the Laguerre polynomials of degree N . The associated Laguerre polynomials are defined by the equation

$$L_n^K = \frac{d^K}{dx^K} L_n \qquad \text{(III.B-32)}$$

where

$$L_n(x) = n! \sum_{j=0}^{n} \binom{n}{n-j} \frac{(-x)^j}{j!} \qquad \text{(III.B-33)}$$

are the Laguerre polynomials.

b. Newton-Cotes Quadrature

The Newton-Cotes formulae are characterized by equally spaced abscissae a_i on the interval (-1,1). This restriction of equal spacing removes N arbitrary constants. Thus,this method is capable of specifying uniquely polynomials of degree N-1. Specific members are Simpson's "three-eighths" rule and Weddle's rule.

In Simpson's "three-eighths" rule, the integral of f(x) is approximated in the following manner:

$$\int_{-1}^{1} f(x)\,dx = \frac{1}{4} f(-1) + \frac{3}{4} f\left(-\frac{1}{3}\right) + \frac{3}{4} f\left(\frac{1}{3}\right) + \frac{1}{4} f(1) \qquad \text{(III.B-34)}$$

Weddle's Rule states that

$$\int_{-1}^{1} f(x)\,dx = \frac{1}{10}\Big[f(-1) + 5 f\left(-\frac{2}{3}\right) + f\left(-\frac{1}{3}\right)$$

$$+ 6 f(0) + f\left(\frac{1}{3}\right) + 5 f(2/3) + f(1)\Big] \qquad \text{(III.B-35)}$$

In general, Gauss quadrature formulae should be used in preference to Newton-Cotes formulae whenever possible. Specific applications of the above formulae are discussed in the next section.

3. Details of Computation

In this section we consider in detail the evaluation of the integrals found in Sections A and B of this chapter. In order to perform numerical integrations efficiently, care must be taken to apply the proper quadrature formula. Generally, a Gauss quadrature formulation will give the best results.

The evaluation of the one-dimensional integrals over the coordinate such as Eq. (III.B-4), was accomplished by first transforming the integral to the range $(0,\infty)$ and then applying a Laguerre Gauss quadrature formula. The final working equation is of the form

$$\int_1^\infty e^{-\alpha\xi} f(\xi)d\xi = \frac{e^{-\alpha}}{\alpha} \sum_i H_i f\left(\frac{a_i}{\alpha}+1\right) \qquad \text{(III.B-36)}$$

where H_i and a_i are the Laguerre weights and point respectively and is an arbitrary function. Integrals involving the η coordinate, such as Eq. (III.B-5), are evaluated by applying a Legendre Gauss quadrature formula resulting in the equation

$$\int_{-1}^{1} g(\eta)d\eta = \sum_i L_i g(a_i) \qquad \text{(III.B-37)}$$

where H_i and a_i are the Legendre Gauss weights and points respectively and g is an arbitrary function.

To evaluate the Φ'_{γ}, Eq. (III.A-77), the inner integral was transformed in the manner

$$\int_1^\xi \longrightarrow \int_1^\infty - \int_\xi^\infty$$

and then evaluated with a Laguerre Gauss quadrature formula leading to the equation

$$\mathcal{J}_{\ell}^{p}(\xi) = \frac{e^{-\delta_\lambda}}{\delta_\lambda} \sum_{i=1}^{N} H_i \left[\bar{\alpha}_{\lambda}^{p}\left(\frac{a_i}{\delta_\lambda}+1\right) - \bar{\alpha}_{\lambda}^{p}\left(\frac{a_i}{\delta_\lambda}+\xi\right) e^{-(\xi-1)\delta_\lambda}\right] \tag{III.B-38}$$

where a_i and H_i are Laguerre Gauss points and weights respectively, and

$$\bar{\alpha}_{\ell}^{p}(x) = x^{p} P_{\ell}(x)\,(x^{2}+1)^{\sigma} \sum_{m} g_m \left(\frac{x-1}{x+1}\right)^{m} \tag{III.B-39}$$

The outer integral was transformed to the range $(0,1)$ by letting

$$\xi' = \frac{1}{\xi} \tag{III.B-40}$$

and then evaluated by applying a Legendre Gauss formula. Thus

$$\Phi_{\ell,\lambda} = \frac{1}{2} \sum_{i} L_i\, g\left(\frac{2}{a_i+1}\right) \tag{III.B-41}$$

where a_i and L_i are Legendre Gauss points and weights respectively and

$$g(x) = \frac{\bar{\alpha}_{\ell}^{p}(x)\,\bar{\alpha}_{\ell}^{q}(x)}{[(1-x^{2})\,P_{\ell}(x)]^{2}} \tag{III.B-42}$$

An alternate procedure for evaluating the Φ's is to use Simpson's rule over both variables.[22] The principle benefit of this method is that it allows for an efficient evaluation of the inner integration.[23]

IV. RESULTS AND DISCUSSION

In this chapter we consider the results of the perturbation calculation of the H_2 molecule. All computations were performed on the CDC 1604 and 3600 computors. The rate of convergence of the perturbation expansion has been found to be extremely rapid at the equilibrium separation, R = 1.4. The energy through fifth order is in good agreement with the accurate variational calculations of Kolos and Roothaan,[29] and of Kolos and Walniewicz[34].

The accuracy of the calculation improves as R decreases; for large R, the perturbation series is ill behaved. This is due primarily to the fact that the degeneracy of the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ states is not treated adequately. The zeroth order wave function dissociates incorrectly.

A. H_2^+ Energy and Wave Function

Bates, Ledsham and Stewart[15] have tabulated accurate wave functions and energies for the ground state of H_2^+, unfortunately a higher degree of accuracy is required in the present calculation. Thus the solution to the H_2^+ equation was determined to eight significant figures.

In Tables I, II and III the electronic energy and wave function corresponding to the $1s\sigma_g$ state of H_2^+ are given

TABLE I

Accurate Values for the Energy of H_2^+ excluding Nuclear Repulsion in units of $e^2/2a_o$

R	ρ	σ	$C-\rho^2$	E
0.4	0.37955279	0.05387184	-0.09573136	-3.60150807
0.6	0.54851367	0.09386517	-0.19922442	-3.34296942
0.8	0.70528975	0.13428559	-0.32789966	-3.10896019
1.0	0.85199364	0.17371769	-0.47594692	-2.90357262
1.2	0.99038460	0.21165050	-0.63922559	-2.72461571
1.4	1.12186623	0.24792061	-0.81469304	-2.56853848
1.6	1.24755747	0.28250605	-1.00004194	-2.43187444
1.8	1.36836066	0.31544267	-1.19347131	-2.31161838
2.0	1.48501462	0.34678809	-1.39353885	-2.20526842
2.2	1.59813388	0.37660557	-1.59906308	-2.11077016
2.4	1.70823724	0.40495708	-1.80905704	-2.02644061
2.6	1.81576876	0.43190039	-2.02268225	-1.95089716
2.8	1.92111309	0.45748837	-2.23921643	-1.88299772
3.0	2.02460685	0.48176917	-2.45803045	-1.82179239
3.8	2.42553823	0.56666259	-3.34596851	-1.62970518

TABLE II

Coefficients Corresponding to the ξ Portion of the H_2^+ Wave Function for Selected Values of the Internuclear Distance

R	g_1	g_2	g_3	g_4
0.4	1.00000	0.00097	0.00010	0.00002
0.6	1.00000	0.00239	0.00019	0.00003
0.8	1.00000	0.00419	0.00027	0.00004
1.0	1.00000	0.00622	0.00033	0.00005
1.2	1.00000	0.00834	0.00037	0.00005
1.4	1.00000	0.01050	0.00040	0.00004
1.6	1.00000	0.01265	0.00041	0.00004
1.8	1.00000	0.01475	0.00041	0.00004
2.0	1.00000	0.01678	0.00040	0.00004
2.2	1.00000	0.01873	0.00039	0.00003
2.4	1.00000	0.02057	0.00038	0.00003
2.6	1.00000	0.02232	0.00036	0.00002
2.8	1.00000	0.02395	0.00033	0.00002
3.0	1.00000	0.02547	0.00031	0.00002
3.8	1.00000	0.03038	0.00023	0.00001

TABLE III

Coefficients Corresponding to the η Portion of the H_2^+ Wavefunction for Selected Values of the Internuclear Separation

R	f_0	f_2	f_4	f_6	f_8	f_{10}
0.4	1.00000	0.01608				
0.6	1.00000	0.03375	0.00017			
0.8	1.00000	0.05613	0.00048			
1.0	1.00000	0.08247	0.00103			
1.2	1.00000	0.11226	0.00190			
1.4	1.00000	0.14518	0.00316	0.00002		
1.6	1.00000	0.18098	0.00489	0.00005		
1.8	1.00000	0.21951	0.00714	0.00010		
2.0	1.00000	0.26065	0.01001	0.00015		
2.2	1.00000	0.30430	0.01356	0.00025		
2.4	1.00000	0.35038	0.01787	0.00037		
2.6	1.00000	0.39883	0.02302	0.00055		
2.8	1.00000	0.44958	0.02908	0.00078	0.00002	
3.0	1.00000	0.50254	0.03615	0.00108	0.00002	
3.8	1.00000	0.73453	0.07956	0.00326	0.00008	

for various values of the internuclear separation.

B. Convergence of Energy Expansion

The rate of convergence at the equilibrium separation was highly satisfactory. In Table IV, the ϵ_n's resulting from a 45 term H set are tabulated. The dissociation energy in electron volts is referred to as D(eV). The symbol $E_{K.W.}$ refers to the 80 term variational calculation of Kolos and Woolnerwic[34] while $E_{K.R.}$ refers to the 50 term calculation of Kolos and Roothaan[29]. These values do not include the internuclear repulsion energy.

The symbol Esum(n) is defined as

$$Esum(n) = \sum_{i=1}^{n} \epsilon_n \qquad \text{(IV.A-1)}$$

The expectation value of $\frac{1}{r_{12}}$ has been determined using a formula derived by Scherr[10] and Knight:

$$\left\langle \frac{1}{r_{12}} \right\rangle_n = (n+1)\, \epsilon_{n+1} \qquad \text{(IV.A-2)}$$

Unless otherwise specified all energies are in atomic units. A comparison with $E_{K.W.}$ and $E_{K.R.}$ shows that the energy through fifth order has converged to five figures. The expectation value of $\left\langle \frac{1}{r_{12}} \right\rangle$ through fourth order agrees exactly

TABLE IV

Electronic Energy of H_2 Through Fifth Order Computed Using a 45-Term H set at R=1.4 with δ =1.2

n	ϵ_n	$-E_{sum(n)}$	D(eV)	$\langle\frac{1}{r_{12}}\rangle$	$E_{K.W.}$	$E_{K.R.}$
0	-2.568538	2.568538		.78088	-1.888760	-1.888733
1	.780882	1.787656		.55913		
2	-.110877	1.898533	5.0133	.59131		
3	.010729	1.887804	4.7214	.58846		
4	-.000714	1.888518	4.7408	.58737		
5	-.000217	1.888735	4.7467			

with the value given by Kolos and Roothaan.

From a comparison with Scherr and Knight, all high order energy coefficients should be negative. This is born out by the fact that as the basis set increases, an increasing number of terms become negative. Thus, the energy series was terminated whenever an ϵ_n beyond ϵ_3 became positive.

In Table V the effect of variation of the non-linear parameter δ in the H set is demonstrated. A 17 term expansion is used. Note that the second order energy demonstrates a minimum around $\delta = 1.2$.

The energies through third order resulting from a 45 term F and H set are compared in Table VI. The roughly optimized value $\delta = 1.2$ is used in the H set. The convergence of the two is approximately the same. However, no non-linear variation of the exponential parameter is required with the F set.

In order to determine the contribution to the second order energy from separate terms in the first order wave function, we have calculated the energy through third order for a 1-36 term F expansion at R = 1.4. The results are given in Table VII. The dissociation energy increases to a maximum and then decreases. At the point where the maximum is reached, ϵ_4 goes from positive to negative.

TABLE V

Variation of Energy of H_2 Through Third Order at R=1.4 Using a 17 Term H-basis Set

δ	$-\epsilon_2$	ϵ_3	$-E(1)$
1.25	.110532	.011013	1.887176
1.20	.110594	.010694	1.887556
1.15	.110569	.010431	1.887795
1.10	.110508	.010274	1.887890

TABLE VI

Comparison of H Method at F Method at R = 1.4 using a
45 term Basis Set with δ =1.2

H Set

n	ϵ_n	Esum(n)	D(eV)
2	-.110877	-1.898534	5.0133
3	.010729	-1.887804	4.7214

F Set

n	ϵ_n	Esum(n)	D(eV)
2	-.110852	-1.898509	5.0126
3	.010730	-1.887778	4.7207

TABLE VII

Electron Energy of H_2 through third order at R=1.4 computed with a 1- to 36-term F basis set.

No.of terms	$\xi_1\xi_2\eta_1\eta_2 r_{12}$	$-\epsilon_2$	ϵ_3	-Esum(n)	D(eV)
1	00001	.102592	.005593	1.884655	4.6357
2	10110	.102594	.005583	1.884667	4.6360
3	01220	.102698	.005884	1.884470	4.6307
4	00020	.102726	.005803	1.884579	4.6336
5	00111	.103167	.007209	1.883614	4.6074
6	01001	.103337	.005692	1.885301	4.6533
7	02000	.109241	.009281	1.887616	4.7163
8	11020	.109244	.009214	1.887685	4.7182
9	01020	.109277	.009293	1.887639	4.7169
10	00110	.109381	.009413	1.887624	4.7165
11	10021	.109449	.009647	1.887458	4.7119
12	11000	.109634	.009001	1.888289	4.7346
13	00002	.110303	.009726	1.888233	4.7331
14	20020	.110350	.009728	1.888278	4.7343
15	10020	.110352	.009740	1.888268	4.7340
16	00220	.110381	.009812	1.888224	4.7328
17	11220	.110387	.009817	1.888225	4.7329
18	02110	.110388	.009831	1.888213	4.7325
19	02001	.110404	.009877	1.888183	4.7317
20	01021	.110404	.009879	1.888181	4.7316
21	20220	.110405	.009879	1.888182	4.7317
22	20200	.110405	.009878	1.888182	4.7317
23	11110	.110521	.010022	1.888155	4.7309
24	01002	.110779	.010627	1.887808	4.7215

TABLE VII (continued)

Electron Energy of H_2 through third order at R=1.4 computed with a 1- to 36-term F basis set.

No. of terms	$\xi_1\xi_2\eta_1\eta_2\rho_{12}$	$-\epsilon_2$	ϵ_3	-Esum(n)	D(eV)
25	21020	.110785	.010633	1.887809	4.7215
26	21200	.110789	.010638	1.887807	4.7215
27	11021	.110803	.010629	1.887830	4.7221
28	00112	.110873	.010750	1.887779	4.7207
29	12000	.110873	.010760	1.887769	4.7204
30	12110	.110889	.010787	1.887758	4.7201
31	11001	.110893	.010805	1.887744	4.7197
32	21220	.110893	.010805	1.887743	4.7197
33	11111	.110897	.010826	1.887726	4.7193
34	10022	.110912	.010861	1.887707	4.7188
35	00022	.110916	.010881	1.887691	4.7183

C. R dependence of Energy Coefficients

In Figure I we illustrate the variation of the energy through third order as a function of R. In the limit of small R, we have the He case where $\epsilon_0 = -4$, $\epsilon_1 = 1.25$, $\epsilon_2 = -.157666$ and $\epsilon_3 = .004349$. The limiting values of the coefficient for large R are $\epsilon_0 = -1$ and $\epsilon_{n\neq 0} = 0$. The calculation of these latter values requires the use of double perturbation theory due to the degeneracy between the ${}^1\Sigma_g^+$ and ${}^3\Sigma_u^+$ states.

The energy coefficients for various values of R determined with a 50 term F basis set are given in Table VIII. The energy expansion is ill-behaved for large R. At R = 2.6 only terms through ϵ_3 are retained.

In Table IX we tabulate the 50 term basis set and the corresponding first order coefficients at R = 0.4 in order to demonstrate the relative importance of various terms in the expansion set. The largest contribution comes from the Π'_{12} term.

D. Members of Isoelectronic Sequence

Our final result is the listing in Table X of the electronic energy of He_2^{+2} at R = 0.4 and 0.2, and, the electronic energy of Li_2^{+4} at R = 0.2. As is apparent, the larger the Z value, the more rapid is the convergence of the perturbation series.

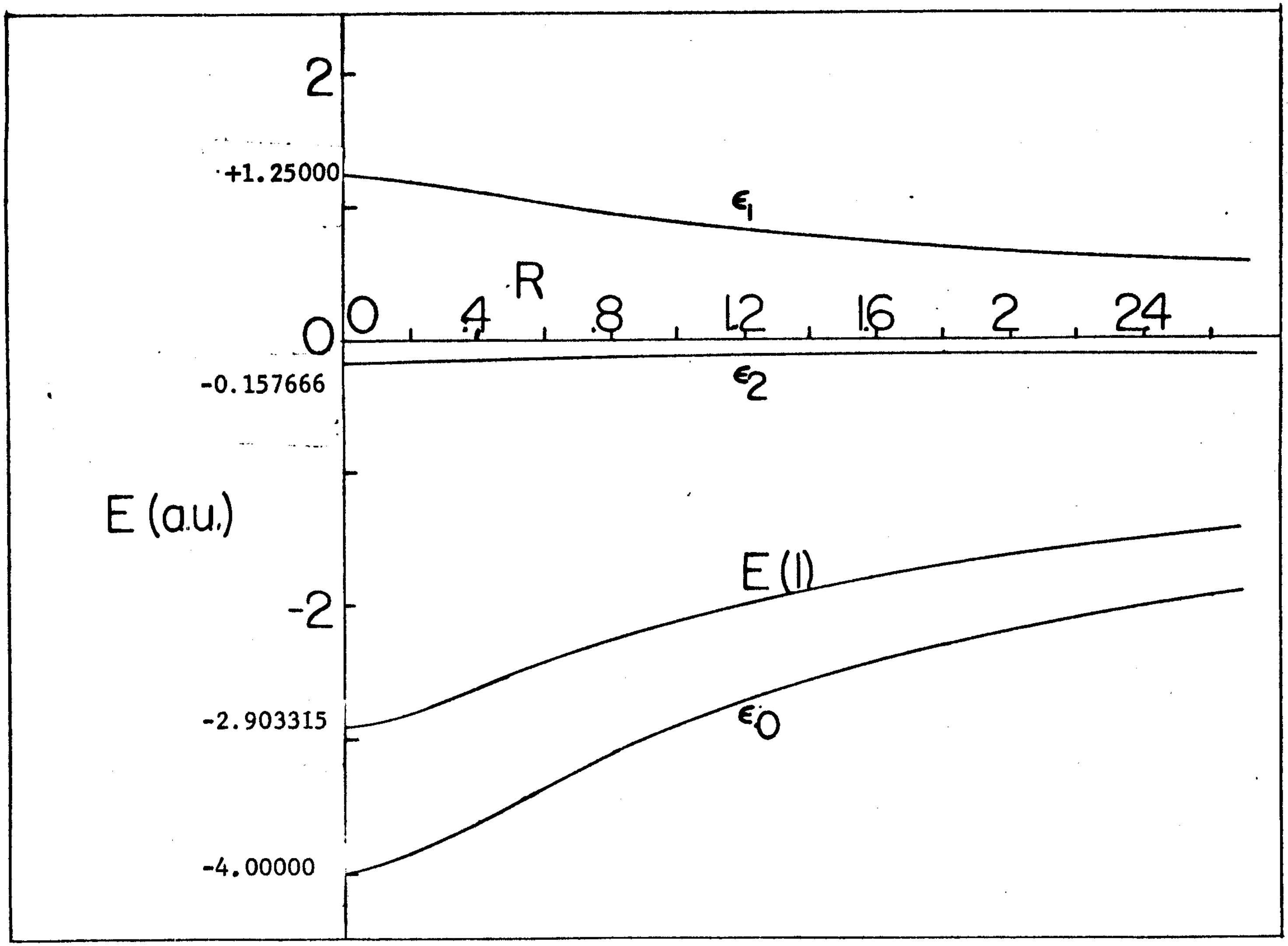

Fig. I Variation with R of the Perturbation Energy Order through

Here $E(1) = \epsilon_o + \epsilon_1 + \epsilon_2 + \epsilon_3$

TABLE VIII

Electronic Energy of H_2 for Various Values of R Using a 50 Term Expansion

R = 0.4

N	ϵ_n	-Esum	D(eV)	$E_{K.R.}$	$E_{K.W.}$
0	-3.601508	3.601508			-2.620203
1	1.118014	2.483494			
2	- .141151	2.624645	23.81817		
3	.004830	2.619815	23.94960		
4	- .000220	2.620035	23.94361		
5	- .000153	2.620188	23.93945		
6	- .000018	2.620206	23.93896		
7	- .000007	2.620214	23.93875		
8	- .000003	2.620216	23.93869		

R = 0.6

N	ϵ_n	-Esum	D(eV)	$E_{K.R.}$	$E_{K.W.}$
0	-3.342969	3.342969			-2.436292
1	1.033259	2.309710			
2	- .131721	2.441432	6.1286		
3	.005615	2.435817	6.2814		
4	- .000303	2.436120	6.2731		
5	- .000151	2.436270	6.2690		
6	- .000011	2.436282	6.2687		
7	- .000007	2.436289	6.2685		
8	- .000002	2.436291	6.2685		

TABLE VIII (continued)

R = 0.8

n	ϵ_n	-Esum	D(eV)	$E_{K.R.}$	$E_{K.W.}$
0	-3.108960	3.108960		-2.270175	-2.270049
1	.956921	2.152039			
2	- .124078	2.276117	.71064		
3	.006644	2.269473	.52985		
4	- .000409	2.269882	.54098		
5	- .000153	2.270035	.54515		
6	- .000003	2.270038	.54524		
7	- .000007	2.270045	.54542		
8	- .000002	2.270047	.54548		

R = 1.0

n	ϵ_n	-Esum	D(ev)	$E_{K.R.}$	$E_{K.W.}$
0	-2.903573	2.903573		-2.124517	-2.1245331
1	.890061	2.013511			
2	- .118192	2.131704	3.5836		
3	.007871	2.123832	3.3694		
4	- .000536	2.124368	3.3840		
5	- .000159	2.124527	3.3883		

TABLE VIII (continued)

R = 1.2

n	ϵ_n	-Esum	D(eV)	$E_{K.R.}$	$E_{K.W.}$
0	-2.724616	2.724616		-1.998264	-1.998264
1	.831796	1.892819			
2	-.113875	2.006694	+4.7171		
3	.009280	1.997414	+4.4646		
4	-.000676	1.998090	+4.4830		
5	-.000178	1.998267	+4.4878		

R = 1.3

n	n	-Esum	D(eV)	$E_{K.R.}$	$E_{K.W.}$
0	-2.643943	2.643943		-1.941553	-1.941572
1	0.805497	1.838446			
2	-0.112251	1.950696	4.9376		
3	0.010058	1.940639	4.6639		
4	-0.000754	1.941393	4.6844		
5	-0.000190	1.941583	4.6896		

TABLE VIII (continued)

R = 1.4

n	ϵ_n	-Esum	D(eV)	$E_{K.R.}$	$E_{K.W.}$
0	-2.568538	2.568538		-1.888728	-1.888756
1	0.780883	1.787656			
2	-0.110968	1.898623	5.0157		
3	0.010937	1.887687	4.7181		
4	-0.000926	1.888613	4.7433		
5	-0.000108	1.888720	4.7463		
6	-0.000066	1.888786	4.7481		

R = 1.5

n	ϵ_n	-Esum	D(eV)	$E_{K.R.}$	$E_{K.W.}$
0	-2.497980	2.497980		-1.839491	-1.839515
1	0.757812	1.740167			
2	-0.109963	1.850131	4.9920		
3	0.011799	1.838331	4.6709		
4	-0.001023	1.839355	4.6988		
5	-0.000142	1.839498	4.7026		

TABLE VIII (continued)

R = 1.6

n	ϵ_n	-Esum	D(eV)	$E_{K.R.}$	$E_{K.W.}$
0	-2.431874	2.431874		-1.793503	-1.793577
1	0.736157	1.695717			
2	-0.109287	1.805004	4.8978		
3	0.012658	1.792347	4.5534		
4	-0.000992	1.793340	4.5804		
5	-0.00266	1.793605	4.5876		

VIII (continued)

R = 1.8

n	ϵ_n	-Esum	D(eV)	$E_{K.R.}$	$E_{K.W.}$
0	-2.311618	2.311618		-1.710540	-1.710617
1	0.696640	1.614979			
2	-0.108934	1.723913	4.5809		
3	0.014792	1.709121	4.1784		
4	-0.001036	1.710157	4.2066		
5	-0.000586	1.710743	4.2226		

R = 2.0

n	ϵ_n	-Esum	D(eV)	$E_{K.R.}$	$E_{K.W.}$
0	-2.205268	2.205208		-1.637999	-1.638123
1	0.661530	1.543739			
2	-0.109846	1.653585	4.1789		
3	-0.017218	1.636367	3.7105		
4	-0.001506	1.637873	3.7514		

VIII (continued)

R = 2.6

n	ϵ_n	-Esum	D(eV)	$E_{K.R.}$	$E_{K.W.}$
0	-1.950897	1.950897		-1.469903	-1.470378
1	0.576813	1.374084			
2	-0.121121	1.495206	3.0091		
3	0.027825	1.467380	2.2520		

R = 3.8

n	ϵ_n	-Esum	D(eV)	$E_{K.R.}$	$E_{K.W.}$
0	-1.629705	1.629705		-1.281663	
1	0.469475	1.160230			
2	-0.213288	1.373517	-3.0028		
3	0.113776	1.259741	0.0929		

TABLE IX

Coefficients of First Order, fifty term wave function at R=0.4

$\xi_1^p \xi_2^q \eta_1^n \eta_2^s \Pi_{12}^{\mu}$	$C_i^{(1)}$
00001	.040971
00020	.009078
01000	.007868
02000	.006484
00110	-.006393
00002	-.003708
11000	-.003420
01001	.002985
00021	-.002664
00111	.001551
10110	-.001317
11020	-.001289
00220	-.001268
11220	.001192
01220	-.001044
02001	-.000815
01021	.000795
10020	.000711
01002	.000622
02110	.000581
20200	-.000430
00112	-.000395
10021	.000313
21220	-.000285
11110	-.000221
21200	.000189
21020	.000179
01022	-.000010
12000	-.000010
10022	.000009
03001	.000004
22110	-.000003
11022	.000002
23000	.000000
03201	.000000

TABLE IX (continued)

Coefficients of First Order, fifty term wave function at R=0.4

$\xi_1^p \xi_2^q \eta_1^r \eta_2^s r_{12}^{\mu}$	$C_i^{(1)}$
11021	-.000159
11111	.000098
00022	-.000093
20220	.000080
12110	-.000074
11001	-.000071
01020	-.000052
12001	.000048
03000	.000044
11002	-.000032
20020	-.000023
22220	.000018
03200	-.000016
22000	-.000016
22200	-.000013

TABLE X

Electronic Energy of He_2^{+2} and L_{12}^{+4} in a.u. for selected values of R using 50 term H basis Set

He_2^{+2}

R = 0.2 50 term basis set

n	ϵ_n	-Esum(n)
0	-14.406032	+14.406032
1	2.236027	+12.170005
2	- .141151	+12.311156
3	- .002415	+12.313571
4	- .000055	+12.313626
5	- .000019	+12.313645
6	- .000001	+12.313646

R = 0.4

n	ϵ_n	-Esum(n)
0	-12.435841	+12.435841
1	1.913842	+10.522000
2	- .124078	+10.646077
3	- .003322	+10.649399
4	- .000102	10.649501
5	- .000019	10.649520

Li_2^{+4}

R = 0.2

	$\mathcal{E}_n$	-Esum(n)
0	-27.980640	+27.980640
1	2.870763	25.109877
2	- .124078	25.233955
3	.002214	25.231741
4	- .000045	25.231286
5	- .000006	25.231292

E. CONCLUSION

Rayleigh Schroedinger Perturbation Theory as a tool for calculating molecular energies, treating the electronic interaction as a perturbation to the remaining Hamiltonian, is capable of giving highly accurate results. However since these results may also be obtained with the aid of variational methods, the real value of perturbation theory lies in the determination of properties other than energy for which no variational bound exists.

