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Two-electron atoms in momentum space.

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TWO-ELECTRON ATOMS IN
MOMENTUM SPACE

by

Philip Eric Regier

A thesis
presented to the University of Waterloo
in partial fulfillment of the
requirements for the degree of
Master of Mathematics
in
Applied Mathematics

Waterloo, Ontario 1983

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ABSTRACT

Philip Eric Regier: Two-Electron Atoms in Momentum Space,
Master's thesis, University of Waterloo, November, 1983.

A Gaussian geminal basis set is employed for calculating approximate eigenfunctions of the Schrodinger equation for two-electron atoms. The basis geminals are non-factorable two-electron functions with explicit correlation terms. Sixteen term variational wavefunctions are obtained for H^-, He and Li^+ and are the best of their type and size. Previous wavefunctions were found to be improperly optimized.

A variation-iteration method for finding solutions to the momentum space Schrodinger equation is also considered. This technique successively iterates an initial wavefunction, producing a sequence of wavefunctions and energies which converge to the exact wavefunction and energy. Using the Fourier transforms of the sixteen term wavefunctions as the initial wavefunctions, first-iterated wavefunctions and half-iterated energies were produced. Previous work using this method with Gaussian orbital basis function was found to be in error.

Gaussian geminal wavefunctions of fifty terms were also constructed, using the generator-coordinate method. This technique uses the motivation of Monte Carlo quadrature to map several variational parameters onto all of the non-linear parameters of the wavefunction. The technique of importance sampling and the control variate method were found to be very useful in this regard.

Compton profiles and one-electron momentum densities were produced from the Gaussian geminal wavefunctions. The most accurate Compton profile yet obtained for helium is presented. The first-iterated wavefunction was not used as the resulting integrals could not be evaluated.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1 Position Space and Momentum Space Wavefunctions.

For the study of atomic and molecular systems in quantum chemistry, we are primarily concerned with the bound state solutions of the time-independent Schrodinger equation in the Born-Oppenheimer approximation (Born and Oppenheimer (1927); Born and Huang (1954)). In operator form, this is expressed as

$$H\chi = E\chi \tag{1.1}$$

where H is the electronic Hamiltonian, E is the electronic energy and χ the wavefunction in an appropriate representation.

The representation most frequently used is that in which χ is a function whose domain is the vector space of the position coordinates $\hat{r}=(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)$ and spin coordinates $\hat{\sigma}= (\sigma_1,\ldots,\sigma_N)$ of the N electrons (called position space). The representation which will be considered in this thesis takes χ to be a function whose domain is the vector space of the electronic momentum coordinates $\hat{p}=(\vec{p}_1,\vec{p}_2,\ldots,\vec{p}_N)$ and the spin coordinates $\hat{\sigma} = (\sigma_1,\ldots,\sigma_N)$ (called momentum space).

These two representations are related by the Dirac-Fourier (Dirac (1958)) transform as follows

$$\Phi(\hat{p},\hat{\sigma}) = (2\pi)^{-3N/2} \int \exp(-i\hat{p}\cdot\hat{r})\ \Psi(\hat{r},\hat{\sigma})\ d\hat{r} \qquad (1.2)$$

Hartree atomic units will be used throughout (Whiffen (1978)).

For two-electron atoms, such as will be considered in this thesis, the spin may be treated as follows. Due to the small nuclear mass of the atoms considered, we may neglect the spin-orbit interaction and the relativistic change in mass. This enables the wavefunction to be factored into a product of a function of spatial or momentum coordinates and a function depending on the spin coordinates (see Bethe and Salpeter (1957) Sec.24). Thus, the spin may be factored out of (1.2) leaving an ordinary Fourier transform. Spin will henceforth be neglected, as it may be incorporated in a two-electron wavefunction merely by multiplication of a normalized spin function of appropriate symmetry.

The electronic Hamiltonian H for a system with N electrons and S nuclei is given by

$$H = \frac{1}{2} \sum_{k=1}^{N} p_k^2 - \sum_{k=1}^{N} \sum_{j=1}^{S} Z_j |\vec{R}_j - \vec{r}_k|^{-1} + \sum_{k<j}^{N} \sum^{N} |\vec{r}_k - \vec{r}_j|^{-1} \quad (1.3)$$

where $\vec{p}_k$ is the momentum vector of electron k, $\vec{r}_k$ is the position vector of electron k, $\vec{R}_k$ is the position vector of nucleus k, $p_k^2 = \vec{p}_k \cdot \vec{p}_k$ and Z_k is the atomic number of nucleus k.

The first term in the Hamiltonian corresponds to the kinetic energy of the electrons, the following term gives the Coulombic potential energy due to the attraction of the electrons to the nuclei and the last term is the potential energy due to the electrostatic repulsion between the electrons.

When a particular representation is chosen for the wavefunction, the operators in the Hamiltonian must be transformed so as to act on the elements of the space under consideration. The solution of the resulting equation will yield the wavefunction (and its associated eigenvalue) in the chosen space.

Wavefunctions are used to calculate expectation values of atomic and molecular properties or observables. In principle, both position space and momentum space wavefunctions contain the same information; in other words, knowledge of either wavefunction enables one to calculate expectation values of all properties. In practice, however, the integrals involved in the calculation of a given observable may be evaluated with greater facility in a particular one of the two representations, depending on the integral under consideration.

1.2 Calculation of Momentum Space Wave Functions.

To determine wavefunctions in momentum space, two main approaches may be employed. The first is the application of the Fourier transform (1.2) to the solution of the Schrodinger equation in position space. In position space, the final two terms of the Hamiltonian remain unchanged, as they are multiplicative operators containing position space coordinates. The kinetic energy term, however, must be transformed to one which operates on the position space coordinates. This is accomplished by representing the p_k^2 operators by the Laplacian operators $-\nabla_k^2$. In the case of hydrogen, the resulting differential equation may be solved exactly, as shown in many textbooks (see Bethe and Salpeter (1957)). Podolsky and Pauling (1929) obtained the momentum space wavefunctions for hydrogen by Fourier transforming the position space solutions.

For systems with more than one electron, the Schrodinger equation may no longer be solved exactly. Various methods have been applied to arrive at a great many approximate wavefunctions for a large number of atoms and molecules (see Richards et al (1971, 1974 and 1978), Ohno (1982)). The majority of these are variational calculations in which the wavefunction has been built from an orbital basis set (one-electron functions). The most common orbital basis sets in use are readily Fourier transformed, as reviewed by Kaijser and Smith (1977). Thus, the Fourier transform technique of obtaining a momentum space wavefunction is widespread.

In the case of helium, an atom with two electrons, the best wavefunctions have been expanded in a basis set of geminals (two-electron functions) which are non-separable because they contain explicitly the inter-electron distance r_{12}. Some geminal basis sets in use are Hylleraas type (Hylleraas (1928); Pekeris (1958)), exponential Hylleraas-Slater type (Hylleraas (1929); Slater (1928); Thakkar and Smith (1977)), Gaussians (Singer (1960); Boys (1960); Poshusta (1978 and 1979)) and others containing negative (Kinoshita (1957)) and fractional (Schwartz (1962)) powers of r_{12} and logarithmic terms (Frankowski and Pekeris (1966)) as well. Unfortunately, the basis sets which yield the best wavefunctions have proven too difficult to Fourier transform.

The second method is to formulate the problem directly in momentum space. In momentum space, it is the kinetic energy operator that is a multiplicative operator and the potential energy operators which must be transformed. This may be done by replacing the position operators by the correspondence $x \Rightarrow i\partial/\partial p_x$, etc. This approach was attempted by Hylleraas (1932), and yielded a differential equation for the radial part of the solution for the hydrogen atom, which he then solved. For atoms other than the hydrogen atom, this method is difficult to handle. A more convenient approach is to use the Fourier transform to express the Schrodinger equation as an integral equation in momentum space. This calculation will be demonstrated in chapter three. While a great deal of work has been done on the position space Schrodinger equation, very few attempts have been made to solve the momentum space Schrodinger equation. All of these attempts relevant to our work will now be reviewed.

Fock (1935) solved the momentum space integral equation for the hydrogen atom. He first made a transformation analagous to a stereographic projection from a plane onto a sphere and his solution was a function of these resulting coördinates. Thus, the hydrogen atom had been solved exactly in both position and momentum space.

McWeeny (1949) attempted an approximate solution to the integral equation for H_2^+ (hydrogen molecule ion). This system now has two force centers (nuclei), although it remains a one electron problem. He employed a variation-iteration (VI) procedure developed by Svartholm (1945) which will be fully described in chapter three. This procedure takes an initial guess at the wave function and then yields successive approximations to the ground-state wavefunction and energy eigenvalue. These approximations converge to the actual values; however, one is limited in practice by the ability to solve the resulting integrals. His initial wavefunction was a combination of atomic orbitals which he iterated to obtain a correction term to the wavefunction. This corrected wavefunction gave a greater spread in the momentum distribution than the initial wavefunction.

Shibuya and Wulfman (1965) used Fock's transformation in their work on the one-electron problem in an arbitrary number of force centers. They attempted to find a solution by expanding the wavefunction in a basis set. Novosadov (1976) obtained the general solution without having to select a form for the wavefunction. The solution is a linear combination of an infinite number of hydrogen-like functions centered on each nucleus. Thus, to obtain numerical results, an approximation is necessary. A simple numerical calculation on H_2^+ was also performed. In a later paper, Novosadov (1979a) presents, in more detail, a numerical method of solution for this one-electron many-center problem. Subsequently, Novosadov (1979b) presented a numerical method for the solution of the momentum space Hartree-Fock equations for ground-state closed shell neutral or positive ion molecules.

Monkhorst and Jeziorski (1979) pointed out that for many-center problems, solving the momentum space integral equation could eliminate the conventional position space difficulties of calculating many-center integrals and instabilities due to overcompleteness of the many-center basis sets. They also presented a method, similar to that of Novosadov, of approximating the energy eigenvalues of a one-electron system. A paper by Duchon et. al. (1982) presents an approximate method of determining the energy levels of a one-electron many-center system which converges more rapidly than the technique of Novosadov.

The first attempt to find an approximate solution for the momentum space integral equation for helium was by McWeeny and Coulson (1949). Here again they used the VI method developed by Svartholm. Their choice of starting function was the momentum space form of the product of two hydrogen s-type (Slater) orbitals with the screening constant as the variational parameter. They were able to calculate an improved eigenvalue estimate but were not able to do the integrations to obtain a new wavefunction. Schreiber (1978) assumed a spherically symmetric wavefunction (i.e. $\phi(\vec{p}_1,\vec{p}_2) = \phi(p_1,p_2)$) and used a series representation of the electrostatic electron repulsion term. Using the same initial wavefunction as McWeeny and Coulson (1949), he obtained a first-iterated wavefunction. This is not an extension of the work of McWeeny and Coulson (1949), as the assumption of spherical symmetry is restrictive and yields a different integral equation.

Henderson and Scherr (1960) also used the VI method, using wavefunctions expressed as a sum of products of Gaussian orbitals (one-electron functions) as their initial functions. They employed one-term, two-term and six-term Gaussian functions with no correlation in their work. They were able to get an improved upper bound to the energy (improved over the variational energy of their initial function) and a first-iterated wavefunction in terms of hypergeometric functions.

Monkhorst and Szalewicz (1981) used the VI method on the Hartree-Fock equations in momentum space developed by Novosadov (1979b). Their initial function was the Fourier transform of a normalized 1s orbital. They obtained a first and second iterated wavefunction and their energy bound was better than that calculated variationally from their initial wavefunction. However, their results would only converge to the Hartree-Fock wavefunction and eigenvalue, not the actual ones.

The usual spherical polar momentum variables (p,θ_p,ϕ_p) are not conjugate to the spherical polar position variables (r,θ,ϕ). Lombardi (1980) has proposed a new set of position and momentum variables which are conjugate variables. He then solved the hydrogen atom in this momentum representation. The functions obtained differ considerably in form from those of Podolsky and Pauling. This is due to the use of a different representation.

Using the same momentum variables, Lombardi (1982) began work on helium by carrying out a self-consistent field calculation on the ground-state. The energy estimate arrived at was in agreement with analagous position space results.

Lombardi (1983) then examined helium using the VI method in conjunction with his momentum variables. He employed a product of Slater orbitals expressed in his momentum variables as his initial function, this being the same as that employed by McWeeny and Coulson (1949) and Schreiber (1978). The momentum space wave equation given by Lombardi uses the assumption of a spherically symmetric wavefunction (as did that of Schreiber). A first-iterated wave function and energy was easily obtained by contour integration, avoiding the difficulties encountered by the previous attempts using the variables (p,θ_p,ϕ_p).

However, the physical interpretation of these new momentum variables is not clear and no formulae are available for calculating other quantities such as Compton profiles.

Other methods aside from the VI method have been advanced to solve the momentum space equations. A recent paper by Navaza and Tsoucaris (1981) investigates the possibility of solving the Hartree-Fock integral equations numerically.

The VI method has not yet yielded good results partly because a good starting function with explicit correlation has never been tried. Gaussian geminals of the Boys (1960) and Singer (1960) type are a good basis set for this type of problem because a Gaussian geminal in position space transforms to a Gaussian geminal in momentum space. In Chapter 2, we construct a good variational wavefunction expanded in a Gaussian geminal basis set containing explicit correlation terms. This wave function will be far more accurate than those yet used in the VI method. It will be shown in Chapter 3 that the use of this basis set presents no complexities greater than those encountered by Henderson and Scherr (1960) who used a basis set of products of Gaussian orbitals.

1.3 Momentum Densities and Compton Profiles.

To attempt comparison between theory and experiment, it is necessary to calculate experimentally observable quantities from the wavefunction. One such quantity is the Compton profile. Compton scattering, along with several other techniques, may also be employed to yield information about the momentum density.

The scattering of a photon from an electron is referred to as Compton scattering. The wavelength of the scattered radiation will then yield information about the momentum of the electron. The formulae for calculating the Compton profile are derived using what is called the impulse approximation. This involves two assumptions. The first is that during the scattering process the electron may be treated as free rather than bound. The second holds that the energy gained by the electron from the collision with the photon is much greater than its binding energy. For more details on the impulse approximation, the reader is referred to the book edited by Williams (1977). It is only through the impulse approximation that a simple relationship exists between the Compton profile and the momentum density of the electrons in the system under investigation. The impulse Compton profile may be calculated from the momentum density which is itself calculated from the wavefunction.

A great many atoms and molecules have had their Compton profiles and momentum densities calculated in this manner. (see Williams (1977)). The majority of these calculations used a momentum space wavefunction which was obtained as the Fourier transform of a position space wavefunction. As mentioned previously, this would not allow use of the best wavefunctions as they are not Fourier transformable. Results of high accuracy for a few systems would be useful for calibrating the experiments and testing the validity of the impulse approximation. Some of the recent attempts at more accurate solutions will be reviewed here.

Eisenberger (1970) calculated the Compton profile of He. Two different wavefunctions were used in this calculation. One was the Hartree-Fock SCF wavefunction of Clementi (1965) and the other was a multiconfigurational SCF wavefunction due to Sabelli and Hinze (1969). Eisenberger also measured the Compton profile of helium experimentally and found that the results were in good agreement with the theoretical calculation.

Benesch (1976) showed how to obtain Compton profiles and momentum densities from position space wavefunctions expanded in a Hylleraas-type basis containing correlation terms. A two-dimensional numerical integration was necessary to obtain these results. He calculated these quantities for helium using wavefunctions given by Bonham and Kohl (1966). These were compared with those obtained from the Hartree-Fock wavefunction of Clementi (1965).

Eisenberger (1970) also examined H_2 using a Hartree-Fock wavefunction due to Cade and Wahl (1974) as well as a multi-configuration SCF wavefunction from Das and Wahl (1966). Here the calculations were not in agreement with experiment over the whole profile. Brown and Smith (1972) used a configuration interaction (CI) function due to Liu (1973) which accounted for most of the correlation energy but their results also did not agree with the experiment of Eisenberger (1970). A new experiment was performed by Lee (1977) which yielded numbers closer to those calculated by Brown and Smith. In a later paper, Smith et al (1977) took into account molecular vibration and rotation as well as electron correlation and found agreement with the experimental data of Lee. Jeziorski and Szalewicz (1979) employed an explicitly correlated Gaussian wavefunction more accurate than that of Liu (1973) and found that the resulting Compton profiles agreed closely with those obtained by Smith et al (1977) prior to vibrational and rotational averaging.

In Chapter 4 of this thesis, wavefunctions of greater accuracy than those produced in Chapter 2 will be generated. Chapter 5 outlines the attempts to obtain Compton profiles and momentum densities from the wavefunctions of Chapters 2,3 and 4. The feasibility of using the highly accurate wavefunctions of Thakkar and Smith (1977) along with the equations derived by Benesch (1976) to generate a momentum density is examined. Some expectation values of various powers of p will also be calculated using some of these wavefunctions.

CHAPTER 2

GAUSSIAN GEMINAL WAVEFUNCTIONS

2.1 Construction of the Wavefunction.

Since Gaussian geminals have the property that their Fourier transform yields another Gaussian geminal (see Appendix 1), we may construct an approximate wavefunction in position space by expansion in a Gaussian geminal basis set which will be easily converted to a momentum space wavefunction.

