Variational calculations for general three-body systems.

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University of Windsor

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UMI
Variational Calculations for General Three-Body Systems

by

Mark Michael Cassar

A Thesis submitted to the Faculty of Graduate Studies and Research through the Department of Physics in Partial Fulfillment of the Requirements for the Degree of Master of Science at the University of Windsor.

Windsor, Ontario, Canada

1998

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ABSTRACT

A general study of the bound states for the quantum mechanical three-body problem is presented over a broad range of particle masses. The purpose is to identify improved methods for constructing the variational wave functions in terms of the Hylleraas interparticle coordinates $r_1$, $r_2$, and $r_{12}$. A new nonlinear parameter is introduced so that distance scales can be set independently for all three coordinates. Significant improvements are found, particularly as the particle masses approach equality and mass polarization effects become large. As a pilot project, high precision variational calculations are carried out for the $1s^2 1S$ ground state of the three-body systems H$^-$ and Ps$^-$. 
Better thine own work is, though done with fault,
Than doing other’s work, ev’n excellently.

Bhagavadgita, Chapter 18
ACKNOWLEDGMENTS

This project would not have materialized or been completed without the expertise and continual guidance of Dr. Gordon W. F. Drake; for this I am very grateful. I would also like to thank the Department of Physics at the University of Windsor and Dr. Gordon W. F. Drake for financial support throughout my studies. I thank all the graduate students in the Department, and in particular, Andrzej Czaikowski (for all the talks and encouragement). Finally, I wish to thank my family and friends for everything they have given me throughout my years at university.
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CHAPTER ONE

1 Introduction

The basic aim of this work is to attempt to extend the accuracy of the calculations carried out on Helium by Drake [1, 2, 3, 4, 5] to the realm of the general three-body atomic system. We are interested in the determination of the nonrelativistic energy levels for these systems, together with the evaluation of the appropriate shifts due to mass polarization. Thus, we wish to solve the general Schrödinger equation for a three-body system in an inertial frame

\[
\left( -\frac{\hbar^2}{2m_1} \nabla^2_1 - \frac{\hbar^2}{2m_2} \nabla^2_2 - \frac{\hbar^2}{m_3} \nabla^2_3 + \frac{q_1q_2}{|r_1 - r_2|} + \frac{q_1q_3}{|r_1 - r_3|} + \frac{q_2q_3}{|r_2 - r_3|} \right) \Psi = E_{NR} \Psi,
\]

(1)

where \( m_i, q_i, r_i, i = 1, 2, 3 \) are the particle masses, charges and positions, respectively.

If we define the centre-of-mass and internal variables by

\[
\begin{align*}
\rho_1 &= r_1 - r_3, \\
\rho_2 &= r_2 - r_3, \\
R &= \frac{m_1 r_1 + m_2 r_2 + m_3 r_3}{m_1 + m_2 + m_3},
\end{align*}
\]

(2)

then

\[
\begin{align*}
r_1 - r_2 &= \rho_1 - \rho_2, \\
\nabla_1 &= \nabla_{\rho_1} + \frac{m_1}{M} \nabla_R, \\
\nabla_2 &= \nabla_{\rho_2} + \frac{m_2}{M} \nabla_R, \\
\nabla_3 &= -\nabla_{\rho_1} - \nabla_{\rho_2} + \frac{m_3}{M} \nabla_R.
\end{align*}
\]

(3)

This casts the Schrödinger equation into the form

\[
\begin{align*}
-\frac{\hbar^2}{2} \left\{ \left( \frac{1}{m_1} + \frac{1}{m_3} \right) \nabla^2_{\rho_1} + \left( \frac{1}{m_2} + \frac{1}{m_3} \right) \nabla^2_{\rho_2} + \frac{2}{m_3} \nabla_{\rho_1} \cdot \nabla_{\rho_2} + \frac{1}{M} \nabla^2_R \\
+ \frac{q_1q_2}{|\rho_1 - \rho_2|} + \frac{q_1q_3}{\rho_1} + \frac{q_2q_3}{\rho_2} \right\} \Psi = E_{NR} \Psi.
\end{align*}
\]

(4)
We now define
\[ \frac{1}{\mu_1} = \frac{1}{m_1} + \frac{1}{m_3}, \]
and
\[ \frac{1}{\mu_2} = \frac{1}{m_2} + \frac{1}{m_3} \]
and drop $\nabla^2_R$ since $R$ is an ignorable coordinate. The centre-of-mass coordinate is ignorable because we assume that no external forces are acting upon the system in question; its inclusion is irrelevant for the calculation at hand.