APPENDIX I

Perturbation Treatment of the Ground State of H_2^+

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Perturbation Treatment of the Ground State of H_2^+ †

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Rayleigh–Schrödinger perturbation calculations are carried out for the ground state of the H_2^+ molecular ion. The zeroth-order wavefunction for this problem is chosen to be the Guillemin and Zener variational function

$$\psi=N[\exp(-\alpha r_A-\beta r_B)+\exp(-\beta r_A-\alpha r_B)].$$

The energies through third order and the expectation value $E(1)$ of the Hamiltonian calculated with the wavefunction accurate through first order are computed for various choices of the parameters. For the optimum choices of both α and β, we obtain for all separations values of $E(1)$ which agree almost perfectly with the accurate series calculations of Bates, Ledsham, and Stewart. Also the values of the wavefunction accurate through the first order agree almost perfectly at most points in configuration space with Bates *et al.*

I. INTRODUCTION

THERE are a number of difficult problems involved in the application of perturbation theory to the calculation of molecular energies. The ground state of the diatomic hydrogen molecular ion H_2^+ is the simplest example since it involves only one electron and two similar nuclei. Starting with the simple Guillemin and Zener[1] wavefunction as zeroth order, the first-order wavefunction is obtained in terms of new transcendental functions. The resulting zeroth-order plus first-order function agrees almost perfectly at most points in configuration space with the very precise series solution wavefunction obtained by Bates, Ledsham, and Stewart.[2] For all separations, the expectation value of the energy corresponding to our zeroth plus first-order wavefunction agrees almost perfectly with the energy obtained by Bates, Ledsham, and Stewart. These results suggest that even first-order corrections to simple trial molecular wavefunctions may provide the energy and other physical properties of molecules with sufficient accuracy for practical purposes. However, even in our H_2^+ example, the energy integrals involved new types of transcendental functions and (except for some special choices of wavefunction parameters) had to be calculated numerically. For many-electron molecules the calculation of the perturbed wavefunctions and the energy integrals requires the use of variation-perturbation techniques.

II. GROUND STATE OF THE H_2^+ ISOELECTRONIC SEQUENCE

Let us consider a molecular ion (isoelectronic with H_2^+) consisting of two nuclei, A and B, and one electron. The nuclei each have a charge Z and are separated by a distance R. The distance from the electron to the two nuclei is r_A and r_B, respectively. It is convenient to describe the system in terms of confocal elliptic coordinates with

$$\lambda=(r_A+r_B)/R, \qquad \mu=(r_A-r_B)/R. \tag{1}$$

Throughout this paper we express energy in units of e^2/a_0 and length in units of a_0.

Kim, Chang, and Hirschfelder[3] have found that the simple Guillemin and Zener wavefunction[1] leads to surprisingly accurate values for the energy of the ground state of H_2^+. It is therefore logical to use it as the zeroth-order function in a Rayleigh–Schrödinger perturbation treatment.[4,5] The Guillemin and Zener function may be written

$$\psi=N\exp(-Ra\lambda/2)\cosh(Rb\mu/2). \tag{2}$$

Here a and b are adjustable parameters and N is the normalization constant. It is easy to show that the Guillemin and Zener function satisfies the Schrödinger equation

$$H_0\psi=\epsilon\psi, \tag{3}$$

where

$$\epsilon=-a^2/2 \tag{4}$$

and

$$H_0=-\tfrac{1}{2}\nabla^2-\left(\frac{2a}{R}\right)\left(\frac{\lambda}{\lambda^2-\mu^2}\right)-\left(\frac{a^2-b^2}{2}\right)\left(\frac{1-\mu^2}{\lambda^2-\mu^2}\right)-\frac{2b\mu}{R(\lambda^2-\mu^2)}\tanh\left(\frac{Rb\mu}{2}\right). \tag{5}$$

The true Hamiltonian for the diatomic molecular ion, neglecting internuclear repulsion, is

$$H=-\tfrac{1}{2}\nabla^2-[4Z\lambda/R(\lambda^2-\mu^2)]. \tag{6}$$

The zeroth-order expectation value of H is the energy

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[1] V. Guillemin and C. Zener, Proc. Natl. Acad. Sci. U. S. **15**, 314 (1929).

[2] D. R. Bates, K. Ledsham, and A. L. Stewart, Phil. Trans. Roy. Soc. London Ser. **A246**, 215 (1953).

[3] S. Kim, T. Y. Chang, and J. O. Hirschfelder, J. Chem. Phys. **43**, 1092 (1965).

[4] A. Dalgarno in *Quantum Theory*, edited by D. R. Bates (Academic Press Inc., New York, 1961), Vol. I, Chap. 5.

[5] J. O. Hirschfelder, W. Byers Brown, and S. T. Epstein, Advan. Quantum Chem. **1**, 255–374 (1964).

calculated in Ref. 3,

$$E(0)=\langle\psi,\ H\psi\rangle. \tag{7}$$

The perturbation potential is

$$V=H-H_0, \tag{8}$$

and the first-order perturbation energy is

$$\epsilon^{(1)}=\langle\psi,\ V\psi\rangle=E(0)-\epsilon. \tag{9}$$

The first-order wavefunction $\psi^{(1)}$ satisfies the differential equation

$$(H_0-\epsilon)\psi^{(1)}+(V-\epsilon^{(1)})\psi=0 \tag{10}$$

and is orthogonal to the zeroth-order function

$$\langle\psi,\ \psi^{(1)}\rangle=0. \tag{11}$$

The second- and third-order energies can be expressed in terms of $\psi^{(1)}$,

$$\epsilon^{(2)}=\langle\psi,\ V\psi^{(1)}\rangle \tag{12}$$

and

$$\epsilon^{(3)}=\langle\psi^{(1)},\ (V-\epsilon^{(1)})\psi^{(1)}\rangle. \tag{13}$$

The expectation value of H calculated with the wavefunction accurate through the first order is then

$$\begin{aligned}E(1)&=\langle(\psi+\psi^{(1)}),\ H(\psi+\psi^{(1)})\rangle/\langle(\psi+\psi^{(1)}),\ (\psi+\psi^{(1)})\rangle\\&=E(0)+(\epsilon^{(2)}+\epsilon^{(3)})/[1+\langle\psi^{(1)},\ \psi^{(1)}\rangle].\end{aligned} \tag{14}$$

By the Rayleigh–Ritz variational principle, $E(1)$ provides an upper bound to the true energy of the ground state of the diatomic molecular ion.

Equation (10) may be separated in confocal elliptic coordinates by making the substitution

$$\psi^{(1)}=[F_1(\lambda)+F_2(\mu)]\psi, \tag{15}$$

where ψ is given by Eq. (2). The resulting one-dimensional differential equations are

$$\begin{aligned}(d/d\lambda)&[(\lambda^2-1)\ \exp(-Ra\lambda)(dF_1/d\lambda)]\\&=\exp(-Ra\lambda)\{C(a,b;R)+[R^2(a^2-b^2)/4]\\&\qquad-R(2Z-a)\lambda-(R^2\epsilon^{(1)}\lambda^2/2)\}\end{aligned} \tag{16}$$

and

$$\begin{aligned}\frac{d}{d\mu}\left[(1-\mu^2)\ \cosh^2\!\left(\frac{Rb\mu}{2}\right)\frac{dF_2}{d\mu}\right]&=\cosh^2\!\left(\frac{Rb\mu}{2}\right)\\\times\{-C(a,b;R)+(R^2\epsilon^{(1)}\mu^2/2)&-[R^2(a^2-b^2)\mu^2/4]\\&+Rb\mu\ \tanh(Rb\mu/2)\},\end{aligned} \tag{17}$$

where C is the separation constant.

The function F_1 is obtained by integrating Eq. (16) twice, and the separation constant is determined by requiring that $[(\lambda^2-1)\ \exp(-Ra\lambda)(dF_1/d\lambda)]$ vanish at $\lambda=1$ and infinity.[6] The integration of Eq. (17) involves the evaluation of two new transcendental functions

$$T_a(\mu)=\int_{-1}^{\mu}\frac{\tanh(ax)}{1-x^2}dx \tag{18}$$

and

$$S_a(\mu)=\int_{-1}^{\mu}\frac{x\ \mathrm{sech}^2(ax)}{1-x^2}dx. \tag{19}$$

To evaluate $T_a(\mu)$, the hyperbolic tangent is expanded in the series[7]

$$\tanh(a\mu)=8a\mu\sum_{n=0}^{\infty}[(2n+1)^2\pi^2+4a^2\mu^2]^{-1}. \tag{20}$$

Then the operations of integration and summation are interchanged, the resulting integrand is expanded in partial fractions, and the integration is carried out term by term to yield

$$\begin{aligned}T_a(\mu)=&-\tfrac{1}{2}\tanh(a)\ \ln(1-\mu^2)\\&+4a\sum_{n=0}^{\infty}[(2n+1)^2\pi^2+4a^2]^{-1}\ln\left[\mu^2+\frac{(2n+1)^2\pi^2}{4a^2}\right].\end{aligned} \tag{21}$$

Once $T_a(\mu)$ has been evaluated, $S_a(\mu)$ may be determined readily by means of the identity

$$S_a(\mu)=(\partial/\partial a)T_a(\mu). \tag{22}$$

The solutions of the differential equations (16) and (17) are then

$$F_1(\lambda)=\{(\epsilon^{(1)}/a^2)+[(2Z-a)/a]\}\ \ln(\lambda+1)+(R\epsilon^{(1)}\lambda/2a)+F_1{}^0 \tag{23}$$

$$\begin{aligned}F_2(\mu)=&\left[\frac{a^2-b^2-2\epsilon^{(1)}}{3b^2}\right]\ln\left[\cosh\left(\frac{Rb\mu}{2}\right)\right]+\left[\frac{R(a^2-b^2)-2R\epsilon^{(1)}}{12b}\right]\mu\ \tanh\left(\frac{Rb\mu}{2}\right)+\sum_{n=0}^{\infty}\frac{\ln\{1-[(1-\mu^2)R^2b^2/(\sigma_n{}^2+R^2b^2)]\}}{\sigma_n{}^2+R^2b^2}\\&\times(\{-(2\epsilon^{(1)}/a^2)-(4/a)-(2R\epsilon^{(1)}/a)-4R+2Ra+(2\epsilon^{(1)}/b^2)-[(a^2-b^2)/b^2]\}+[(\sigma_n{}^2-R^2b^2)/(\sigma_n{}^2+R^2b^2)]\\&\times\{-(2\epsilon^{(1)}/a^2)-(4/a)+2Ra-4R-(2R\epsilon^{(1)}/a)-(2R^2\epsilon^{(1)}/3)+(2\epsilon^{(1)}/b^2)-[(a^2-b^2)/b^2]+[R^2(a^2-b^2)/3]\})\\&+\{-(2\epsilon^{(1)}/a^2)-(4/a)+2Ra-4R-(2R\epsilon^{(1)}/a)-(2R^2\epsilon^{(1)}/3)+(2\epsilon^{(1)}/b^2)-[(a^2-b^2)/b^2]+[R^2(a^2-b^2)/3]\}\\&\times\frac{[\mu\ \tanh(Rb\mu/2)-\tanh(Rb/2)]}{2Rb(1-\mu^2)}+F_2{}^0,\end{aligned} \tag{24}$$

where $\sigma_n=(2n+1)\pi$.

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[6] R. L. Matcha, W. D. Lyon, and J. O. Hirschfelder, University of Wisconsin Theoretical Chemistry Institute Report No. 57 (1964). This has been deposited as Document number 8448 with the ADI Auxiliary Publications Project, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting \$8.75 for photoprints, or \$3.00 for 35 mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

[7] B. O. Pierce, *A Short Table of Integrals* (Ginn and Company, Boston, Massachusetts, 1956), Formulas 678 and 880.

The constant $F^0=F_1^0+F_2^0$ is determined by requiring that Eq. (11) be satisfied. It is possible with a great deal of care to evaluate F^0 explicitly. Logarithmic singularities and simple poles have to be isolated and shown to vanish identically. Integrals involving the infinite series may be summed by making use of one integration by parts and an expansion into partial fractions; details of this procedure are given in Appendix II to Ref. 8. However, taking this into account, F^0 is more conveniently determined from Eq. (11) by a numerical integration procedure such as Gaussian quadrature,[9] as

$$F^0=-\langle\psi,\,[F_1(\lambda)+F_2(\mu)-F_1^0-F_2^0]\psi\rangle. \tag{25}$$

The series in F_2 converges sufficiently well that only a small number of terms need be summed, and the entire integration may be done quickly and easily on a computer.

Transcendental functions of the above type may be expected to appear in the application of perturbation techniques to more complicated molecules. For the special choice of parameters $a=2$, $b=0$, the function F_2 may be determined in closed form. In this case the solutions are

$$F_1(\lambda)=R\epsilon^{(1)}\lambda/4+(\epsilon^{(1)}/4)\ \ln(\lambda+1)+F_1^0, \tag{26a}$$

$$F_2(\mu)=(R^2/6)\,(1-\epsilon^{(1)}/2)\mu^2+F_2^0, \tag{26b}$$

and

$$\begin{aligned}F^0&=F_1^0+F_2^0\\&=-\{3R[\epsilon^{(1)}]^2/16\}\{(11/15)+(23/15R)+(5/3R^2)+(37/24R^3)+\ln(2)[(2/3R)+(1/R^2)+(1/2R^3)]\\&\qquad-\exp(4R)\,Ei(-4R)[(2/3R)-(1/R^2)+(1/2R^3)]\}.\end{aligned} \tag{27}$$

From these equations we obtain, with relatively little effort, expressions for the energies up through third order[10]

$$\epsilon=-2 \tag{28}$$

$$\epsilon^{(1)}=8R^2/(4R^2+6R+3) \tag{29}$$

$$\epsilon^{(2)}=(3R\epsilon^{(1)}/2)\;((2F^0/3R)+(R/45)+(\epsilon^{(1)}/6)\{1+(1/2R)-(R/15)+[\ln(2)/R]-[\exp(4R)Ei(-4R)/R]\}) \tag{30}$$

$$\begin{aligned}\epsilon^{(3)}={}&2F^0\epsilon^{(2)}-(F^0)^2\epsilon^{(1)}+(3\epsilon^{(1)}R/2)\;([(\epsilon^{(1)})^2/12]\{(R/2)+\tfrac{1}{2}+(3/4R)+M\ \exp(4R)/R\\&+[1+(1/2R)]\ \ln(2)+[1-(1/2R)]\ \exp(4R)\,Ei(-4R)\}\\&+(R\epsilon^{(1)}/90)[1-(\epsilon^{(1)}/2)][R+\tfrac{1}{2}+\ln(2)-\exp(4R)\,Ei(-4R)]+[1-(\epsilon^{(1)}/2)]^2(R^3/630))\\&+3R(\epsilon^{(1)}/2)^2(2F^0\{F^0+(R^2/9)[1-(\epsilon^{(1)}/2)]\}[(1/2R)+(1/2R^2)+(1/4R^3)]-(F^0/3R)\{F^0+(R^2/5)[1-(\epsilon^{(1)}/2)]\}\\&+[(\epsilon^{(1)})^2/8]\{(R/3)+\tfrac{5}{6}+(7/4R)+(7/4R^2)+(19/8R^3)+\ln(2)[\tfrac{2}{3}+(4/3R)+(3/2R^2)+(3/2R^3)]\\&+\exp(4R)\,Ei(-4R)[\tfrac{2}{3}-(4/3R)+(5/2R^2)-(3/2R^3)]\\&+M\ \exp(4R)[(2/3R)-(1/R^2)+(1/2R^3)]+[\ln(2)/R]^2\}\\&+(R^4/36)[1-(\epsilon^{(1)}/2)]^2[(2/35R)+(1/5R^2)+(1/10R^3)]+\epsilon^{(1)}\{F^0+(R^2/18)[1-(\epsilon^{(1)}/2)]\}\\&\times\{\tfrac{1}{2}+(3/4R)+(3/4R^2)+(3/4R^3)+\ln(2)[(1/2R)+(1/2R^2)+(1/4R^3)]\\&-\exp(4R)\,Ei(-4R)[(1/2R)-(1/2R^2)+(1/4R^3)]\}-(\epsilon^{(1)}/6R)\{F^0+(R^2/10)[1-(\epsilon^{(1)}/2)]\}\\&\times[R+\tfrac{1}{2}+\ln(2)-\exp(4R)\,Ei(-4R)]),\end{aligned} \tag{31}$$

where

$$\begin{aligned}M={}&(\gamma[(\gamma/2)+\ln(2)]+(\pi^2/12)+\gamma\ \ln(2R)+\{[\ln(2R)]^2/2\}\\&+\ln(2)[\ln(4R)-Ei(-4R)]-[1-\exp(-4R)]\{[\ln(2)]^2/2\}\\&-\{4R-[(4R)^2/2^2 2!]+[(4R)^3/3^2 3!]-[(4R)^4/4^2 4!]+\cdots\}),\end{aligned} \tag{32}$$

and γ is Euler's constant.

It is much easier to evaluate the second-order energy $\epsilon^{(2)}$ numerically than to express it in explicit form. The difficulties in the explicit evaluation are similar to those encountered with F^0. Closed-form expressions for both F^0 and $\epsilon^{(2)}$ are given in Appendix II to Ref. 8 for the special choice of parameters $a=b=s$. Still, the procedure leading to these expressions is very tedious, and the analytic evaluation of the third-order energy is virtually hopeless. For this reason the integrals in-

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[8] W. A. Sanders, W. J. Meath, and J. O. Hirschfelder, University of Wisconsin Theoretical Chemistry Institute Report No. 44 (1964). This has been deposited as Document number 8448 with the ADI Auxiliary Publications Project. For further information, see Ref. 6.

[9] Z. Kopal, *Numerical Analysis* (Chapman and Hall, Ltd., London, 1955), Chap. 7.

[10] It should be noted that this work is basically different from that of I. N. Levine, J. Chem. Phys. **41**, 2044 (1964), who used a single-center expansion of the perturbation about the united-atom nucleus and derived the energy only through second order.

TABLE I. Perturbation energies[a,b] for the ground state of H_2^+, neglecting internuclear repulsion and using the unperturbed function $\psi=N\exp(-Ra\lambda/2)\cosh(Rb\mu/2)$.

R/a_0	$-E(0)$	$-\epsilon^{(2)}$	$\epsilon^{(3)}$	$-E(1)$	$-E_{BLS}$
0.0	2.0000000	0.0000000	0.0000000	2.0000000	2.00000
0.2	1.9285376	0.0000831	0.0000005	1.9286203	1.9287_0
0.4	1.8005254	0.0002311	0.0000025	1.8007540	1.8007_8
0.6	1.6711853	0.0003040	0.0000047	1.6714846	1.6715_0
1.0	1.4514847	0.0003081	0.0000068	1.4517860	1.4517_8
1.4	1.2840155	0.0002601	0.0000068	1.2842688	1.2842_6
1.6	1.2157074	0.0002358	0.0000064	1.2159368	1.2159_3
1.8	1.1556003	0.0002144	0.0000059	1.1558088	1.1558
1.9	1.1282219	0.0002049	0.0000057	1.1284212	···
2.0	1.1024428	0.0001964	0.0000054	1.1026338	1.10263
2.1	1.0781414	0.0001889	0.0000052	1.0783250	···
2.2	1.0552074	0.0001823	0.0000049	1.0553847	1.05538
2.5	0.9936591	0.0001683	0.0000042	0.9938232	···
3.0	0.9107355	0.0001636	0.0000032	0.9108960	0.91089
4.0	0.7958779	0.0002082	0.0000014	0.7960848	···
5.0	0.7241507	0.0002686	−0.0000009	0.7244202	0.72442
6.0	0.6783593	0.0002719	−0.0000042	0.6786355	0.67863
8.0	0.6274265	0.0001371	−0.0000062	0.6275698	0.62757
10.0	0.6005292	0.0000469	−0.0000024	0.6005785	···
∞	0.5000000	0.0000000	0.0000000	0.5000000	0.50000

[a] As was stated in Ref. 2, the fifth decimal place of E_{BLS} is probably in error by at least one unit. Furthermore, in the range of 0.2 to 1.8, little significance can be attached to the last figure; we have indicated this by writing it as a subscript. The energies are in units of (e^2/a_0). The Bates, Ledsham, and Stewart energies, E_{BLS}, were the best by previously determined energy calculations.

[b] *Note added in proof:* H. Wind [J. Chem. Phys. **42**, 2371 (1965)] extended the BLS calculations to seven decimal places in the energy. Our $E(1)$ agrees with his up to the last figure.

volved in calculation of $\epsilon^{(2)}$ for general a and b, and $\epsilon^{(3)}$ for all cases (except when $b=0$) were determined numerically on the CDC 1604 computer of the University of Wisconsin Computing Center. The accuracy of the numerical integrations to the number of figures given in the tables has been assured by comparing numerical values of $\epsilon^{(2)}$ with those obtained from the explicit expression.

III. RESULTS AND DISCUSSION

The flexibility provided by the parameters in the Guillemin–Zener zeroth-order wavefunction allows extremely accurate determination of the energy through third order. Kim, Chang, and Hirschfelder[3] determined these parameters for the H_2^+ molecule by the use of the variational principle, minimizing Eq. (7). We have used their values for $E(0)$, a and b.