The approximation to the wavefunction will be written in the following form:

$$\psi(\vec{r}_1,\vec{r}_2) = \frac{\pi^{-3/2}}{\sqrt{2}}(1+P_{12}) \sum_{k=1}^{N} C_k \exp(-\alpha_k r_1{}^2 - \beta_k r_2{}^2 - \gamma_k r_{12}{}^2) \qquad (2.1)$$

where $r_1{}^2 = \vec{r}_1\cdot\vec{r}_1$
$r_2{}^2 = \vec{r}_2\cdot\vec{r}_2$
$r_{12}{}^2 = (\vec{r}_1 - \vec{r}_2)\cdot(\vec{r}_1 - \vec{r}_2)$
$P_{12}\, f(\vec{r}_1,\vec{r}_2) = f(\vec{r}_2,\vec{r}_1)$
and $(\alpha_k,\beta_k,\gamma_k,C_k)$ are parameters to be determined.

This form is useful as the r_{12} dependence may be clearly seen.

Another way of writing this, which will also be of some use is:

$$\psi(\vec{r}_1,\vec{r}_2) = \frac{\pi^{-3/2}}{\sqrt{2}}(1+P_{12})$$

$$\sum_{k=1}^{N} C_k \exp(-\zeta_k\eta_k r_1^2 - \zeta_k/\eta_k r_2^2 - 2\zeta_k\theta_k\vec{r}_1\cdot\vec{r}_2) \qquad (2.2)$$

Here $(\zeta_k,\eta_k,\theta_k,C_k)$ are parameters to be determined.

The first form was used by Longstaff and Singer (1964) and the second was used by Poshusta (1979). We shall use one or the other as convenience dictates. These two different parametrizations are related by the following transformation:

$$\begin{aligned}\alpha_k &= \zeta_k(\eta_k+\theta_k)\\ \beta_k &= \zeta_k(1/\eta_k+\theta_k)\\ \gamma_k &= -\zeta_k\theta_k\end{aligned} \qquad (2.3)$$

If the wavefunction is to be square-integrable, we must have the following conditions: $\zeta_k>0$, $\eta_k>0$, $|\theta_k|<1$ for $k=1,\ldots,N$. Since replacing η_k by $1/\eta_k$ does not change the wavefunction,we may write the restrictions on the parameters as follows:

$$\left.\begin{array}{l}\zeta_k>0\\ \eta_k\geqslant 1\\ |\theta_k|<1\end{array}\right. \qquad k=1,\ldots,N \tag{2.4}$$

The parameters are obtained variationally as follows:

Define

$$\psi_k = \exp(-\zeta_k\eta_k r_1{}^2 - \zeta_k/\eta_k r_2{}^2 - 2\zeta_k\theta_k\vec{r}_1\cdot\vec{r}_2) \tag{2.5}$$

Then

$$\psi = \frac{\pi^{-3/2}}{\sqrt{2}}\,(1+P_{12})\sum_{k=1}^{N} C_k\psi_k(\vec{r}_1,\vec{r}_2) \tag{2.6}$$

or, in matrix form

$$= \frac{\pi^{-3/2}}{\sqrt{2}}\,\underline{\Psi}\,\underline{C} \tag{2.7}$$

where $\underline{\Psi} = [(1+P_{12})\psi_1,\ldots,(1+P_{12})\psi_N]$
and $\underline{C} = \begin{bmatrix} C_1\\ C_2\\ \cdot\\ C_N\end{bmatrix}$

The Hamiltonian we will be using is the sum of the kinetic energy T and the potential energy V. For a two-electron atom of nuclear charge Z, the Hamiltonian is given by:

$$H = T + V \qquad (2.8)$$

$$T = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2$$

$$V = -\frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}$$

When values are assigned to the parameters $(\zeta_k, \eta_k, \theta_k)$ and the resulting wavefunction (2.7) is substituted into the Ritz quotient and the latter is minimized with respect to the vector $\underline{C}$, we obtain (McWeeny and Sutcliffe (1976)):

$$\underline{\underline{H}}\,\underline{C} = E\underline{\underline{S}}\,\underline{C} \qquad (2.9)$$

where $\underline{\underline{H}}$ and $\underline{\underline{S}}$ are defined by:

$$H_{kl} = \langle (1+P_{12})\psi_k |\, H \,| \psi_l \rangle \qquad (2.10)$$

$$S_{kl} = \langle (1+P_{12})\psi_k | \psi_l \rangle \qquad (2.11)$$

This is a generalized eigenvalue equation, where the unknowns are the eigenvalues E, and their corresponding eigenvectors $\underline{C}$. The lowest energy eigenvalue E of this equation gives an upper bound to the ground state energy of the atom. The parameters $(\zeta_k, \eta_k, \theta_k)$ should be chosen so as to yield the minimum value of E. Calculation of the corresponding eigenvector $\underline{C}$ (with the condition that $\langle\psi|\psi\rangle=1$) will then determine the approximate wavefunction.

The method of calculation will now be outlined.

To solve this generalized eigenvalue problem in matrix form, one proceeds as follows:

Since $\underline{\underline{S}}$ is a positive definite matrix, the Choleski decomposition may be used (Wilkinson and Reinsch (1971)).

$\underline{\underline{S}} = \underline{\underline{L}}\ \underline{\underline{L}}^T$ where $\underline{\underline{L}}$ is lower triangular

The equation (2.9) becomes:

$$\underline{\underline{H}}\ \underline{C} = E\ \underline{\underline{L}}\ \underline{\underline{L}}^T\ \underline{C}$$

Since $\underline{\underline{S}}$ is invertible, so is $\underline{\underline{L}}$.

$$\underline{\underline{L}}^{-1}\ \underline{\underline{H}}\ \underline{C} = E\ \underline{\underline{L}}^{-1}\ \underline{\underline{L}}\ \underline{\underline{L}}^T\ \underline{C} \qquad (2.12)$$

Let $\underline{\underline{G}} = \underline{\underline{L}}^{-1}\ \underline{\underline{H}}\ \underline{\underline{L}}^{-T}$

and $\underline{D} = \underline{\underline{L}}^T\ \underline{C}$

and (2.12) becomes

$$\underline{\underline{G}}\ \underline{D} = E\ \underline{D} \qquad (2.13)$$

which is now an eigenvalue problem and the lowest eigenvalue E may be found. The corresponding eigenvector $\underline{D}$ may also be calculated, which will allow calculation of the vector $\underline{C}$ by the following formula:

$$\underset{\sim}{C} = \underset{\approx}{L}^{-T} \underset{\sim}{D} \tag{2.14}$$

The calculation of the matrix elements (2.10) and (2.11) is outlined in Appendix 2. The calculation of the generalized eigenvalue equation (2.9) was done using computer routines taken from the EISPACK program library (Smith et al (1976)). These routines use the algorithm described above. Equation (2.13) is then solved by reducing the matrix $\underset{\approx}{G}$ to symmetric tridiagonal form using the method of Householder. The eigenvalues of this matrix are determined by the method of Sturm sequencing, and the eigenvectors by inverse iteration. The $\underset{\sim}{C}$ eigenvector is calculated such that the wavefunction ψ is normalized.

Two computer minimization routines were used to vary the parameters $\zeta_k, \eta_k, \theta_k$ in an attempt to minimize the eigenvalue E. One of these was the program VA04AD from the HARWELL subroutine library, using a conjugate direction method given by Powell (1965). The other program was ZXMIN from the IMSL subroutine library which uses a quasi-Newton method described by Fletcher (1972). These programs must be used with care, as there is no algorithm which will guarantee finding the absolute minimum in this type of problem. Local minima may be found and this is highly dependent on the starting values supplied to the programs.

Finally, the wavefunction may be scaled to satisfy the virial theorem (Pilar (1968)). To perform this scaling, one must calculate the following quantities:

$$\langle T\rangle = \langle\psi|T|\psi\rangle \tag{2.15}$$

$$\langle V\rangle = \langle\psi|V|\psi\rangle \tag{2.16}$$

We define a norm-preserving scaling of the wavefunction by

$$\psi_\eta(\vec{r}_1,\vec{r}_2) = \eta^3\psi(\eta\vec{r}_1,\eta\vec{r}_2) \tag{2.17}$$

It follows that

$$\langle T\rangle_\eta = \eta^2\langle T\rangle \tag{2.18}$$

$$\langle V\rangle_\eta = \eta\langle V\rangle \tag{2.19}$$

$$E_\eta = \eta^2\langle T\rangle + \eta\langle V\rangle \tag{2.20}$$

Minimizing E_η with respect to η yields

$$\eta = -\langle V\rangle/(2\langle T\rangle) \tag{2.21}$$

Note that $E \geqslant E_\eta \geqslant E(\text{exact})$ and that

$$\langle T\rangle_\eta = \eta^2\langle T\rangle = \langle V\rangle^2/(4\langle T\rangle) \tag{2.22}$$

$$\langle V\rangle_\eta = -\langle V\rangle^2/(2\langle T\rangle) \tag{2.23}$$

from which we see that

$$-2\langle T\rangle_\eta = \langle V\rangle_\eta \tag{2.24}$$

in other words, ψ_η satisfies the virial theorem.

This scaling is necessary only because perfect optimization with respect to the non-linear parameters $\zeta_k, \eta_k, \theta_k$ is not possible.

2.2 Results.

For the purpose of testing the parameter optimizing program and succeeding programs, one- and two-term wavefunctions were produced for helium (Z=2). Several random guesses for the parameter values were used to start the minimization. The best wavefunctions obtained are presented in tables 1 and 2. To produce the scaled wavefunction from the tabulated parameters, simply multiply each ζ_k by η^2 (where η is the scale factor given in the table). The tabulated energy eigenvalue is that obtained after scaling. The method of obtaining more accurate wavefunctions will now be presented.

Longstaff and Singer (1964) worked with a 16-term wavefunction of the form (2.1). They obtained parameters $(\alpha_k, \beta_k, \gamma_k, C_k)$ which yielded an energy of -2.90233 E_h (hartree). Another 16-term wavefunction of the form (2.2) was independently constructed by Poshusta (1979). He arrived at a set of parameters for which the corresponding energy was -2.902446 E_h. It is clear that the wavefunction of Longstaff and Singer (1964) was not fully-optimized; in other words, there is a set of parameters different from theirs which yields a lower energy. The wavefunction of Poshusta (1979) was claimed to be fully-optimized.

When the coefficients C_k are calculated, an analysis may be undertaken to calculate an approximate measure of the weight that each basis function contributes to the wavefunction (see Appendix 3). In attempting to add a 17th basis function to Poshusta's 16-term function, this analysis made it clear that a term of the 16-term wavefunction could be replaced by another with consequent lowering of the energy. Upon this discovery, it was decided to ascertain how much lowering of the energy could be obtained with just 16 terms.

When the 16-term parameters of Longstaff and Singer (1964) were used as starting values to the routine ZXMIN, the resulting energy was substantially lower than that obtained by Poshusta (1979). The resulting parameters were then put through VA04AD and the energy was lowered yet again. However, two of the basis functions had become close to being linearly dependent, as their parameters were almost equal. This was not desirable because of the possibility of numerical instability in the ensuing calculations. The problem was remedied by changing the parameters in one of the two functions to an arbitrary value and then using this resulting set of parameters as a starting value. Several more iterations of the two routines with re-setting of parameters when this became necessary resulted in a 16-term wavefunction with an energy of -2.9034048 E_h. The parameters of this function are listed in Table 3. By way of comparison, the best variational estimate of Frankowski and Pekeris (1966) is -2.903724377 E_h. The wavefunction of Poshusta was most likely a local minimum rather than a global minimum. It is not claimed that our result is a global minimum, as the results are highly dependent on the algorithm used in the minimization and the choice of starting parameters.

Wavefunctions for H^- and Li^+ were also produced in this manner, as the only change required in the program is to the parameter Z, which is 1 for H^- and 3 for Li^+. The starting non-linear parameters were chosen by virial scaling the corresponding parameters for helium. The parameters and energies of these wavefunctions are listed in Tables 4 and 5. The energies for these H^- and Li^+ wavefunctions respectively are -0.5275907 E_h and -7.2794137 E_h as compared with the best variational estimates of Frankowski and Pekeris (1966) of -0.527751016 E_h and -7.279913413 E_h.

TABLE 1.

1-Term Gaussian Geminal Wavefunction for Helium.

ζ_k	η_k	θ_k	C_k
0.76709D+0	0.20733D+1	0.77656D-1	0.1556223964253462D+1

η = 1.000005474502231D+0

E = -2.570885510460622D+0

TABLE 2.

2-Term Gaussian Geminal Wavefunction for Helium.

ζ_k	η_k	θ_k	C_k
0.21262D+1	0.31608D+1	0.47654D-1	0.2099432236690439D+1
0.62377D+0	0.18233D+1	0.82271D-1	0.9037566063862591D+0

η = 1.000001233068744D+0

E = -2.816253182514283D+0

TABLE 3

16-Term Gaussian Geminal Wavefunction for Helium.

ζ_k	η_k	θ_k	C_k
0.27406D+0	0.17537D+1	0.13495D+0	0.7834309794628184D-1
0.59431D+0	0.36160D+1	-0.27228D-2	0.1676512602867212D+0
0.58169D+0	0.15507D+1	0.51985D-1	0.3992914766677912D+0
0.14694D+1	0.38294D+1	0.99758D-2	0.5497096714246338D+0
0.15280D+1	0.94714D+1	0.44024D-2	0.1117496479692804D+0
0.45716D+1	0.16483D+2	0.20879D-2	0.2007585069357208D+0
0.11818D+1	0.11394D+1	-0.57116D+0	-0.9263129489481611D-1
0.13279D+1	0.15803D+1	0.52959D-1	0.8968829761696726D+0
0.40864D+1	0.52673D+1	0.62901D-2	0.6901086242048394D+0
0.15142D+2	0.88235D+1	0.96287D-3	0.5076369840966206D+0
0.17297D+2	0.37974D+2	0.22808D-2	0.1979673096630049D+0
0.36280D+1	0.17395D+1	0.79803D-1	0.9965723414331877D+0
0.23142D+2	0.10000D+1	-0.91316D+0	-0.1751783181217316D+0
0.29556D+0	0.18840D+1	0.30430D+0	-0.2949136827472741D-1
0.41201D+1	0.11206D+1	-0.71306D+0	-0.2055838800345489D+0
0.12762D+2	0.22128D+1	0.12932D+0	0.6340978907609876D+0

η = 1.000023157772717580D+0

E = -2.903404758453900280D+0

TABLE 4.

16-Term Gaussian Geminal Wavefunction for H^-.

ζ_k	η_k	θ_k	C_k
0.10764D+0	0.36857D+1	0.23514D-1	-0.2118219070958106D-1
0.93527D-1	0.86037D+1	-0.97138D-3	-0.6854177628108106D-2
0.11325D+0	0.15640D+1	0.75911D-1	-0.3059306620704317D-2
0.42778D-1	0.42127D+1	-0.61919D-2	-0.3963989030906066D-2
0.22471D+0	0.14861D+2	-0.21259D-2	-0.9869661031178129D-2
0.61039D+0	0.30728D+2	0.14973D-2	-0.9051876416704338D-2
0.15182D+0	0.12909D+1	-0.45030D+0	0.1181921355114989D-1
0.29736D+0	0.17140D+1	0.13637D+0	-0.5898343498764227D-1
0.27521D+0	0.48645D+1	0.21178D-1	-0.4134837501070204D-1
0.25834D+1	0.97931D+1	0.24075D-1	-0.3320430356170277D-1
0.24141D+1	0.51040D+2	-0.76145D-2	-0.1231589642926121D-1
0.73289D+0	0.80306D+1	0.12070D-1	-0.3813148584167367D-1
0.28798D+1	0.10635D+1	-0.85174D+0	0.2677383327375646D-1
0.44447D-1	0.17871D+1	0.11862D+0	-0.3666679948965567D-2
0.54738D+0	0.12002D+1	-0.63871D+0	0.2640970814876181D-1
0.96528D+0	0.21210D+1	0.18354D+0	-0.5661629089258670D-1

η = 1.000017094530687790+0

E = -0.527590692653241725D+0

TABLE 5.

16-Term Gaussian Geminal Wavefunction for Li$^+$.

ζ_k	η_k	θ_k	C_k
0.40690D+2	0.22667D+1	0.74682D-1	-0.2454997368339620D+1
0.23786D+1	0.37194D+1	0.90124D-2	-0.1133930352454319D+1
0.17953D+1	0.14680D+1	-0.51822D-1	-0.4180091584050366D+1
0.54079D+1	0.39475D+1	0.10815D-2	-0.2150403006885588D+1
0.46347D+1	0.97742D+1	0.17035D-2	-0.4609152227833256D+0
0.14035D+2	0.17617D+2	0.23727D-2	-0.7264727500106591D+0
0.18660D+1	0.13660D+1	-0.16997D+0	0.2072147338137456D+1
0.41646D+1	0.15897D+1	0.42559D-1	-0.3959544794961287D+1
0.13511D+2	0.57121D+1	0.29386D-2	-0.2428456590899977D+1
0.49061D+2	0.99546D+1	0.7722DD-3	-0.1744788642472862D+1
0.52705D+2	0.42408D+2	0.10260D-2	-0.6588257693389918D+0
0.78096D+0	0.15028D+1	0.39765D-1	-0.3277403114080187D+0
0.41813D+2	0.10397D+1	-0.89049D+0	0.5454566337361895D+0
0.10866D+1	0.32998D+1	-0.48325D+1	-0.1836948144148076D+0
0.76137D+1	0.11162D+1	-0.72536D+0	0.4536483235045034D+0
0.11488D+2	0.17564D+1	0.67759D-1	-0.3702152587673132D+1

η = 0.9999898370489983D+0

E = -7.279413716535168D+0

CHAPTER 3

VARIATION-ITERATION METHOD

3.1 Wave Equation in Momentum Space (Two-Electron Atom).

The Hamiltonian for a two-electron atom is

$$H = \frac{p_1^2}{2} + \frac{p_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}$$

To write the Schrodinger equation in momentum space, the operators $1/r_1$, $1/r_2$ and $1/r_{12}$ must be transformed to operate on a momentum space function.