Then the Schrödinger equation becomes
\[
\left\{ \begin{array}{c}
- \frac{\hbar^2}{2\mu_1} \nabla^2_{\rho_1} - \frac{\hbar^2}{2\mu_2} \nabla^2_{\rho_2} - \frac{\hbar^2}{m_3} \nabla_{\rho_1} \cdot \nabla_{\rho_2} + \frac{q_1 q_2}{|\rho_1 - \rho_2|} + \frac{q_1 q_3}{\rho_1} + \frac{q_2 q_3}{\rho_2}
\end{array} \right\} \Psi = E_{NR} \Psi.
\]
\[ (5) \]

We now put $q_i = eZ_i$, and measure distances in units of $a_1 = \hbar^2/(\mu_1 e^2)$, so that the above becomes [6]
\[
\left\{ \begin{array}{c}
- \frac{1}{2} \nabla^2_1 - \frac{\mu_1}{2\mu_2} \nabla^2_2 - \frac{\mu_1}{m_3} \nabla_1 \cdot \nabla_2 + \frac{Z_1 Z_2}{r_{12}} + \frac{Z_1 Z_3}{r_1} + \frac{Z_2 Z_3}{r_2}
\end{array} \right\} \Psi = E \Psi,
\]
\[ (6) \]
where $E = (a_1/e^2)E_{NR}$. For the atomic systems dealt with here, $Z_3 = Z$ and $Z_1 = Z_2 = -1$, $m_3 = M$ and $\mu_1 = \mu_2 = \mu_e$ so that we are left with
\[
\left( - \frac{1}{2} \nabla^2_1 - \frac{1}{2} \nabla^2_2 - \frac{\mu}{M} \nabla_1 \cdot \nabla_2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \right) \Psi(r_1, r_2) = E\Psi(r_1, r_2).
\]
\[ (7) \]

The price we pay for transforming into the above coordinate system is that we introduce a cross-term in the Hamiltonian $(\mu/M)\nabla_1 \cdot \nabla_2$, called the mass polarization term. This term plays a crucial role in this thesis.

Under the assumption that $\mu/M << 1$ we may drop the mass polarization term and solve the Schrödinger equation for the infinite nuclear mass case:
\[
\left( - \frac{1}{2} \nabla^2_1 - \frac{1}{2} \nabla^2_2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \right) \Psi(r_1, r_2) = E\Psi(r_1, r_2).
\]
\[ (8) \]

Even with the above assumption $(\mu/M << 1)$ the mass polarization term has a non-negligible role with respect to the accuracy of the energies; but as we move from the atomic regime into the molecular regime it is obvious that the mass polarization term stands on an equal footing with all the other terms in the Hamiltonian [e.g. He $(\mu/M \approx 0.000137) \rightarrow \mu D_2$ $(\mu/M \approx
Thus, it is essential that we add in the mass polarization term as a correction to the infinite nuclear mass case.

Microscopic three-body systems can, in a rough way, be classified as falling into (i) the atomic regime, where one particle is much more massive than the other two, or (ii) the molecular regime, where one particle is much less massive than the other two. In this scheme we can clearly see that \( H^- \), consisting of one proton and two electrons \( (p^+e^-e^-) \), is on the atomic side, while \( H^+_2 \), containing two protons and one electron \( (p^+p^+e^-) \), is on the molecular side. A system such as \( Ps^- \) however, consisting of one positron and two electrons \( (e^+e^-e^-) \), resides on the cusp between these two regimes.