In Table I we have listed for the H_2^+ molecule the second- and third-order energies and the energy expectation value $E(1)$ given by Eq. (14). Here $E(1)$ is an upper bound to the exact energy. It may be observed that our calculated energies are extremely accurate throughout the entire range of R. The energy through $\epsilon^{(2)}$ agrees to all places with E_{BLS}, the energy of Bates, Ledsham, and Stewart[2] determined by means of an accurate series expansion, while $\epsilon^{(3)}$ affects the energy in the sixth decimal place. Since E_{BLS} is given

TABLE II. Calculated values of the normalized wavefunctions.[a]

		$R=0.2\ a_0$			$R=2.0\ a_0$			$R=9.0\ a_0$		
μ	λ	ψ	$\Psi(1)$	Ψ_{BLS}	ψ	$\Psi(1)$	Ψ_{BLS}	ψ	$\Psi(1)$	Ψ_{BLS}
0.0	1.0	1.26697	1.25739	1.25749	0.31719	0.31473	0.31469	0.01020	0.01159	0.01175
	2.0	1.04373	1.04098	1.04103	0.08190	0.08251	0.08250	0.00010	0.00011	0.00011
	3.0	0.85983	0.85992	0.85994	0.02115	0.02069	0.02071	0.00000	0.00000	0.00000
	4.0	0.70834	0.70950	0.70951	0.00546	0.00505	0.00507	0.00000	0.00000	0.00000
0.7	1.0	1.27097	1.26136	1.26147	0.38512	0.38092	0.38089	0.10749	0.10664	0.10665
	2.0	1.04703	1.04427	1.04432	0.09944	0.09986	0.09986	0.00108	0.00103	0.00103
	3.0	0.86255	0.86263	0.86266	0.02568	0.02502	0.02506	0.00000	0.00001	0.00001
	4.0	0.71057	0.71174	0.71175	0.00663	0.00611	0.00614	0.00000	0.00000	0.00000
1.0	1.0	1.27513	1.26551	1.26561	0.46083	0.45793	0.45789	0.39568	0.39688	0.39679
	2.0	1.05046	1.04770	1.04775	0.11899	0.12004	0.12005	0.00397	0.00382	0.00383
	3.0	0.86538	0.86547	0.86549	0.03072	0.03010	0.03013	0.00000	0.00003	0.00003
	4.0	0.71290	0.71407	0.71409	0.00793	0.00735	0.00738	0.00000	0.00000	0.00000

[a] The wavefunction ψ is given by Eq. (2), $\Psi(1)=N(\psi+\psi^{(1)})$, and Ψ_{BLS} is the normalized wavefunction of Bates, Ledsham, and Stewart.

only through the fifth decimal place, it is not possible to determine the degree of accuracy of our energies by comparison. (See Footnote b, Table I.)

To see how well perturbation theory has improved the zeroth-order wavefunction ψ, we compare in Table II the "exact" normalized wavefunction Ψ_{BLS} of Bates, Ledsham, and Stewart with $\Psi(1)=N(\psi+\psi^{(1)})$, where $N=(1+\langle\psi^{(1)},\psi^{(1)}\rangle)^{-\frac{1}{2}}$. It is clear that the Guillemin–Zener function corrected through first order is in much closer agreement with Ψ_{BLS} than is the zeroth-order function. Since the functions $\Psi(1)$ and Ψ_{BLS} have nearly the same values over all space, $\Psi(1)$ will undoubtedly give good values for properties other than energy.

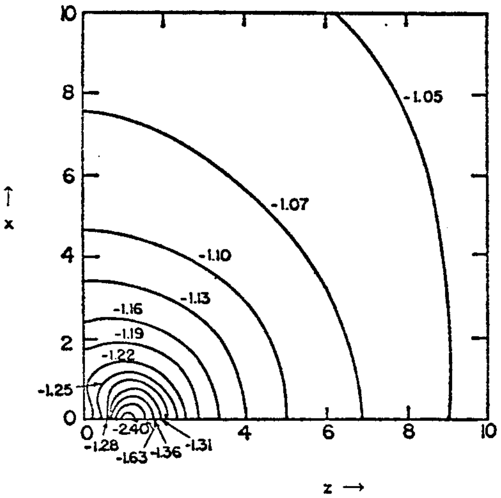

FIG. 1. Contour mapping of $H\Psi(1)/\Psi(1)$ at the equilibrium separation $R=1.9973a_0$. Here $E_{\text{BLS}}=-1.1026$. The electronic coordinate $r=(x, y, z)$ is measured from the origin of the confocal elliptic system, with z oriented along the internuclear axis.

To determine further the quality of $\Psi(1)$, we have investigated the local energy[11,12]

$$\epsilon_{\text{LOC}}=H\Psi(1)/\Psi(1)=\epsilon+V-[(V-\epsilon^{(1)})/(1+F_1+F_2)]. \tag{33}$$

Comparison with the energy averaged over all space, given as E_{BLS}, shows that the wavefunction is most accurate when the electron is 4 to $6a_0$ from the nuclei and least accurate near the nuclei. Sample results are given in a contour map, Fig. 1, at the equilibrium separation.

TABLE III. Perturbation energies for the ground state of H_2^+, neglecting internuclear repulsion, using the "united atom" unperturbed function $\psi=N\exp(-r_A-r_B)$.

R/a_0	$-E(0)$	$-\epsilon^{(2)}$	$-\epsilon^{(3)}$	$-E(1)$	$-E_{\text{BLS}}$
0.0	2.00000	0.00000	0.00000	2.00000	2.00000
0.2	1.92661	0.00205	−0.00004	1.92862	1.9287_0
0.4	1.78808	0.01296	−0.00027	1.80071	1.8007_8
0.6	1.64179	0.03003	−0.00024	1.67125	1.6715_0
1.0	1.38462	0.06499	0.00252	1.45038	1.4517_8
1.4	1.18503	0.09105	0.00824	1.28041	1.2842_6
2.0	0.96774	0.11434	0.01847	1.09314	1.10263
2.5	0.83721	0.12462	0.02672	0.97838	···
3.0	0.73684	0.13028	0.03431	0.88862	0.91089
5.0	0.49624	0.13490	0.05994	0.66733	0.72442
10.0	0.27214	0.12682	0.11510	0.45024	···

Limiting Values

Some interesting limiting forms of the Guillemin–Zener function are obtained from the following special choices of the parameters a and b:

(1) $a=2$, $b=0$,

(2) $a=b=1$,

(3) $a=b=s$, a variational parameter.

A brief discussion of these limits follows.

1. $a=2$, $b=0$, *the United-Atom Function*

The resulting zeroth-order wavefunction

$$\psi=N\exp(-r_A-r_B)\rightarrow N\exp(-2r) \tag{34}$$

becomes accurate in the united-atom limit. Table III contains the results for this case. As expected, the energies are quite good for small R but become increasingly bad as R becomes large. In order to demonstrate the asymptotic behavior of the perturbation energies, we have derived the expressions for Eqs. (28) through (31) in the limit of large R

$$\epsilon=-2$$

$$\epsilon^{(1)}=2+\mathcal{O}(R^{-1})$$

$$\epsilon^{(2)}=-\tfrac{1}{10}+\mathcal{O}(R^{-1})$$

$$\epsilon^{(1)}=-4R/350+\mathcal{O}(R^0).$$

A comparison of these limits with the asymptotic value of the exact energy, $-\frac{1}{2}$, shows that the perturbation calculation diverges for large R. For example, the

TABLE IV. Perturbation energies for the ground state of H_2^+, neglecting internuclear repulsion, using the "separated atom" or Pauling unperturbed function $\psi=N[\exp(-r_A)+\exp(-r_B)]$.

R/a_0	$-E(0)$	$-\epsilon^{(2)}$	$\epsilon^{(3)}$	$-E(1)$	$-E_{\text{BLS}}$
0.2	1.48353	0.46513	0.01967	1.74436	1.9287_0
1.0	1.28837	0.20117	0.05012	1.40112	1.4517_8
2.0	1.05377	0.06027	0.01525	1.09429	1.10263
3.0	0.89242	0.02127	0.00346	0.90952	0.91089
4.0	0.78687	0.00967	0.00055	0.79582	···
5.0	0.71920	0.00507	−0.00012	0.72433	0.72442
6.0	0.67573	0.00270	−0.00017	0.67859	0.67863
8.0	0.62673	0.00078	−0.00005	0.62756	0.62757
10.0	0.60030	0.00027	−0.00001	0.60058	···
∞	0.50000	0.00000	0.00000	0.50000	0.50000

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TABLE V. Perturbation energies for the ground state of H_2^+, neglecting internuclear repulsion, using Finkelstein–Horowitz unperturbed function $\psi = N[\exp(-sr_A)+\exp(-sr_B)]$.

R/a_0	$-E(0)$	$-\epsilon^{(2)}$	$-\epsilon^{(3)}$	$-E(1)$	$-E_{BLS}$
0.0	2.0000000	0.0000000	0.0000000	2.0000000	2.00000
0.2	1.9283280	0.0002936	−0.0000014	1.9286203	1.9287_0
0.6	1.6667478	0.0047684	−0.0000330	1.6714790	1.6715_0
1.4	1.2696254	0.0146429	0.0000429	1.2841976	1.2842_6
1.8	1.1397320	0.0160749	0.0000701	1.1556836	1.1558
2.0	1.0865060	0.0161327	0.0000676	1.1024824	1.10263
2.2	1.0395174	0.0158792	0.0000590	1.0552106	1.05538
3.0	0.8977816	0.0131115	0.0000348	0.9106872	0.91089
4.0	0.7873345	0.0086428	0.0000920	0.7959307	···
5.0	0.7192055	0.0050392	0.0001441	0.7243330	0.72442
8.0	0.6267342	0.0007835	0.0000436	0.6275597	0.62757
10.0	0.6002979	0.0002689	0.0000101	0.6005767	···
∞	0.5000000	0.0000000	0.0000000	0.5000000	0.50000

energy through third order is above E_{BLS} in the range $R=0$ to $R\approx 25$ but for $R>25$ it falls below E_{BLS}, approaching minus infinity. Equations (28) through (31) go to the correct limit, -2, as R approaches zero, since the zeroth-order wavefunction becomes identical with the exact wavefunction in this limit. Note that although the energy through third order diverges, the energy $E(1)$ remains finite and gives an upper bound to the exact energy over the full range of R, approaching zero asymptotically. This behavior results from the fact that the denominator of $E(1)$ goes as R^2 in the limit of large R while the numerator goes as R.

2. $a=b=1$, *the Pauling Function*

The resulting zeroth-order wavefunction[13]

$$\psi = N\,[\exp(-r_A)+\exp(-r_B)]$$

is accurate in the separated atom limit. We would expect that the resultant energies in this case would be nearly exact for large R and become progressively worse as R approaches zero. As shown in Table IV such is actually the situation.

3. $a=b=s$, *the Finkelstein–Horowitz Function*

The energies resulting from this choice of parameters,[14] with s variationally determined,[3] are fairly accurate throughout the entire range of R, as seen in Table V. For this case, the expression for the perturbation energy to second order was expanded in powers of R (through terms in R^3) in the limit of small R. The results agree with the exact energy expansion for H_2^+ as determined by Byers Brown and Steiner.[15] For large R, ignoring exponentially decreasing terms, the expansion of $\epsilon^{(2)}$ agrees with the result of Dalgarno and Lynn[16] and of Robinson.[17]

Comparison of Tables IV and V shows the advantage to be gained by using a variationally optimized zeroth-order wavefunction. The superiority of the scaled function is particularly striking at small internuclear separations, where the scaling parameter is significantly different from unity. These results support the view that the rate of convergence of the perturbation series is strongly dependent upon the quality of the zeroth-order wavefunction.

IV. SUMMARY

The ease of solution of the perturbation equations depends very greatly upon the form of the zeroth-order function. The one-electron homonuclear diatomic molecule probably represents the limiting case in which analytic solutions can be obtained for a reasonable unperturbed function. For systems with two or more electrons, the variables are not separable and one cannot solve the perturbation differential equations exactly. It appears, therefore, that the extension of perturbation calculations to more complicated systems can only be accomplished by means of variational techniques.[4,6,18]

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The authors would like to thank Mrs. Wanda Giese for assistance with the numerical calculations. We would also like to thank Dr. Robert A. Sack for several helpful suggestions and comments.

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Computor Programs

As the role of computors in atomic and molecular calculations becomes increasingly important, the computor programs themselves are gaining added stature. Often the mathematical formalism for a particular computation may take less than a month to develop while the programs for implementing the calculation may require over a year to complete. Subsequently, the mathematics is made available to others in the field through the various journals while the computor programs are completely inaccessible. This inaccessibility is due partly to the fact that programs written for a given computor are incompatible with most of the other computors. This situation has been partially alleviated by the development of the fortran language. The fact that listings of programs generally are not published also tends to make them inaccessible.

In order to make available for general use the computor programs developed in this calculation, their listing with a detailed explanation of symbols and operating procedures is given in this section.

Symbols and Arrays

Certain symbols and arrays are common to all programs. These are listed here for convenience. The arrays wtgaus(m), ptgaus(m), wtlag(m), and ptlag(m) contain the Legendre Gauss weights and points and the Laguerre Gauss weights and points respectively.

The symbols and arrays corresponding to the zeroth order wave function Eqs(II.B-16) and (II.B-26), are as follows: f(m+1) = f_m; P(ℓ+1, ν+1) = P_ℓ^ν ; sigma = σ ; P = ρ ; gtau(ℓ+1) = g_ℓ. The maximum number of terms in the ξ summation is denoted by wavelam and in the η summation by wavemu; energy = ϵ_o.

The arrays corresponding to the matrix elements, Eqs(II.E-18) - (II.E-22) and Eqs(II.E-48) - (II.E-53), are the following:
coeffl(m+1,n+1) = $H_{m,n}$; cofrho(m+1,n+1) = $V_{m,n}$; cofnom(m+1,n+1) = $S_{m,n}$; summit(m+1) = $N_{m,o}$; VA(m+1) = $V_{m,o}$.

Additional symbols are: PI = π; alp2 = 2α where α and ρ are defined by Eqs(II.E-3) and II.B-26). The subroutines Ktime and Pclock are used to determine the time required for various operations. Ktime is a library subroutine. The library subroutine Matinv is used for all necessary matrix inversions.

General Procedure

The procedure for determining the ϵ_n consists of three parts: the determination of the basic integrals; the evaluation of the matrix elements; and the determination of the various energy orders. Each of these is accomplished by separate programs. Data is transferred between programs by magnetic tape and punched cards. The order of the program listings are as follows:

1. Fmethod
    a. Program Htauint
    b. Program Energy
2. Hmethod
    a. Program Htauint
    b. Program Energy
    c. Program Enermat
3. Program Highen

The programs Htauint are used to calculate the basic integrals while the programs Energy and Enermat are used to determine the various matrix elements. The program Highen determines the perturbation energy coefficients.

1. Fmethod

a. Program Htauint

Definition of Symbols and Arrays

$$R(\tau+1, m+1, \nu+1) = \left[\frac{(2\tau+1)(\tau-\nu)!}{2(\tau+\nu)!}\right]^{-\frac{1}{2}} \mathcal{P}^{\nu,\nu}_{2\tau}(m) - (\text{III.D}-49)$$

$$\left.\begin{aligned} H(m+1, n+1, \tau+1) &= \Phi^{0}_{2,\tau}(m,n) \\ H1(m+1, n+1, \tau+1) &= \Phi^{1}_{2,\tau}(m,n) \\ H2(m+1, n+1, \tau+1) &= \Phi^{2}_{2,\tau}(m,n) \end{aligned}\right\} - (\text{III}.A-66)$$

$$A1(m+1) = A_2(m) \quad - (\text{III}.A-15)$$

$$A2(m+1) = B_2(m) \quad - (\text{III}.A-26)$$

Subroutines and Functions

1. Rtaun(mmax,nmax,R,wtgaus,ptgaus,maxgaus) determines the array R(m,n,ν) for ν = 1,2, and 3 and all m and n $\leq$ mmax and nmax.

2. Bint(mmax,A2,wtgaus,ptgaus,maxgaus) determines the integrals A2(m) for all m $\leq$ mmax.

3. GetA(wtlag,ptlag,maxlag,mmax,A1,A1p) determines the integrals A1(m) for all m $\leq$ mmax.

4. Htau(mmax,nmax,tmax,A1p,nu,H,wtgaus,ptgaus,maxgaus,wtlag,ptlag, maxlag) is used to calculate H(m,n,t) for all n,m, and t $\leq$ mmax,nmax, and tmax.

5. Htau12(m1max,n1max,t1max,m2max,n2max,t2max,H,H1,H2,mmax,nmax, tmat) determines H1(m1,n1,t1) and H2(m2,n2,t2) for all m1,n1,t1 $\leq$ m1max,n1max,t1max and m2,n2,t2 $\leq$ m2max,n2max,t2max.