We will first examine the transformation of $1/r_1$ to a momentum space operator. In position space the operator $1/r_1$ is a multiplicative operator:

$$(1/r_1)\psi(\vec{r}_1,\vec{r}_2) = g(\vec{r}_1,\vec{r}_2) \tag{3.1}$$

Let us represent the momentum space form of this operator by M:

$$M\ \phi(\vec{p}_1,\vec{p}_2) = f(\vec{p}_1,\vec{p}_2) \tag{3.2}$$

where the functions ψ and ϕ and also f and g are related by the Fourier transform:

$$\phi(\vec{p}_1,\vec{p}_2) = (2\pi)^{-3} \int \psi(\vec{r}_1,\vec{r}_2) \exp(-i(\vec{p}_1\cdot\vec{r}_1 + \vec{p}_2\cdot\vec{r}_2))\, d\vec{r}_1 d\vec{r}_2 \quad (3.3)$$

$$f(\vec{p}_1,\vec{p}_2) = (2\pi)^{-3} \int g(\vec{r}_1,\vec{r}_2) \exp(-i(\vec{p}_1\cdot\vec{r}_1 + \vec{p}_2\cdot\vec{r}_2))\, d\vec{r}_1 d\vec{r}_2 \quad (3.4)$$

Substitution of (3.1) into (3.4) yields:

$$f(\vec{p}_1,\vec{p}_2) = (2\pi)^{-3} \int (\psi(\vec{r}_1,\vec{r}_2)/r_1) \exp(-i(\vec{p}_1\cdot\vec{r}_1 + \vec{p}_2\cdot\vec{r}_2))\, d\vec{r}_1 d\vec{r}_2 \quad (3.5)$$

We must use the Fourier integral representation of $1/r_1$:

$$1/r_1 = 1/(2\pi^2) \int \exp(i\vec{p}\cdot\vec{r}_1)/p^2\, d\vec{p} \quad (3.6)$$

Substituting (3.6) into (3.5) and using (3.3) gives:

$$f(\vec{p}_1,\vec{p}_2) = 1/(2\pi^2) \int \phi(\vec{p}_1-\vec{p},\vec{p}_2)/p^2\, d\vec{p}$$

Therefore, using (3.2):

$$M\, \phi(\vec{p}_1,\vec{p}_2) = \frac{1}{2\pi^2} \int \frac{\phi(\vec{p}_1-\vec{p},\vec{p}_2)}{p^2}\, d\vec{p} \quad (3.7)$$

The operator $1/r_1$ becomes an integral operator in momentum space. By a similar calculation, we find that:

$$\frac{1}{r_2}\,\phi(\vec{p}_1,\vec{p}_2) = \frac{1}{2\pi^2}\int \frac{\phi(\vec{p}_1,\vec{p}_2-\vec{p})}{p^2}\,d\vec{p} \tag{3.8}$$

and

$$\frac{1}{r_{12}}\,\phi(\vec{p}_1,\vec{p}_2) = \frac{1}{2\pi^2}\int \frac{\phi(\vec{p}_1-\vec{p},\vec{p}_2+\vec{p})}{p^2}\,d\vec{p} \tag{3.9}$$

3.2 Description of the VI Method.

Using the results of section 3.1, we may write the Schrodinger equation in momentum space for a two-electron atom as:

$$(p_0^2+p_1^2+p_2^2)\ \phi(\vec{p}_1,\vec{p}_2) = \lambda[ZI_1(\phi)+ZI_2(\phi)-I_{12}(\phi)] \qquad (3.10)$$

where $p_0^2 = -2E$ (3.11)

$$\lambda = \pi^{-2} \qquad (3.12)$$

$$I_1(\phi) = \int p^{-2}\ \phi(\vec{p}_1-\vec{p},\vec{p}_2)\ d\vec{p}$$

$$I_2(\phi) = \int p^{-2}\ \phi(\vec{p}_1,\vec{p}_2-\vec{p})\ d\vec{p} \qquad (3.13)$$

$$I_{12}(\phi) = \int p^{-2}\ \phi(\vec{p}_1-\vec{p},\vec{p}_2+\vec{p})\ d\vec{p}$$

An iterative method of solution based on the Gauss-Hilbert variational principle and the Kellogg theory of iterated functions will be applied to equation (3.10). This technique was first described by Svartholm (1945) and will be referred to as the variation-iteration (VI) method.

In this procedure, λ is regarded as an eigenvalue parameter. An initial function, ϕ^0, is chosen and the following integrals are formed:

$$\phi^{n+1} = (p_0^2+p_1^2+p_2^2)^{-1}[ZI_1(\phi^n)+ZI_2(\phi^n)-I_{12}(\phi^n)] \qquad (3.14)$$

$$W_n = \int \phi^{n+1}(p_0{}^2+p_1{}^2+p_2{}^2)\ \phi^n\ d\vec{p_1}\ d\vec{p_2} \tag{3.15}$$

$$T_n = \int \phi^{n}(p_0{}^2+p_1{}^2+p_2{}^2)\ \phi^n\ d\vec{p_1}\ d\vec{p_2} \tag{3.16}$$

If we let

$$\lambda_n = \frac{T_n}{W_n} \tag{3.17}$$

and

$$\lambda_{n+1/2} = \frac{W_n}{T_{n+1}} \tag{3.18}$$

then $\lambda_0, \lambda_{1/2}, \lambda_1, \ldots$ is a monotonically decreasing sequence which converges to λ, the smallest eigenvalue of (3.10). Also, the sequence $\phi^0, \phi^1, \ldots$ converges to ϕ, the eigenfunction of (3.10) corrresponding to λ. In practice, the number of iterations performed is limited by the ability to solve the resulting integrals of (3.14). The iteration will then be stopped at some ϕ^s and some λ_t. The quantity λ_t is now a function of p_0. Here we may use the actual value of λ and choose p_0 such that

$$\lambda_t = 1/\pi^2 \tag{3.19}$$

This yields a value for E (see eq. (3.11)) which is an upper bound to the actual ground state energy of the system.

3.3 Application of the VI Method to a Gaussian Geminal Wavefunction.

If the wavefunction (2.1) is Fourier transformed, we will obtain a wavefunction in momentum space. This will be labelled ϕ^0 and used as our initial wavefunction for the VI method. Using the result of Appendix 1, we will get a momentum space wavefunction of the following form.

$$\phi^0(\vec{p}_1,\vec{p}_2) = \frac{\pi^{-3/2}}{\sqrt{2}} (1+P_{12}) \sum_{k=1}^{N} \frac{C_k}{(\Delta k)^{3/2}} \exp\left[-\frac{\beta_k}{\Delta k} p_1^2 - \frac{\alpha_k}{\Delta k} p_2^2 - \frac{\gamma_k}{\Delta k} (\vec{p}_1+\vec{p}_2)^2 \right] \tag{3.20}$$

where $\Delta k = (\alpha_k\beta_k + \alpha_k\gamma_k + \beta_k\gamma_k)4$.

We now wish to redefine some of these quantities to simplify the succeeding analysis.

Let $$d_k = \frac{\pi^{-3/2}}{\sqrt{2}} \frac{C_k}{(\Delta k)^{3/2}} \tag{3.21}$$

$$a_k = \frac{\alpha_k}{\Delta k}, \quad b_k = \frac{\beta_k}{\Delta k}, \quad g_k = \frac{\gamma_k}{\Delta k} \tag{3.22}$$

Then

$$\phi^0(\vec{p}_1,\vec{p}_2) = (1+P_{12}) \sum_{k=1}^{N} d_k \exp[-b_k p_1{}^2 - a_k p_2{}^2 - g_k(\vec{p}_1+\vec{p}_2)^2] \tag{3.23}$$

Clearly, interchanging $\vec{p}_1$ and $\vec{p}_2$ with the P_{12} operator is the same as interchanging a_k and b_k with a new operator which we shall call t_k which does the following:

$$t_k\, f(a_k,b_k) = f(b_k,a_k) \tag{3.24}$$

This operator does not change the value of Δk. The wavefunction is now written:

$$\phi^0(\vec{p}_1,\vec{p}_2) = \sum_{k=1}^{N} (1+t_k) d_k \exp[-b_k p_1{}^2 - a_k p_2{}^2 - g_k(\vec{p}_1+\vec{p}_2)^2] \tag{3.25}$$

Finally, we define

$$h_k = \exp[-b_k p_1{}^2 - a_k p_2{}^2 - g_k(\vec{p}_1+\vec{p}_2)^2] \tag{3.26}$$

Thus our wavefunction is written as:

$$\phi^0(\vec{p}_1,\vec{p}_2) = \sum_{k=1}^{N} (1+t_k)\, d_k\, h_k \tag{3.27}$$

The first-iterated wavefunction, ϕ^1, is given as follows:

$$\phi^1 = (p_0{}^2+p_1{}^2+p_2{}^2)^{-1}[ZI_1(\phi^0)+ZI_2(\phi^0)-I_{12}(\phi^0)] \tag{3.28}$$

$$\phi^1 = \sum_{k=1}^{N} (1+t_k)\, d_k \frac{[ZI_1(h_k)+ZI_2(h_k)-I_{12}(h_k)]}{(p_0{}^2+p_1{}^2+p_2{}^2)} \qquad (3.29)$$

We now wish to calculate $\lambda_{1/2}$. The quantities W_0 and T_1 must be calculated to obtain this result. The first of these quantities is given by:

$$W_0 = \sum_{k=1}^{N} \sum_{j=1}^{N} (1+t_k)(1+t_j)\, d_k d_j \int d\vec{p}_1 d\vec{p}_2\, [ZI_1(h_k)+ZI_2(h_k)-I_{12}(h_k)]\, h_j \qquad (3.30)$$

and if we define

$$J_n(k,j) = \int d\vec{p}_1 d\vec{p}_2\, I_n(h_k)\, h_j \qquad (3.31)$$

then

$$W_0 = \sum_{k=1}^{N} \sum_{j=1}^{N} (1+t_k)(1+t_j) d_k d_j [ZJ_1(k,j)+ZJ_2(k,j)-J_{12}(k,j)] \qquad (3.32)$$

We may also use the fact that $(1+t_k)(1+t_j)J_1(k,j) = (1+t_k)(1+t_j)J_2(k,j)$. This is derived by inserting the actual expression for I_1 and I_2 (see Appendix 4) into the J_1 and J_2 integrals. Another such relation is $(1+t_k)(1+t_j)J_{12}(k,j) = 2(1+t_j)J_{12}(k,j)$. The expression for W_0 may now be written:

$$W_0 = 2 \sum_{k=1}^{N} \sum_{j=1}^{N} d_k d_j [Z(1+t_k)(1+t_j)J_1(k,j) - (1+t_j)J_{12}(k,j)] \tag{3.33}$$

Using the calculation of J_n given in Appendix 5, W_0 may be calculated algebraically given the parameters $(\alpha_k, \beta_k, \gamma_k, C_k)$ of a wavefunction.

The quantity T_1 is calculated as follows:

$$T_1 = \int \phi^1 (p_0{}^2 + p_1{}^2 + p_2{}^2) \phi^1 \, d\vec{p}_1 d\vec{p}_2$$

$$= \sum_{k=1}^{N} \sum_{j=1}^{N} (1+t_k)(1+t_j) d_k d_j \int d\vec{p}_1 d\vec{p}_2 \tag{3.34}$$

$$\frac{[ZI_1(h_k)+ZI_2(h_k)-I_{12}(h_k)][ZI_1(h_j)+ZI_2(h_j)-I_{12}(h_j)]}{(p_0{}^2+p_1{}^2+p_2{}^2)}$$

Define

$$K_{m,n}(k,j) = \int \frac{I_m(h_k) I_n(h_j)}{(p_0{}^2+p_1{}^2+p_2{}^2)} d\vec{p}_1 d\vec{p}_2 \tag{3.35}$$

so that

$$T_1=\sum_{k=1}^{N}\sum_{j=1}^{N}(1+t_k)(1+t_j)d_kd_j[Z^2K_{1,1}(k,j)+Z^2K_{1,2}(k,j)$$
$$-ZK_{1,12}(k,j)+Z^2K_{1,2}(j,k)+Z^2K_{2,2}(k,j)-ZK_{2,12}(k,j)$$
$$-ZK_{1,12}(j,k)-ZK_{2,12}(j,k)+K_{12,12}(k,j)] \qquad (3.36)$$

We may take advantage of the symmetry in this summation and write

$$T_1=\sum_{k=1}^{N}\sum_{j=1}^{N}(1+t_k)(1+t_j)d_kd_j[Z^2K_{1,1}(k,j)+Z^2K_{2,2}(k,j)$$
$$+K_{12,12}(k,j)+2Z^2K_{1,2}(k,j)-2ZK_{1,12}(k,j)-2ZK_{2,12}(k,j)] \qquad (3.37)$$

As is the case with the J integrals, there are further symmetries which may be applied to the K integrals. These are

$$(1+t_k)(1+t_j)K_{1,1}(k,j) = (1+t_k)(1+t_j)K_{2,2}(k,j)$$
$$(1+t_k)(1+t_j)K_{1,12}(k,j) = (1+t_k)(1+t_j)K_{2,12}(k,j) \qquad (3.38)$$
$$(1+t_k)(1+t_j)K_{12,12}(k,j) = 2(1+t_j)K_{12,12}(k,j)$$

so we may write

$$T_1=2\sum_{k=1}^{N}\sum_{j=1}^{N} d_k d_j[(1+t_k)(1+t_j)(Z^2K_{1,1}(k,j)+Z^2K_{1,2}(k,j)$$
$$-2ZK_{1,12}(k,j)) + (1+t_j)K_{12,12}(k,j)] \qquad (3.39)$$

These K integrals are reduced in Appendix 6 to one-dimensional integrals. Thus, for a given value of p_0, the quantity T_1 may be calculated with the aid of a single one-dimensional numerical integration.

If the above analysis were to be simplified by using an uncorrelated wavefunction (such as any of those used by Henderson and Scherr (1960)), one need only set the parameters γ_k to zero. It is found in this case that our evaluation of the J, K and I integrals agrees with that of Henderson and Scherr. However, Henderson and Scherr claim that all dependence on p_0 may be factored from the K integrals. As a consequence, these integrals need not be re-evaluated for different values of p_0, resulting in the saving of a great deal of computation time. Unfortunately, this dependence on p_0 cannot be factored and their numerical results are in error. The actual results will be given in the next section.

The computational effort involved in obtaining $\lambda_{1/2}$ from a correlated Gaussian geminal wavefunction is similar to that involved in using wavefunctions of the type used by Henderson and Scherr. The J integrals may be done analytically in both cases, and the K integrals involve a one-dimensional quadrature in both cases. Thus there is no advantage to using initial wavefunctions such as those of Henderson and Scherr.

To obtain an energy bound, we must find a value of p_0 such that

$$\pi^2 W_0 - T_1 = 0 \tag{3.40}$$

The energy corresponding to this value of p_0 will be closer to the true energy of the system than the variational energy E_0 of the initial wavefunction ϕ^0.

To obtain an even better bound on the energy, the technique of Henderson and Scherr could be followed to minimize $\lambda_{1/2}$. Write eqns. (3.30) and (3.34) as

$$W_0 = \sum_{k=1}^{N} \sum_{j=1}^{N} d_k d_j W_{kj} \tag{3.41}$$

$$T_1 = \sum_{k=1}^{N} \sum_{j=1}^{N} d_k d_j T_{kj} \tag{3.42}$$

The equation

$$\lambda_{1/2} = W_0/T_1 \tag{3.43}$$

could be solved as a generalized eigenvalue problem:

$$(\underline{\underline{W}} - \lambda_{1/2}\underline{\underline{T}})\ \underline{D} = 0 \tag{3.44}$$

where the matrix elements of $\underline{\underline{W}}$ and $\underline{\underline{T}}$ are W_{kj} and T_{kj} respectively and $\underline{D}$ is a column vector of the d_k coefficients.

For given values of the non-linear parameters of the wavefunction and of p_0, the eigenvalue $\lambda_{1/2}$ may be obtained. The value given to p_0 should be such that the lowest eigenvalue equals $1/\pi^2$. The non-linear parameters may now be varied, yielding a p_0 with every different set. The highest of these values for p_0 may then be used to calculate an energy bound. The corresponding non-linear parameters and their associated eigenvector would give a wavefunction ϕ^0 that was optimized with respect to $\lambda_{1/2}$. This is a useful approach for wavefunctions with few parameters and terms. Each element of the $\underline{\underline{T}}$ matrix requires a numerical integration for every value of p_0, instead of just one integration per value as in the method previously illustrated. For wavefunctions with more than a few terms, this method becomes too costly. For this reason we used the linear and non-linear parameters of our initial wavefunction ϕ^0 in the calculation of $\lambda_{1/2}$.