Normally, \( H^+_2 \) is treated as a molecule and calculations done on this system incorporate certain molecular approximations (e.g. the Born-Oppenheimer approximation, where the nucleus is assumed stationary for each calculation of the electron cloud [7]). In contrast, we wish to treat \( H^+_2 \) as a general three-body atomic system. In doing so, we anticipate that the states of \( H^- \) should transform into the states of \( H^+_2 \) as the mass ratios change, thereby allowing a one-to-one mapping of atomic states onto molecular states. The parameter that would govern such a continuous evolution is the atomic mass ratio \( \mu/M \). Each infinitesimal increment of \( \mu/M \) would be accompanied by an optimization of all nonlinear parameters; and thus, the nonlinear parameters would be smooth functions of \( \mu/M \).

This work applies the variational principle to solve the above problem for the nonrelativistic energy eigenvalues for the \( 1s^2 \ 1S \) ground state of \( H^- \) and \( Ps^- \). The wave functions used in the calculations are constructed so that they mirror the physical nature of the problem, i.e. they allow distance scales along the three radial coordinates to be set independently. Such a characteristic is absolutely necessary for systems in which the atomic mass ratio is on the order of one.
2 Historical Survey

The helium atom, with its nucleus and two electrons, holds a very fundamental position within the scheme of atomic theory. Since it is the simplest atomic system with a three-body structure, it therefore serves as a testing ground for other, more general, three-body systems. Unlike the situation for hydrogen, the Schrödinger equation for helium is nonseparable; and is thus not exactly solvable.

The early work of Hartree [8] and Hylleraas [9] – only four years after the introduction of the Schrödinger equation – set the stage for much of the later work done in this field. Hylleraas first suggested (in 1928) writing the wave function (for S states) in the explicitly correlated form

$$\Psi(r_1, r_2) \sum_{ijk} a_{ijk} r_i^j r_2^k r_{12} e^{-ar_1 - br_2} \pm \text{exchange}. $$

Wave functions of this same general type have been used on the Helium system up to the present day calculations of Drake, who has calculated the nonrelativistic energy levels of Helium, for all intents and purposes, exactly.

The positronium atom was demonstrated to be theoretically stable against break-up in 1946 by Wheeler [10]. The classical variational method of Hylleraas was extended to this system in the early 1960s [11, 12].

It was not, however, until 1981 when Mills Jr. [13] provided the first experimental evidence for this particle. Shortly after this, in 1983, Ho [14] did calculations for the $1S^e$ state of Ps− using a basis set defined by

$$\Psi = \sum_{l, m \geq 0, k \geq 0} c_{klm} e^{-\alpha(r_{1p} + r_{2p})} r_{12}^{-k}(r_{1p}^{l} r_{2p}^{m} + r_{1p}^{m} r_{2p}^{l}). $$

Calculations were carried out with basis sets up to 125 terms that yielded an energy accurate to 1 part in 10^8. In the same year, Bhatia and Drachman [15] carried out a variational calculation for the same state using 220 terms in the basis set expansion

$$\Psi(r_1, r_2) = \sum_{l, m, n \geq 0} c_{lmn}(r_1^l r_2^m e^{-\gamma r_1 - \delta r_2} + r_1^m r_2^l e^{-\delta r_1 - \gamma r_2}) r_{12}^{n} D_0^{0+}. $$
For the $^1S^e$ ground state, they calculated an energy of $-0.262\,005\,057$ a.u. In 1987, Petelenz and Smith [16] used a modified integral method for the same calculation. Their method is equivalent to a variational treatment using the wave function

$$\Psi(r_1, r_2, r) = (4\pi)^{-1} \sum_{k=1}^{N} c_k (1 + P_{12}) e^{-\alpha_k r_1 - \beta_k r_2 - \gamma_k r},$$

where the $\alpha_k$, $\beta_k$, and $\gamma_k$ are generated in a pseudo-random manner from a set of six nonlinear parameters. Using 150 terms in their expansion, they achieved an energy $E_{\text{extrap}} = -0.262\,005\,070$ a.u. A correlation function hyperspherical harmonic method was employed two years later by Haftel and Mandelzweig [17]. In this method, the wave function is written as

$$\Psi = \chi \phi,$$

where $\chi$ is chosen to account for the singular and/or clustering structure of the system, and $\phi$ is expanded in terms of hyperspherical harmonics. The correlation function $\chi$ is of the form (for $S$ states of two-electron systems)