Operating Procedure

The program requires the input of maxgaus,maxlag,ptgaus,wtgaus, ptlag,wtlag,Rzero,lamwave,muwave,p,sigma,aprime,energy,f,and gtau. The basic integrals R,A1,H,H1,H2, and A2 are automatically calculated and stored on tape.

```
      PROGRAM HTAUINT
      DIMENSION R(15,15,3),H(13,13,15),H1(11,11,15),H2(9,9,15),A1(40),
     1 A2(40)
      DIMENSION WTGAUS(99),PTGAUS(99),WTLAG(99),PTLAG(99)
      DIMENSION STRLAG(100)
      COMMON /BLOCK 12/ICOUNTP
      COMMON/H2PLUS/F(30),GTAU(30),MUWAVE,LAMWAVE,SIGMA,P,RZERO
 862  FORMAT(1H1)
   43 FORMAT(3X, 5E17.8)
 514  FORMAT (2(/),4X,I2,3X,6HRZERO=F7.5,2X,2E17.10)
 142  FORMAT(1H1, 4(/),14X,7HMAXLAG=,I2,4X,8HMAXGAUS= I2//)
 973  FORMAT(35HTHIS PACKET CONTAINS H,S FOR RZERO= F7.5)
 972  FORMAT(4X,6HRZERO= F8.5/13HR(LTAU,J,NU)= /135(5E16.9/)/3HA1=/
     1  8(5E16.9/)/3HH= /507(5E16.9/),3HH1=,/363(5E16.9/),/3HH2=,/243(
     2  5E16.9/),(5E16.9))
 1111 FORMAT(90X,I2,3HMIN, 2X,I2,3HSEC, 3X,I2,6HSEC/60)
 919  FORMAT(3X,2HR=,F5.2,2X,25HNUMBER OF TERMS IN LAMBDA ,I2,9HAND IN M
     1U,I2,/4X,2HP=F17.10,6HSIGMA=F17.10,2X,7HAPRIME= F17.10/4X,7HENERGY
     2= F17.10,6X,19HTHE FS ARE EQUAL TO /(4F20.10))
 920  FORMAT (4X,19HTHE GS ARE EQUAL TO /(4F20.10))
  187 FORMAT(3X,8HMAXGAUS= I2,7HMAXLAG=I2/,(4E17.10) )
  150 FORMAT(90X,2F7.2)
  905 FORMAT(5E16.9)


C    READ IN THE GAUS LAGUERRE AND GAUS LEGENDRE POINTS
      READ  187 , MAXGAUS,MAXLAG,(PTGAUS(I),I=1,MAXGAUS),(WTGAUS(I),I=1,
     1MAXGAUS),(PTLAG(I),I=1,MAXLAG),(WTLAG(I),I=1,MAXLAG)
 917  CONTINUE



C     READ IN THE ZEROTH ORDER WAVE FUNCTION
      READ 919, RZERO,LAMWAVE,MUWAVE,P,SIGMA,APRIME,ENERGY,(F (I),I=1,
     1MUWAVE)
      IF(EOF, 60)101,102
 101   STOP
 102  CONTINUE
      READ 920, (GTAU(I),I = 1,LAMWAVE)


      MLO = 1$MHIGH = 3
      DELTA = P


C     IGOGET DETERMINES THE  POWER OF PSIZERO IN THE INTEGRAND
C  FOR IGOGET = 1 INTEGRAND CONTAINS PSIZERO SQUARE
```

```
      IGOGET = 1
      GO TO (350,349,348),IGOGET
 348  CONTINUE
      ALP = DELTA + DELTA
      ICOUNT P= 1
      GO TO 351
 349  CONTINUE
      ALP = DELTA+P
      ICOUNTP = 2
      GO TO 351
 350  CONTINUE
      ICOUNTP = 3
      ALP = P+P
 351  CONTINUE
      DO 10 I = 1,15
      DO 10 J = 1,15
      DO 10 K = 1,3
  10  R(I,J,K) = 0.
      DO 11 I = 1,40
      A2(I) = 0.
  11  A1(I) = 0.
      PRINT 862
      CALL KTIME(MIN,KSEC,DD)  $ PRINT 1111,MIN,KSEC,DD
C R(MAXMUM,LMAX,3)
      CALLRTAUN(15,15,R,WTGAUS,PTGAUS,MAXGAUS)
      CALL KTIME(MIN,KSEC,DD)  $ PRINT 1111,MIN,KSEC,DD
      CALL BINT (38,A2,WTGAUS,PTGAUS,MAXGAUS)
      CALL KTIME(MIN,KSEC,DD)  $ PRINT 1111,MIN,KSEC,DD
      CALL GETA(WTLAG,PTLAG,MAXLAG,38, A1, ALP)
      CALL KTIME(MIN,KSEC,DD)  $ PRINT 1111,MIN,KSEC,DD
      CALL HTAU(13,13,15,ALP,1,H,WTGAUS,PTGAUS,MAXGAUS,WTLAG,PTLAG,
     1MAXLAG)
      CALL KTIME(MIN,KSEC,DD)  $ PRINT 1111,MIN,KSEC,DD
      CALL HTAU12(11,11,15,9,9,15,H,H1,H2,13,13,15)
      CALL KTIME(MIN,KSEC,DD)  $ PRINT 1111,MIN,KSEC,DD
      PRINT 142, MAXLAG, MAXGAUS
      ENZERO = ENERGY
      WRITE TAPE 23,RZERO,R,A1,H,H1,H2,A2,ENZERO,DELTA
 467    CONTINUE
      GO TO 917
      END
```

```
      SUBROUTINE BINT(NUMINTS,BZ,WTGAUS,PTGAUS,MAXGAUS)
      DIMENSION BZ(40),WTGAUS(99),PTGAUS(99),G(99),X(99),P(30,4)
      COMMON /BLOCK 12/ICOUNTP
      COMMON/H2PLUS/F(30),GTAU(30),MUWAVE,LAMWAVE,SIGMA,PEE,RZERO
      DO 39 K = 1,MAXGAUS
      G(K) = WTGAUS(K)
      X(K) = PTGAUS(K)
      G(K+MAXGAUS) = G(K)
39    X(K+MAXGAUS) = -X(K)
       DO 11 J = 1, NUMINTS
 11   BZ(J) = 0.
      MXGAUSS = 2*MAXGAUS
      DO 43 M = 1,MXGAUSS
      FP2 = 0.
      MAXKAT = MUWAVE
      CALL PTN(MAXKAT,1,P,X(M))
      DO 47 IQ = 1, MAXKAT,2
47    FP2 = FP2 + F(IQ)*P(IQ,1)
      GO TO (335,336,337),ICOUNTP
 335  CONTINUE
      FSQUAR = 1
      GO TO 338
336   CONTINUE
      FSQUAR = FP2
      GO TO 338
337   CONTINUE
      FSQUAR = FP2*FP2
338   CONTINUE
      DO 43 IA = 1,NUMINTS
      BZ(IA)= BZ(IA) + X(M)**(IA-1)*FSQUAR*G(M)
 43   CONTINUE
      END
```

```
      SUBROUTINE GETA(WTLAG,PTLAG,MAXLAG,NUMINTS,ARRAY,SCALE)
      DIMENSION WTLAG(99), PTLAG(99), ARRAY(40)
      ALIMIT = 1
      EAL = EXPF(-ALIMIT*SCALE)/SCALE
      DO 38 L = 1, NUMINTS
```

```
 38   ARRAY (L) = 0.
      DO 43 M = 1,MAXLAG
      Y = PTLAG(M)/SCALE + ALIMIT
      WAVEFU = GNO((Y-1.)/(Y+1.),Y+1.)
      DO 43 N = 1, NUMINTS
 43   ARRAY(N) = ARRAY(N)    +     Y   **(N-1)*WAVEFU*WTLAG(M)*EAL
      END
```

```
      SUBROUTINE HTAU(MMAX,NMAX,ITAUMX,ALP,NU,H,WTGAUS,PTGAUS,MAXGAUS,
     1 WTLAG,PTLAG,MAXLAG)
      DIMENSION P(30,4),G(99),X(99),D(15,15,3),WTGAUS(99),PTGAUS(99),
     1 WTLAG(99),PTLAG(99)
      DIMENSION H(13,13,15)
C     DIMENSION H(NMAX,MMAX,ITAUMX)
      DO 39 K = 1,MAXGAUS
      G(K) = WTGAUS(K)
      X(K) = PTGAUS(K)*(1./2.) + 1./2.
      G(K + MAXGAUS) = G(K)
 39   X(K + MAXGAUS)= -X(K) + 1.
      DO 8 M=1,MMAX
      DO 8 N= 1,NMAX
      DO 8 ITAU = 1,ITAUMX
  8   H(M,N,ITAU) = 0.
       MAXTWO = 2*MAXGAUS
      DO 3 I = 1,MAXTWO
      T = X(I)
 12   MAX = NMAX
 13   CALL PTN (ITAUMX,NU, P,1./T)
      Z = 1./T
      CALL ETAUN (MAX,D,NU,ALP,1./T,ITAUMX,WTLAG,PTLAG,MAXLAG)
      DO 3 ITAU = 1, ITAUMX
      GT = ((1.-T*T) *P(ITAU,NU)*P(ITAU,NU))**(-1)
      DO 3 N= 1,NMAX
      DO 3 M = 1,N
  3   H(M,N,ITAU) = H(M,N,ITAU) + GT*D(ITAU,M,NU)*D(ITAU,N,NU)* G(I)*1./
     1 2.
      DO 81 ITAU = 1,ITAUMX
      TAU = ITAU - 1
      FNU = NU - 1
      KP = 1
```

```
      LIM1 = TAU - FNU + 1.
      LIM 2 = TAU + FNU
      DO 82 I = LIM1,LIM2
   82 KP = KP*I
      COF = (-1)**(NU-1)*KP
      DO 81 N = 1,NMAX
      DO 81 M = 1,N
   81 H(M,N,ITAU) = COF*H(M,N,ITAU)
      DO 30 ITAU = 1, ITAUMX
      DO 30 N = 1,NMAX
      DO 30 M = 1,N
   30 H(N,M,ITAU) = H(M,N,ITAU)
      END
```

```
      SUBROUTINE ETAUN(JMAX,D,NU,ALP,Y,ITAUMX,WTLAG,PTLAG,MAXLAG)
      DIMENSION G(99),X1(99),X2(99),WTLAG(99), PTLAG(99)
      DIMENSION D(15,15,3),P1(30,4),P2(30,4)
      EAL = EXPF(-ALP)/ALP
      U = EXPF(-(Y-1.)*ALP)
      DO 39 K = 1,MAXLAG
      G(K) = WTLAG(K)
      X1(K)= PTLAG(K)/ALP +1.
   39 X2(K) = PTLAG(K)/ALP +Y
      DO 38 J= 1,JMAX
      DO 38 LTAU = 1, ITAUMX
    38 D(LTAU,J,NU) = 0.
      DO 43 M = 1,MAXLAG
      CALL PTN(ITAUMX,NU,P2,X2(M))
      CALL PTN(ITAUMX,NU,P1,X1(M))
      GN1 = GNO((X1(M)-1.)/(X1(M)+1.),X1(M)+1.)
      GN2 = GNO((X2(M)-1.)/(X2(M)+1.),X2(M)+1.)
      COFFA = GN1*G(M)*EAL
C
      W = U*GN2/GN1
      DO 43 J = 1,JMAX
      COFX1J = X1(M)**(J-1)*COFFA
      COFX2J = X2(M)**(J-1)*W*COFFA
      DO 43 LTAU = 1, ITAUMX
   43 D(LTAU,J,NU)=D(LTAU,J,NU)+P1(LTAU,NU)*COFX1J-P2(LTAU,NU)*COFX2J
      END
```

```
      FUNCTION GNO(W,Z)
      COMMON/H2PLUS/F(30),GTAU(30),MUWAVE,LAMWAVE,SIGMA,P,RZERO
      COMMON /BLOCK 12/ICOUNTP
      SUM = 0
      DO 1 I = 1,LAMWAVE
    1 SUM = SUM + GTAU(I)*W**(I-1)
      GO TO (335,336,337),ICOUNTP
  335 CONTINUE
      GNO = 1
      GO TO 338
  336 CONTINUE
      GNO = (Z**SIGMA*SUM)
      GO TO 338
  337 CONTINUE
      GNO = (Z**SIGMA*SUM)**2
 338  CONTINUE
      END
C
```

```
      SUBROUTINE RTAUN(MAXMUM,LMAX,RTAUV,WTGAUS,PTGAUS,MAXPT)
      DIMENSION P(30,4),G(99),X(99),RTAUV(15,15,3),WTGAUS(99)
      DIMENSION PTGAUS(99),RA(15,15)
      COMMON/H2PLUS/F(30),GTAU(30),MUWAVE,LAMWAVE,SIGMA,PEE,RZERO
      COMMON /BLOCK 12/ICOUNTP
      DO 39 K = 1,MAXPT
      G(K) = WTGAUS(K)
      X(K) = PTGAUS(K)
      G(K+ MAXPT) = G(K)
   39 X(K+MAXPT) = -X(K)
C     MAXMUM = 2*KMAX + 7
```

```
      DO 11 J = 1, MAXMUM
      DO 11 K = 1,LMAX
      DO 11 M = 1,3
11    RTAUV(J,K,M) = 0.
      DO 10 NU = 1,3
      DO 38 J = 1,MAXMUM
      DO 38 K = 1,LMAX
 38   RA (J,K) = 0.
      MAXPTS = 2*MAXPT
      DO 43 M = 1,MAXPTS
      FP2 = 0.
      MAXKAT = MUWAVE
      CALL PTN (MAXKAT,1,P,X(M))
      DO 47 IQ = 1,MAXKAT ,2
 47   FP2 = FP2 + F(IQ)*P(IQ,1)
      GO TO (335,336,337),ICOUNTP
 335  CONTINUE
      FSQUAR = 1
      GO TO 338
336   CONTINUE
      FSQUAR = FP2
      GO TO 338
 337  CONTINUE
      FSQUAR = FP2*FP2
338   CONTINUE
      CALL PTN (MAXMUM,NU,P,X(M))
      PROD = FSQUAR*G(M)*(SQRTF(1.-X(M)*X(M)))**(NU-1)
      DO 43 IA = 1,LMAX
      PRODUCT = PROD*X(M)**(IA-1)
      DO 43 LTAU = 1,MAXMUM
      RA(LTAU,IA) = RA(LTAU,IA) + PRODUCT*P(LTAU,NU)
 43   CONTINUE
      DO 10 J = 1,MAXMUM
      DO 10 K = 1, LMAX
      RTAUV(J,K,NU) = RA(J,K)
10    CONTINUE
      END
```

```
      SUBROUTINE HTAU12(MMAX,NMAX,IMAX,NMAX2,MMAX2,IMAX2,H,H1,H2,MZERMAX
     1 ,NZERMAX,IZERMAX)
```

```
      DIMENSION H(13,13,15),H1(11,11,15),H2(9,9,15)
C     DIMENSION H(MZERMAX,NZERMAX,IZERMAX),H1(MMAX,NMAX,IMAX),H2(NMAX2,
C    1 MMAX2,IMAX2)
      DO 49 I = 1,MMAX
      DO 49 J = 1,NMAX
      DO 49 K = 1,IMAX
  49  H1(I,J,K) = 0.
      DO 48 I = 1,NMAX2
      DO 48 J = 1,MMAX2
      DO 48 K = 1,IMAX2
  48  H2(I,J,K) = 0.
      DO 50  I=2,IMAX
      DO 50 N = 1,NMAX
      DO 50  M=1,N
      T = I-1
  50 0 H1(M,N,I) = T*(T+1.)/(2.*T + 1.)*(( T + 1.)*H(M,N,I+1) -
     1(2.*T+ 1.)* H(M + 1,N+1, I) + T*H(M,N,I - 1))
      DO 30 ITAU = 2,IMAX
      DO 30 N = 1,NMAX
      DO 30 M = 1,N
 30   H1(N,M,ITAU) = H1(M,N,ITAU)
      DO 51 I = 3,IMAX2
      DO 51 N = 1,NMAX2
      DO 51 M = 1,N
      T = I-1
  51 0H2(M,N,I) = (T+2.)*(T+1.)*T*(T-1.)/((2. *T +3.)*
     1(2.*T + 1.)* (2.*T-1.))*(T*(2.*T - 1.)*((2.*T + 3.)/
     2 ((T + 1.)*(T + 2.)))*
     3H1(M,N,I + 1)- (2.*T + 3.)*(2.*T-1.)* ((2.*T+1.)/(T*(T + 1.)))*
     4H1(M+1,N+1,I) +(T+1.)*(2.*T + 3.)*((2.*T-1.)/((T - 1.)*T))
     5 *H1(M, N, I - 1))
      DO 40 ITAU = 3,IMAX 2
      DO 40 N = 1,NMAX2
      DO 40 M = 1,N
 40   H2(N,M,ITAU) = H2(M,N,ITAU)
      END
```

```
      SUBROUTINE PTN(LTAUMX,NU,P,X)
C     CALCULATES ASSOCIATED LEGENDRE POLYNOMIALS PTAUNU
      DIMENSION P(30,4)
```

```
      DO 1 M = 1,30
      DO 1 N = 1,4
1     P(M,N) = 0.
      P(1,1) = 1.
      P(2,1) = X
      P(2,2) = SQRTF(ABSF(1.-X*X))
      P(3,2) = 3.*X*P(2,2)
      P(3,3) = 3.*(1. - X*X)
      P(4,3) = 5.*P(3,3)*X
      FNU = NU
      LIMU = NU + 1
      DO 44  LTAU = LIMU,L TAUMX
      TAU = LTAU
440P(LTAU + 1,NU) = 1./(TAU - FNU +1.)*((2.*TAU -1.)*X*
     1P(LTAU,NU) - (TAU + FNU - 2.)*P(LTAU - 1,NU))
      END
      END
```

b. Program Energy

Definition of Symbols and Arrays

Man(i), nan(i), jan(i), and ipan(i) contain the powers of $\xi_1, \xi_2, \eta_1, \eta_2$ and r_{12} for the i^{th} term in the basis set. Equivalent arrays are m(i), n(i), j(i), k(i) and ip(i). The array bmat contains the first order wave function coefficients. Fnorm =1/ $\sqrt{\langle\psi_0|\psi_0\rangle}$, Enone = ϵ_1 , Etwo = ϵ_2, and, Entre = ϵ_3 .

Subroutines and Functions

1. The function X(m,n,j,k,ip) is used to calculate the integrals M_2^o(m,n,j,k,ip).

2. The functions Z2zer, Z1zer, Zone, Z1one, Ztwo,Z1two, Ztre, Zneg, Z1neg, Z2neg, and Zzer are all part of function X.

3. The subroutine Amatsav is used to call the matrix inversion subroutine.

4. The function Hsmall calculates Hij-(II.E-31)

Operating Procedure

The basis set is inputed from punched cards and stored in the arrays m,n,j,k, and ip. Rzero, R, A1, H, H1, H2, A2, enzero, and delta is then inputed from tape. The program subsequently calculates the energy through third order and stores the matrix elements on tape for use by program Highen.