3.4 Results.

The limits on the K integrals are zero and infinity. The natural choice of numerical method for this type of integral is Gauss-Laguerre quadrature; however, the results obtained from this method were not sufficiently accurate. An adaptive quadrature algorithm which was suited for an integral over a finite range was employed. This quadrature routine was developed by Thakkar (unpublished) and uses a global acceptance criterion and data representation as a binary tree, as suggested by Malcolm and Simpson (1975). It differs from their technique by the use of a 7-point Clenshaw-Curtis quadrature as the interval integrator and a refined Oliver estimate as the interval error estimator. A number A was chosen and the total integral was split into a sum of an integral from zero to A and another from A to infinity. The selection of A was such that the major contribution to the total integral came from the finite integral. Next, the second integral was transformed to a finite range. Calling the integration variable x, the transformation $x=-1/p_0{}^2 \ln y$ gives us an integral from zero to $\exp(-Ap_0{}^2)$. In this manner, the total integral could be evaluated in two pieces by the adaptive quadrature algorithm. Care had to be taken to ensure that the integrand was correctly evaluated at all points. In some places, the use of series representations of the integrand became necessary to avoid numerical instabilities. This method gave us the accuracy that we needed.

Solving eq.(3.40) was accomplished with a root-finding subroutine using the algorithm of Bus and Dekker (1975). Two values of p_0 must be supplied to the routine, such that the root lies between them. As one bound, the p_0 derived from ϕ^0 was used. As the other bound, p_0 was taken from the best theoretical results of Frankowski and Pekeris (1966).

Henderson and Scherr (1960) used three wavefunctions in their work. These wavefunctions were sums of products of Gaussian orbitals. These consisted of a one-term, one-parameter function (which we refer to as HS1), a one-term, two-parameter function (HS2) and a six-term, three non-linear parameter function (HS3). The ground state energies, E_0, given in Table 6 are the energies of these wavefunctions when they have been optimized variationally. Henderson and Scherr also optimized the parameters with respect to $\lambda_{1/2}$, for which the resulting energy is referred to as $E_{1/2}$. These half-iterated energies which they calculated from their wavefunctions are given in Table 6. The half-iterated energies given in Table 6 for these wavefunctions were recalculated by us using the parameters which they gave. No attempt was made to re-optimize these parameters. We see that their values of this half-iterated energy are in error, probably due to the fact that p_0 does not factor from the K integrals as they claimed.

The remaining wavefunctions in Table 6 are those given in Tables 1,2,3,4 and 5 in Chapter 2. The variational energy obtained earlier is given along with the half-iterated energy which was calculated. This half-iterated energy is not the energy corresponding to ϕ^1 (this corresponding energy would be E_1, the energy calculated from λ_1), but is an upper limit to E_1. The "exact" energies listed at the bottom of the table are due to Frankowski and Pekeris (1966).

It may be seen that for the three 16-term wavefunctions, the energy difference $E_{1/2}$-E(exact) is approximately a factor of 10 less than E_0-E(exact). This continues the trend noted by Henderson and Scherr; that the better the initial wavefunction, the greater is the decrease in absolute error. It must be noted, however, that our $E_{1/2}$ results would be even lower had we varied parameters to minimize $\lambda_{1/2}$ as Henderson and Scherr did.

TABLE 6.

Zeroth Order and Half-Iterated Energies of Several Wavefunctions.

	E_0	$E_{1/2}$	$E_{1/2}$ (Henderson and Scherr)
HS1 (He)	-2.3010	-2.5942	-2.5995
HS2 (He)	-2.5566	-2.7755	-2.7815
HS3 (He)	-2.8511	-2.8818	-2.8915

	E_0	$E_{1/2}$
1-term He (Table 1)	-2.5709	-2.7730
2-term He (Table 2)	-2.8163	-2.8760
16-term H^- (Table 4)	-0.52759	-0.52773
16-term He (Table 3)	-2.90340	-2.90369
16-term Li^+ (Table 5)	-7.27941	-7.27987

H^- E (exact) = -0.527751016

He E (exact) = -2.903724377

Li^+ E (exact) = -7.279913413

CHAPTER 4

CONSTRUCTION OF WAVEFUNCTIONS USING THE GENERATOR COORDINATE METHOD

4.1 The Generator Coordinate Method.

The construction of wavefunctions using the technique given in Chapter 2 rapidly becomes more difficult and time-consuming as the number of terms in the wavefunction rises. To avoid having to optimize all of the non-linear parameters, we make use of what is called the generator coordinate method (GCM). This was first employed in the construction of accurate electronic wavefunctions by Thakkar and Smith (1977) (for the form of these wavefunctions, see eq. (5.8)). Using the GCM, they produced very accurate and compact two-electron Hylleraas-type wavefunctions. The method has been fruitfully employed since then (see, for example, Thakkar (1981)). The GCM will be described and used to generate larger wavefunctions than the 16-term wavefunctions obtained thus far.

Poshusta (1979) refers to the technique of generating parameters as tempering. He presents some tempering functions for Gaussian geminals and the resulting wavefunctions which they generate. However, he did not work within the GCM framework and does not present a method for obtaining his tempering functions.

Wavefunctions are generated using the GCM in the following manner:

$$\psi(\vec{r}) = \int_D K(\vec{t})\ G(\vec{t},\vec{r})\ d\vec{t} \qquad (4.1)$$

where the integration is carried out over the domain D, G is a known generator function and $K(\vec{t})$ is to be determined. To obtain a wavefunction as a sum of a finite number of terms, we may numerically integrate eq.(4.1) to get

$$\psi = \sum_{j=1}^{N} W_j\ K(\vec{t}_j)\ G(\vec{t}_j,\vec{r}) \qquad (4.2)$$

where $\{W_j\}$ and $\{\vec{t}_j\}$ are the weights and abscissae of an integration formula for the domain D. We may combine the known W_j and the unknown $K(\vec{t}_j)$ into unknown linear coefficients D_j.

$$\psi = \sum_{j=1}^{N} D_j\ G(\vec{t}_j,\vec{r}) \qquad (4.3)$$

If we make the association

$$\vec{t} = (\zeta,\eta,\theta) \qquad (4.4)$$

and we make the choice

$$G(\zeta,\eta,\theta,\vec{r}_1,\vec{r}_2)=\frac{\pi^{-3/2}}{\sqrt{2}}\,(1+P_{12})\,\exp(-\zeta\eta r_1^2-\zeta/\eta r_2^2-2\zeta\theta\vec{r}_1\cdot\vec{r}_2) \qquad (4.5)$$

then our wavefunction is of the same form as (2.2), except the parameters $(\zeta_j,\eta_j,\theta_j)$ are now chosen to be the abscissae of some numerical integration formula.

As in chapter two, the domain of integration will be

$$\begin{array}{ll} \zeta_j>0 & \\ \eta_j\geqslant 1 & j=1,\ldots N \\ |\theta_j|<1 & \end{array} \qquad (4.6)$$

The method of integration we choose is a pseudo-random number quadrature (see Hammersley and Handscomb (1964)). However, it is seen from the parameters of the 16-term wavefunction that none of the three sets $\{\zeta_j\}$, $\{\eta_j\}$ or $\{\theta_j\}$ is uniformly distributed. For example, the values of the θ parameter tend to cluster around zero. This suggests that our abscissae $(\zeta_j,\eta_j,\theta_j)$ not be generated by a uniform distribution of pseudo-random numbers. We may make use of this knowledge and the fact that we already have a good 16-term wavefunction (which is better than the 100-term wavefunction with E =-2.90309 E_h obtained by Poshusta (1979) using his tempering methods) by the following methods.

Let us write our wavefunction (4.1) as:

$$\psi = \int_D [K(\vec{t}) - K_{16}(\vec{t})]\, G(\vec{t},\vec{r})\, d\vec{t} + \int_D K_{16}(\vec{t})\, G(\vec{t},\vec{r})\, d\vec{t} \tag{4.7}$$

Define G as in (4.5) and use the domain as given by (4.6). Then choose $K_{16}(\vec{t})$ such that the last integral becomes a sum of 16 unknown coefficients, each multiplied by one of the 16 basis functions used in our 16-term wavefunction. Let us refer to these 16 basis functions as $(\psi_{N+1},\ldots,\psi_{N+16})$. The kernel K_{16} would then have the form of a sum of delta functions. Let us rename the unknown function $K(\vec{t})-K_{16}(\vec{t})$, and call it $K_1(\vec{t})$. We now have

$$\psi = \int_D K_1(\vec{t})\, G(\vec{t},\vec{r})\, d\vec{t} + \sum_{j=N+1}^{N+16} C_j \psi_j \tag{4.8}$$

By incorporating the known 16-term wavefunction in this manner, we have utilized the control variate method (see Hammersley and Handscomb (1964)).

In the remaining integral we wish to proceed as from eq.(4.1), but we wish to distribute the $\vec{t}_j$ non-uniformly. This method, called importance sampling (see Hammersley and Handscomb (1964)), is now outlined.

First we may introduce normalized frequency distribution functions for ζ,η and θ which we will call $u(\zeta)$, $v(\eta)$ and $w(\theta)$. The integral of each of these functions over the domain of their independent variable must be unity for normalization. Equation (4.8) may now be written as:

$$\psi = \int_D \frac{K_1(\zeta,\eta,\theta)\ G(\zeta,\eta,\theta,\vec{r_1},\vec{r_2})}{u(\zeta)v(\eta)w(\theta)}\ u(\zeta)v(\eta)w(\theta)\ d\zeta d\eta d\theta + \sum_{j=N+1}^{N+16} C_j\psi_j \qquad (4.9)$$

This may be approximated by

$$\psi = \frac{1}{N}\sum_{j=1}^{N} \frac{K_1(\zeta_j,\eta_j,\theta_j)}{u(\zeta_j)v(\eta_j)w(\theta_j)}\ G(\zeta_j,\eta_j,\theta_j,\vec{r_1},\vec{r_2}) + \sum_{j=N+1}^{N+16} C_j\psi_j \qquad (4.10)$$

where the ζ_j,η_j,θ_j are distributed according to their frequency functions.

We may now write $K_1/(Nuvw)$ as a coefficient:

$$\psi = \sum_{j=1}^{N} C_j\ G(\zeta_j,\eta_j,\theta_j,\vec{r_1},\vec{r_2}) + \sum_{j=N+1}^{N+16} C_j\psi_j \qquad (4.11)$$

Using this importance sampling scheme, the ζ_j,η_j,θ_j are obtained as follows. Calculate the cumulative probability distributions:

$$U(\zeta)=\int_0^{\zeta} u(x)dx \ , \quad V(\eta)=\int_1^{\eta} v(x)dx \ , \quad W(\theta)=\int_{-1}^{\theta} w(x)dx \qquad (4.12)$$

As our sequences of pseudo-random numbers uniformly distributed on [0,1], we take

$$\begin{aligned} R_{1j} &= \langle\langle\, j(j+1)/2\ \sqrt{2}\,\rangle\rangle \\ R_{2j} &= \langle\langle\, j(j+1)/2\ \sqrt{3}\,\rangle\rangle \\ R_{3j} &= \langle\langle\, j(j+1)/2\ \sqrt{5}\,\rangle\rangle \end{aligned} \qquad (4.13)$$

where $\langle\langle x\rangle\rangle$ denotes the fractional part of x.

Solving the equations

$$\begin{aligned} U(\zeta_j) - R_{1j} &= 0 \qquad j=1,\ldots,N \\ V(\eta_j) - R_{2j} &= 0 \qquad j=1,\ldots,N \\ W(\theta_j) - R_{3j} &= 0 \qquad j=1,\ldots,N \end{aligned} \qquad (4.14)$$

gives us the ζ_j,η_j,θ_j distributed according to their frequency functions, as required for eq. (4.11). Thus, to get a wavefunction of the type (4.11), we must define the frequency functions u, v and w to obtain the 3N parameters $\{\zeta,\eta,\theta\}$. The N+16 coefficients, C_j, may be obtained by using the variational principle, as in Chapter 2. This type of wavefunction may be further improved by introducing constants in the three frequency functions that may be optimized such that the wavefunction yields the minimum variational energy. In this fashion, a wavefunction containing a large number of non-linear parameters may be constructed which requires optimization of only a few non-linear parameters.

4.2 Results.

First a variety of frequency functions were examined by the following exploratory calculations. The frequency function schemes used are given in Table 7. Each set of frequency functions chosen was used to create a 16-term helium wavefunction with parameters generated solely by the GCM (without making use of the 16-term wavefunction of Chapter 2). Each set is listed with the 16-term variational energy obtained with that scheme and the corresponding values of the frequency function parameters. The programs ZXMIN and VA04AD, as described in Chapter 2, were used to vary these frequency function parameters so as to obtain the minimum energy. In the cases where the inverse functions for U, V or W could not be solved explicitly, equations (4.14) were solved using the root-finding program employed in Chapter 3. The value of the parameter ζ,η or θ was then obtained to 5 significant figure accuracy.

Scheme number 5 is a set of frequency functions given by Poshusta (1979). This is his MC1 scheme, with the functions for ζ and η re-written in our notation. In this case, the frequency function parameters are used to tailor the domain of the frequency function. Scheme 8 is also due to Poshusta, as well as the ζ function in scheme 9. Note that schemes 5 and 8 produce values of $\eta>0$ and not $\eta\geq1$. These could not be re-written in our notation.

The remainder of the frequency functions were obtained by attempting to fit a function to histograms of the ζ,η,θ parameters produced from the 16-term wavefunction for helium given earlier in Table 3.

Those sets of frequency functions with the best 16-term variational energy were used to generate a 50-term wavefunction of the form (4.11). Table 8 lists the schemes tested on a 50-term wavefunction of the form (4.11) along with the resulting energies. The frequency function parameters were re-optimized for these wavefunctions. The scheme which yielded the best variational energy, scheme 5, was then used to create 50-term wavefunctions for H^- and Li^+ as well. These 50-term wavefunctions are given in Tables 9, 10 and 11. The first 34 terms are generated from the frequency functions and the last 16 terms use the scaled ζ,η,θ parameters given in Chapter 2. The scaled C values for all 50 terms are presented in the tables. To obtain the scaled 50-term wavefunction, all 50 ζ parameters must be multiplied by the square of the given virial scale factor. For the purposes of comparison, the best variational energies obtained by Frankowski and Pekeris (1966) are also listed in Tables 9,10 and 11.

TABLE 7.

Frequency Function Schemes.

N,M and P represent normalization constants.

1. $u(\zeta) = N\,\zeta\exp(-\zeta/a^2)$
   $v(\eta) = M\,(1+b^2\eta)\,\exp(-\eta/c^2)$
   $w(\theta) = P\,[\cos((\pi/2)\theta) + d(1-\theta^2)]$

   4 parameters
   $a^2 = 0.83513D+0$
   $b^2 = 0.37938D-2$
   $c^2 = 0.16049D+1$
   $d = -0.95213D+0$

   $E_{16} = -2.8655$

2. $u(\zeta) = N\,\zeta^2\,\exp(-\zeta/a^2)$
   $v(\eta)$ as in 1.
   $w(\theta)$ as in 1.

   4 parameters
   $a^2 = 0.37671D+0$
   $b^2 = 0.21881D+2$
   $c^2 = 0.14421D+1$
   $d = -0.38517D+1$

   $E_{16} = -2.8416$

TABLE 7 (cont.)

3. $u(\zeta) = N[\zeta^2\exp(-\zeta/a^2)+(\zeta^2\exp(-\zeta/b^2))/c^2]$
$v(\eta) = M[\eta^2\exp(-\eta/d^2)+(\eta^2\exp(-\eta/f^2))/g^2]$
$w(\theta) = P(1-\theta^2)\exp(-|\theta|)$

6 parameters
$a^2 = 0.16850D+0$
$b^2 = 0.75888D+0$
$c^2 = 0.32423D+2$
$d^2 = 0.99439D+0$
$f^2 = 0.38482D+0$
$g^2 = 0.18030D+0$

$E_{16} = -2.8692$

4. $u(\zeta)$ as in 3.
$v(\eta)$ as in 3.
$w(\theta) = P\cos((\pi/2)\theta)$

6 parameters
$a^2 = 0.15644D+0$
$b^2 = 0.10504D+1$
$c^2 = 0.13347D+3$
$d^2 = 0.11123D+1$
$f^2 = 0.45719D+0$
$g^2 = 0.13974D+0$

$E_{16} = -2.8778$

TABLE 7 (cont.)

5. $$u(\zeta) = \frac{1}{\zeta(b-a)} \qquad \exp(a)<\zeta<\exp(b);\ a<b$$

$$v(\eta) = \frac{1}{\eta(d-c)} \qquad \exp(c)<\eta<\exp(d);\ c<d$$

$\eta_j = (g-f)r_{3j} + f$

6 parameters
$a = -0.17827D+1$
$b = 0.24736D+1$
$c = -0.39728D+1$
$d = 0.55036D-1$
$f = -0.20213D-1$
$g = 0.21210D+0$

$E_{16} = -2.8885$

6. $u(\zeta)$ as in 5.
$v(\eta) = M[(1+c^2\eta)\exp(-\eta/d^2)]$
$w(\theta)$ as in 5.

6 parameters
$a = -0.20539D+1$
$b = 0.39017D+1$
$c^2 = 0.73379D-3$
$d^2 = 0.26055D+1$
$f = 0.48649D-1$
$g = 0.10492D+0$

$E_{16} = -2.8873$

TABLE 7 (cont.)