Note

During the calculation certain M_2^o are required more than once. To prevent a repeated evaluation of these integrals a number of memory locations are reserved for their storage. Upon entering function X, a search is made of these to determine whether or not the desired primitive integral has been previously calculated. If not, it is consequently evaluated and stored. Common block 4 which is located in bank 1 is reserved for this storage. Since this program was written, approximately 500 memory locations in bank 1 have been taken over by the computing center in order to store tape handling subroutines. As time proceeds, more locations in Bank 1 will be removed from user access. Because of this the program as it now stands overflows the memory. This condition can be corrected by decreasing the size of Xmattwo, Xmat and Xmatzer in common block 4. Unfortunately this removes some of the storage locations for the M_2^o and forces the recalculation of certain of these integrals. The array sizes are decreased according to the formulas Xmattwo($2(\text{mattwo} + 1)^4$), Xmat($2(\text{mat} + 1)^4$) and Xmatzer($2(\text{matzer} + 1)^4$) where mattwo, mat and matzer are integers. Their value as of now is mattwo = 6, mat = 7, and matzer = 8.

```
      PROGRAM ENERGY
C     PROGRAM READS FROM TAPE, THR BASIC INTEGRALS.  THE BASIS SET
C     EXPANSION TERMS ARE READ FROM CARDS.  THE PROGRAM THEN CALCULATES
C     MATRIX ELEMENTS WHICH IT STORES ON TAPE.  FINALLY, THE ENERGY
C     THROUGH THIRD ORDER IS CALCULATED.
      DIMENSION MAN(50), NAN(50),JAN(50),KAN(50),IPAN(50)
      DIMENSION STRBMAT(50), MSTOR(50)
      DIMENSION SUMMIT(60),COEFF1(50,50),BMAT(50),EONE(2),VA(60)
      BANK,(1),/4/,/3/,(0),/7/,/2/,ENERGY,AMATSAV,ZZER,Z2ZER,MATINV,
     1 ZNEG,Z1NEG,HSMALL,X,Z1ZER,ZONE,Z1ONE,ZTWO,KTIME
      COMMON/7/VCHECK(50),COFNOM(50,50),COFRHO(50,50)
      COMMON/  1   /FNORM,PI,RZERO
      COMMON / 2    /M(100),N(100),J(100),K(100),IP(100)
      COMMON/    3 /A1(40), A2(40),R(15,15,3),H(13,13,15),H1(11,11,15),
     1 H2(9,9,15)
      COMMON/  4   /XMATTWO(4802),XMAT(8192),XMATZER(13122),MATZER,
     1 MAT, MATTWO
 461  FORMAT(4(/),7X,5HEZERO,12X,4HEONE,13X,4HETWO,12X,6HETHREE,12X,
     1 4HESUM,12X,6HEEXACT,12X,4HDIFF,/,7(2X,F13.10,2X))
 460  FORMAT(1H1,5(/)55X,3HR =,F5.2,2(/),37X,42HTHE NUMBER OF TERMS IN T
     1HE WAVEFUNCTION IS ,I2,3(/),40X,12HWAVEFUNCTION, 20X,11HCOEFFICIEN
     2T , 2(/),(41X,5I2,20X,F12.9))
 827  FORMAT(3X,6HRZERO= , E16.9, 4X,E16.9)
 972  FORMAT(4X,6HRZERO= F8.5/13HR(LTAU,J,NU)= /135(5E16.9/)/3HA1=/
     18(5E16.9/)/3HH= /253(5E16.9/),254(5E16.9/),3HH1= ,/200(5E16.9/),
     2 163(5E16.9/),/3HH2= ,/243(5E16.9/),(5E16.9))
 1111 FORMAT(90X,I2,3HMIN, 2X,I2,3HSEC, 3X,I2,6HSEC/60)
 29   FORMAT(1H1,12X,6HRZERO=, F8.5,4X,6HENONE=,E20.10,4X,
     1 7HENZERO=, E20.10, 3X,6HFNORM=, E20.10)
  99  FORMAT (3X,F5.3)
 47     FORMAT(3X,//6HDELTA=F7.5)
 596  FORMAT (1H1)
 407  FORMAT(3X,6HRZERO= , F5.2,3X,14HFUNCTION SIZE= ,I2,40HCOFRHO COFNO
     1M COEFF VA AND SUMMIT FOLLOW /(4E20.10))
 20   FORMAT(3X,I2/(13(5I1,1X)))
  22  FORMAT(6X,3(7HCOEFF1(I2,1H,I2,2H)=  E17.10))
  56  FORMAT(7X,26HTHE DETERMINANT OF COEFF1= E17.10)
 67   FORMAT(8X,  5HETWO=E17.10)

      X1(MO,NO,JO,KO,IO)= X(MO,NO+2,JO,KO,IO)-X(MO,NO,JO,KO+2,IO)

C XMATTWO(4,802),XMAT(8,192),XMATZER(13,122)COFNOM(50,50), COFRHO(50,50)
CMATTWO = 6, MAT= 7, MATZER= 8
C XMATTWO(2*(MATTWO + 1)**4),XMAT(2*(MAT+1)**4), XMATZER(2*(MATZER+1)**4)
      MATTWO= 6$MAT=7$MATZER=8
      PI = 3.141592653589
      CALL KTIME(MIN,KSEC,DD)  $ PRINT 1111,MIN,KSEC,DD

C     READ TERM IN BASIS EXPANSION
```

```
      READ 20,MN,(M(I),N(I),J(I),K(I),IP(I),I=1,MN)
      IF(EOF,60)163,164
  163 STOP
  164 CONTINUE
      DO 300  I = 1,MN
      M(I+MN) = N(I)
      N(I + MN) = M(I)
      J(I + MN) = K(I)
      K(I + MN) = J(I)
  300 IP(I + MN) = IP(I)
  19  CONTINUE
C       INPUT BASIS INTEGRALS FROM TAPE
      READ  TAPE 23,RZERO,R,A1,H,H1,H2,A2,ENZERO,DELTA
      IF(EOF,23)263,264
  263 STOP
  264 CONTINUE
      CALL KTIME(MIN,KSEC,DD)  $ PRINT 1111,MIN,KSEC,DD
      LIMIT1= 2*(MAT+1)**4
      LIMIT2 = 2*(MATZER+1)**4
      LIMIT 3 = 2*(MATTWO + 1)**4
      DO 999 I = 1,LIMIT1
  999 XMAT(I) = 0.
      DO 998 I = 1,LIMIT2
  998 XMATZER(I) = 0.
      DO 997 I = 1,LIMIT3
  997 XMATTWO(I) = 0.
      CALL KTIME(MIN,KSEC,DD)  $ PRINT 1111,MIN,KSEC,DD
      FRONT = (RZERO**3*PI/4.)**2
C
C
C     CALCULATION OF NORMALIZATION INTEGRAL
C
      FNORM = 1/SQRTF(FRONT*X1(0,0,0,0,0))
      RBI = (RZERO**3*PI/4)**2*FNORM**2
C     CALCULATION OF FIRST ORDER ENERGY
      ENONE = RBI*2./RZERO*X1(0,0,0,0,-1)
      CALL KTIME(MIN,KSEC,DD)  $ PRINT 1111,MIN,KSEC,DD
C       CALCULATION OF MATRIX ELEMENTS
      DO 881 I = 1,MN
      DO 881 L = 1,I
      IF(M(I+MN).EQ.M(I).AND.N(I+MN).EQ.N(I).AND.J(I+MN).EQ.J(I).AND.
     1K(I+MN).EQ.K(I).AND.IP(I+MN).EQ.IP(I))190,191
```

```
190  IF(M(L+MN).EQ.M(L).AND.N(L+MN).EQ.N(L).AND.J(L+MN).EQ.J(L).AND.
    1K(L+MN).EQ.K(L).AND.IP(L+MN).EQ.IP(L))192,193
192  W1 = HSMALL(I,L,XMATRX) $ W2=W1$W3=W1$W4=W1
      GO TO 196
193  W1=HSMALL(I,L,XMATRX)$W2=W1$W3=HSMALL(I,L+MN,XMATRX)$W4=W3
      GO TO 196
191  IF(M(L+MN).EQ.M(L).AND.N(L+MN).EQ.N(L).AND.J(L+MN).EQ.J(L).AND.
    1K(L+MN).EQ.K(L).AND.IP(L+MN).EQ.IP(L))194,195
194  W1=HSMALL(I,L,XMATRX)$W2=HSMALL(I+MN,L,XMATRX) $W3=W1$W4=W2
     GO TO 196
195  CONTINUE
     W1 = HSMALL(I,L,XMATRX)
     W2 = HSMALL(I+MN,L,XMATRX)
     W3 = HSMALL(I,L+MN,XMATRX)
     W4 = HSMALL(I+MN,L+MN,XMATRX)
196  CONTINUE
     COEFF1(I,L) = W1+W2+W3+W4
 881 COEFF1(L,I) = COEFF1(I,L)
C    PRINT 22,((MO,NO,COEFF1(MO,NO),MO=1,MN),NO=1,MN)
C    CALCULATION OF (0,1) AND (0,V,1)
     CALL KTIME(MIN,KSEC,DD)  $ PRINT 1111,MIN,KSEC,DD
     DO 60 I = 1,MN
     SUMMIT (I) = 0.
     VA(I) = 0.
     VYA = X1(M(I),N(I),J(I),K(I),IP(I)-1)
     VYB = X1(M(I),N(I),J(I),K(I),IP(I))
390  VYC = VYA $ VYD = VYB
     SUMMIT(I) = RBI*(VYB+VYD)
60   VA(I) = -RBI*(2./RZERO*(VYA+VYC) - ENONE*(VYB+VYD))
     CALL KTIME(MIN,KSEC,DD)  $ PRINT 1111,MIN,KSEC,DD
 913 CONTINUE
     CALL AMATSAV(MN,COEFF1,BMAT,VA,PI,DET)
     EP = 0.

C    CALCULATION OF SECOND ORDER ENERGY

      DO 15 I = 1,MN
15   EP = EP + BMAT(I)*VA(I)
     ETWO = -EP
     SUM2 = 0.
     SUM1 = 0.
     CALL KTIME(MIN,KSEC,DD)  $ PRINT 1111,MIN,KSEC,DD
     MNTWO = 2*MN
     DO 9 JQ = 1,MN
     DO 9 IQ = 1,JQ
     JUCK = J(IQ) + J(JQ)
     KUCK = K(IQ) + K(JQ)
     MUCK = M(IQ) + M(JQ)
     NUCK = N(IQ) + N(JQ)
```

```
      IPUCK = IP(IQ) +IP(JQ)
      JU = J(IQ) + J(JQ + MN)
      KU = K(IQ) + K(JQ+MN)
      MU = M(IQ) + M(JQ+MN)
      NU = N(IQ) + N(JQ +MN)
      IPU = IP(IQ) + IP(JQ+MN)
      PORK = (X1(MUCK,NUCK,JUCK,KUCK,IPUCK-1)
     1 + X1(MU,NU,JU,KU,IPU-1))*2
      FORK =(X1(MUCK,NUCK,JUCK, KUCK, IPUCK)
     1 + X1(MU,NU,JU,KU,IPU  ))*2
      COFNOM(IQ,JQ) = RBI*FORK
      COFRHO(IQ,JQ) = RBI*PORK*2/RZERO
      COFNOM(JQ,IQ) = COFNOM(IQ,JQ)
      COFRHO(JQ,IQ) = COFRHO(IQ,JQ)
    9 CONTINUE
      DO 910 IQ= 1,MN
      DO 910 JQ = 1,MN
      SUM1 = SUM1 + BMAT(IQ)*BMAT(JQ)*(COFRHO(IQ,JQ)-
     1 ENONE*COFNOM(IQ,JQ))
  910 CONTINUE
      DO 11 I = 1,MN
      SUM2 = SUM2 + BMAT(I)*SUMMIT(I)
   11 CONTINUE

C       CALCULATION OF THIRD ORDER ENERGY

      ENTRE = SUM1-2.*ETWO*SUM2
      EEXACT = -1.888734
      ESUMM= ENZERO + ENONE + ETWO + ENTRE
      DIFF = -1.88873 - (ENZERO + ENONE + ETWO + ENTRE)
      PRINT 460,RZERO,MN,(M(I),N(I),J(I),K(I),IP(I),BMAT(I),I=1,MN)
      PRINT 461, ENZERO,ENONE,ETWO,ENTRE,ESUMM,EEXACT,DIFF
      PRINT 596
      DO 747 JJ = 1,MN
  747 STRBMAT(JJ) = 0.
      DO 748 JJ = 1,MN
      TRY = ABSF(BMAT(1))
      NUMKP = 1
      DO 749 I = 1,MN
C     IF(TRY-ABSF(BMAT(I)))749,749,731
      IF(TRY-ABSF(BMAT(I)))731,749,749
  731 TRY = ABSF(BMAT(I))
      NUMKP = I
  749 CONTINUE
      MSTOR(JJ) = NUMKP
      STRBMAT(JJ) = BMAT(NUMKP)
       BMAT(NUMKP) = 0.0
  748 CONTINUE
      DO 395 I = 1,MN
```

```
      MAN(I)=M(MSTOR(I))$NAN(I)=N(MSTOR(I))$JAN(I)=J(MSTOR(I))
      KAN(I) = K(MSTOR(I))
395   IPAN(I) = IP(MSTOR(I))
      PRINT 460, RZERO,MN,(MAN(I),NAN(I),JAN(I),KAN(I),IPAN(I),
     1STRBMAT(I),I=1,MN)
257    CONTINUE
431    CONTINUE
      WRITE TAPE 47,
     1          RZERO,MN,ENZERO,((COFRHO(I,JO),I=1,MN),JO= 1,MN),((COFNO
     2M(I,JO), I = 1,MN),JO= 1,MN),((COEFF1(I,JO),I = 1,MN),JO= 1,MN),
     3 (VA(I),I=1,MN),(SUMMIT(I),I=1,MN),ENZERO,ENONE,
     4 (M(I),N(I),J(I),K(I),IP(I),I=1,MN)
1199  CONTINUE
      GO TO 19
      END





      FUNCTION ZNEG(M,N,J,K)
      DIMENSION TE(2)
      COMMON/    3 /A1(40), A2(40),R(15,15,3),H(13,13,15),H1(11,11,15),
     1 H2(9,9,15)
 90   FORMAT(    2E17.10,I2, 23HTOO MANY TAUS IN VZNEG )
      IF (J-2*(J/2))38,39,38
38    IF(K-2*(K/2))40,41,40
41    ZNEG = 0.
      RETURN
39    IF(K-2*(K/2))41,40,41
40    CONTINUE
18    FORMAT(//,14X,17HOVERLOAD IN Z NEG, 2HM=I2,2HN=I2)
      IF(M-12)17,17,15
17    IF(N-12)19,19,15
15    PRINT 18,M,N
19    CONTINUE
      TERM = 0.
      SUMM = 0.
      LTAU = 0
      I = 0
      TE1KP = 1.E128
      TE2KP = 1.E128
3     LTAU = LTAU + 1
      T = LTAU - 1
```

```
      I = I+1
      TE(I) = (2.*T+1.)*R(LTAU,J+1,1)*R(LTAU,K+1,1)*H(M+1,N+1,LTAU)
      IF(I-2) 3,5,5
 5    I = 0
      TERM = TE(1) + TE(2)
C     PRINT 71, TE(1) , TE(2),SUMM
      IF(TE(1) - TE(2))191,191,190
 190  CONTINUE
      IF(ABSF(TE(1))-ABSF(TE1KP))192,1,1
 192  TE1KP = TE(1)
      GO TO 193
 191  IF(ABSF(TE(2))- ABSF(TE2KP))194,1,1
 194  TE2KP = TE(2)
 193  CONTINUE
 71   FORMAT (17HTE(1),TE(2),SUMM= , 3E16.9)
      TE(1) = 0.
      TE(2) = 0.
  4   SUMM = SUMM + TERM
      IF(LTAU - 14) 8,9,9
   9   CONTINUE
      PRINT 90, TERM,SUMM,LTAU
      GO TO 1
  8     CONTINUE
      IF (ABSF(TERM/SUMM)-.1E-7)1,3,3
   1  CONTINUE
      ZNEG = SUMM
      END
```

```
      FUNCTION Z1NEG(M,N,J,K)
      DIMENSION TE(2)
      COMMON/    3 /A1(40), A2(40),R(15,15,3),H(13,13,15),H1(11,11,15),
     1 H2(9,9,15)
  90  FORMAT(   2E17.10,I2 ,23HTOO MANY TAUS IN VZ1NEG)
      IF (J-2*(J/2))38,39,38
 38   IF(K-2*(K/2))40,41,40
 41   Z1NEG = 0.
      RETURN
 39   IF(K-2*(K/2))41,40,41
 40   CONTINUE
 18   FORMAT(//,14X,17HOVERLOAD IN Z1NEG, 2HM=I2,2HN=I2)
```

```
      IF(M-10)17,17,15
 17   IF (N-10) 19,19,15
 15   PRINT 18,M,N
 19   CONTINUE
      SUMM = 0.
      TERM = 0.
      I = 0
      TE1KP = 1.E128
      TE2KP = 1.E128
      LTAU = 1
  3   LTAU = LTAU + 1
      T = LTAU - 1
      I = I+1
      TE(I) = -1./(T*(T+1.))*R(LTAU,J+1,2)*R(LTAU,K+1,2)*
     1(2.*T+1.)/(T*(T+1.))*H1(M+1,N+1,LTAU)
      IF(I-2) 3,5,5
  5   I = 0
      TERM = TE(1) + TE(2)
C     PRINT 73, SUMM, TE(1) , TE(2)
      IF(TE(1) - TE(2))191,191,190
 190  CONTINUE
      IF(ABSF(TE(1))-ABSF(TE1KP))192,1,1
 192  TE1KP = TE(1)
      GO TO 193
 191  IF(ABSF(TE(2))- ABSF(TE2KP))194,1,1
 194  TE2KP = TE(2)
 193  CONTINUE
 73   FORMAT (11HSUMM,T1,T2= , 3E17.10)
      TE(1) = 0.
      TE(2) = 0.
  4   SUMM = SUMM + TERM
      IF(LTAU-15)8,9,9
   9   CONTINUE
      PRINT 90, TERM,SUMM,LTAU
      GO TO 1
  8     CONTINUE
C THE LIMIT .1E-7 SHOULD BE EXPERIMENTED WITH
      IF (ABSF(TERM/SUMM)-.1E-7)1,3,3
  1   CONTINUE
      Z1NEG = SUMM
      END
```

```
      FUNCTIONZ2NEG(M,N,J,K)
      COMMON/    3 /A1(40), A2(40),R(15,15,3),H(13,13,15),H1(11,11,15),
     1 H2(9,9,15)
400   FORMAT(//4X,20HLTAU IN Z2NEG EQUALS I3,//)
8     FORMAT(17HOVERLOAD IN Z2NEG  ,2HM=I2,2HN=I2,4HLIM=I2)
      IF(J-2*(J/2))38,39,38
 38   IF(K-2*(K/2))40,41,40
 41   Z2NEG = 0.
      RETURN
39    IF(K-2*(K/2))41,40,41
 40   CONTINUE
      IF (J - K) 17,17,18
 17   LIM = J + 3
      GO T O 19
 18   LIM = K + 3
19    IF(LIM-12)6,6,5
6     IF(M-8)7,7,5
7     IF(N-8)9,9,5
5     PRINT 8,M,N,LIM
      LIM = 6
 9    CONTINUE
      SUMM1 = 0.
      SUMM2 = 0.
      SUMM KP = 0
      CONST = 1
      DO 171 KTAU = 3,13,2
      IF (CONST-1) 109,109,171
109   CONTINUE
      JAKE = KTAU + 1
      DO 209 LTAU = KTAU,JAKE
      T = LTAU - 1
      SUMM 1 = SUMM1 + (1./((2.*T + 3.)*(2.*T - 1.)* (T + 2.)*(T + 1.)
     1 *T*(T - 1.)))*R(LTAU , J + 1, 3)*R(LTAU, K + 1, 3)*((2.*T + 3.)
     2 *(2.*T + 1.)*(2.*T - 1.)/((T + 2.)*(T + 1.)*T*(T - 1.))) * H2
     3  (M + 1,N+1,LTAU)
 209  CONTINUE
      IF ( ABSF((SUMM1-SUMMKP)/SUMM1) - 1.E-08) 110,110,111
110   CONTINUE
      CONST = 2
      IF(KTAU-13)171,183,183
183   CONTINUE
      PRINT 400, LTAU
      GO TO 171
 111  CONTINUE
      SUMM KP = SUMM1
 171  CONTINUE
      CONST = 1
```

```
      SUMM KP = 0.
      DO 172 KTAU = 1,13,2
      IF ( CONST-1) 113,113,172
113   CONTINUE
      JAIL = KTAU + 1
      DO 210 LTAU = KTAU,JAIL
      T = LTAU - 1
      SUMM 2 = SUMM2 + (2.*T + 1.)*(R(LTAU,J + 1,1) -R(LTAU ,J + 3,1))
     1* ( R(LTAU,K + 1,1) -R(LTAU, K+ 3,1))*     (H(M+3,N + 3,LTAU)
     2  -H(M + 3, N + 1,LTAU) - H(M+1,N + 3,LTAU)
     3    + H(M+1,N+1,LTAU))
210   CONTINUE
      IF(ABSF((SUMM2-SUMMKP)/SUMM2)-1.E-08)  114,114,115
114   CONTINUE
      CONST = 2
      IF(KTAU-13)172,184,184
184   CONTINUE
      PRINT 400, LTAU
      GO TO 172
 115  CONTINUE
      SUMMKP = SUMM2
 172  CONTINUE
      Z = 1./2.*(SUMM1 + SUMM2)
      Z2NEG = Z
      RETURN
      END
```

```
      FUNCTION ZZER(M,N,J,K)
      COMMON/    3 /A1(40), A2(40),R(15,15,3),H(13,13,15),H1(11,11,15),
     1 H2(9,9,15)
      IF (J-2*(J/2)) 2,2,3
 2    IF (K-2*(K/2)) 4,4,3
 3    ZZER = 0.
      RETURN
 4    ZZER = A1(M+1)*A1(N+1)*A2(J+1)*A2(K+1)
      END
```

```
      FUNCTION X(M,N,J,K,IP)
      COMMON/  4   /XMATTWO(4802),XMAT(8192),XMATZER(13122),MATZER,
     1 MAT, MATTWO
C              ,REZTAM,)0062(REZTAMX,)5521(TAMX  ,)025(OWTTAMX/4KCOLB/ NOMMOC
 199  FORMAT(/10X,5I3)
 200  FORMAT(40X,E17.10)
      IF(J-2*(J/2))38,39,38
 38   IF(K-2*(K/2))40,41,40
 41   X = 0.
      RETURN
 39   IF(K-2*(K/2))41,40,41
  40  IF(IP)42,43,42
  43  IF(J-2*(J/2))41,42,41
 42   IF(IP) 60,60,61
 60   IF(M-MATZER)74,74,3
 74   IF(N-MATZER) 75,75,3
  75  IF(J-MATZER)76,76,3
 76   IF(K-MATZER)77,77,3
 77   Y = XMATZER(M+1+(MATZER+1)*N + (MATZER+1)**2*J +(MATZER+1)**3*K
     1 +(MATZER+1)**4*(IP+1))
      PRINT 200,Y
      IF(Y) 48,79,48
 79   COUNT = 0.
      GO TO 2
 61   IF(IP-2) 62,62,63
 62   IF(M-MAT)44,44,3
 44   IF (N-MAT)45,45,3
 45   IF(J-MAT)46,46,3
 46   IF(K-MAT)47,47,3
 47   Y = XMAT(M+1+(MAT+1)*N +(MAT+1)**2*J + (MAT+1)**3*K + (MAT+1)**4
     1 *(IP-1))
      IF(Y) 48,49,48
 48   X = Y
      RETURN
 49   COUNT = 1.
      GO TO 2
 63   IF(M-MATTWO)84,84,3
 84   IF(N-MATTWO)85,85,3
 85   IF(J-MATTWO)86,86,3
 86   IF (K-MATTWO)87,87,3
 87   Y = XMATTWO(M+1+(MATTWO+1)*N + (MATTWO+1)**2*J+(MATTWO+1)**3*K
     1 +(MATTWO +1)**4*(IP-3))
      IF(Y) 48,89,48
```

```
 89   COUNT = 2.
      GO TO 2
 160  XX= ZZER(M+2,N,J,K) - ZZER(M,N,J+2,K)
      GO TO 50
  3   CONTINUE
C     PRINT 106,M,N,J,K,IP
 106  FORMAT (23HOVERFLOW IN FUNCTION X 3X,5(I2,2X))
      COUNT = 3.
  2   IF(IP)159,160,161
 159  XX= ZNEG(M+2,N,J,K) - ZNEG(M,N,J+2,K)
      GO TO 50
 161  IF(IP-2)162,163,164
  162 XX= ZONE(M+2,N,J,K ) - ZONE(M,N,J+2,K)
      GO TO 50
 163  XX= ZTWO(M+2,N,J,K) - ZTWO(M,N,J+2,K)
      GO TO 50
 164  IF(IP-4) 165,166,166
 165  XX= ZTRE(M+2,N,J,K) - ZTRE(M,N,J+2,K)
      GO TO 50
 166  XX= ZFOR(M+2,N,J,K) - ZFOR(M,N,J+2,K)
 50   IF(COUNT - 1.)53,52,54
 53   NUMBER =    (M+1+(MATZER+1)*N + (MATZER+1)**2*J +(MATZER+1)**3*K
     1 +(MATZER+1)**4*(IP+1))
      XMATZER(NUMBER) = XX
      GO TO 51
 54   IF(COUNT - 2.) 55,55,51
 55   NUMBER =    (M+1+(MATTWO+1)*N + (MATTWO+1)**2*J+(MATTWO+1)**3*K
     1 +(MATTWO +1)**4*(IP-3))
      XMATTWO(NUMBER) = XX
      GO TO 51
 52   NUMBER =(M+1+(MAT+1)*N +(MAT+1)**2*J + (MAT+1)**3*K + (MAT+1)**4
     1 *(IP-1))
      XMAT(NUMBER) = XX
 51   X = XX
       END
```

```
      SUBROUTINE AMATSAV(MN,COEFF1,BMAT,VA,PI,DET)
      DIMENSION AMAT(50,50),COEFF1(50,50),BMAT(50 ),VA(60)
      DO 50 I = 1,MN
      DO 50 J = 1,MN
```

```
50    AMAT(I,J) = COEFF1(I,J)
      DO 51 I = 1,MN
51    BMAT(I) = VA(I)
      NQ = 1
      CALL MATINV(AMAT,MN,BMAT,NQ,DET,50)
      END
```

```
      FUNCTIONZ2ZER(M,N,J,K)
      COMMON/    3 /A1(40), A2(40),R(15,15,3),H(13,13,15),H1(11,11,15),
     1 H2(9,9,15)
      FJ = J
      FK = K
      IF (J-2*(J/2)) 2,2,3
2     IF (K-2*(K/2)) 4,4,3
3     Z2ZER = 0.
      RETURN
4     Z2ZER = (A1(M+3)-A1(M+1))*(A1(N+3)-A1(N+1))*(A2(J+1)-A2(J+3))*
     1(A2(K+1)-A2(K+3))/2.
      END
```

```
      FUNCTION HSMALL(IQ,JQ,XMATRX)
      DIMENSION TERM(8) ,CO(8)
      COMMON/  1   /FNORM,PI,RZERO
      COMMON/2/MW(100),NW(100),JW(100),KW(100),IPW(100)
      NA = NW(IQ)
      MA = MW(IQ)
      JA = JW(IQ)
      KA = KW(IQ)
      IPA = IPW(IQ)
      NB = NW(JQ)
      MB = MW(JQ)
```

```
      JB = JW(JQ)
      KB = KW(JQ)
      IPB = IPW(JQ)
      CO(1) = NA*NB-KA*KB
      CO (2) = IPA*NB + IPB*NA
      CO(3) = -NA*NB
      CO (4) = KA*KB
      CO (5) = IPA*IPB
      CO (6) = -(IPA*KB+KA*IPB)
      CO (7) = -(CO(6) + CO(2))
      CO(8) = CO(7)
      N = NA + NB
      M = MA + MB
      J = JA + JB
      K = KA + KB
      IP = IPA + IPB
      DO 10 I = 1,8
 10   TERM(I) = 0.
      DO 11 I = 1,8
      IF (CO(I) - 0.)14,11,14
 11   CONTINUE
      GO TO  38
 14   GO TO (1,2,3,4,5,6,7,8),I
  1   TERM(1) = CO(1)*X(M,N,J,K,IP)
      GO TO 11
  2   TERM(2) = CO(2)*(X(M,N+2,J,K,IP-2)+X(M+1,N-1,J+1,K+1,IP-2))
      GO TO 11
 3    TERM(3) = CO(3)*X(M,N-2,J,K,IP)
      GO TO 11
  4   TERM(4) = CO(4)*X(M,N,J,K-2,IP)
      GO TO 11
  5   TERM(5) = CO(5)*(X(M,N+2,J,K,IP-2)-X(M,N,J,K+2,IP-2))
      GO TO 11
  6   TERM(6) = CO(6)*(X(M,N,J,K+2,IP-2)+X(M+1,N+1,J+1,K-1,IP-2))
      GO TO 11
  7   TERM(7) = CO(7)*(X(M+1,N+1,J+1,K+1,IP-2)+X(M,N,J,K,IP-2))
      GO TO 11
  8   TERM(8) = CO(8)*(X(M+2,N,J,K,IP-2)+X(M,N+2,J,K,IP-2)+X(M,N,J+2,K,
     1IP-2)+X(M,N,J,K+2,IP-2)-2*X(M,N,J,K,IP-2)-2*X(M+1,N+1,J+1,K+1,
     2 IP-2)-X(M,N,J,K,IP))/2.
      GO TO 11
  38  SUMM = 0.
      DO 17 I = 1,8
   17 SUMM = SUMM +TERM(I)
      HSMALL = (RZERO**2*PI*FNORM/2)**2*SUMM
      END
```

```
       FUNCTION Z1ZER(M,N,J,K)
       Z1ZER          = M*(2-2)
       END

       FUNCTION ZONE(M,N,J,K)
       ZONE               = ZNEG (M+2,N,J,K) + ZNEG (M,N,J+2,K)+ZNEG (M,N,J,
      1K+2) -2.*ZNEG (M,N,J,K) -2.*ZNEG (M+1,N+1,J+1,K+1) -2.*Z1NEG(M,
      2N,J,K) + ZNEG (M,N+2,J,K)
       END

       FUNCTION Z1ONE(M,N,J,K)
       Z1ONE              = Z1NEG(M+2,N,J,K) + Z1NEG(M,N,J+2,K)+Z1NEG(M,N,J,
      1K+2) -2.*Z1NEG(M,N,J,K) -2.*Z1NEG(M+1,N+1,J+1,K+1) -2.*Z2NEG(M,
      2N,J,K) + Z1NEG(M,N+2,J,K)
       END

       FUNCTION ZTWO(M,N,J,K)
       ZTWO               = ZZER (M+2,N,J,K) + ZZER (M,N,J+2,K)+ZZER (M,N,J,
      1K+2) -2.*ZZER (M,N,J,K) -2.*ZZER (M+1,N+1,J+1,K+1) -2.*Z1ZER(M,
      2N,J,K) + ZZER (M,N+2,J,K)
       END

       FUNCTION Z1TWO(M,N,J,K)
       Z1TWO              = Z1ZER(M+2,N,J,K) + Z1ZER(M,N,J+2,K)+Z1ZER(M,N,J,
      1K+2) -2.*Z1ZER(M,N,J,K) -2.*Z1ZER(M+1,N+1,J+1,K+1) -2.*Z2ZER(M,
      2N,J,K) + Z1ZER(M,N+2,J,K)
       END

       FUNCTION ZTRE(M,N,J,K)
       ZTRE               = ZONE (M+2,N,J,K) + ZONE (M,N,J+2,K)+ZONE (M,N,J,
      1K+2) -2.*ZONE (M,N,J,K) -2.*ZONE (M+1,N+1,J+1,K+1) -2.*Z1ONE(M,
      2N,J,K) + ZONE (M,N+2,J,K)
       END
```

```
 ZFOR            = ZTWO (M+2,N,J,K) + ZTWO (M,N,J+2,K)+ZTWO (M,N,J,
1K+2) -2.*ZTWO (M,N,J,K) -2.*ZTWO (M+1,N+1,J+1,K+1) -2.*Z1TWO(M,
2 N,J,K) + ZTWO(M,N+2,J,K)
 END
```

2. Hmethod

a. Program Htauint

Definition of Symbols and Arrays

$$R(\tau+1,m+1,\nu) = \left[\frac{(2\tau+1)(\tau-\nu)!}{2(\tau+\nu)!}\right]^{-1/2} \mathcal{Q}_{0,\tau}^{\nu,\nu}(m) - (\text{III}.A-51)$$

$$\left.\begin{aligned} H(m+1,n+1,\tau+1) &= \mathcal{H}_{0,\tau}^{0}(m,n) \\ H1(m+1,n+1,\tau+1) &= \mathcal{H}_{0,\tau}^{1}(m,n) \\ H2(m+1,n+1,\tau+1) &= \mathcal{H}_{0,\tau}^{2}(m,n) \end{aligned}\right\} -(\text{III}.A-16)$$

$$A1(m+1) = A_0(m) - (\text{III}.A-15)$$

Subroutines and Functions

1. Rtaun(jmax,R,nu,wtgaus,ptgaus,maxgaus) determines the array R(m,n, ν) for ν = 1,2, and 3 and all m $\leq$ jmax + nu and N $\leq$ jmax + 1.

2. Aint(lmax,A,X) determines the integrals A1 for all m $\leq$ lmax.

3. Htau and Htaui2 - see page 127.

Operating Procedure

Besides the input parameters listed on page 127, this program requires a value for delta $= \alpha$ -(II.E-3). The basic integrals R,A1,H,H1,H2, and A2 are automatically calculated and punched on cards along with delta.

```
      PROGRAM HTAUINT
C     PROGRAM CALCULATED BASIC INTEGRALS FOR H METHOD
      DIMENSION R(12,10,3),H(10,10,10),H1(8,8,8),H2(6,6,7),A1(40)
      DIMENSION WTGAUS(32),PTGAUS(32),WTLAG(16),PTLAG(16)
 972  FORMAT(6HDELTA=F8.5/13HR(LTAU,J,NU)= /72(5E16.9/)/3HA1=/8(5E16.9/
     1 )/ 3HH= /200(5E16.9/)     3HH1=,/102(5E16.9/),2E16.9,/3HH2=
     2 /50(5E16.9/),2E16.9)
 973  FORMAT(35HTHIS PACKET CONTAINS H,S FOR DELTA= F7.5,)
  905 FORMAT(5E16.9)
 47    FORMAT(3X,//6HDELTA=F7.5)
  99  FORMAT (3X,F5.3)
  187 FORMAT(3X,8HMAXGAUS= I2,7HMAXLAG=I2,3E16.9,10(/5E16.9))
  150 FORMAT(90X,2F7.2)
  187 FORMAT(3X,8HMAXGAUS= I2,7HMAXLAG=I2/,(4E17.10) )
C     READ IN GAUS POINTS AND WEIGHTS
C     FOR N POINT LEGENDRE INTEGRATION , READ IN N/2 POINTS.
C     WTLAG REFERS TO LAGUERRE WEIGHTS, AND WTGAUS REFERS TO LEGENDRE
C     GAUS WEIGHTS
      READ  187 , MAXGAUS,MAXLAG,(PTGAUS(I),I=1,MAXGAUS),(WTGAUS(I),I=1,
     1MAXGAUS),(PTLAG(I),I=1,MAXLAG),(WTLAG(I),I=1,MAXLAG)
      READ 99,DELTA
      PRINT 47, DELTA
      ALP = 2.*DELTA
      CALL RTAUN(8 ,R,1,WTGAUS,PTGAUS,MAXGAUS)
      CALL RTAUN(8 ,R,2,WTGAUS,PTGAUS,MAXGAUS)
      CALL RTAUN(8 ,R,3,WTGAUS,PTGAUS,MAXGAUS)
      CALL AINT (38,A1,ALP)
      CALLHTAU(10,10,10,ALP ,1,H,WTGAUS,PTGAUS,MAXGAUS,WTLAG,PTLAG,
     1 MAXLAG)
      CALL HTAU12(8,8,8,6,6,7,H,H1,H2,10,10,10)
      PRINT 973 , DELTA
      PUNCH 972,DELTA,R,A1,H,H1,H2
      GO TO 9999
      END
```

```
      SUBROUTINE AINT (LMAX, A, X)
      DIMENSION A (40)
      A(1) = EXPF(-X)/X
      DO2 I =  1, LMAX
      FI = I
    2 A(I + 1) = A(1) + FI*A(I)/X
      END
```

```
C
       SUBROUTINE HTAU(MMAX,NMAX,ITAUMX,ALP,NU,H,WTGAUS,PTGAUS,MAXGAUS,
     1 WTLAG,PTLAG,MAXLAG)
       DIMENSION P(12,4 ),G(32),X(32),D(20,20,3 ) ,WTGAUS(32),PTGAUS(32),
     1 WTLAG(16),PTLAG(16)
       DIMENSION H(10,10,10)
C      DIMENSION H(NMAX,MMAX,ITAUMX)
       DO 39 K = 1,MAXGAUS
       G(K) = WTGAUS(K)
       X(K) = PTGAUS(K)*(1./2.) + 1./2.
       G(K + MAXGAUS) = G(K)
 39    X(K + MAXGAUS)= -X(K) + 1.
       DO 8 M=1,MMAX
       DO 8 N= 1,NMAX
       DO 8 ITAU = 1,ITAUMX
  8    H(M,N,ITAU) = 0.
        MAXTWO = 2*MAXGAUS
       DO 3 I = 1,MAXTWO
       T = X(I)
  12   MAX = NMAX
  13   CALL PTN (ITAUMX,NU, P,1./T)
  43   FORMAT(5E16.9)
       Z = 1./T
       CALL ETAUN (MAX,D,NU,ALP,1./T,ITAUMX,WTLAG,PTLAG,MAXLAG)
       DO 3 ITAU = 1, ITAUMX
       GT = ((1.-T*T) *P(ITAU,NU)*P(ITAU,NU))**(-1)
       DO 3 N= 1,NMAX
       DO 3 M = 1,N
  3    H(M,N,ITAU) = H(M,N,ITAU) + GT*D(ITAU,M,NU)*D(ITAU,N,NU)* G(I)*1./
     1 2.
       DO 81 ITAU = 1,ITAUMX
       TAU = ITAU - 1
       FNU = NU - 1
       KP = 1
       LIM1 = TAU - FNU + 1.
       LIM 2 = TAU + FNU
       DO 82 I = LIM1,LIM2
  82   KP = KP*I
       COF = (-1)**(NU-1)*KP
       DO 81 N = 1,NMAX
       DO 81 M = 1,N
  81   H(M,N,ITAU) = COF*H(M,N,ITAU)
       DO 30 ITAU = 1, ITAUMX
       DO 30 N = 1,NMAX
       DO 30 M = 1,N
```

```
   30 H(N,M,ITAU) = H(M,N,ITAU)
      END
```

```
      SUBROUTINE ETAUN(JMAX,D,NU,ALP,Y,ITAUMX,WTLAG, PTLAG,MAXLAG)
      DIMENSION P1(12,4 ), P2(12,4 ), G(16),X1(16), X2(16), D(20,20,3),
     1 WTLAG(16), PTLAG(16)
      EAL = EXPF(-ALP)/ALP
      DO 39 K = 1,MAXLAG
      G(K) = WTLAG(K)
      X1(K)= PTLAG(K)/ALP +1.
   39 X2(K) = PTLAG(K)/ALP +Y
      DO 38 J= 1,JMAX
      DO 38 LTAU = 1, ITAUMX
   38 D(LTAU,J,NU) = 0.
      DO 43 M = 1,MAXLAG
      CALL PTN(ITAUMX,NU,P2,X2(M))
      CALL PTN(ITAUMX,NU,P1,X1(M))
      DO 43 J = 1,JMAX
      DO 43 LTAU = 1, ITAUMX
      FNU = NU
      U = EXPF(-(Y-1.)*ALP)
      GNU = (FNU - 1.) /2.
   43 D(LTAU,J,NU) = D(LTAU,J,NU) + ((X1(M)*X1(M) -1.)**GNU*
     1 P1(LTAU,NU)*X1(M)**(J-1) - EXPF(-(Y-1.)*ALP)*
     2 (X2(M)*X2(M)-1.)**GNU*P2(LTAU,NU)*X2(M)**(J-1))*G(M)*EAL
      END
```

```
      SUBROUTINE HTAU12(MMAX,NMAX,IMAX,NMAX2,MMAX2,IMAX2,H,H1,H2,MZERMAX
     1 ,NZERMAX,IZERMAX)
      DIMENSION H(10,10,10),H1(8,8,8),H2(6,6,7)
C     DIMENSION H(MZERMAX,NZERMAX,IZERMAX),H1(MMAX,NMAX,IMAX),H2(NMAX2,
C    1 MMAX2,IMAX2)
      DO 49 I = 1,MMAX
      DO 49 J = 1,NMAX
      DO 49 K = 1,IMAX
   49 H1(I,J,K) = 0.
      DO 48 I = 1,NMAX2
      DO 48 J = 1,MMAX2
      DO 48 K = 1,IMAX2
   48 H2(I,J,K) = 0.
```

```
       DO 50  I=2,IMAX
       DO 50 N = 1,NMAX
       DO 50  M=1,N
       T = I-1
   50 0 H1(M,N,I) = T*(T+1.)/(2.*T + 1.)*(( T + 1.)*H(M,N,I+1) -
      1(2.*T+ 1.)* H(M + 1,N+1, I) + T*H(M,N,I - 1))
       DO 30 ITAU = 2,IMAX
       DO 30 N = 1,NMAX
       DO 30 M = 1,N
  30   H1(N,M,ITAU) = H1(M,N,ITAU)
       DO 51 I = 3,IMAX2
       DO 51 N = 1,NMAX2
       DO 51 M = 1,N
       T = I-1
   51 0H2(M,N,I) = (T+2.)*(T+1.)*T*(T-1.)/((2. *T +3.)*
      1(2.*T + 1.)* (2.*T-1.))*(T*(2.*T - 1.)*((2.*T + 3.)/
      2 ((T + 1.)*(T + 2.)))*
      3H1(M,N,I + 1)- (2.*T + 3.)*(2.*T-1.)* ((2.*T+1.)/(T*(T + 1.)))*
      4H1(M+1,N+1,I) +(T+1.)*(2.*T + 3.)*((2.*T-1.)/((T - 1.)*T))
      5 *H1(M, N, I - 1))
       DO 40 ITAU = 3,IMAX 2
       DO 40 N = 1,NMAX2
       DO 40 M = 1,N
  40   H2(N,M,ITAU) = H2(M,N,ITAU)
       END




C
       SUBROUTINE RTAUN(JMAX,R,NU,WTGAUS,PTGAUS,MAXGAUS)
       DIMENSION P(12,4), G(32),X(32),R(12,10,3)  ,WTGAUS(32),PTGAUS(32)
C     0THIS SUBROUTINE CALCULATES THE INTEGRAL OFTHE ASSOCIATED LEGENDRE
C     1POLYNOMIALS
       DO 39 K = 1,MAXGAUS
       G(K) = WTGAUS(K)
       X(K) = PTGAUS(K)
       G(K+MAXGAUS) = G(K)
  39   X(K+MAXGAUS) = -X(K)
       LIMNU = JMAX + NU + 1
       LIM = JMAX + 1
       DO 38 J = 1, LIM
       DO 38 LTAU = 1,LIMNU
  38    R(LTAU,J,NU) = 0.
       MNTWO = 2*MAXGAUS
       DO 43 M = 1,MNTWO
       CALL PTN (JMAX+NU,NU,P,X(M))
```

```
      DO 43 J=1,LIM
      JNUONE = J + NU-1
      DO 43 LTAU = NU,JNUONE
      FNU = NU
      GNU = (FNU - 1.) /2.
   43 OR(LTAU,J,NU) = R(LTAU,J,NU) +((1. - X(M)*X(M))**  GNU*P(LTAU,NU)
     1*X(M)**(J-1)*G(M))
      END



C
      SUBROUTINE PTN(LTAUMX,NU,P,X)
C     CALCULATES ASSOCIATED LEGENDRE POLYNOMIALS PTAUNU
       DIMENSION P(12,4 )
      DO 1 M= 1,12
      DO 1 N = 1,4
    1 P(M,N) = 0.
      P(1,1) = 1.
      P(2,1) = X
      P(2,2) = SQRTF(ABSF(1.-X*X))
      P(3,2) = 3.*X*P(2,2)
      P(3,3) = 3.*(1. - X*X)
      P(4,3) = 5.*P(3,3)*X
      FNU = NU
      LIMU = NU + 1
      DO 44  LTAU = LIMU,L TAUMX
      TAU = LTAU
   440P(LTAU + 1,NU) = 1./(TAU - FNU +1.)*((2.*TAU -1.)*X*
     1P(LTAU,NU) - (TAU + FNU - 2.)*P(LTAU - 1,NU))
      END
```

b. Program Energy

Definition of Symbols and Arrays

M(i), n(i), j(i), k(i), and ip(i) contain the powers of and r_{12} for the i^{th} term in the basis set H. The array bmat contains the first order wave function coefficient. Fnorm is proportional to the integral $\langle \psi_d | \psi_0 \rangle$. Enzero $=\epsilon_o$, Enone $=\epsilon_1$, Etwo $=\epsilon_2$ and Entreϵ_3.

Subroutines and Functions

1. The function X(m,n,j,k,ip,xmatrx) is used to calculate the integrals M_o^o(m,n,j,k,ip).

2. The functions Zzer, Z2zer, Zneg, Z1neg, and Z2neg are all part of function X.

3. The function Hsmall calculates H_{ij}-(II.E-4) and Ssmall calculates S_{ij}-(II.E-19).

Operating Procedure

The basis set H is inputed from punched cards and stored in the arrays m,n,j,k and ip. Delta, R, A1, H, H1, and H2 and finally, the matrix elements Summit and VA are read from cards. These latter elements are gotten from Program Enermat. The program Energy subsequently calculates the energy through third order and stores the matrix elements on tape for use by program Highen.

```
      PROGRAM ENERGY
C     CALCULATES MATRIX ELEMENTS FOR FMETHOD, ALSO CALCULATES ENERGY
C     THROUGH THIRD ORDER
      DIMENSION VCHECK(50),COFNOM(26,26) ,COFRHO(26,26)
      DIMENSION              BMAT(50),EONE(2),VA(60),PTLAG(16)
      DIMENSION GTAU(3),F(15),          WTGAUS(16),PTGAUS(16),WTLAG(16)
      DIMENSION XMATTWO(520),XMAT(1255),XMATZER(2600),
     1 R(12,10,3),H(9,9,9),H1(7,7,7),H2(5,5,6),A1(40),A2(40),M(100),N
     2(100),J(100),K(100),IP(100),CA(30),CB(30),SUMMIT(60),COEFF1(50,50)
      COMMON XMATTWO,XMAT,XMATZER,  SUMMIT,COEFF1,MN,PI,CA,CB,RZERO, M
      COMMON N,J,K,IP,A1,A2,H,H1,H2,R,DELTA
      X1(MO,NO,JO,KO,IO,XMATRX) = X(MO,NO+2,JO,KO,IO,XMATRX)-
     1     X(MO,NO,JO,KO+2,IO,XMATRX)
 302  FORMAT (6HDELTA=F7.5,3X,3HMN=I2,7HCOFNOM=/500(5E16.9/))
 303  FORMAT (6HDELTA=F7.5,3X,3HMN=I2,7HCOFRHO=/500(5E16.9/))
  139 FORMAT(X6HENTRE=,E17.10)
 201  FORMAT(//38HTHE ENERGY DIFFERENCE IS NOW EQUAL TO ,E17.10)
 93   FORMAT(X7HENZERO=E17.10, 6HENONE= E17.10)
 467  FORMAT(3X,/,3(7HVCHECK( I2,2H)=,E17.10,4X))
 198  FORMAT(3X,5E17.10)
 41   FORMAT(X6HDELTA=,F7.5,4E16.9,9(/5E16.9))
 42   FORMAT(X6HDELTA=,F7.5   ,7HSUMMIT=3E16.9,9(/5E16.9))
 301  FORMAT (6HDELTA=F7.5,3X,3HMN=I2,7HCOEFF1=/500(5E16.9/))
 972  FORMAT(6HDELTA=F8.5/13HR(LTAU,J,NU)= /72(5E16.9/)/3HA1=/8(5E16.9/
     1 )/ 3HH= /145(5E16.9/)4E16.9/3HH1=,/68(5E16.9/),3E16.9,/3HH2=
     2 / 30(5E16.9/))
 973  FORMAT(35HTHIS PACKET CONTAINS H,S FOR DELTA= F7.5,)
  99  FORMAT (3X,F5.3)
 47    FORMAT(3X,//6HDELTA=F7.5)
  28  FORMAT(3X,4E18.10)
 29   FORMAT(1H1,12X,6HRZERO=, F8.5,4X,6HENONE=,E20.10,4X,
     1 7HENZERO=, E20.10, 3X,6HFNORM=, E20.10)
 20   FORMAT(3X,I2/13(5I1,1X)/13(5I1,1X))
  21  FORMAT( 13(5I1,1X))
   22 FORMAT(X3(7HCOEFF1(I2,1H,I2,2H)=E17.10))
   40 FORMAT(5E17.10)
  56  FORMAT(X26HTHE DETERMINANT OF COEFF1= E17.10)
  67  FORMAT(X5HETWO=E17.10)
  150 FORMAT(90X,2F7.2)
  16  FORMAT(X4(2HV(,I2,2H)= E17.10))
  4   FORMAT(X4(7HSUMMIT(,I2,2H)= E17.10))
      PI = 3.141592653589
      XMATRX = 0.
      ALP = 2.*DELTA
      CALL PCLOCK (TM,ELAPTM)
      PRINT 150,TM,ELAPTM
      READ  972,DELTA,R,A1,H,H1,H2
      DO 999 I = 1,1255
 999  XMAT(I) = 0.
```

```
      DO 998 I = 1,2600
  998 XMATZER(I) = 0.
      DO 997 I = 1,520
  997 XMATTWO(I) = 0.
      CALL PCLOCK (TM,ELAPTM)
      PRINT 150,TM,ELAPTM
  19  CONTINUE
C     READ WAVE FUNCTION TERMS
      READ 20,MN,(M(I),N(I),J(I),K(I),IP(I),I=1,MN)
      PRINT20,MN,(M(I),N(I),J(I),K(I),IP(I),I=1,MN)
      DO 300  I = 1,MN
      M(I+MN) = N(I)
      N(I + MN) = M(I)
      J(I + MN) = K(I)
      K(I + MN) = J(I)
  300 IP(I + MN) = IP(I)
      DO 881 I = 1,MN
      DO 881 L = 1,MN
      W1 = HSMALL(I,L,XMATRX)
      W2 = HSMALL(I+MN,L,XMATRX)
      W3 = HSMALL(I,L+MN,XMATRX)
      W4 = HSMALL(I+MN,L+MN,XMATRX)
      S1 = SSMALL(I,L,XMATRX)
      S2 = SSMALL(I+MN,L,XMATRX)
      S3 = SSMALL(I,L+MN,XMATRX)
      S4 = SSMALL(I+MN,L+MN,XMATRX)
      COEFF1(I,L) = W1+W2+W3+W4-ENZERO*(S1+S2+S3+S4)
  881 COEFF1(L,I) = COEFF1(I,L)
      PUNCH 301, DELTA,MN,((COEFF1(I,JO),I=1,MN),JO=1,MN)
C     READ PUNCHED CARDS CONTAINING THE VMATRX ELEMENTS
      READ   42,DELTA,(SUMMIT(I),I=1,MN)
      READ  41, DELTA,(VA(I),I=1,MN)
      CALL PCLOCK (TM,ELAPTM)
      PRINT 150,TM,ELAPTM
  913 CONTINUE
      CALL AMATSAV(MN,COEFF1,BMAT,VA,PI,DET)
      SUM1 = 0.
      SUM 2 = 0.
      DO 66 I = 1,MN
      SUM1 = SUM1 - BMAT(I)  * VA(I)
      DO 66 JO = 1,MN
   66 SUM2 = SUM2 + BMAT(I)*BMAT(JO)*COEFF1(I,JO)
      ETWO =(SUM1/PI +4.*PI*PI*SUM2)/FNORM
      SUM2 = 0.
      SUM1 = 0.
      CALL PCLOCK (TM,ELAPTM)
      PRINT 150,TM,ELAPTM
      MNTWO = 2*MN
      DO 9 JQ = 1, MNTWO
```

```
      DO 9 IQ = 1,MNTWO
      JUCK = J(IQ) + J(JQ)
      KUCK = K(IQ) + K(JQ)
      MUCK = M(IQ) + M(JQ)
      NUCK = N(IQ) + N(JQ)
      IPUCK = IP(IQ) +IP(JQ)
      PORK = X1(MUCK,NUCK,JUCK,KUCK,IPUCK - 1, XMATRX)
      FORK = X1(MUCK,NUCK,JUCK,KUCK,IPUCK, XMATRX)
      COFNOM(IQ,JQ) = FORK
      COFRHO(IQ,JQ) = PORK
      IF(IQ -MN) 180,180,181
  180 IO = IQ
      GO TO 182
  181 IO = IQ-MN
  182 IF(JQ-MN)183,183,184
  183 JO = JQ
      GO TO 185
  184 JO = JQ-MN
  185 CONTINUE
      SUM1 = SUM1+BMAT(IO)*BMAT(JO)*(2./RZERO*PORK - ENONE*FORK )
    9 CONTINUE
      DO 11 I = 1,MN
      SUM2 = SUM2 + BMAT(I)*SUMMIT(I)
   11 CONTINUE
      ENTRE = 4.*PI*PI*RZERO**6 /(64.*FNORM)*(SUM1 - 2.*ETWO*SUM2)
      PRINT 93,   ENZERO,ENONE
      PRINT 67, ETWO
      PRINT 139 ,ENTRE
      DIFF = -1.88873 - (ENZERO + ENONE + ETWO + ENTRE)
      PRINT 201, DIFF
      PUNCH 302, DELTA,MN,((COFNOM(I,JO),I=1,MN),JO=1,MN)
      PUNCH 303, DELTA,MN,((COFRHO(I,JO),I=1,MN),JO=1,MN)
  600 CALL PCLOCK (TM,ELAPTM)
      PRINT 150,TM,ELAPTM
  257  CONTINUE
  431  CONTINUE
      GO TO 19
      END
```

```
      SUBROUTINE AMATSAV(MN,COEFF1,BMAT,VA,PI,DET)
      DIMENSION AMAT(50,50),COEFF1(50,50),BMAT(50 ),VA(60)
      DO 50 I = 1,MN
      DO 50 J = 1,MN
   50 AMAT(I,J) = COEFF1(I,J)
```

```
      DO 51 I = 1,MN
   51 BMAT(I) = VA(I) /(8.*PI**3)
      NQ = 1
      CALL MATINV(AMAT,MN,BMAT,NQ,DET,50)
      END
```

```
      FUNCTION X(M,N,J,K,IP,XMATRX)
      DIMENSION XMATTWO(520),XMAT(1255),XMATZER(2600),
     1 R(12,10,3),H(9,9,9),H1(7,7,7),H2(5,5,6),A1(40),A2(40),W(100),U
     2(100),V(100),S(100),IQ(100),CA(30),CB(30),SUMMIT(60),COEFF1(50,50)
      COMMON XMATTWO,XMAT,XMATZER,  SUMMIT,COEFF1,MN,PI,CA,CB,RZERO, W
      COMMON S,U,V,IQ,A1,A2,H,H1,H2,R,DELTA
      Z1ZER(M,N,J,K) = 0.
      ZONE (M,N,J,K) = ZNEG (M+2,N,J,K) + ZNEG (M,N,J+2,K)+ZNEG (M,N,J,
     1K+2) -2.*ZNEG (M,N,J,K) -2.*ZNEG (M+1,N+1,J+1,K+1) -2.*Z1NEG(M,
     2N,J,K) + ZNEG (M,N+2,J,K)
      Z1ONE(M,N,J,K) = Z1NEG(M+2,N,J,K) + Z1NEG(M,N,J+2,K)+Z1NEG(M,N,J,
     1K+2) -2.*Z1NEG(M,N,J,K) -2.*Z1NEG(M+1,N+1,J+1,K+1) -2.*Z2NEG(M,
     2N,J,K) + Z1NEG(M,N+2,J,K)
      ZTWO (M,N,J,K) = ZZER (M+2,N,J,K) + ZZER (M,N,J+2,K)+ZZER (M,N,J,
     1K+2) -2.*ZZER (M,N,J,K) -2.*ZZER (M+1,N+1,J+1,K+1) -2.*Z1ZER(M,
     2N,J,K) + ZZER (M,N+2,J,K)
      Z1TWO(M,N,J,K) = Z1ZER(M+2,N,J,K) + Z1ZER(M,N,J+2,K)+Z1ZER(M,N,J,
     1K+2) -2.*Z1ZER(M,N,J,K) -2.*Z1ZER(M+1,N+1,J+1,K+1) -2.*Z2ZER(M,
     2N,J,K) + Z1ZER(M,N+2,J,K)
      ZTRE (M,N,J,K) = ZONE (M+2,N,J,K) + ZONE (M,N,J+2,K)+ZONE (M,N,J,
     1K+2) -2.*ZONE (M,N,J,K) -2.*ZONE (M+1,N+1,J+1,K+1) -2.*Z1ONE(M,
     2N,J,K) + ZONE (M,N+2,J,K)
      ZFOR (M,N,J,K) = ZTWO (M+2,N,J,K) + ZTWO (M,N,J+2,K)+ZTWO (M,N,J,
     1K+2) -2.*ZTWO (M,N,J,K) -2.*ZTWO (M+1,N+1,J+1,K+1) -2.*Z1TWO(M,
     2 N,J,K) + ZTWO(M,N+2,J,K)
      IF(J-2*(J/2))38,39,38
   38 IF(K-2*(K/2))40,41,40
   41 X = 0.
      RETURN
   39 IF(K-2*(K/2))41,40,41
    40 IF(IP)42,43,42
    43 IF(J-2*(J/2))41,42,41
   42 IF(IP) 60,60,61
   60 IF(M-5) 74,74,3
   74 IF(N-5)75,75,3
   75 IF(J-5) 76,76,3
    76 IF(K-5) 77,77,3
   77 Y = XMATZER(M+1+6*N+36*J+216*K+1296*(IP+1))
```

```
      IF(Y) 48,79,48
 79   COUNT = 0.
      GO TO 2
 61   IF(IP-2) 62,62,63
   62 IF(M-4)44,44,3
  44  IF(N-4)45,45,3
  45  IF(J-4) 46,46,3
  46  IF(K-4) 47,47,3
  47  Y = XMAT(M+1+5*N+25*J+125*K+625*(IP-1))
      IF(Y) 48,49,48
 48   X = Y
      RETURN
 49   COUNT = 1.
      GO TO 2
  63  IF(M-3)84,84,3
  84  IF(N-3)85,85,3
  85  IF(J-3)86,86,3
  86  IF(K-3)87,87,3
  87  Y = XMATTWO (M+1+4*N+16*J+64*K+256*(IP-3))
      IF(Y) 48,89,48
 89   COUNT = 2.
      GO TO 2
  3   CONTINUE
C     PRINT 106,M,N,J,K,IP
 106  FORMAT (23HOVERFLOW IN FUNCTION X 3X,5(I2,2X))
      COUNT = 3.
  2   IF(IP)159,160,161
 160  XW= ZZER(M+2,N,J,K) - ZZER(M,N,J+2,K)
      GO TO 50
 159  XW= ZNEG(M+2,N,J,K) - ZNEG(M,N,J+2,K)
      GO TO 50
 161  IF(IP-2)162,163,164
  162 XW= ZONE(M+2,N,J,K ) - ZONE(M,N,J+2,K)
      GO TO 50
 163  XW= ZTWO(M+2,N,J,K) - ZTWO(M,N,J+2,K)
      GO TO 50
 164  IF(IP-4) 165,166,166
 165  XW= ZTRE(M+2,N,J,K) - ZTRE(M,N,J+2,K)
      GO TO 50
 166  XW= ZFOR(M+2,N,J,K) - ZFOR(M,N,J+2,K)
 50   IF(COUNT - 1.)53,52,54
 53   NUMBER = M+1+6*N+36*J+216*K+1296*(IP+1)
      XMATZER(NUMBER) = XW
      GO TO 51
 54   IF(COUNT - 2.) 55,55,51
  55  NUMBER = M+1+4*N+16*J+64*K+256*(IP-3)
      XMATTWO(NUMBER) = XW
      GO TO 51
 52   NUMBER = M+1+5*N+25*J+125*K+625*(IP-1)
```

```
      XMAT(NUMBER) = XW
   51 X = XW
       END


      FUNCTION ZZER(M,N,J,K)
      DIMENSION XMATTWO(520),XMAT(1255),XMATZER(2600),
     1 R(12,10,3),H(9,9,9),H1(7,7,7),H2(5,5,6),A1(40),A2(40),W(100),U
     2(100),V(100),S(100),IP(100),CA(30),CB(30),SUMMIT(60),COEFF1(50,50)
      COMMON XMATTWO,XMAT,XMATZER,  SUMMIT,COEFF1,MN,PI,CA,CB,RZERO, W
      COMMON S,U,V,IP,A1,A2,H,H1,H2,R,DELTA
      IF (J-2*(J/2)) 2,2,3
    2 IF (K-2*(K/2)) 4,4,3
    3 ZZER = 0.
      RETURN
    4 ZZER = 4.*A1(M+1)*A1(N+1)/((FLOATF(J) + 1.)*(FLOATF(K) + 1.))
      END


      FUNCTIONZ2ZER(M,N,J,K)
      DIMENSION XMATTWO(520),XMAT(1255),XMATZER(2600),
     1 R(12,10,3),H(9,9,9),H1(7,7,7),H2(5,5,6),A1(40),A2(40),W(100),U
     2(100),V(100),S(100),IP(100),CA(30),CB(30),SUMMIT(60),COEFF1(50,50)
      COMMON XMATTWO,XMAT,XMATZER,  SUMMIT,COEFF1,MN,PI,CA,CB,RZERO, W
      COMMON S,U,V,IP,A1,A2,H,H1,H2,R,DELTA
      FJ = J
      FK = K
      IF (J-2*(J/2)) 2,2,3
    2 IF (K-2*(K/2)) 4,4,3
    3 Z2ZER = 0.
      RETURN
    4 Z = 8.*(A1(M+ 3) -A1(M+1))*(A1(N+3)-A1(N+1))/((FJ+1.)*(FJ+3.)*(FK
     1 + 1.)*(FK+3.))
      Z2ZER = Z
      END


C
      FUNCTION ZNEG(M,N,J,K)
      DIMENSION XMATTWO(520),XMAT(1255),XMATZER(2600),
     1 R(12,10,3),H(9,9,9),H1(7,7,7),H2(5,5,6),A1(40),A2(40),W(100),U
     2(100),V(100),S(100),IP(100),CA(30),CB(30),SUMMIT(60),COEFF1(50,50)
      COMMON XMATTWO,XMAT,XMATZER,  SUMMIT,COEFF1,MN,PI,CA,CB,RZERO, W
      COMMON S,U,V,IP,A1,A2,H,H1,H2,R,DELTA
      IF(J-2*(J/2))38,39,38
```

```
 38   IF(K-2*(K/2))40,41,40
41    ZNEG = 0.
      RETURN
39    IF(K-2*(K/2))41,40,41
 40   CONTINUE
      IF(J-K) 97,97,98
 97   LIM = J +1
      GO TO 99
  98 LIM = K + 1
8     FORMAT(17HOVERLOAD IN ZNEG    ,2HM=I2, 2HN=I2,4HLIM=I2)
      IF(LIM-9)6,6,5
6     IF(M-8)7,7,5
7     IF(N-8)9,9,5
5     PRINT 8,M,N,LIM
 9    CONTINUE
 99   SUMM = 0.
      DO 49 LTAU = 1,LIM
      T = LTAU -1
  49 SUMM = SUMM + (2.*T + 1.)*R(LTAU,J+1,1)*R(LTAU, K + 1,1)*H(M+1,
     1N+1, LTAU)
      ZNEG = SUMM
      END



C
      FUNCTIONZ1NEG(M,N,J,K)
      DIMENSION XMATTWO(520),XMAT(1255),XMATZER(2600),
     1 R(12,10,3),H(9,9,9),H1(7,7,7),H2(5,5,6),A1(40),A2(40),W(100),U
     2(100),V(100),S(100),IP(100),CA(30),CB(30),SUMMIT(60),COEFF1(50,50)
      COMMON XMATTWO,XMAT,XMATZER,  SUMMIT,COEFF1,MN,PI,CA,CB,RZERO, W
      COMMON S,U,V,IP,A1,A2,H,H1,H2,R,DELTA
      IF(J-2*(J/2))38,39,38
 38   IF(K-2*(K/2))40,41,40
41    Z1NEG = 0.
      RETURN
39    IF(K-2*(K/2))41,40,41
 40   CONTINUE
      IF (J-K) 27,27,28
 27   LIM = J + 2
       GO TO 29
 28   LIM = K + 2
8     FORMAT(17HOVERLOAD IN Z1NEG   ,2HM= I2,2HN=I2,4HLIM=I2)
      IF(LIM-7)6,6,5
6     IF(M-6)7,7,5
7     IF(N-6)9,9,5
5     PRINT 8,M,N,LIM
 9    CONTINUE
```

```
 29   SUMM = 0.
      DO 170 LTAU = 2,LIM
      T = LTAU - 1
 170  SUMM = SUMM - 1./(T * (T + 1.))* R(LTAU , J + 1,2)*R(LTAU, K+ 1,
     1 2)* (2.*T + 1.)/(T*(T + 1.))*H1(M + 1, N + 1, LTAU)
      Z1NEG = SUMM
      END




C
      FUNCTIONZ2NEG(M,N,J,K)
      DIMENSION XMATTWO(520),XMAT(1255),XMATZER(2600),
     1 R(12,10,3),H(9,9,9),H1(7,7,7),H2(5,5,6),A1(40),A2(40),W(100),U
     2(100),V(100),S(100),IP(100),CA(30),CB(30),SUMMIT(60),COEFF1(50,50)
      COMMON XMATTWO,XMAT,XMATZER,  SUMMIT,COEFF1,MN,PI,CA,CB,RZERO, W
      COMMON S,U,V,IP,A1,A2,H,H1,H2,R,DELTA
 8    FORMAT(17HOVERLOAD IN Z2NEG   ,2HM=I2,2HN=I2,4HLIM=I2)
      IF(J-2*(J/2))38,39,38
 38   IF(K-2*(K/2))40,41,40
 41   Z2NEG = 0.
      RETURN
 39   IF(K-2*(K/2))41,40,41
 40   CONTINUE
      IF (J - K) 17,17,18
 17   LIM = J + 3
      GO T O 19
 18   LIM = K + 3
 19   IF(LIM-6)6,6,5
 6    IF(M-4)7,7,5
 7    IF(N-4)9,9,5
 5    PRINT 8,M,N,LIM
      LIM = 6
 9    CONTINUE
      SUMM1 = 0.
      SUMM2 = 0.
      DO 171 LTAU = 3,LIM
      T = LTAU - 1
 171  SUMM 1 = SUMM1 + (1./((2.*T + 3.)*(2.*T - 1.)* (T + 2.)*(T + 1.)
     1 *T*(T - 1.)))*R(LTAU , J + 1, 3)*R(LTAU, K + 1, 3)*((2.*T + 3.)
     2 *(2.*T + 1.)*(2.*T - 1.)/((T + 2.)*(T + 1.)*T*(T - 1.))) * H2
     3  (M + 1,N+1,LTAU)
      DO 172 LTAU = 1, LIM
      T = LTAU - 1
 172  SUMM 2 = SUMM2 + (2.*T + 1.)*(R(LTAU,J + 1,1) -R(LTAU ,J + 3,1))
     1* ( R(LTAU,K + 1,1) -R(LTAU, K+ 3,1))*     (H(M+3,N + 3,LTAU)
```

```
     2  -H(M + 3, N + 1,LTAU) - H(M+1,N + 3,LTAU)
     3   + H(M+1,N+1,LTAU))
      Z = 1./2.*(SUMM1 + SUMM2)
      Z2NEG = Z
      RETURN
      END




      FUNCTION SSMALL (IQ,JQ,XMATRX)
      DIMENSION XMATTWO(520),XMAT(1255),XMATZER(2600),
     1 R(12,10,3),H(9,9,9),H1(7,7,7),H2(5,5,6),A1(40),A2(40),M(100),N
     2(100),J(100),K(100),IP(100),CA(30),CB(30),SUMMIT(60),COEFF1(50,50)
      COMMON XMATTWO,XMAT,XMATZER,  SUMMIT,COEFF1,MN,PI,CA,CB,RZERO, M
      COMMON N,J,K,IP,A1,A2,H,H1,H2,R,DELTA
      SSMALL = 1./64.*RZERO**6*(X(M(IQ)+M(JQ),N(IQ)+N(JQ)+2,J(IQ)+J(JQ),
     1 K(IQ)+K(JQ),IP(IQ)+IP(JQ),XMATRX) - X(M(IQ)+M(JQ),N(IQ)+N(JQ),
     2   J(IQ)+J(JQ),K(IQ)+K(JQ)+2,IP(IQ)+IP(JQ) ,XMATRX) )
      END



C
      FUNCTION HSMALL(IQ,JQ,XMATRX)
      DIMENSION TERM(8) ,CO(8)
      DIMENSION XMATTWO(520),XMAT(1255),XMATZER(2600),
     1 R(12,10,3),H(9,9,9),H1(7,7,7),H2(5,5,6),A1(40),A2(40),MW(100),
     2NW(100),JW(100),KW(100),IPW(100),CA(30),CB(30),SUMMIT(60),COEFF1
     3(50,50)
      COMMON XMATTWO,XMAT,XMATZER,  SUMMIT,COEFF1,MN,PI,CA,CB,RZERO, MW
      COMMON NW,JW,KW,IPW,A1,A2,H,H1,H2,R,DELTA
      NA = NW(IQ)
      MA = MW(IQ)
      JA = JW(IQ)
      KA = KW(IQ)
      IPA = IPW(IQ)
      NB = NW(JQ)
      MB = MW(JQ)
      JB = JW(JQ)
      KB = KW(JQ)
      IPB = IPW(JQ)
      CO(1) = ((NA -NB)*(NA-NB)-(KA-KB)*(KA-KB)+(NA+NB)-(KA+KB)+
     1 (IPA-IPB)*(NA-NB-KA+KB))
      CO(2)  = (8.*RZERO-4.*DELTA)
      CO(3)  = - ((NA -NB)*(NA -NB) -(NA +NB))
      CO(4)= ((KA -KB)*(KA-KB)-(KA +KB))
```

```
      CO(5) =((IPA-IPB)*(IPA-IPB)+IPA +IPB + (IPA -IPB)*(NA -NB +KA-KB))
      CO(6)= -(IPA-IPB)*(NA-NB-(KA-KB))
      CO(7)  = 2 *(IPA -IPB)*(NA-NB)
      CO(8)= -2 *( IPA-IPB)*(KA-KB)
      N = NA + NB
      M = MA + MB
      J = JA + JB
      K = KA + KB
      IP = IPA + IPB
      DO 10 I = 1,8
 10   TERM(I) = 0.
      DO 11 I = 1,8
      IF (CO(I) - 0.)14,11,14
 11   CONTINUE
      GO TO  38
 14   GO TO (1,2,3,4,5,6,7,8),I
  1   TERM(1) =CO(1)*X(M,N,J,K, IP,XMATRX)
      GO TO 11
 2    TERM(2) =CO(2) *X(M,N+1,J,K,IP,XMATRX)
      GO TO 11
  3   TERM(3) = CO(3) *X(M,N-2,J,K,IP,XMATRX)
      GO TO 11
  4   TERM(4) = CO(4)*X(M,N,J,K-2,IP,XMATRX)
      GO TO 11
   5  TERM(5)=CO(5)*(X(M,N+2,J,K,IP-2,XMATRX)-X(M,N,J,K+2,IP-2,XMATRX))
      GO TO 11
  6   TERM(6)=CO(6)*(X(M+2,N,J,K,IP-2,XMATRX)+X(M,N,J+2,K,IP-2,XMATRX))
      GO TO 11
 7    TERM(7)=CO(7)*X(M+1,N-1,J+1,K+1,IP-2,XMATRX)
      GO TO 11
  8   TERM(8) = CO(8)*X(M+1,N+1,J+1,K-1,IP-2,XMATRX)
      GO TO 11
  38  SUMM = 0.
      DO 17 I = 1,8
   17 SUMM = SUMM +TERM(I)
      HSMALL =-(RZERO**4*SUMM/64.)
      END


         FINIS
-EXECUTE.
(  *P        -))*N
* P*X-0 ((X-X X=X=X9X-0 U90 0 0 X*49-5X V577W--5((P T-*(S5--((((     */
(  **     ))*N
(  *7     **)V
(  (7        7
-
```