7. $u(\zeta)$ as in 5.
$v(\eta)$ as in 6.
$w(\theta) = P[f\cos((\pi/2)\theta) + (1-\theta^2)\exp(-g^2|\theta|)]$

6 parameters
$a = 0.34181D+0$
$b = 0.11973D+1$
$c^2 = 0.17316D-1$
$d^2 = 0.19510D+1$
$f = 0.87073D-1$
$g = 0.12503D+2$

$E_{16} = -2.8733$

8. $\zeta_j = \exp(ar_{1j} + br_{4j})$
$\eta_j = \exp(cr_{2j} + dr_{5j})$
$\theta_j = \sin(fr_{3j} + gr_{6j})$

where $r_{nj} = \langle\langle\, j(j+1)/2 \sqrt{\text{n-th prime}} \,\rangle\rangle$

6 parameters
$a = -0.15980D+1$
$b = 0.23520D+1$
$c = -0.43882D+1$
$d = 0.20279D+1$
$f = 0.39170D+0$
$g = -0.18400D+0$

$E_{16} = -2.8905$

9. $\zeta_j = a^2 d^j$ $\quad d>0$
$v(\eta)$ as in 2. (solve using r_{1j})
$w(\theta)$ as in 5. (solve using r_{2j})

6 parameters
$a^2 = 0.22641D+0$
$b^2 = 0.18230D+1$
$c^2 = 0.16169D+1$
$d = 0.12141D+1$
$f = 0.88094D-1$
$g = 0.11022D+0$

$E_{16} = -2.8768$

TABLE 8.

Helium 50-Term GCM Wavefunctions.

scheme 5.
a = -0.88911D+0
b = 0.46896D+1
c = -0.48744D+1
d = -0.61306D+0
f = 0.91202D-2
g = 0.14272D-2

E_{50} = -2.9035403

scheme 8.
a = -0.23111D+1
b = 0.37841D+1
c = -0.40833D+1
d = 0.17611D+1
f = 0.26565D-2
g = 0.12810D-1

E_{50} = -2.9035083

scheme 6.
a = -0.21528D+1
b = 0.35959D+1
c^2= 0.29998D+0
d^2= 0.28094D+1
f = 0.10030D+0
g = 0.21013D-3

E_{50} = -2.9034939

TABLE 9.

H^- 50-Term GCM Wavefunction.

Scaled C_j
-0.6973159882613982D-01
0.5765894424798000D-03
0.6354085026286149D-02
0.9330235426230553D-03
-0.1185541770415685D-01
0.1302365388874927D-02
0.9496570405005006D-02
0.8354259942526741D-02
-0.5299596166016247D-02
0.3876140541411643D-02
-0.2558896606950276D-03
0.2360205668810851D-03
0.8210858865191725D-02
-0.3057435719427838D-01
-0.1968691555044590D-01
0.1214485506628942D+00
0.2982036446372525D-04
0.9921614159545529D-02
0.9249324820678532D-03
0.1168671902450335D-01
0.5135706976650327D-03
-0.1044387559891311D-01
-0.2750161096602315D-03
-0.5555145003776513D-02
0.4243332132486493D-01
0.3678184518082852D-01
0.2256171780897080D-01
-0.3868462459515158D-03
-0.1141638450893223D-02
0.7783289681930299D-04
0.6399013757489044D-03
0.7549021777770289D-02
0.7745272777340250D-01
0.2048499975522868D-01
0.2103326403176208D-01
0.6968701937464148D-02
0.3037631734240636D-01
0.3985689222784572D-02
0.9660006913329909D-02

TABLE 9 (cont.)

0.5971828765146128D-02
-0.1171511063252401D-01
0.6437753434906017D-01
0.4154004513992137D-01
-0.3443371088982349D-02
0.6416806221128636D-02
-0.1166847997855307D+00
-0.2729872040450338D-01
0.3662636302404848D-02
-0.2585767386360977D-01
0.4424064794637419D-01

The first 34 $\zeta_j, \eta_j, \theta_j$ are generated by scheme 8 with

a = -0.19591D+1
b = 0.27927D+1
c = -0.57545D+1
d = 0.67720D+0
f = 0.48333D-3
g = 0.77444D-1

The last 16 $\zeta_j, \eta_j, \theta_j$ are the scaled parameters from Table 4.

For this 50-term wavefunction

η = 0.9998026999743541
E = -0.5276490714302323

E (exact) = -0.527751016

TABLE 10.

He 50-Term GCM Wavefunction.

Scaled C_j
-0.2044849692548567D+01
0.1638134040063559D-02
0.8410181029456954D-01
0.1591524656650429D-02
0.2921928756872029D-01
0.5854348342452844D-02
0.1330628825756143D+00
0.6611231646619084D-01
0.2212650930438624D+00
0.2404905260678761D+00
0.9768499075473357D-02
-0.7556989709028050D-02
0.4503389659690509D+00
0.2404861612260007D-01
0.8973348921218027D-01
0.1332865116234977D+00
-0.3512878259311028D-02
0.3232059721941153D+00
0.7015079206625750D-01
0.2400403013660101D+00
-0.3197999925458807D-01
-0.4788426059332739D+00
0.7008309149703888D-02
-0.2549500550705289D+00
-0.4560896070772198D+00
-0.1292036934417369D+00
0.4711878312494276D+00
-0.8862275384122093D-03
-0.6088236317964243D-02
-0.1974354534551892D-01
0.5013504499162201D-02
-0.7194474664480702D-02
0.3492274751215179D+00
0.2519260122097870D+00
0.7833207518978851D-01
0.1669775886472045D+00
0.3994481139480899D+00
0.5309209518317787D+00
0.2579723692030408D+00
-0.7685188701656463D-01
-0.9331227322743397D-01

TABLE 10 (cont.)

0.8786033790756235D+00
0.2295992414956630D+01
-0.3458040227603057D+00
0.9858676046927818D-01
0.1060605386850110D+01
-0.1744076248418728D+00
-0.2943803221666693D-01
-0.2026603919946295D+00
0.7106931725602302D+00

The first 34 $\zeta_j, \eta_j, \theta_j$ are generated by scheme 8 with

a = -0.88911D+0
b = 0.46896D+1
c = -0.48744D+1
d = -0.61306D+0
f = 0.91202D-2
g = 0.14272D-2

The last 16 $\zeta_j, \eta_j, \theta_j$ are the scaled parameters from Table 3.

For this 50-term wavefunction

η = 0.9999587801679417
E = -2.903540316632166

E (exact) = -2.903724377

TABLE 11.

Li$^+$ 50-Term Wavefunction.

Scaled C_j
0.1551822399486184D+00
0.3505140368128134D-05
-0.3317831396308162D-02
0.5727946746535948D-03
0.3296883308068918D-02
-0.3038264302497086D-01
-0.3613625436313713D+00
-0.1553886161063876D+01
-0.2665172133158871D+01
-0.8210395158300870D+00
-0.6394508562872439D-03
0.9894266426500836D-03
-0.8464339304195829D+00
-0.2648147840257026D+01
-0.1412447414883455D+01
0.4264966096643472D-02
0.5320119917025612D-03
-0.6100388438369612D+00
-0.2967731712026773D-01
-0.7191552991324749D+00
0.1279602246884527D-01
0.1003336115112577D+01
-0.1025588107539613D-02
0.6321328964742434D-02
-0.2998683790558917D+01
-0.1593937413177974D+00
-0.6403310149787437D+00
-0.2040221207925509D-03
-0.1443415208727508D-02
0.4694752496447185D-01
-0.4084523388829902D-03
-0.6395852658557166D+00
-0.1413016363937362D+00
0.4231240143398764D-01
-0.2273420669298360D+01
-0.9851183680516158D+00
-0.4167477469436565D+01
0.8783830172437716D+00
-0.3341033075685406D+00
0.6228958323627976D+00
0.2070196944196083D+01

TABLE-11 (cont.)

-0.3913370820578325D+01
-0.4254104083479847D+00
-0.9516261920520188D+00
0.1124843060413084D+01
-0.3284290725065104D+00
0.5373293157833873D+00
-0.1934462281368806D+00
0.4528219226240417D+00
-0.3878740112981642D+01

The first 34 $\zeta_j, \eta_j, \theta_j$ are generated by scheme 8 with

a = -0.13507D+1
b = 0.46964D+1
c = -0.51795D+1
d = -0.80685D+0
f = 0.42967D-2
g = 0.44753D-3

The last 16 $\zeta_j, \eta_j, \theta_j$ are the scaled parameters from Table 5.

For this 50-term wavefunction

η = 0.9999977473342717
E = -7.279570470472180

E (exact) = -7.279913413

CHAPTER FIVE

MOMENTUM DENSITIES AND COMPTON PROFILES

5.1 Formulae.

From a two-electron wavefunction, one may calculate the following quantities.

The one-electron momentum density, $\Pi(\vec{p})$, is

$$\Pi(\vec{p}) = 2 \int \phi^*(\vec{p},\vec{p}_2)\phi(\vec{p},\vec{p}_2)\, d\vec{p}_2 \qquad (5.1)$$

The spherically averaged momentum density, $\bar{\Pi}(p)$, is

$$\bar{\Pi}(p) = \frac{1}{4\pi} \int_0^{\pi} d\theta \int_0^{2\pi} d\phi\, \Pi(p,\theta,\phi) \sin\theta \qquad (5.2)$$

The radial momentum density, $I(p)$, is given by

$$I(p) = 4\pi p^2 \bar{\Pi}(p) \qquad (5.3)$$

The spherically averaged Compton profile, $J(q)$, which is the experimentally accessible quantity if measurements are taken on the liquid or gas phase, is given within the impulse approximation by (see Williams (1977))

$$J(q) = \frac{1}{2} \int_{|q|}^{\infty} \frac{I(p)}{p}\, dp \qquad (5.4)$$

The momentum expectation values may be derived from

$$\langle p^k \rangle = \int_0^\infty I(p) p^k \, dp \qquad (-3<k<5) \qquad (5.5)$$

The function J(q) may be expanded about the origin in a Taylor series, in the form

$$J(q) = \sum_{k=0}^{\infty} \frac{J^{(k)}(0)\, q^k}{k!} \qquad (5.6)$$

The coefficients of the odd powers of q must vanish, as J(q) is an even function. The even order derivatives of J(q) may be calculated in terms of $\Pi(p)$ using eqns. (5.4) and (5.3). The following expansion is obtained:

$$J(q) = J(0) - 2\pi \sum_{n=1}^{\infty} \frac{(2n-1)}{(2n)!} \, \overline{\Pi}^{(2n-2)}(0)\, q^{2n} \qquad (5.7)$$

Thus, calculation of the first few even order derivatives of $\overline{\Pi}(p)$ at p=0 along with J(0) would allow us to approximate the function J(q) near to the origin.

5.2 Momentum Densities from Hylleraas-Type Wavefunctions.

The two-electron wavefunctions obtained by Thakkar and Smith (1977) are highly accurate with only a few terms. These wavefunctions have the following form:

$$\psi = (4\pi)^{-1} \sum_{k=1}^{N} C_k(1+P_{12})\exp(-\alpha_k r_1 - \beta_k r_2 - \gamma_k r_{12}) \tag{5.8}$$

A paper by Benesch (1976) describes how to calculate the momentum density and Compton profile from a class of wavefunctions which includes those of Thakkar and Smith as a special case. Benesch calculated the momentum density and Compton profile for He using the RHF wavefunction of Clementi (1965) and a Hylleraas-type wavefunction of Bonham and Kohl (1966). The variational energy of this second wavefunction was -2.903486 E_h.

The calculation of a momentum density from the Thakkar and Smith wavefunctions involves performing a two-dimensional quadrature. The integrand given by Benesch is a complicated function which had to be successively differentiated with respect to five different variables. These differentiations involved large expressions and were done with the help of the symbolic algebra computer language, MACSYMA.

Two computer routines were used to perform the double integration. Both routines, DMLIN and DBLIN, were taken from the IMSL library.

The integrand was found to be highly unstable. Even simple rearrangements of the integrand resulted in different answers. It became clear that the attempt to cast the problem in a form where the numerics became stable would involve a great deal of computer time if, in fact, it could be done at all. This approach was abandoned in favor of attempting to use the momentum space wavefunctions which have been calculated.

5.3 The First-Iterated Wavefunction ϕ^1.

The momentum density of the first-iterated wavefunction is obtained by substituting equation (3.29) for ϕ^1 into the formula (5.1). A typical integral which results is:

$$\int \frac{I_1(h_k)\ I_1(h_j)}{(p_0{}^2+p_1{}^2+p_2{}^2)^2}\, d\vec{p}_2 \qquad (5.9)$$

Substitution of the integral representation for I_1 given in Appendix 4, enabled this integral to be reduced to:

$$\frac{8\pi^4}{\sqrt{(b_k+g_k)(b_j+g_j)}} \int_0^1 du \cdot \int_0^1 dy\ \frac{\exp(-Lp_1{}^2)}{Np_1} \int_{-\infty}^{\infty} dp_2\ \frac{p_2\exp(-Mp_2{}^2+Np_1p_2)}{(p_0{}^2+p_1{}^2+p_2{}^2)^2} \qquad (5.10)$$

where $L = (b_k+g_k)(1-u^2) + (b_j+g_j)(1-y^2)$

$M = a_k+g_k+a_j+g_j-g_k{}^2/(b_k+g_k)-g_j{}^2y^2/(b_j+g_j)$

$N = g_k(2-u^2) + g_j(2-y^2)$

Attempts to reduce this integral further were unsuccessful. Integrals such as these would also require evaluation to normalize ϕ^1, except they would have to be integrated over p_1 as well. Thus, no numerical results for the momentum density could be obtained using ϕ^1.

5.4 Gaussian Geminal Wavefunctions.

The evaluation of $\overline{\Pi}(p)$ and J(q) using Gaussian geminal wavefunctions of the form (2.1) is found to be quite simple. All of the resulting integrals may be evaluated analytically. The derivatives of $\overline{\Pi}(p)$ at the origin and the expectation values $<p^k>$ may also be evaluated analytically. These results are given in Appendix 7.

The results of these calculations using the 16-term wavefunctions of He (Table 3), H^- (Table 4) and Li^+ (Table 5) are given in Tables 12, 17 and 19 respectively. These calculations were also performed using the three 50-term wavefunctions of Tables 9, 10 and 11. These results are presented in Tables 13, 18 and 20.

Included for comparison are some Compton profiles and momentum densities for helium which have been calculated previously. Table 15 contains the data of Benesch (1976), who used the wavefunction of Bonham and Kohl (1966) which has a variational energy of -2.903486 E_h. Evaluation of the momentum density required a two-dimensional quadrature. Another numerical integration is required to obtain J(q). Table 16 contains the helium Compton profile given by Eisenberger (1970) using the wavefunction of Sabelli and Hinze (1969). Table 14 gives a momentum density and Compton profile calculated analytically by us from a HF wavefunction produced by Szalewicz and Monkhorst (1981).

The values obtained for $<p^4>$ for helium may be compared with the best theoretical result of 108.17604 due to Pekeris (1959). The 50-term wavefunction has a value of $<p^4>$ closest to this result although it is still not very accurate. It is known that the expectation values $<p^{-2}>$ and $<p^4>$ converge very slowly when Gaussian orbitals are used (Simas et al (1982)). This is also true of Gaussian geminals as even 50 terms does not give very good accuracy. It has been shown that the momentum density behaves asymptotically as p^{-8} (Thakkar et al (1981)). Our expression of the momentum density (see Appendix 7) decays as a Gaussian. This leads one to suspect that the value of $<p^4>$ when using Gaussians should be underestimated.

The graph in Figure 1 shows the Compton profiles of the 16-term, 50-term, Benesch and Sabelli-Hinze helium wavefunctions after subtracting the HF Compton profile and multiplying by 100. It is seen that the Compton profiles from the 16-term and 50-term wavefunctions vary only slightly from each other while the others are considerably different.

TABLE 12.

Momentum Density and Compton Profile of a He 16-Term Scaled Wavefunction

p	$\bar{\Pi}(p)$	I(p)	J(p)
0.00	0.4322424D+00	0.0000000D+00	0.1067073D+01
0.04	0.4310468D+00	0.8666711D-02	0.1064904D+01
0.08	0.4274840D+00	0.3438030D-01	0.1058430D+01
0.10	0.4248351D+00	0.5338635D-01	0.1053611D+01
0.14	0.4178673D+00	0.1029211D+00	0.1040903D+01
0.18	0.4087899D+00	0.1664390D+00	0.1024283D+01
0.20	0.4035126D+00	0.2028276D+00	0.1014586D+01
0.30	0.3707735D+00	0.4193349D+00	0.9538178D+00
0.40	0.3301803D+00	0.6638669D+00	0.8768488D+00
0.50	0.2856598D+00	0.8974268D+00	0.7899726D+00
0.60	0.2408387D+00	0.1089528D+01	0.6992725D+00
0.70	0.1985723D+00	0.1222713D+01	0.6098899D+00
0.80	0.1607344D+00	0.1292702D+01	0.5256268D+00
0.90	0.1282449D+00	0.1305374D+01	0.4488759D+00
1.00	0.1012554D+00	0.1272413D+01	0.3807905D+00
1.20	0.6202612D-01	0.1122398D+01	0.2708235D+00
1.40	0.3777571D-01	0.9304191D+00	0.1914535D+00
1.60	0.2315674D-01	0.7449504D+00	0.1354964D+00
1.80	0.1435793D-01	0.5845838D+00	0.9639547D-01
2.00	0.9020267D-02	0.4534081D+00	0.6912104D-01
2.50	0.3016609D-02	0.2369239D+00	0.3146390D-01
3.00	0.1119480D-02	0.1266102D+00	0.1531016D-01
3.50	0.4557532D-03	0.7015776D-01	0.7906329D-02
4.00	0.2003219D-03	0.4027711D-01	0.4299766D-02
4.50	0.9396853D-04	0.2391208D-01	0.2446822D-02
5.00	0.4656546D-04	0.1462897D-01	0.1449658D-02
5.50	0.2421062D-04	0.9203247D-02	0.8909870D-03
6.00	0.1316504D-04	0.5955724D-02	0.5660912D-03
6.50	0.7465081D-05	0.3963429D-02	0.3702091D-03
7.00	0.4391610D-05	0.2704143D-02	0.2481040D-03
7.50	0.2662733D-05	0.1882175D-02	0.1698033D-03
8.00	0.1654197D-05	0.1330385D-02	0.1184465D-03
8.50	0.1049119D-05	0.9525168D-03	0.8414214D-04
9.00	0.6784537D-06	0.6905818D-03	0.6085264D-04
9.50	0.4475571D-06	0.5075812D-03	0.4478110D-04
10.00	0.3014219D-06	0.3787779D-03	0.3349620D-04

TABLE 12 (cont.)