c. Program Enermat

Operating Procedure

The program requires the input of the basis set H from punched cards. It also requires the parameter delta. The program then calculates the matrix elements VA and Summit and outputs them on punched cards for use by program Energy.

```
      PROGRAM ENERMAT
C     CALCULATES THE V MATRIX ELEMENTS FOR H METHOD
      DIMENSION GTAU(3),F(15),WTGAUS(16),PTGAUS(16),WTLAG(16),PTLAG(16)
      DIMENSION VA(60) ,SUMMIT(60)
      DIMENSION FZ(20),BZ(20),RTAUV(15,15,2),HPHI(8,8,15),HPHIA(8,8,15),
     1VXMAT(5190),M (100),N (100),J (100),K (100),IP (100)
      COMMON VXMAT,RTAUV,HPHI,HPHIA,FZ,BZ,M,N,J,K,IP
      VX1(M,N,J,K,IP) = VX(M,N+2,J,K,IP) - VX(M,N,J,K+2,IP)
 93   FORMAT(X7HENZERO=E17.10, 6HENONE= E17.10)
 41   FORMAT(X6HDELTA=,F7.5,4E16.9,9(/5E16.9))
 42   FORMAT(X6HDELTA=,F7.5  ,7HSUMMIT=3E16.9,9(/5E16.9))
 28   FORMAT (5E17.10)
 441  FORMAT(3X,6HDELTA= F5.2,3X,I2,/,4X,22HTHE V,S AND SUMMIT ARE/
     1 (40I2))
 442  FORMAT(4E20.11)
  99  FORMAT (3X,F5.3)
 47    FORMAT(3X,//6HDELTA=F7.5)
  29  FORMAT(1H1,//20X,6HDELTA=F5.3//,20X,3HMN=,I2,//,(13(1X,5I1)))
 917  FORMAT(52HMATFCOF,RZERO,GTAU,SIGMA,DELTA1,ANDF ARE AS FOLLOWS  /
     1        3X,I2,2XF5.3,3F7.4,2F8.5/3X,2(6F9.6/))
 20   FORMAT(3X,I2/(13(5I1,1X)))
  21  FORMAT( 13(5I1,1X))
   22 FORMAT(X3(7HCOEFF1(I2,1H,I2,2H)=E17.10,2X))
   40 FORMAT(5E17.10)
  56  FORMAT(X26HTHE DETERMINANT OF COEFF1= E17.10)
  67  FORMAT(X5HETWO=E17.10)
  150 FORMAT(90X,2F7.2)
  16  FORMAT(X4(2HV(,I2,2H)= E17.10))
  4   FORMAT( 4(7HSUMMIT(,I2,2H)= E17.10,2X))
C     THE LEGENDRE GAUSS WEIGHTS ARE
      WTGAUS(01)=   .0271524594
      WTGAUS(02)=   .0622535239
      WTGAUS(03)=   .0951585117
      WTGAUS(04)=   .1246289713
      WTGAUS(05)=   .1495959888
      WTGAUS(06)=   .1691565194
      WTGAUS(07)=   .1826034150
      WTGAUS(08)=   .1894506105
C     AND THE CORRESPONDING POINTS ARE
      PTGAUS(01)= - .9894009350
      PTGAUS(02)= - .9445750231
      PTGAUS(03)= - .8656312024
      PTGAUS(04)= -.7554044084
      PTGAUS(05)= - .6178762444
      PTGAUS(06)=  -.4580167777
      PTGAUS(07)= - .2816035508
      PTGAUS(08)= - .0950125098
      MAXGAUS = 8
C    THE LAGUERRE GAUSS WEIGHTS ARE
```

```
            WTLAG (01) = .3691885893E+0
            WTLAG(02) = .4187867808E+0
            WTLAG (03) = .17579498664E+0
            WTLAG (04) = .3334349226E-1
            WTLAG (05) = .2794536235E-2
            WTLAG(06) = .9076508773E-4
            WTLAG (07) = .8485746716E-6
            WTLAG (08) = .1048001175E-8
C            AND THE CORRESPONDING POINTS ARE
            PTLAG (01) = .1702796323E+0
            PTLAG (02) = .9037017768E+0
            PTLAG (03) = .2251086630E+1
            PTLAG (04) = .4266700170E+1
            PTLAG (05) = .7045905402E+1
            PTLAG (06) = .1075851601E+2
            PTLAG (07) = .1574067864E+2
            PTLAG (08) = .2286313173E+2
            MAXLAG = 8
            PTLAG (01) = .8764941048E-1
            PTLAG (02) = .4626963289E+0
            PTLAG (03) = .1141057775E+1
            PTLAG (04) = .2129283645E+1
            PTLAG (05) = .3437086634E+1
            PTLAG (06) = .5078018615E+1
            PTLAG (07) = .7070338535E+1
            PTLAG (08) = .9438314336E+1
            PTLAG (09) = .1221422337E+2
            PTLAG (10) = .1544152737E+2
            PTLAG (11) = .1918015686E+2
            PTLAG (12) = .2351590569E+2
            PTLAG (13) = .2857872974E+2
            PTLAG (14) = .3458339870E+2
            PTLAG (15) = .4194045264E+2
            PTLAG (16) = .5170116034E+2
            WTLAG (01) = .2061517150E+0
            WTLAG (02) = .3310578550E+0
            WTLAG (03) = .2657957776E+0
            WTLAG (04) = .1362969343E+0
            WTLAG (05) = .4732892869E-1
            WTLAG (06) = .1129990008E-1
            WTLAG (07) = .1849070943E-2
            WTLAG (08) = .2042719153E-3
            WTLAG (09) = .1484458687E-4
            WTLAG (10) = .6828319331E-6
            WTLAG (11) = .1881024841E-7
            WTLAG (12) = .2862350243E-9
            WTLAG (13) = .2127079033E-11
            WTLAG (14) = .6297967003E-14
            WTLAG (15) = .5050473700E-17
```

```
      WTLAG (16) = .4161462370E-21
      MAXLAG = 16
      ENONE = .7808816326
      ENZERO = -2.568538484
      RZERO = 1.4
      PI = 3.141592653589
      FNORM = .5806108281
      MAXFCOF = 7
C   KMAX EQUALS THE NUMBER OF F,S MINUS THREE
      KMAX = MAXFCOF - 3
C MAXMUM EQUALS THE TOTAL NUMBER OF TAU ,S DESIRED
C  LMAX INDICATES THE POWER OF MU DESIRED
      LMAX = 8
      MMAX = 8
      NMAX = 8
      MAXMUM = 15
      DELTA1 = 1.12186623
C     ZEROTH ORDER WAVE FUNCTION COEFFICIENTS
      SIGMA = .2479206
      F(1) = 1.0769
      F(3) = 0.15634
      F(5) = 0.003407
      F(7) = 0.000031
      GTAU(1) = 1.
      GTAU(2) = 0.0105
      GTAU (3) = 0.0004
C     READ F, GTAU
      CALL PCLOCK (TM,ELAPTM)
      PRINT 150,TM,ELAPTM
      ALP2 = 2.*DELTA1
      READ 99,DELTA
   19 CONTINUE
      READ 20,MN,(M(I),N(I),J(I),K(I),IP(I),I=1,MN)
      DO 300  I = 1,MN
      M(I+MN) = N(I)
      N(I + MN) = M(I)
      J(I + MN) = K(I)
      K(I + MN) = J(I)
  300 IP(I + MN) = IP(I)
      XMATRX = 0.
C ALP GOES INTO 1ST ORDER W.F.  ALP1 IS USED TO CALC V,S ALP2 TO CALC EZEF
      ALP = 2.*DELTA
      ALP1 = DELTA1 + DELTA
      CALL PCLOCK (TM,ELAPTM)
      PRINT 150,TM,ELAPTM
      CALL QUADLEG(KMAX+3,F,BZ,10,WTGAUS,PTGAUS,MAXGAUS)
      CALL QUADLAG(1.,ALP1,10,16,FUNCT,FZ,GTAU,SIGMA,WTLAG,PTLAG,MAXLAG)
      CALL PCLOCK (TM,ELAPTM)
      PRINT 150,TM,ELAPTM
```

```
      CALL RTAU(KMAX,F,RTAUV,LMAX,MAXMUM,WTGAUS,PTGAUS,MAXGAUS)
      CALL PCLOCK (TM,ELAPTM)
      PRINT 150,TM,ELAPTM
      CALL TROT (NMAX,MMAX,MAXMUM, ALP1,1,HPHI ,SIGMA,GTAU,FINT1,FINT2,
     1WTGAUS,PTGAUS,MAXGAUS,WTLAG,PTLAG,MAXLAG)
      CALL PCLOCK (TM,ELAPTM)
      PRINT 150,TM,ELAPTM
      DO 990 I = 1,5190
990   VXMAT(I) = 0.
      LMAXXX = NMAX - 2
      MXXMUM = MAXMUM - 1
      DO 73 I = 2,MXXMUM
      DO 73 NO = 1,LMAXXX
      DO 73 MO = 1,NO
      T = I -1
      HPHIA(MO,NO,I) = T*(T+1.)/(2.*T+1.)*((T+1.)*HPHI(MO,NO,I+1)-
     1 (2.*T+1.)*HPHI(MO+1,NO+1,I) + T*HPHI(MO,NO,I-1))
73    HPHIA(NO,MO,I) = HPHIA(MO,NO,I)
      CALL PCLOCK (TM,ELAPTM)
      PRINT 150,TM,ELAPTM
      DO 30 I = 1,MN
 30   SUMMIT(I) = 0.
      DO 60 I = 1,MN
      VYA = VX1(M(I), N(I), J(I), K(I), IP(I)-1)
      VYB = VX1(M(I),N(I),J(I),K(I),IP(I))
      VYC = VX1( M(I+MN),N(I+MN),J(I+MN),K(I+MN),IP(I+MN)-1)
      VYD = VX1(M(I+MN),N(I+MN),J(I+MN),K(I+MN),IP(I+MN))
      SUMMIT(I) = SUMMIT(I) + VYB + VYD
       VA(I) = 2./RZERO*(VYA + VYC) - ENONE*(VYB + VYD)
60    CONTINUE
      DO 8 I = 1,MN
 8    VA(I) = -8.*PI**3*RZERO**6/64.*VA(I)
      PRINT 16, (I,VA(I),I = 1,MN)
      PRINT 4, (I,SUMMIT(I), I = 1,MN)
      PUNCH 441,DELTA,MN,(M(I),N(I),J(I),K(I),IP(I),I=1,MN)
      PUNCH 442,(VA(I),I=1,MN),(SUMMIT(I),I=1,MN),ENZERO,ENONE
 800  CALL PCLOCK (TM,ELAPTM)
      PRINT 150,TM,ELAPTM
      END


      SUBROUTINE TROT(MMAX,NMAX,ITAUMX,ALP,NU,H,SIGMA, GTAU,FINT1,FINT2,
     1WTGAUS,PTGAUS,MAXPT   ,WTLAG,PTLAG,MAXLAG)
      DIMENSION G(32),X(32),WTGAUS(16),PTGAUS(16),WTLAG(16),PTLAG(16)
      DIMENSION D(15,12,2),P(30,2),H(8,8,15),GTAU(3)
      DO 39 K = 1,MAXPT
      G(K) = WTGAUS(K)
      X(K) = PTGAUS(K)*(1./2.) + 1./2.
```

```
      G(K+MAXPT ) = G(K)
 39   X(K+MAXPT) = -X(K) + 1.
      DO 8 M = 1,8
      DO 8 N = 1,8
      DO 8 ITAU = 1,6
  8   H(M,N,ITAU) = 0.
      MAXPTS = 2*MAXPT
      DO 3 I = 1,MAXPTS
      T = X(I)
      IF (NMAX-MMAX) 11,11,12
  11  MAX = MMAX
      GO TO 13
  12  MAX = NMAX
  13  CALL RTN (ITAUMX,NU, P,1./T)
      Z = 1./T
      CALL VTAUN (MAX,D,NU,ALP,1./T,ITAUMX,GTAU,SIGMA,FINT1,FINT2,
     1 WTLAG,PTLAG,MAXLAG)
      DO 3 ITAU = 1, ITAUMX
      GT = ((1.-T*T) *P(ITAU,NU)*P(ITAU,NU))**(-1)
  141  CONTINUE
      DO 3 N= 1,NMAX
      DO 3 M = 1,N
  3   H(M,N,ITAU) = H(M,N,ITAU) + GT*D(ITAU,M,NU)*D(ITAU,N,NU)* G(I)*1./
     1 2.
      DO 81 ITAU = 1,ITAUMX
      TAU = ITAU - 1
      FNU = NU - 1
      KP = 1
      LIM1 = TAU - FNU + 1.
      LIM 2 = TAU + FNU
      DO 82 I = LIM1,LIM2
  82  KP = KP*I
      COF = (-1)**(NU-1)*KP
      DO 81 N = 1,NMAX
      DO 81 M = 1,N
  81  H(M,N,ITAU) = COF*H(M,N,ITAU)
      DO 30 ITAU = 1,ITAUMX
      DO 30 N = 1,NMAX
      DO 30 M = 1,N
 30   H(N,M,ITAU) = H(M,N,ITAU)
      END


C
      SUBROUTINE VTAUN(JMAX,D,NU,ALP,Y,ITAUMX, GTAU,SIGMA,FINT1,FINT2,
     1 WTLAG,PTLAG,MAXLAG)
      DIMENSION G(16),X1(16),X2(16),WTLAG(16), PTLAG(16)
      DIMENSION D(15,12,2),P1(30,2) ,P2(30,2), GTAU(3)
```

```
      GNO(W,Z)= Z**SIGMA*(GTAU(1) + GTAU(2)*W + GTAU(3)*W*W)
      EAL = EXPF(-ALP)/ALP
      DO 39 K = 1,MAXLAG
      G(K) = WTLAG(K)
      X1(K)= PTLAG(K)/ALP +1.
   39 X2(K) = PTLAG(K)/ALP +Y
      DO 38 J= 1,JMAX
      DO 38 LTAU = 1, ITAUMX
   38 D(LTAU,J,NU) = 0.
      DO 43 M = 1,MAXLAG
      CALL RTN(ITAUMX,NU,P2,X2(M))
      CALL RTN(ITAUMX,NU,P1,X1(M))
      GN1 = GNO((X1(M)-1.)/(X1(M)+1.),X1(M)+1.)
      GN2 = GNO((X2(M)-1.)/(X2(M)+1.),X2(M)+1.)
      U = EXPF(-(Y-1.)*ALP)
      COFFA = GN1*G(M)*EAL
      W = U*GN2/GN1
      DO 43 J = 1,JMAX
      COFX1J = X1(M)**(J-1)*COFFA
      COFX2J = X2(M)**(J-1)*W*COFFA
      DO 43 LTAU = 1, ITAUMX
   43 D(LTAU,J,NU)=D(LTAU,J,NU)+P1(LTAU,NU)*COFX1J-P2(LTAU,NU)*COFX2J
      END
C


      SUBROUTINE RTAU (KMAX,F,RTAUV,LMAX,MAXMUM,WTGAUS,PTGAUS,MAXPT)
      DIMENSION P(30,2) , G(16) , X(16), RTAUV(15,15,2), WTGAUS(16)
      DIMENSION PTGAUS(16), F(15),RA(15,15)
      DO 39 K = 1,MAXPT
      G(K) = WTGAUS(K)
      X(K) = PTGAUS(K)
      G(K+ MAXPT) = G(K)
   39 X(K+MAXPT) = -X(K)
C     MAXMUM = 2*KMAX + 7
      DO 11 J = 1, MAXMUM
      DO 11 K = 1,LMAX
      DO 11 M = 1,2
   11 RTAUV(J,K,M) = 0.
      DO 10 NU = 1,2
      DO 38 J = 1,MAXMUM
      DO 38 K = 1,LMAX
   38 RA (J,K) = 0.
      MAXPTS = 2*MAXPT
      DO 43 M = 1,MAXPTS
      FP2 = 0.
      MAXKAT = KMAX + 3
      CALL RTN(MAXKAT,1,P,X(M))
      DO 47 IQ = 1,MAXKAT ,2
```

```
 47   FP2 = FP2 + F(IQ)*P(IQ,1)
      FSQUAR = FP2
      CALL RTN (MAXMUM , NU, P, X(M))
      PROD = FSQUAR*G(M)*(SQRTF(1.-X(M)*X(M)))**(NU-1)
      DO 43 IA = 1,LMAX
      PRODUCT = PROD*X(M)**(IA-1)
      DO 43 LTAU = 1,MAXMUM
      RA(LTAU,IA) = RA(LTAU,IA) + PRODUCT*P(LTAU,NU)
 43   CONTINUE
      DO 10 J = 1,MAXMUM
      DO 10 K = 1, LMAX
      RTAUV(J,K,NU) = RA(J,K)
10    CONTINUE
      END


C
      SUBROUTINE RTN(LTAUMX,NU,P,X)
C     CALCULATES ASSOCIATED LEGENDRE POLYNOMIALS PTAUNU
      DIMENSION P(30,2)
      DO 1  M = 1,30
  1   P(M,NU) = 0.
      P(1,1) = 1.
      P(2,1) = X
      P(2,2) = SQRTF(ABSF(1.-X*X))
      P(3,2) = 3.*X*P(2,2)
      FNU = NU
      LIMU = NU + 1
      DO 44  LTAU = LIMU,L TAUMX
      TAU = LTAU
   44OP(LTAU + 1,NU) = 1./(TAU - FNU +1.)*((2.*TAU -1.)*X*
     1P(LTAU,NU) - (TAU + FNU - 2.)*P(LTAU - 1,NU))
      END


C
      SUBROUTINE QUADLEG(MAXKAT, F, BZ, NUMINTS,WTGAUS,PTGAUS,MAXGAUS)
      DIMENSIONF(15),BZ(20),WTGAUS(50),PTGAUS(16),G(16),X(50),P(30,2)
      DIMENSION FZ(20)
      DO 39 K = 1,MAXGAUS
      G(K) = WTGAUS(K)
      X(K) = PTGAUS(K)
      G(K+MAXGAUS) = G(K)
 39   X(K+MAXGAUS) = -X(K)
       DO 11 J = 1, NUMINTS
  11  BZ(J) = 0.
      MXGAUSS = 2*MAXGAUS
```

```
      DO 43 M = 1,MXGAUSS
      FP2 = 0.
      CALL RTN(MAXKAT, 1, P,X(M))
      DO 47 IQ = 1, MAXKAT,2
 47   FP2 = FP2 + F(IQ)*P(IQ,1)
      DO 43 IA = 1,NUMINTS
      BZ(IA) = BZ(IA) + X(M)**(IA-1) *FP2*G(M)
  43  CONTINUE
      END


C
      SUBROUTINEQUADLAG(ALIMIT,SCALE,NUMINTS,LAGPTS,F,ARRAY,GTAU,SIGMA,
     1 WTLAG,PTLAG,MAXLAG)
      DIMENSION WTLAG(16 ),PTLAG(16 ), ARRAY(20), GTAU(3)
      GNO(Y,Z) = Z**SIGMA*(GTAU(1)+GTAU(2)*Y + GTAU(3)*Y*Y)
      EAL = EXPF(-ALIMIT*SCALE)/SCALE
      DO 38 L = 1, NUMINTS
  38  ARRAY (L) = 0.
      DO 43 M = 1,MAXLAG
      Y = PTLAG(M)/SCALE + ALIMIT
      WAVEFU = GNO((Y-1.)/(Y+1.),Y+1.)
      DO 43 N = 1, NUMINTS
 43   ARRAY(N) = ARRAY(N)    +     Y  **(N-1)*WAVEFU*WTLAG(M)*EAL
      END


C
      FUNCTION VX(M,N,J,K,IP)
      DIMENSION FZ(20),BZ(20),RTAUV(15,15,2),HPHI(8,8,15),HPHIA(8,8,15),
     1VXMAT(5190),MA(100),NA(100),JA(100),KA(100),IPA(100)
      COMMON VXMAT,RTAUV,HPHI,HPHIA,FZ,BZ,MA,NA,JA,KA,IPA
      VZ1ZER(M,N,J,K) = 0.
      VZTWO(M,N,J,K) = VZZER(M+2,N,J,K) +VZZER(M,N,J+2,K) +
     1VZZER(M,N,J,K+2) -2.*VZZER(M,N,J,K) - 2.*VZZER(M+1,N+1,J+1,K+1)
     2 -2.*VZ1ZER(M,N,J,K) +VZZER(M,N+2,J,K)
      VZONE(M,N,J,K) = VZNEG(M+2,N,J,K) + VZNEG(M,N,J+2,K) + VZNEG(M,N,J
     1,K+2) - 2.*VZNEG(M,N,J,K) - 2.*VZNEG(M+1,N+1,J+1,K+1)-2.*VZ1NEG
     2(M,N,J,K) +VZNEG(M,N+2,J,K)
  169 FORMAT(X52HTHE PROGRAM HAS EXCEEDED THE AVAILABLE NUMBER OF P,S)
  10  FORMAT(X  2HX(,1I2,1H,1I2,1H,1I2,1H,1I2,1H,1I2,2H)=1F17.10)
      IF(J-2*(J/2))38,39,38
 38   IF(K-2*(K/2))40,41,40
 41   VX = 0.
      RETURN
 39   IF(K-2*(K/2))41,40,41
  40  IF(IP)42,43,42
```

```
   43  IF(J-2*(J/2))41,42,41
   42  IF(M-5)44,44,3
  44   IF(N-5)45,45,3
  45   IF(J-5)46,46,3
  46   IF(K-5)47,47,3
  47   IF(IP-2)70,70,3
  70   Y = VXMAT(M+1+6*N+36*J+216*K+1296*(IP+1))
       IF(Y) 48,49,48
   48  CONTINUE
       VX = Y
       RETURN
  49   COUNT = 1.
       GO TO 2
  3    COUNT = 3.
       PRINT 106,M,N,J,K,IP
  106  FORMAT(24HOVERFLOW IN FUNCTION VX  3X,5(I2,2X))
   2   IF(IP)159,160,161
  160  VXW= VZZER(M+2,N,J,K) - VZZER(M,N,J+2,K)
       GO TO 50
  159  VXW= VZNEG(M+2,N,J,K) - VZNEG(M,N,J+2,K)
       GO TO 50
  161  IF (IP-2) 162,163,163
  162  VXW= VZONE(M+2,N,J,K) - VZONE(M,N,J+2,K)
       GO TO 50
  163  VXW= VZTWO(M+2,N,J,K) - VZTWO(M,N,J+2,K)
  50   IF(COUNT -2.) 52,52,51
   52  NUMBER = M+1+6*N+36*J+216*K+1296*(IP+1)
       VXMAT(NUMBER) = VXW
   51  VX = VXW
       END


C
       FUNCTION VZZER(MO,NO,JO,KO)
       DIMENSION FZ(20),BZ(20),RTAUV(15,15,2),HPHI(8,8,15),HPHIA(8,8,15),
      1VXMAT(5190),MA(100),NA(100),JA(100),KA(100),IPA(100)
       COMMON VXMAT,RTAUV,HPHI,HPHIA,FZ,BZ,MA,NA,JA,KA,IPA
       IF(JO-2*(JO/2))2,2,3
     2 IF(KO-2*(KO/2))4,4,3
    3  VZZER = 0.
       RETURN
    4  VZZER = FZ(MO+1)*FZ(NO+1)*BZ(JO+1)*BZ(KO+1)
       END


C
       FUNCTION VZNEG(M,N,J,K)
```

```
      DIMENSION TE(2)
      DIMENSION FZ(20),BZ(20),RTAUV(15,15,2),HPHI(8,8,15),HPHIA(8,8,15),
     1VXMAT(5190),MA(100),NA(100),JA(100),KA(100),IPA(100)
      COMMON VXMAT,RTAUV,HPHI,HPHIA,FZ,BZ,MA,NA,JA,KA,IPA
   90 FORMAT(///2E17.10,///,23HTOO MANY TAUS IN VZNEG )
      IF (J-2*(J/2))38,39,38
   38 IF(K-2*(K/2))40,41,40
   41 VZNEG = 0.
      RETURN
   39 IF(K-2*(K/2))41,40,41
   40 CONTINUE
      TERM = 0.
      SUMM = 0.
      LTAU = 0
      I = 0
    3 LTAU = LTAU + 1
      T = LTAU - 1
      I = I+1
      TE(I)= (2.*T+1.)*RTAUV(LTAU,J+1,1)* RTAUV(LTAU,K+1,1)*
     1 HPHI(M+1,N+1,LTAU)
      IF(I-2) 3,5,5
    5 I = 0
      TERM = TE(1) + TE(2)
      TE(1) = 0.
      TE(2) = 0.
    4 SUMM = SUMM + TERM
      IF(LTAU-15)8,9,9
    9  CONTINUE
      PRINT 90, TERM,SUMM
      GO TO 1
    8   CONTINUE
      IF (ABSF(TERM/SUMM)-.1E-7)1,3,3
    1 CONTINUE
      VZNEG = SUMM
      END
C


      FUNCTION VZ1NEG(M,N,J,K)
      DIMENSION TE(2)
      DIMENSION FZ(20),BZ(20),RTAUV(15,15,2),HPHI(8,8,15),HPHIA(8,8,15),
     1VXMAT(5190),MA(100),NA(100),JA(100),KA(100),IPA(100)
      COMMON VXMAT,RTAUV,HPHI,HPHIA,FZ,BZ,MA,NA,JA,KA,IPA
   90 FORMAT(///2E17.10,///,23HTOO MANY TAUS IN VZ1NEG)
      IF (J-2*(J/2))38,39,38
   38 IF(K-2*(K/2))40,41,40
   41 VZ1NEG = 0.
      RETURN
```

```
 39    IF(K-2*(K/2))41,40,41
 40    CONTINUE
       SUMM = 0.
       TERM = 0.
       I = 0
       LTAU = 1
  3    LTAU = LTAU + 1
       T = LTAU - 1
       I = I+1
       TE(I)= -1./(T*(T+1.) )*RTAUV(LTAU,J+1,2)*RTAUV (LTAU,K+1,2)*
      1 (2.*T+1.) /(T*(T+1.))  * HPHIA(M+1,N+1,LTAU)
       IF(I-2) 3,5,5
  5    I = 0
       TERM = TE(1) + TE(2)
       TE(1) = 0.
       TE(2) = 0.
  4    SUMM = SUMM + TERM
       IF(LTAU-15)8,9,9
   9    CONTINUE
       PRINT 90, TERM,SUMM
       GO TO 1
  8      CONTINUE
C THE LIMIT .1E-7 SHOULD BE EXPERIMENTED WITH
       IF (ABSF(TERM/SUMM)-.1E-7)1,3,3
  1    CONTINUE
       VZ1NEG = SUMM
       END
```