$\bar{\Pi}^{(2)}(0) = -1.49692927059849565\text{D}{+}00$

$\bar{\Pi}^{(4)}(0) = 1.87005608248628361\text{D}{+}01$

$\bar{\Pi}^{(6)}(0) = -4.37038484702093022\text{D}{+}02$

$\bar{\Pi}^{(8)}(0) = 1.54577226125649377\text{D}{+}04$

$\bar{\Pi}^{(10)}(0) = -7.43318992093996669\text{D}{+}05$

$\langle p^{-2} \rangle = 4.06261675825547675\text{D}{+}00$

$\langle p^{-1} \rangle = 2.13414659758152403\text{D}{+}00$

$\langle p^{0} \rangle = 2.00000000000000028\text{D}{+}00$

$\langle p \rangle = 2.81515096549407073\text{D}{+}00$

$\langle p^{2} \rangle/2 = 2.90340475845379697\text{D}{+}00$

$\langle p^{3} \rangle = 1.83769673304682835\text{D}{+}01$

$\langle p^{4} \rangle = 1.03604044985572354\text{D}{+}02$

TABLE 13.

Momentum Density and Compton Profile of a He 50-Term Scaled Wavefunction.

p	$\bar{\Pi}(p)$	I(p)	J(p)
0.00	0.4327687D+00	0.0000000D+00	0.1067273D+01
0.04	0.4315682D+00	0.8677193D-02	0.1065101D+01
0.08	0.4279909D+00	0.3442107D-01	0.1058620D+01
0.10	0.4253315D+00	0.5344873D-01	0.1053795D+01
0.14	0.4183370D+00	0.1030368D+00	0.1041073D+01
0.18	0.4092267D+00	0.1666168D+00	0.1024435D+01
0.20	0.4039314D+00	0.2030380D+00	0.1014727D+01
0.30	0.3710945D+00	0.4196980D+00	0.9539013D+00
0.40	0.3304088D+00	0.6643262D+00	0.8768726D+00
0.50	0.2858108D+00	0.8979010D+00	0.7899435D+00
0.60	0.2409252D+00	0.1089920D+01	0.6992031D+00
0.70	0.1986054D+00	0.1222917D+01	0.6097967D+00
0.80	0.1607276D+00	0.1292648D+01	0.5255282D+00
0.90	0.1282146D+00	0.1305066D+01	0.4487881D+00
1.00	0.1012173D+00	0.1271935D+01	0.3807238D+00
1.20	0.6200085D-01	0.1121941D+01	0.2708030D+00
1.40	0.3776968D-01	0.9302705D+00	0.1914573D+00
1.60	0.2315979D-01	0.7450485D+00	0.1355010D+00
1.80	0.1436160D-01	0.5847332D+00	0.9639195D-01
2.00	0.9021684D-02	0.4534793D+00	0.6911136D-01
2.50	0.3015311D-02	0.2368219D+00	0.3145796D-01
3.00	0.1119017D-02	0.1265578D+00	0.1531219D-01
3.50	0.4558398D-03	0.7017108D-01	0.7909627D-02
4.00	0.2004703D-03	0.4030694D-01	0.4301401D-02
4.50	0.9404471D-04	0.2393146D-01	0.2446938D-02
5.00	0.4657995D-04	0.1463352D-01	0.1449147D-02
5.50	0.2419743D-04	0.9198234D-02	0.8905111D-03
6.00	0.1314740D-04	0.5947741D-02	0.5659181D-03
6.50	0.7452831D-05	0.3956926D-02	0.3703364D-03
7.00	0.4386403D-05	0.2700937D-02	0.2484141D-03
7.50	0.2662776D-05	0.1882205D-02	0.1701669D-03
8.00	0.1657028D-05	0.1332661D-02	0.1187700D-03
8.50	0.1052788D-05	0.9558474D-03	0.8437798D-04
9.00	0.6817972D-06	0.6939850D-03	0.6099033D-04
9.50	0.4500714D-06	0.5104327D-03	0.4483319D-04
10.00	0.3030231D-06	0.3807901D-03	0.3348551D-04

TABLE 13 (cont.)

$\overline{\Pi}^{(2)}(0) = -1.50311334931482063\mathrm{D}{+}00$
$\overline{\Pi}^{(4)}(0) = 1.89647658410584987\mathrm{D}{+}01$
$\overline{\Pi}^{(6)}(0) = -4.53537462161925767\mathrm{D}{+}02$
$\overline{\Pi}^{(8)}(0) = 1.51714377179646049\mathrm{D}{+}04$
$\overline{\Pi}^{(10)}(0) = 1.03082143646830846\mathrm{D}{+}05$
$\langle p^{-2}\rangle = 4.06494178097705672\mathrm{D}{+}00$
$\langle p^{-1}\rangle = 2.13454699955583432\mathrm{D}{+}00$
$\langle p^{0}\rangle = 2.00000000000000800\mathrm{D}{+}00$
$\langle p\rangle = 2.81502329479204283\mathrm{D}{+}00$
$\langle p^{2}\rangle/2 = 2.90354031663256112\mathrm{D}{+}00$
$\langle p^{3}\rangle = 1.83996638378424993\mathrm{D}{+}01$
$\langle p^{4}\rangle = 1.06076272511062569\mathrm{D}{+}02$

TABLE 14.

Momentum Density and Compton Profile from the HF Wavefunction of Szalewicz and Monkhorst (1981).

p	$\overline{\Pi}(p)$	I(p)	J(p)
0.00	0.4398504D+00	0.0000000D+00	0.1070484D+01
0.04	0.4385594D+00	0.8817760D-02	0.1068276D+01
0.08	0.4347158D+00	0.3496192D-01	0.1061692D+01
0.10	0.4318618D+00	0.5426936D-01	0.1056791D+01
0.14	0.4243693D+00	0.1045225D+00	0.1043880D+01
0.18	0.4146399D+00	0.1688208D+00	0.1027012D+01
0.20	0.4090000D+00	0.2055858D+00	0.1017179D+01
0.30	0.3742743D+00	0.4232942D+00	0.9557135D+00
0.40	0.3318248D+00	0.6671734D+00	0.8781956D+00
0.50	0.2859884D+00	0.8984589D+00	0.7910629D+00
0.60	0.2405239D+00	0.1088105D+01	0.7003825D+00
0.65	0.2188331D+00	0.1161849D+01	0.6553289D+00
0.70	0.1981765D+00	0.1220276D+01	0.6111609D+00
0.80	0.1605861D+00	0.1291510D+01	0.5270326D+00
0.90	0.1284386D+00	0.1307346D+01	0.4502677D+00
1.00	0.1017259D+00	0.1278325D+01	0.3819769D+00
1.20	0.6264934D-01	0.1133676D+01	0.2711902D+00
1.30	0.4893299D-01	0.1039198D+01	0.2276595D+00
1.40	0.3818817D-01	0.9405779D+00	0.1909541D+00
1.60	0.2331840D-01	0.7501508D+00	0.1344722D+00
1.80	0.1437141D-01	0.5851327D+00	0.9520763D-01
2.00	0.8978890D-02	0.4513282D+00	0.6798136D-01
2.50	0.2974641D-02	0.2336278D+00	0.3065797D-01
3.00	0.1092550D-02	0.1235645D+00	0.1479699D-01
3.50	0.4404606D-03	0.6780364D-01	0.7603997D-02
4.00	0.1924043D-03	0.3868517D-01	0.4129005D-02
4.50	0.9000356D-04	0.2290312D-01	0.2352036D-02
5.00	0.4464672D-04	0.1402618D-01	0.1396803D-02
5.50	0.2329908D-04	0.8856741D-02	0.8603056D-03
6.00	0.1270812D-04	0.5749018D-02	0.5471459D-03
6.50	0.7206001D-05	0.3825876D-02	0.3580102D-03
7.00	0.4229093D-05	0.2604073D-02	0.2402612D-03
7.50	0.2559287D-05	0.1809053D-02	0.1649379D-03
8.00	0.1591967D-05	0.1280335D-02	0.1155635D-03
8.50	0.1015115D-05	0.9216437D-03	0.8247699D-04
9.00	0.6619845D-06	0.6738182D-03	0.5985729D-04
9.50	0.4406052D-06	0.4996969D-03	0.4410891D-04
10.00	0.2987789D-06	0.3754566D-03	0.3296039D-04

TABLE 14 (cont.)

$\bar{\Pi}^{(2)}(0) = -0.1616838423772048D+01$
$\bar{\Pi}^{(4)}(0) = 0.2317224196265785D+02$
$\bar{\Pi}^{(6)}(0) = -0.6809283361710810D+03$
$\bar{\Pi}^{(8)}(0) = 0.3323886323791572D+05$
$\bar{\Pi}^{(10)}(0) = -0.2412896247057461D+07$
$\langle p^{-2} \rangle = 4.09233$
$\langle p^{-1} \rangle = 2J(0)$ (These expectation values are
$\langle p \rangle = 2.798956$ due to Simas et al (1983)).
$\langle p^{2} \rangle/2 = 2.8616794$
$\langle p^{3} \rangle = 17.9903$
$\langle p^{4} \rangle = 105.6156$

TABLE 15.

Momentum Density and Compton Profile
from Benesch (1976).

p	I(p)	J(p)
0.00	0.00000D+0	0.10685D+1
0.04	0.89703D-2	0.10662D+1
0.08	0.35557D-1	0.10595D+1
0.10	0.55181D-1	0.10545D+1
0.14	0.10622D+0	0.10414D+1
0.18	0.17144D+0	0.10243D+1
0.20	0.20868D+0	0.10143D+1
0.30	0.42850D+0	0.95198D+0
0.40	0.67298D+0	0.87365D+0
0.50	0.90250D+0	0.78594D+0
0.60	0.10881D+1	0.69505D+0
0.70	0.12148D+1	0.60603D+0
0.80	0.12803D+1	0.52246D+0
0.90	0.12913D+1	0.44650D+0
1.00	0.12591D+1	0.37915D+0
1.20	0.11139D+1	0.27020D+0
1.40	0.92600D+0	0.19131D+0
1.60	0.74280D+0	0.13646D+0
1.80	0.58426D+0	0.97374D-1
2.00	0.45498D+0	0.70067D-1
2.50	0.24090D+0	0.32060D-1
3.00	0.12937D+0	0.14795D-1
3.50	0.71544D-1	0.80250D-2
4.00	0.40926D-1	0.43528D-2
4.50	0.24221D-1	0.24729D-2
5.00	0.14806D-1	0.14635D-2
5.50	0.9327D-2	0.8980D-3
6.00	0.6037D-2	0.5686D-3
6.50	0.4009D-2	0.3702D-3
7.00	0.2723D-2	0.2469D-3
7.50	0.1888D-2	0.1683D-3
8.00	0.1334D-2	0.1168D-3
8.50	0.9589D-3	0.8234D-4
9.00	0.7003D-3	0.5882D-4
9.50	0.5188D-3	0.4246D-4
10.00	0.3896D-3	0.3089D-4

$\Pi(0) = 0.447$ (see Simas (1982))

$\langle p^{-2}\rangle = 4.111$ These expectation values come from unpublished results of Thakkar, Smith and Simas.

$\langle p\rangle = 2.843$

$\langle p^{2}\rangle = 6.040$

$\langle p^{3}\rangle = 20.37$

$\langle p^{4}\rangle = 128.1$

TABLE 16.

Compton Profile from the Wavefunction of Sabelli and Hinze (1969).

p	J(p)
0.00	0.1068D+1
0.10	0.1055D+1
0.20	0.1015D+1
0.30	0.954D+0
0.40	0.876D+0
0.50	0.788D+0
0.60	0.698D+0
0.70	0.609D+0
0.80	0.525D+0
0.90	0.449D+0
1.00	0.381D+0
1.20	0.271D+0
1.40	0.191D+0
1.60	0.135D+0
1.80	0.096D+0
2.00	0.069D+0
2.50	0.031D+0
3.00	0.015D+0

TABLE 17.

Momentum Density and Compton Profile of a H^- 16-Term Scaled Wavefunction.

p	$\bar{\Pi}(p)$	I(p)	J(p)
0.00	0.1723720D+02	0.0000000D+00	0.3218702D+01
0.04	0.1650038D+02	0.3317599D+00	0.3133927D+01
0.08	0.1451290D+02	0.1167197D+01	0.2900491D+01
0.10	0.1321616D+02	0.1660792D+01	0.2743831D+01
0.14	0.1041121D+02	0.2564290D+01	0.2389690D+01
0.18	0.7761457D+01	0.3160080D+01	0.2027734D+01
0.20	0.6602357D+01	0.3318707D+01	0.1856762D+01
0.30	0.2788833D+01	0.3154095D+01	0.1179925D+01
0.40	0.1251340D+01	0.2515968D+01	0.7699058D+00
0.50	0.6268279D+00	0.1969238D+01	0.5197528D+00
0.60	0.3409368D+00	0.1542362D+01	0.3599393D+00
0.70	0.1971148D+00	0.1213739D+01	0.2539482D+00
0.80	0.1190979D+00	0.9578420D+00	0.1846057D+00
0.90	0.7421552D-01	0.7554220D+00	0.1312700D+00
1.00	0.4735564D-01	0.5950885D+00	0.9578891D-01
1.20	0.2041488D-01	0.3694189D+00	0.5233657D-01
1.40	0.9339921D-02	0.2300431D+00	0.2952714D-01
1.60	0.4486279D-02	0.1443232D+00	0.1719934D-01
1.80	0.2258266D-02	0.9194538D-01	0.1033801D-01
2.00	0.1187793D-02	0.5970500D-01	0.6395733D-02
2.50	0.2778493D-03	0.2182223D-01	0.2152173D-02
3.00	0.7825856D-04	0.8850835D-02	0.8361506D-03
3.50	0.2594291D-04	0.3993601D-02	0.3646349D-03
4.00	0.9699618D-05	0.1950224D-02	0.1738346D-03
4.50	0.3985172D-05	0.1014103D-02	0.8941945D-04
5.00	0.1784421D-05	0.5605925D-03	0.4910798D-04
5.50	0.8627563D-06	0.3279619D-03	0.2843019D-04
6.00	0.4437940D-06	0.2007677D-03	0.1715053D-04
6.50	0.2392015D-06	0.1269991D-03	0.1069907D-04
7.00	0.1336337D-06	0.8228523D-04	0.6877934D-05
7.50	0.7697205D-07	0.5440833D-04	0.4551598D-05
8.00	0.4566247D-07	0.3672394D-04	0.3099388D-05
8.50	0.2792925D-07	0.2535754D-04	0.2169194D-05
9.00	0.1763480D-07	0.1795005D-04	0.1556725D-05
9.50	0.1149535D-07	0.1303705D-04	0.1141696D-05
10.00	0.7722869D-08	0.9704843D-05	0.8523696D-06

TABLE 17 (cont.)

$\bar{\Pi}^{(2)}(0) = -9.46154011132922903D+02$

$\bar{\Pi}^{(4)}(0) = 1.92380770607384835D+05$

$\bar{\Pi}^{(6)}(0) = -7.29792932724249177D+07$

$\bar{\Pi}^{(8)}(0) = 4.16584772151196289D+10$

$\bar{\Pi}^{(10)}(0) = -3.21517550114579478D+13$

$\langle p^{-2} \rangle = 4.27004883298870839D+01$

$\langle p^{-1} \rangle = 6.43740331669148202D+00$

$\langle p^{0} \rangle = 2.00000000000000056D+00$

$\langle p \rangle = 1.11485282148915082D+00$

$\langle p^{2} \rangle / 2 = 5.27590692653263194D-01$

$\langle p^{3} \rangle = 1.65457330236620045D+00$

$\langle p^{4} \rangle = 4.67214541490788626D+00$

TABLE 18.

Momentum Density and Compton Profile of a H^- 50-Term Scaled Wavefunction.

p	$\overline{\Pi}(p)$	I(p)	J(p)
0.00	0.1733569D+02	0.0000000D+00	0.3222255D+01
0.04	0.1659113D+02	0.3335845D+00	0.3137005D+01
0.08	0.1458350D+02	0.1172874D+01	0.2902359D+01
0.10	0.1327429D+02	0.1668097D+01	0.2744973D+01
0.14	0.1044479D+02	0.2572561D+01	0.2389476D+01
0.18	0.7775868D+01	0.3165948D+01	0.2026596D+01
0.20	0.6610021D+01	0.3322559D+01	0.1855365D+01
0.30	0.2784744D+01	0.3149472D+01	0.1178675D+01
0.40	0.1248948D+01	0.2511159D+01	0.7694055D+00
0.50	0.6260432D+00	0.1966773D+01	0.5196622D+00
0.60	0.3407404D+00	0.1541473D+01	0.3599962D+00
0.70	0.1971016D+00	0.1213658D+01	0.2540398D+00
0.80	0.1191393D+00	0.9581749D+00	0.1816876D+00
0.90	0.7426479D-01	0.7559235D+00	0.1313264D+00
1.00	0.4739460D-01	0.5955780D+00	0.9581857D-01
1.20	0.2042608D-01	0.3696215D+00	0.5233306D-01
1.40	0.9338153D-02	0.2299995D+00	0.2951844D-01
1.60	0.4483192D-02	0.1442239D+00	0.1719627D-01
1.80	0.2256914D-02	0.9189036D-01	0.1033971D-01
2.00	0.1187692D-02	0.5969991D-01	0.6398959D-02
2.50	0.2781301D-03	0.2184429D-01	0.2153472D-02
3.00	0.7831054D-04	0.8856713D-02	0.8361782D-03
3.50	0.2593256D-04	0.3992007D-02	0.3645482D-03
4.00	0.9687111D-05	0.1947709D-02	0.1739085D-03
4.50	0.3981782D-05	0.1013240D-02	0.8959833D-04
5.00	0.1786445D-05	0.5612284D-03	0.4928937D-04
5.50	0.8655949D-06	0.3290409D-03	0.2856696D-04
6.00	0.4456641D-06	0.2016137D-03	0.1724407D-04
6.50	0.2401496D-06	0.1275024D-03	0.1076580D-04
7.00	0.1341557D-06	0.8260666D-04	0.6929950D-05
7.50	0.7740017D-07	0.5471096D-04	0.4593188D-05
8.00	0.4609570D-07	0.3707236D-04	0.3130519D-05
8.50	0.2834179D-07	0.2573209D-04	0.2189255D-05
9.00	0.1797539D-07	0.1829672D-04	0.1566342D-05
9.50	0.1173378D-07	0.1330745D-04	0.1142877D-05
10.00	0.7857621D-08	0.9874178D-05	0.8478758D-06

TABLE 18 (cont.)

$\bar{\Pi}^{(2)}(0) = -9.56189997715263402D+02$
$\bar{\Pi}^{(4)}(0) = 1.95057429577937415D+05$
$\bar{\Pi}^{(6)}(0) = -7.40103621757408939D+07$
$\bar{\Pi}^{(8)}(0) = 4.20066019536668644D+10$
$\bar{\Pi}^{(10)}(0) = -3.18633992604584531D+13$
$\langle p^{-2}\rangle = 4.28358613966412945D+01$
$\langle p^{-1}\rangle = 6.44451043912338006D+00$
$\langle p^{0}\rangle = 1.99999999999999914D+00$
$\langle p\rangle = 1.11466439233682726D+00$
$\langle p^{2}\rangle/2 = 5.27649071429998118D-01$
$\langle p^{3}\rangle = 1.65782428851877103D+00$
$\langle p^{4}\rangle = 4.82636181207409998D+00$

TABLE 19.

Momentum Density and Compton Profile of a Li^+ 16-Term Scaled Wavefunction.

p	$\bar{\Pi}(p)$	I(p)	J(p)
0.00	0.9648737D-01	0.0000000D+00	0.65[illegible]1960D+00
0.04	0.9639084D-01	0.1938053D-02	0.6537112D+00
0.08	0.9610198D-01	0.7728980D-02	0.6522598D+00
0.10	0.9588603D-01	0.1204939D-01	0.6511742D+00
0.14	0.9531306D-01	0.2347569D-01	0.6482910D+00
0.18	0.9455561D-01	0.3849835D-01	0.6444735D+00
0.20	0.9410936D-01	0.4730452D-01	0.6422212D+00
0.30	0.9123699D-01	0.1031866D+00	0.6276655D+00
0.40	0.8739407D-01	0.1757162D+00	0.6080277D+00
0.50	0.8274096D-01	0.2599384D+00	0.5839828D+00
0.60	0.7746065D-01	0.3504237D+00	0.5563143D+00
0.70	0.7174553D-01	0.4417746D+00	0.5258643D+00
0.80	0.6578476D-01	0.5290725D+00	0.4934847D+00
0.90	0.5975361D-01	0.6082177D+00	0.4599936D+00
1.00	0.5380536D-01	0.6761380D+00	0.4261404D+00
1.20	0.4263342D-01	0.7714762D+00	0.3598618D+00
1.40	0.3293337D-01	0.8111517D+00	0.2985676D+00
1.60	0.2495691D-01	0.8028616D+00	0.2444482D+00
1.80	0.1866011D-01	0.7597473D+00	0.1982747D+00
2.00	0.1383466D-01	0.6954056D+00	0.1598500D+00
2.50	0.6465322D-02	0.5077852D+00	0.9230340D-01
3.00	0.3052069D-02	0.3451808D+00	0.5353056D-01
3.50	0.1481479D-02	0.2280560D+00	0.3160753D-01
4.00	0.7452919D-03	0.1498498D+00	0.1911843D-01
4.50	0.3896471D-03	0.9915310D-01	0.1186592D-01
5.00	0.2113865D-03	0.6640904D-01	0.7552023D-02
5.50	0.1185789D-03	0.4507571D-01	0.4923259D-02
6.00	0.6858764D-04	0.3102832D-01	0.3284324D-02
6.50	0.4085641D-04	0.2169186D-01	0.2239403D-02
7.00	0.2504394D-04	0.1542086D-01	0.1557941D-02
7.50	0.1576971D-04	0.1114695D-01	0.1103436D-02
8.00	0.1017044D-04	0.8179550D-02	0.7939188D-03
8.50	0.6694673D-05	0.6078229D-02	0.5792814D-03
9.00	0.4483734D-05	0.4563885D-02	0.4281555D-03
9.50	0.3048881D-05	0.3457781D-02	0.3203615D-03
10.00	0.2102606D-05	0.2642212D-02	0.2425737D-03

TABLE 19 (cont.)

$\bar{\Pi}^{(2)}(0) = -1.20727981777734467\text{D}-01$

$\bar{\Pi}^{(4)}(0) = 5.54776412286796153\text{D}-01$

$\bar{\Pi}^{(6)}(0) = -4.89979724868112521\text{D}+00$

$\bar{\Pi}^{(8)}(0) = 6.73260793124566739\text{D}+01$

$\bar{\Pi}^{(10)}(0) = -1.29050721268732619\text{D}+03$

$\langle p^{-2}\rangle = 1.50795097613571150\text{D}+00$

$\langle p^{-1}\rangle = 1.30839190605437120\text{D}+00$

$\langle p^{0}\rangle = 1.99999999999999964\text{D}+00$

$\langle p\rangle = 4.50843991305116043\text{D}+00$

$\langle p^{2}\rangle/2 = 7.27941371653506974\text{D}+00$

$\langle p^{3}\rangle = 7.04649279629268275\text{D}+01$

$\langle p^{4}\rangle = 6.00128544816338803\text{D}+02$

TABLE 20.

Momentum Density and Compton Profile of a Li^+ 50-Term Scaled Wavefunction.

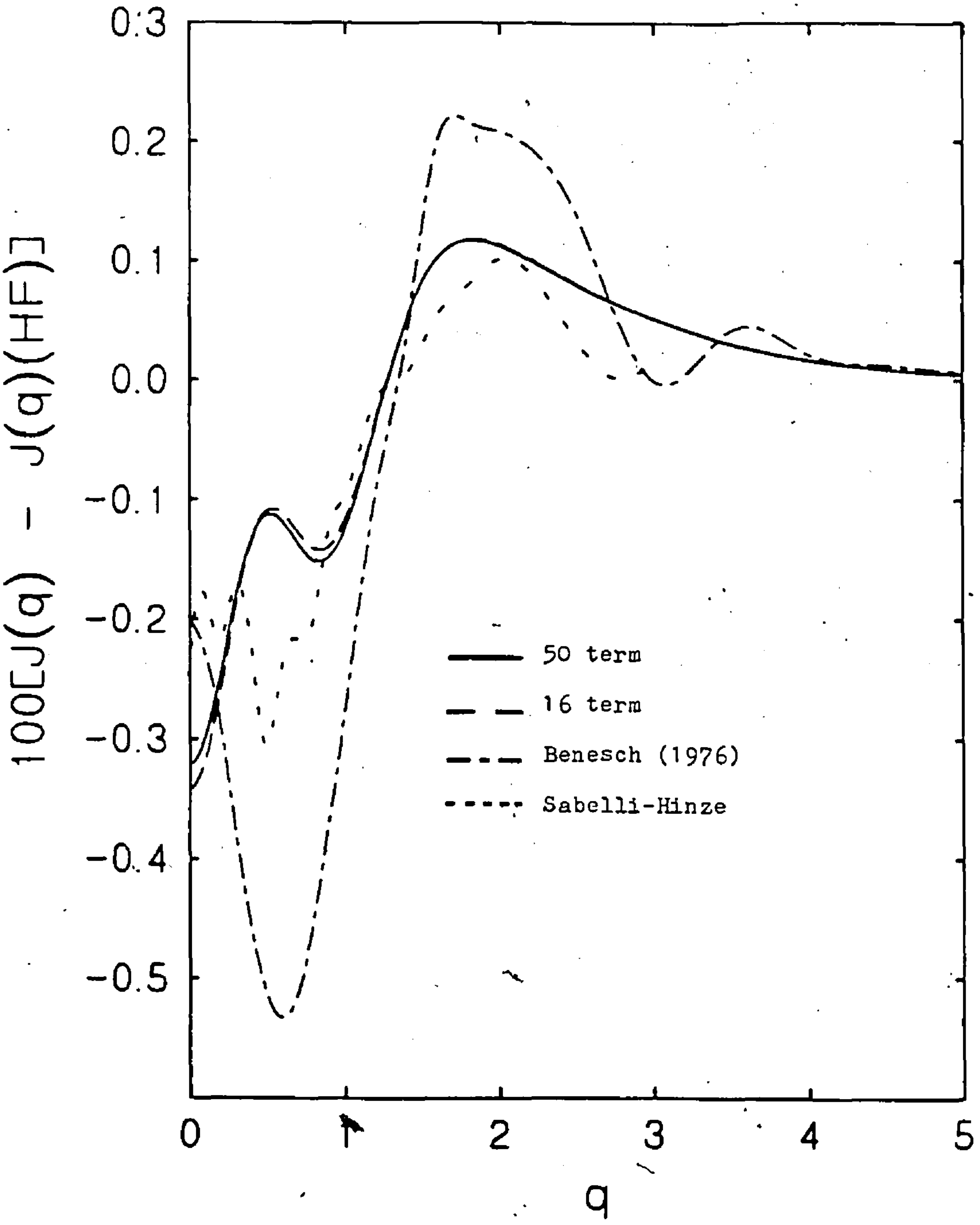
p	$\bar{\Pi}(p)$	I(p)	J(p)
0.00	0.9679352D-01	0.0000000D+00	0.6545160D+00
0.04	0.9670201D-01	0.1944309D-02	0.6540297D+00
0.08	0.9642689D-01	0.7755110D-02	0.6525736D+00
0.10	0.9622000D-01	0.1209136D-01	0.6514842D+00
0.14	0.9566651D-01	0.2356274D-01	0.6485906D+00
0.18	0.9492585D-01	0.3864910D-01	0.6447585D+00
0.20	0.9448543D-01	0.4749356D-01	0.6424973D+00
0.30	0.9160277D-01	0.1036003D+00	0.6278825D+00
0.40	0.8769277D-01	0.1763168D+00	0.6081714D+00
0.50	0.8296249D-01	0.2606344D+00	0.5840536D+00
0.60	0.7762552D-01	0.3511696D+00	0.5563193D+00
0.70	0.7187218D-01	0.4425545D+00	0.5258104D+00
0.80	0.6587989D-01	0.5298375D+00	0.4933787D+00
0.90	0.5981764D-01	0.6088694D+00	0.4598453D+00
1.00	0.5383880D-01	0.6765584D+00	0.4259633D+00
1.20	0.4261802D-01	0.7711975D+00	0.3596759D+00
1.40	0.3289637D-01	0.8102405D+00	0.2984288D+00
1.60	0.2492187D-01	0.8017342D+00	0.2443800D+00
1.80	0.1863804D-01	0.7588485D+00	0.1982682D+00
2.00	0.1382604D-01	0.6949725D+00	0.1598792D+00
2.50	0.6470237D-02	0.5081713D+00	0.9232684D-01
3.00	0.3053930D-02	0.3453914D+00	0.5352187D-01
3.50	0.1480797D-02	0.2279509D+00	0.3159586D-01
4.00	0.7445355D-03	0.1496977D+00	0.1911667D-01
4.50	0.3894223D-03	0.9909591D-01	0.1187060D-01
5.00	0.2114652D-03	0.6643374D-01	0.7557364D-02
5.50	0.1187141D-03	0.4512710D-01	0.4926596D-02
6.00	0.6868016D-04	0.3107017D-01	0.3285550D-02
6.50	0.4089765D-04	0.2171376D-01	0.2239345D-02
7.00	0.2505294D-04	0.1542640D-01	0.1557392D-02
7.50	0.1576461D-04	0.1114335D-01	0.1102872D-02
8.00	0.1016194D-04	0.8172720D-02	0.7935353D-03
8.50	0.6687458D-05	0.6071679D-02	0.5791067D-03
9.00	0.4479055D-05	0.4559122D-02	0.4281445D-03
9.50	0.3046495D-05	0.3455076D-02	0.3204515D-03
10.00	0.2101826D-05	0.2641232D-02	0.2427101D-03

TABLE 20 (cont.)

$\bar{\Pi}^{(2)}(0)$ = -1.14310628354540629D-01
$\bar{\Pi}^{(4)}(0)$ =-5.22006223563693403D-01
$\bar{\Pi}^{(6)}(0)$ = 1.58212879638312849D+02
$\bar{\Pi}^{(8)}(0)$ =-1.51845946984049585D+04
$\bar{\Pi}^{(10)}(0)$ =-8.97715703419174743D+06
$\langle p^{-2} \rangle$ = 1.51050308499113420D+00
$\langle p^{-1} \rangle$ = 1.30903204647602991D+00
$\langle p^{0} \rangle$ = 2.00000000000000050D+00
$\langle p \rangle$ = 4.50810916318400279D+00
$\langle p^{2} \rangle/2$ = 7.27957047047271899D+00
$\langle p^{3} \rangle$ = 7.04990576843794123D+01
$\langle p^{4} \rangle$ = 6.04423062855430587D+02

FIGURE 1.

Plot of Helium Compton Profiles.



CHAPTER 6

CONCLUSIONS AND SUGGESTIONS

6.1 Conclusions.

The 16-term Gaussian geminal wavefunction for helium which was calculated in Chapter 2 is considerably better, to our knowledge, than any other like calculation. If one is careful with the application of the minimizing routines then good results may be achieved. When the number of terms in the wavefunction becomes large, it is no longer feasible to attempt to optimize all of its parameters. The work on the GCM suggests that this is a good method to increase the size of the wavefunction without an undue amount of computer work. Use of a small wavefunction that has been "fully-optimized" within the GCM-produced wavefunction is found to be very useful. This suggests that construction of a large wavefunction should start with the calculation of a small "fully-optimized" wavefunction and then proceed with GCM-produced parameters.

The VI method does not seem to be particularly well-suited for a Gaussian basis set. A great deal of computer time is required to produce an estimate of the half-iterated energy. The first-iterated wavefunction is complicated and of questionable value, although it may be useful in calculating other expectation values. We have shown that the use of Gaussian geminals with explicit correlation presents no difficulty greater than the use of products of Gaussian orbitals, and thus should be the choice if Gaussians are to be employed.

The 50-term helium wavefunction produced in Chapter 5 is the most accurate wavefunction used to produce a helium Compton profile to date. Gaussian geminals are ideal for this type of calculation as all results may be obtained analytically.

6.2 Suggestions for Further Research.

The area which lends itself most readily to future work is the GCM. We have presented nine frequency function schemes but many more could be tested. It would be instructive to examine a greater number of frequency functions to gain more insight into this method. These frequency functions may be given more parameters to be varied, with both the shape of the function and its endpoints varied.

The VI method also deserves more scrutiny. Since the use of Gaussians is questionable, perhaps a good momentum space basis set could be found in which the integrals involved in the iteration do not become too complicated. The feasibility of using the first-iterated wavefunction of Chapter 3 in calculating properties other than the momentum density or Compton profile could be examined.

APPENDIX 1

FOURIER TRANSFORM OF A GAUSSIAN GEMINAL BASIS FUNCTION

Take as our Gaussian geminal:

$$g(\vec{r}_1,\vec{r}_2) = \exp(-ar_1^2-br_2^2-cr_{12}^2)$$

The Fourier transform is:

$$\phi(\vec{p}_1,\vec{p}_2) = \frac{1}{(2\pi^3)} \int \exp(-ar_1^2-br_2^2-cr_{12}^2) \exp(-i\vec{p}_1\cdot\vec{r}_1-i\vec{p}_2\cdot\vec{r}_2)\, d\vec{r}_1 d\vec{r}_2$$

Splitting into Cartesian coordinates and performing the integrations yields:

$$\phi(\vec{p}_1,\vec{p}_2) = \frac{1}{(\Delta)^{3/2}} \exp\left[\frac{-bp_1^2-ap_2^2-c(\vec{p}_1+\vec{p}_2)^2}{\Delta}\right]$$

where $\Delta = 4(ab+ac+bc)$
with the conditions $a+c>0$, $\Delta>0$.