3. Program Highen

Definition of Symbols and Arrays

Nthlim designates the order of the wave function desired. The basis set is stored in the Arrays mat(i), nat(i), jat(i), kat(i), and ipat(i). Cterm(m,n) contains the m^{th} coefficient of the n^{th} order wave function. Eps(n) contains the n^{th} order energy.

Operating Procedure

The program calculates the n^{th} order wave function from Eqs(II.D-9) and (II.D-10). Rzero, mn - the number of terms in the basis set-, enzero, cofrho, cofnom, coeffl, va, summit, enzero, enone, mat, nat, jat, kat, and ipat are read from tape or punched cards. The energy through $(2n + 1)^{th}$ order is then calculated.

```
      PROGRAM HIGHEN
      DIMENSION            COEFF1(50,50),MAT(100),NAT(100),JAT(100)
      DIMENSION KAT(100),IPAT(100),BMAT(50),VCHECK(50),CX(50),CY(50)
      COMMON/BLOCK3/ZEREPS(81),EPS(80),CTERM(50,40),COFNOM(50,50),
     1COFRHO(50,50),MNTERM(40)
      COMMON/BLOCK4/SUMMIT(50),VA(50),STOREN(40,40)
      EQUIVALENCE(EPS(1),ZEREPS(2))
   20 FORMAT(3X,I2/,(13(5I1,1X)))
  30  FORMAT(//,20X,26HTHE DISSOCIATION ENERGY IS,  F7.5//)
   67 FORMAT(X5HETWO=E17.10)
  72  FORMAT(1H1,4(/),40X,39HTHE VALUES OF THE VARIOUS ORDERS OF THE/40X
     1,40HCOEFFICIENTS ARE LISTED BELOW ALONG WITH /,51X,15HTHE TOTAL VA
     2LUE)
    74 FORMAT(
     1      4(/),35X,11HCOEFFICIENT,20X,18HTOTAL CONTRIBUTION /35X,5I2,
     2 23X,F15.10//,22X,4(5HORDER,1X, 12HCONTRIBUTION,2X)/(22X,4(1X,
     3 I2,2X,F15.10)))
  93  FORMAT(X7HENZERO=E17.10, 6HENONE= E17.10)
   139 FORMAT(X6HENTRE=,E17.10)
  197  FORMAT(1H1,4(/),57X,2HR=,F5.2,4(/),4X,5HORDER,9X,6HENERGY,10X,9HES
     1UM A.U.,9X,9H D(E.V.) ,10X,7H(1/R12),12X,4HDIFF,11X,9HW.F.TERMS//)
  297  FORMAT(1H1,2(/),52X,16HENERGY OF HEHE+2,
     1            4(/),57X,2HR=,F5.2,4(/),4X,5HORDER,9X,6HENERGY,10X,9HES
     2UM A.U.,9X,9H D(E.V.) ,10X,7H(1/R12),9X,10HESUM + 1/R,8X,9HW.F.TER
     3MS//)
  291  FORMAT(1H1)
  198  FORMAT(6X,I2,4X,5(2X,F14.10,2X),8X,I3)
  201  FORMAT(//38HTHE ENERGY DIFFERENCE IS NOW EQUAL TO ,E17.10)
  467  FORMAT(3X,/,3(7HVCHECK( I2,2H)=,E17.10,4X))
  1111 FORMAT(90X,I2,3HMIN, 2X,I2,3HSEC, 3X,I2,6HSEC/60)
  407  FORMAT(3X,6HRZERO= , F5.2,3X,14HFUNCTION SIZE= ,I2,40HCOFRHO COFNO
     1M COEFF VA AND SUMMIT FOLLOW /(4E20.10))
  916  FORMAT(3X,4E17.10)
   769 CONTINUE


C        NTHLIM IS THE ORDER OF THE WAVE FUNCTION DESIRED
       NTHLIM = 5



       READ  TAPE 47,
     1           RZERO,MN,ENZERO,((COFRHO(I,JO),I=1,MN),JO= 1,MN),((COFNO
     2M(I,JO), I = 1,MN),JO= 1,MN),((COEFF1(I,JO),I = 1,MN),JO= 1,MN),
     3 (VA(I),I=1,MN),(SUMMIT(I),I=1,MN),ENZERO,ENONE,
     4 (MAT(I),NAT(I),JAT(I),KAT(I),IPAT(I),I=1,MN)
        IF(EOF,47)1742,1743
  1742 STOP
  1743 CONTINUE
```

```
      PI = 3.141592653
      DO 987 I = 1,50
      DO 987 J = 1,40
987   CTERM(I,J) = 0.
      DO 505 I = 1,MN
      DO 505 J = 1,MN
505   COFRHO(I,J) = COFRHO(I,J) - ENONE*COFNOM(I,J)
      MORE = 1
      MN = MN + 1
      DO 71 IDONT = 1,MORE
      MN = MN - 1
      IF(MN)71,71,1139
1139  CONTINUE
      DO 307 I = 1,MN
      MAT(I+MN) = NAT(I)
      NAT(I+MN) = MAT(I)
      JAT(I+MN) = KAT(I)
      KAT(I+MN) = JAT(I)
 307  IPAT(I+MN) = IPAT(I)
      DO 506 I = 1,MN
506   BMAT(I) = VA(I)
      CALL AMATSAV(MN,COEFF1,BMAT,VA,PI,DET)
      DO 508 I = 1,MN
 508  VCHECK(I) = 0.
      DO 507 I = 1,MN
      DO 507 J = 1,MN
507   VCHECK(I) = VCHECK(I) + BMAT(J)*COEFF1(I,J)
      DO 509 I = 1,MN
      VCHECK(I) = (VCHECK(I) - VA(I))/VA(I)
      IF(VCHECK(I) - 1.E-8) 509,509,520
 520  CONTINUE
      PRINT 467,I,VCHECK(I)
509   CONTINUE
      SUM1 = 0.
      SUM2 = 0.
      DO 511 I = 1,MN
      SUM1 = SUM1 + BMAT  (I)*VA(I)
      DO 511 J = 1,MN
511   SUM2 = SUM2 + BMAT(I)*BMAT(J)*COEFF1(I,J)
      ETWO = SUM2 -2.*SUM1
      SUM11 = 0.
      SUM22 = 0.
      DO 512 I = 1,MN
      SUM11 = SUM11 + SUMMIT(I)*BMAT(I)
      DO 512 J = 1,MN
512   SUM22 = SUM22 + BMAT(I)*BMAT(J)*COFRHO(I,J)
      PSI 10 = SUM11
```

```
      PSI01 = PSI10
      PSIZR1 = PSI10
      ENTRE = SUM22 -2.*ETWO*SUM11
      DIFF = -1.888734- (ENZERO + ENONE + ETWO + ENTRE)
      DIS = -(DIFF+ .888734-1./RZERO)*27.20974
      DO 525 I = 1,MN
  525 CTERM(I,1) = BMAT(I)
      DO 576 I = 1,40
  576 MNTERM(I) = MN
      DO 577 I = 1,40
      DO 577 J = 1,40
  577 STOREN (I,J) =0
      EPS(1) = ENONE
      EPS(2) = ETWO
      EPS (3) = ENTRE
      DO 550 NORDER = 2,NTHLIM
      CALL KTIME(MIN,KSEC,DD)  $ PRINT 1111,MIN,KSEC,DD
      MN = MNTERM(NORDER)
      CALL BMATGET(BMAT,MN,NORDER)
      DO 551 I = 1,MN
  551 CTERM(I,NORDER) = BMAT(I)
      CALL AMATSAV(MN,COEFF1, BMAT,VA,PI,DET)
      DO 552 I = 1,MN
      VCHECK(I) = 0
      DO 553 J = 1,MN
  553 VCHECK(I) = VCHECK(I) + BMAT(J) * COEFF1(I,J)
  552 VCHECK(I) = VCHECK(I) - CTERM(I,NORDER)
C                                  )NM,1 = I , )I(KCEHCV,I( ,764 TNIR
      DO 554 I = 1,MN
  554 CTERM(I, NORDER) = BMAT(I)
      SUM1 = 0
      LIM2 = 2*NORDER - 1
      DO 560 I = 2,LIM2
      SUM 2 = 0.
      LIM3 = NORDER - I
      DO 561 J = LIM3,NORDER
  561 SUM2 = SUM2 + FNORMAL(J,2*NORDER-I-J)
  560 SUM1 = SUM1 + EPS(I)*SUM2
      NTWO = 2*NORDER
      MINORD = NORDER - 1
      DO 569 I = 1,MN
      CX(I ) = CTERM(I,NORDER)
  569 CY(I) = CTERM(I,MINORD)
      MNT = MNTERM(NORDER-1)
      EPS(NTWO) = ADDMAT(CX,CX,COEFF1,VA,1,MN,MN)
     1 + 2*ADDMAT(CX,CY,COFRHO,VA,1,MN,MNT)- SUM1
      LIM1 = 2*NORDER
      SUM4 = 0
      DO 563 I = 2,LIM1
```

```
      SUM 5 = 0
      LIM2 = NORDER + 1 - I
      DO 564 J = LIM2,NORDER
564   SUM5 = SUM5 + FNORMAL (J,2*NORDER + 1 - I - J)
563   SUM4 = SUM4 + EPS(I) * SUM5
      NTWO ONE = NTWO + 1
      EPS (NTWOONE) = ADDMAT (CX,CX, COFRHO,VA,1,MN,MN) - SUM4
550   CONTINUE
      PRINT 197 , RZERO
      ZEREPS(1) = ENZERO
      SUM = 0
      LOW = 0
      EEXACT = -1.888734
      RAV = 0
      DO 570 I = LOW,NTWOONE
      RAV = RAV + (I+1)*EPS(I+1)
571   SUM = SUM + EPS(I)
      DIFF = EEXACT - SUM
      DIS = -(DIFF+ .888734-1./RZERO)*27.20974
      PRINT 198,I,EPS(I),SUM,DIS,RAV,DIFF,MN
570   CONTINUE
      PRINT 72
      RHALF = RZERO/2
      PRINT 297,RHALF
      EKR = 1.5
      HE2KP = 0
      R12 = 0
      DO 572 I = LOW,NTWOONE
      IPRIME = 2-I
      HE2ENER=2.**IPRIME*EPS(I)
      HE2KP = HE2KP + HE2ENER
      FINALEN = -4
      ENPLR = HE2KP + 4/RHALF
      DISOSEN = (FINALEN - ENPLR)*27.20974
      DIFF = EKR-HE2ENER
      R12 = R12 + I*HE2ENER
      PRINT 198,I,HE2ENER,HE2KP,DISOSEN,R12,ENPLR,MN
572   CONTINUE
      PRINT 291
      DO 71 I = 1,MN
      SUMC = 0
      DO 70 J = 1,NTHLIM
70    SUMC = SUMC + CTERM(I,J)
      PRINT 74, MAT(I),NAT(I),JAT(I),KAT(I),IPAT(I),SUMC,(II,CTERM(I,II),
     1,II=1,NTHLIM)
71    CONTINUE
777   CONTINUE
      GO TO 769
      END
```

```
      SUBROUTINE AMATSAV(MN,COEFF1,BMAT,VA,PI,DET)
      DIMENSION AMAT(50,50),COEFF1(50,50),BMAT(50 ),VA(50)
      DO 50 I = 1,MN
      DO 50 J = 1,MN
50    AMAT(I,J) = COEFF1(I,J)
      NQ = 1
      CALL MATINV(AMAT,MN,BMAT,NQ,DET,50)
      END
```

```
      SUBROUTINE BMATGET(BMAT,MN,NORDER)
      COMMON/BLOCK3/ZEREPS(81),EPS(80),CTERM(50,40),COFNOM(50,50),
     1COFRHO(50,50),MNTERM(40)
      COMMON/BLOCK4/SUMMIT(50),VA(50),STOREN(40,40)
      EQUIVALENCE(EPS(1),ZEREPS(2))
      DIMENSION BMAT(50)
      DO 1 I = 1,MN
      SUM1 = 0
      SUM3 = 0
      DO 2 J = 1,MN
      SUM3 = SUM3 + CTERM(J,NORDER-1)*COFRHO(I,J)
      LIM = NORDER-1
      SUM2 = 0
      DO 3 K = 2,LIM
3     SUM2 = SUM2 + EPS(K)*CTERM(J,NORDER-K)
2     SUM1 = SUM1 + SUM2 *COFNOM(I,J)
1     BMAT(I) = EPS(NORDER)*SUMMIT(I) + SUM1 - SUM3
      END
```

```
      FUNCTION FNORMAL (J, K)
      COMMON/BLOCK3/ZEREPS(81),EPS(80),CTERM(50,40),COFNOM(50,50),
     1COFRHO(50,50),MNTERM(40)
      COMMON/BLOCK4/SUMMIT(50),VA(50),STOREN(40,40)
      DIMENSION CX(50), CY(50)
      EQUIVALENCE(EPS(1),ZEREPS(2))
      M = XMAXOF(J,K)
      N = XMINOF(J,K)
      MONE = M+ 1
      NONE = N+1
      MN = MNTERM(M)
      MX = MNTERM(N)
      IF(N) 1,3,3
 3    IF ( STOREN(MONE,NONE)) 4,5,4
 5    DO 7 I = 1,50
      CX(I) = CTERM(I,M)
 7    CY(I) = CTERM(I,N)
      IF(N) 8,8,9
 8    STOREN(MONE,NONE) = ADDMAT(CX,CY,COFNOM,SUMMIT,2,MN,MX)
      FNORMAL = STOREN(MONE,NONE)
      RETURN
 9    STOREN(MONE,NONE) = ADDMAT(CX,CY,COFNOM,VA,1,MN,MX)
      FNORMAL = STOREN(MONE,NONE)
      RETURN
 1    FNORMAL = 0
      RETURN
 4    FNORMAL = STOREN(MONE,NONE)
      RETURN
      END
```

```
      FUNCTION ADDMAT(COF1,COF2,SQRMAT,VECT,IPAR,MN,M1)
      DIMENSION COF1(50),COF2(50),SQRMAT(50,50),VECT(50)
      IF(IPAR-1)1,1,2
```

```
 1   SUMM = 0.
      DO 21 I = 1,MN
     DO 21 J = 1,M1
21   SUMM = SUMM + COF1(I)*COF2(J)* SQRMAT(I,J)
     ADDMAT = SUMM
     RETURN
2    SUMM = 0.
     DO 22 I = 1,MN
22   SUMM = SUMM + COF1(I)*VECT(I)
     ADDMAT = SUMM
     END
     END
```