APPENDIX 2

MATRIX ELEMENTS WITH GAUSSIAN GEMINALS

Take two Gaussian geminals as follows:

$$g_1 = \exp\,(-ar_1{}^2-br_2{}^2-cr_{12}{}^2)$$

$$g_2 = \exp\,(-dr_1{}^2-er_2{}^2-fr_{12}{}^2)$$

1. Overlap Matrix Elements.

$$\langle g_1 | g_2 \rangle = \int \exp(-(a+d)r_1{}^2-(b+e)r_2{}^2-(c+f)r_{12}{}^2)\, d\vec{r}_1 d\vec{r}_2$$

Splitting $\vec{r}_1$ and $\vec{r}_2$ into Cartesian coordinates, we find

$$= \left[\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \exp[-(a+d)x_1{}^2-(b+e)x_2{}^2-(c+f)(x_1-x_2)^2]\, dx_1 dx_2\right]^3$$

The double integral may be evaluated using:

$$\int_{-\infty}^{\infty} \exp(-tx^2-ux)dx = \sqrt{\frac{\pi}{t}}\, \exp\left(\frac{u^2}{4t}\right) \qquad t>0$$

The result is

$$\langle g_1 | g_2 \rangle = \frac{\pi^3}{t^{3/2}}$$

with the conditions $a+d+c+f>0$, $t>0$
and where $t = (a+d)(b+e)+(a+d)(c+f)+(b+e)(c+f)$.

2. Kinetic Energy Matrix Elements.

These integrals are evaluated by first performing the differentiations and integrating in Cartesian coordinates. The result is:

$$-\frac{1}{2}\langle g_1|\nabla_1^2+\nabla_2^2|g_2\rangle = \frac{3\pi^3}{t^{5/2}}[(d+e+2f)t-2fd(b+e)$$
$$-2fe(a+d)-d^2(b+c+e+f)-e^2(a+d+c+f)-2f^2(a+d+b+e)]$$

where t is given above.

3. Potential Energy Matrix Elements.

If the potential energy operators are replaced by their Fourier integral representations (as in eq. (3.6)), the integrals are readily evaluated in Cartesian coordinates. The results are:

$$-Z\langle g_1|\ 1/r_1\ |g_2\rangle = \frac{-2Z\pi^{5/2}}{t\sqrt{b+e+c+f}} \qquad \begin{matrix}(b+e+c+f)>0\\ t>0\end{matrix}$$

$$-Z\langle g_1|\ 1/r_2\ |g_2\rangle = \frac{-2Z\pi^{5/2}}{t\sqrt{a+d+c+f}} \qquad \begin{matrix}(a+d+c+f)>0\\ t>0\end{matrix}$$

$$\langle g_1 | \; 1/r_{12} \; | g_2 \rangle = \frac{2\pi^{5/2}}{t\sqrt{a+d+b+e}} \qquad \begin{array}{c} (a+d+b+e)>0 \\ t>0 \end{array}$$

where t is given above.

APPENDIX 3

IMPORTANCE OF EACH WAVEFUNCTION TERM

Let us take an L-term wavefunction as follows:

$$\psi_L = \sum_{k=1}^{L} C_k \phi_k \tag{A3.1}$$

The variational energy, E_L, of this wavefunction is given by

$$E_L = \frac{\langle \psi_L | H | \psi_L \rangle}{\langle \psi_L | \psi_L \rangle} . \tag{A3.2}$$

The linear coefficients are calculated by solving

$$\underline{\underline{H}}\ \underline{C} = E\ \underline{\underline{S}}\ \underline{C} \tag{A3.3}$$

or

$$\sum_n H_{mn} C_n = E_L \sum_n S_{mn} C_n \tag{A3.4}$$

for each $m=1,\ldots,L$
and where $H_{mn} = \langle \phi_m | H | \phi_n \rangle$
$S_{mn} = \langle \phi_m | \phi_n \rangle$.

The solution of (A3.4) is constrained by requiring that ψ_L be normalized. This condition may be written as

$$\sum_{m,n} C_m C_n S_{mn} = 1 \qquad \text{(A3.5)}$$

Let us define $\psi_{L/j}$ as the wavefunction resulting when the j-th basis function is deleted from (A3.1) and for which the linear coefficients have been re-calculated variationally. We also define $\chi_{L/j}$ as the wavefunction resulting when the j-th basis function is deleted from (A3.1) and the remaining linear coefficients are unchanged.

We will approximate $\psi_{L/j}$ by $\chi_{L/j}$:

$$\psi_{L/j} \approx \chi_{L/j} = \sum_{k\neq j}^{L} C_k \phi_k \qquad \text{(A3.6)}$$

Define $E_{L/j}$ as the variational energy of $\psi_{L/j}$ and $\varepsilon_{L/j}$ as the variational energy of $\chi_{L/j}$. We know that

$\varepsilon_{L/j} \geq E_{L/j} \geq E_L \geq$ true energy.

The energy gained by the wavefunction when the j-th basis function is deleted is given by $E_{L/j}-E_L$. An over-estimate of this energy is given by:

$$\Delta_{L/j} = \varepsilon_{L/j} - E_L \geq E_{L/j} - E_L$$

$$\Delta_{L/j} = \frac{\langle \chi_{L/j}|H|\chi_{L/j}\rangle - E_L\langle \chi_{L/j}|\chi_{L/j}\rangle}{\langle \chi_{L/j}|\chi_{L/j}\rangle} \tag{A3.7}$$

Now

$$\langle \chi_{L/j}|\chi_{L/j}\rangle = \sum_{m,n} C_m C_n S_{mn} - \sum_{m} C_m C_j S_{mj} - \sum_{n} C_n C_j S_{jn} + C_j^2 S_{jj}$$

$$\langle \chi_{L/j}|\chi_{L/j}\rangle = 1 - 2C_j \sum_{m} C_m S_{mj} + C_j^2 S_{jj} \tag{A3.8}$$

using (A3.5) and the fact that $\underline{\underline{S}}$ is symmetric.

$$\langle \chi_{L/j}|H|\chi_{L/j}\rangle - E_L\langle \chi_{L/j}|\chi_{L/j}\rangle = \sum_{m,n} C_m C_n (H_{mn} - E_L S_{mn}) - 2C_j \sum_{m} C_m (H_{mj} - E_L S_{mj}) + C_j^2 (H_{jj} - E_L S_{jj})$$

$$= C_j^2 (H_{jj} - E_L S_{jj}) \tag{A3.9}$$

using (A3.4).

So we have

$$\Delta_{L/j} = \frac{C_j^2 (H_{jj} - E_L S_{jj})}{1 - 2C_j \sum_{m} C_m S_{mj} + C_j^2 S_{jj}} \tag{A3.10}$$

This technique, first developed by Brown (1967), gives an over-estimate, $\Delta_{L/j}$, of the variational energy increase when the j-th basis function is removed from eq. (A3.1). Since the quantities required in (A3.10) will already have been calculated in obtaining (A3.1), it is a quick method to get an idea of the importance of the j-th basis function. Calculation of the exact energy increase would require the solution of a new set of linear coefficients. This approximate energy increase is computed in the program which calculates eigenvectors.

APPENDIX 4

CALCULATION OF I_1, I_2 AND I_{12}.

For use in the evaluation of these quantities, the following integral will be evaluated:

$$\int \frac{d\vec{p}}{p^2} \exp(-ap^2+2\vec{q}\cdot\vec{p}) \qquad \text{(A4.1)}$$

Define spherical polar coordinates (p,θ,ϕ) such that $\vec{q}$ lies along the axis from which θ is measured. The integral now becomes

$$\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \int_0^{\infty} dp \frac{p^2 \sin\theta}{p^2} \exp(-ap^2+2qp\cos\theta)$$

Integrate over the ϕ variable and transform the θ variable by $u=\cos\theta$ to get:

$$2\pi \int_{-1}^{1} du \int_0^{\infty} dp \exp(-ap^2+2qpu)$$

Using integral tables, we get:

$$= \frac{\pi^{3/2}}{a^{1/2}} \int_{-1}^{1} du \left[\exp\left(\frac{q^2u^2}{a}\right) + \exp\left(\frac{q^2u^2}{a}\right) \operatorname{erf}\left(\frac{qu}{\sqrt{a}}\right) \right] \qquad a>0$$

The term containing the error function is an odd function of u and it will integrate to zero. We are left with:

$$= \frac{\pi^{3/2}}{a^{1/2}} \int_{-1}^{1} du \exp\left(\frac{q^2u^2}{a}\right)$$

$$= \frac{2\pi^{3/2}}{a^{1/2}} \int_{0}^{1} du \exp\left(\frac{q^2u^2}{a}\right)$$

$$= \frac{2\pi^{3/2}}{a^{1/2}} F\left(\frac{1}{2},\frac{3}{2},\frac{q^2}{a}\right) \qquad a>0$$

where $F(1/2,3/2,x)$ is the confluent hypergeometric function defined as:

$$F\left(\frac{1}{2},\frac{3}{2},x\right) = \int_{0}^{1} \exp(xu^2)du$$

1. Calculation of I_1.

Let $\quad g(\vec{p}_1,\vec{p}_2) = \exp[-bp_1{}^2-ap_2{}^2-c(\vec{p}_1+\vec{p}_2)^2]$

$$I_1(g) = \int \frac{d\vec{p}}{p^2}\, g(\vec{p}_1-\vec{p},\vec{p}_2)$$

Substituting the actual expression for g yields:

$$I_1(g) = g(\vec{p}_1,\vec{p}_2) \int \frac{d\vec{p}}{p^2} \exp[-(b+c)p^2+2((b+c)\vec{p}_1+c\vec{p}_2)\cdot\vec{p}]$$

$$I_1(g) = \frac{2\pi^{3/2}}{\sqrt{b+c}} g(\vec{p}_1,\vec{p}_2) F\left(\frac{1}{2},\frac{3}{2},\frac{((b+c)\vec{p}_1+c\vec{p}_2)^2}{b+c}\right)$$

A similar calculation gives

$$I_2(g) = \frac{2\pi^{3/2}}{\sqrt{a+c}} g(\vec{p}_1,\vec{p}_2) F\left(\frac{1}{2},\frac{3}{2},\frac{(c\vec{p}_1+(a+c)\vec{p}_2)^2}{a+c}\right)$$

$$I_{12}(g) = \frac{2\pi^{3/2}}{\sqrt{a+b}} g(\vec{p}_1,\vec{p}_2) F\left(\frac{1}{2},\frac{3}{2},\frac{(b\vec{p}_1-a\vec{p}_2)^2}{a+b}\right)$$

APPENDIX 5

CALCULATION OF J INTEGRALS

Let

$$g = \exp[-ap_1{}^2 \; -bp_2{}^2 \; -c(\vec{p}_1+\vec{p}_2)^2]$$

$$h = \exp[-dp_1{}^2 \; -ep_2{}^2 \; -f(\vec{p}_1+\vec{p}_2)^2]$$

Calculate

$$J_1 = \int d\vec{p}_1 d\vec{p}_2 \; I_1(g) \; h$$

Substitute for $I_1(g)$ and h and use the integral representation of I_1 given in Appendix 4 to get:

$$= \frac{2\pi^{3/2}}{\sqrt{a+c}} \int_0^1 du \int d\vec{p}_1 d\vec{p}_2 \; \exp[-((a+c)(1-u^2)+d+f)p_1{}^2$$

$$-(b+e+c+f-c^2u^2/(a+c))p_2{}^2$$

$$-2(c(1-u^2)+f)\vec{p}_1\cdot\vec{p}_2]$$

First evaluate the integral over $\vec{p}_1$ and $\vec{p}_2$ by expanding these two vectors in Cartesian coordinates and using integral tables:

$$= 2\pi^{9/2}(a+c) \int_0^1 du((a+c)v-wu^2)^{-3/2}$$

where $v = (b+e)(a+d+c+f) + (a+d)(c+f)$
$w = (a+c)^2(b+e) + a^2(c+f) + c^2(a+d)$
with the condition that $(a+c)v-w>0$.

Performing the last integral gives:

$$J_1 = \frac{2\pi^{9/2}}{v\sqrt{(a+c)v-w}}$$

Similarly

$$J_{12} = \frac{2\pi^{9/2}}{v\sqrt{(a+b)v-y}}$$

where $y = (a+b)^2(c+f)+b^2(a+d)+a^2(b+e)$
v is given above
with the condition $(a+b)v-y>0$.

APPENDIX 6

CALCULATION OF K INTEGRALS

Let

$$g = \exp[-ap_1{}^2 - bp_2{}^2 - c(\vec{p}_1+\vec{p}_2)^2]$$

$$h = \exp[-dp_1{}^2 - ep_2{}^2 - f(\vec{p}_1+\vec{p}_2)^2]$$

Calculate

$$K_{1,1} = \int d\vec{p}_1 d\vec{p}_2 \frac{I_1(g) I_1(h)}{(p_0{}^2+p_1{}^2+p_2{}^2)}$$

Use the integral representation of I_1 given in Appendix 4 and use

$$\frac{1}{p_0{}^2+p_1{}^2+p_2{}^2} = \int_0^\infty \exp(-m(p_0{}^2+p_1{}^2+p_2{}^2))\, dm$$

All variables with the exception of m are easily integrated. The result is

$$K_{1,1} = \frac{4\pi^6}{\sqrt{(a+c)(d+f)}} \int_0^\infty dm \frac{\exp(-mp_0{}^2)}{\sqrt{PQ}} \tan^{-1}\sqrt{\frac{Q}{PN}}$$

where

$$P = (a+d+m)(b+e+m)+(c+f)(a+b+d+e+2m)$$

$$N = m(m+b+e+ac/(a+c)+df/(d+f))$$

$Q =$

$((a+c)(d+f)(b+e+m)+ac(d+f)+df(a+c)+cfm)^2/((a+c)(d+f))$

$P, Q, N > 0$

Similarly

$$K_{1,2} = \int d\vec{p}_1 d\vec{p}_2 \frac{I_1(g) I_2(h)}{(p_0{}^2+p_1{}^2+p_2{}^2)}$$

$$= \frac{4\pi^6}{\sqrt{(a+c)(e+f)}} \int_0^\infty dm \frac{\exp(-mp_0{}^2)}{\sqrt{PQ}} \tan^{-1}\sqrt{\frac{Q}{PN}}$$

where

P is as above

$N = ((a+c)(b+m)+ac)((e+f)(d+m)+ef)/((a+c)(e+f))$

$Q = (f(a+c)(b+m)+c(e+f)(d+m)+cf(a+e))^2/((a+c)(e+f))$

$P, Q, N > 0$

$$K_{1,12} = \int d\vec{p}_1 d\vec{p}_2 \frac{I_1(g) I_{12}(h)}{(p_0{}^2+p_1{}^2+p_2{}^2)}$$

$$= \frac{4\pi^6}{\sqrt{(a+c)(d+e)}} \int_0^\infty dm \frac{\exp(-mp_0{}^2)}{\sqrt{PQ}} \tan^{-1}\sqrt{\frac{Q}{PN}}$$

where

P is as above

$N = m^2 + (2f+b+2de/(d+e)+ac/(a+c))m$

$bf + acf/(a+c) + bde/(d+e) + acde/((a+c)(d+e))$

$Q = (d(b+m)(a+c)+af(d+e)+ad(c+e)-cem)^2/((a+c)(d+e))$

$P,\ Q,\ N > 0$

$$K_{12,12} = \int d\vec{p}_1 d\vec{p}_2 \frac{I_{12}(g)\, I_{12}(h)}{(p_0^2+p_1^2+p_2^2)}$$

$$= \frac{4\pi^6}{\sqrt{(a+b)(d+e)}} \int_0^\infty dm \frac{\exp(-mp_0^2)}{\sqrt{PQ}} \tan^{-1}\sqrt{\frac{Q}{PN}}$$

where

P is as above

$N = m^2 + 2m(c+f+de/(d+e)+ab/(a+b))$

$Q =$

$((ae+bd)(c+f)+(be(a+d+c+f+m)+ad(b+e+c+f+m)))^2/((a+b)(d+e))$

$P,\ N,\ Q > 0$

APPENDIX 7

MOMENTUM DENSITY AND COMPTON PROFILE FROM GAUSSIAN GEMINALS

Take

$$\phi = \sum_{k=1}^{N} d_k(1+t_k)\exp(-b_k p_1{}^2 - a_k p_2{}^2 - g_k(\vec{p}_1+\vec{p}_2)^2)$$

as in equation (3.25).

Now use equation (5.1) to calculate $\Pi(\vec{p})$ with the result

$$\Pi(\vec{p}) = 2\pi^{3/2} \sum_{k=1}^{N} \sum_{j=1}^{N} d_k d_j (1+t_k)(1+t_j) \frac{\exp(-up^2/v)}{v^{3/2}}$$

where $v = a_k+g_k+a_j+g_j$
$u = (a_k+a_j)(b_k+g_k+b_j+g_j) + (b_k+b_j)(g_k+g_j)$

In this case $\bar{\Pi}(p) = \Pi(\vec{p})$.

Now

$$J(q) = 2\pi \int_{|q|}^{\infty} p\bar{\Pi}(p)dp$$

$$= 4\pi^{5/2} \sum_{k=1}^{N} \sum_{j=1}^{N} d_k d_j (1+t_k)(1+t_j) \frac{\exp(-uq^2/v)}{2uv^{1/2}}$$

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