$$\chi = e^{-\gamma (r_{13} + r_{23}) - \delta r_{12}}.$$

Including 169 hyperspherical functions and choosing the parameters via a 'minimal energy configuration' the authors calculated an energy of $E = -0.262\,004\,486$. In the same year, to much better success, Frolov and Yeremin [18] used a 700-term variational expansion of the form

$$\Psi_{L=0}(r_{13}, r_{23}, r_{12}) = \frac{1}{\sqrt{2}} (1 + P_{12}) \sum_{i=1}^{N} c_i e^{-\alpha_i (r_{23} - \alpha_1^{i} r_{13} - \alpha_2^{i} r_{13} - \alpha_3^{i} r_{12})}.$$ 

The $\alpha_k^{i}$ were chosen quasirandomly and their resultant energy was $E = -0.262\,005\,070\,232$. Again in the same year, Ho [19] carried out another variational calculation using wave functions of the form

$$\Psi = \sum_{l \geq m \geq 0} \sum_{k \geq 0} c_{klm} e^{-\alpha (r_{1p} + r_{2p})} r_{12}^{l} r_{2p}^{m} r_{1p}^{m} r_{2p}^{l},$$

where $(k + l + m) \leq \omega$ and $\omega$ is some integer. With 969 terms and $\alpha = 0.510$, he determined a value of $E = -0.262\,005\,070\,21$ for the ground state. In
Table 1: Summary of past results for Ps$^-$.

<table>
<thead>
<tr>
<th>Author</th>
<th>Year</th>
<th>Method</th>
<th>Energy (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ho</td>
<td>1983</td>
<td>variational</td>
<td>-0.262 004 90</td>
</tr>
<tr>
<td>Bhatia and Drachman</td>
<td>1983</td>
<td>variational</td>
<td>-0.262 005 057</td>
</tr>
<tr>
<td>Petelenz and Smith</td>
<td>1987</td>
<td>modified integral transform</td>
<td>-0.262 005 070</td>
</tr>
<tr>
<td>Haftel and Mandelweig</td>
<td>1989</td>
<td>correlation function</td>
<td>-0.262 004 86</td>
</tr>
<tr>
<td></td>
<td></td>
<td>hyperspherical harmonic</td>
<td></td>
</tr>
<tr>
<td>Frolov and Yeremin</td>
<td>1989</td>
<td>variational</td>
<td>-0.262 005 070 232</td>
</tr>
<tr>
<td>Ho</td>
<td></td>
<td>variational</td>
<td>-0.262 005 070 21</td>
</tr>
<tr>
<td>Ackermann and Shertzer</td>
<td>1996</td>
<td>adaptive finite-element</td>
<td>-0.262 005 070 23</td>
</tr>
</tbody>
</table>

1996, Ackermann and Shertzer [20] carried out an adaptive finite-element calculation. This method is like a variational calculation in that the energy values are true upper bounds to the exact energies. The wave function is expanded in terms of the Lagrange polynomials \( \phi_i^{(p)} \), \( i = 1, 2, \ldots, M \):

\[
\Psi \approx \Psi_{\text{FEM}}^{(p)} = \sum_{i=0}^{M} c_i \phi_i^{(p)}.
\]

With 2267 gridpoints they calculated an energy of \( E = -0.262 005 070 23 \).

The results of all the above are shown in Table 1.

The hydrogen negative ion, in contrast to the positronium negative atom, has been a subject of study almost since the beginning of quantum mechanics. Early calculations were done on H$^-$ by Bethe, Hylleraas, Heinrich, and Chandresekhar using standard Hylleraas type wave functions as well as slight modifications. The best result obtained [21], for the ground state, was \( E = -0.527 56 \) a.u.

Calculations, much closer to the present day, were carried out by Frolov and Yeremin using the same wave functions as mentioned above for the infinite nuclear mass ground state of H$^-$. Their estimate of the total energy is \( E = -0.527 751 016 52 \) a.u. In 1992, Frolov and Bishop [22], carried out the same calculation as Frolov and Yeremin with no improvement in the H$^-$ energy.

Ackermann and Shertzer, in the same 1996 paper as mentioned previously, calculated an energy of \( E = -0.527 445 881 110 \), which is for the finite nuclear mass case, while the values of Frolov and Yeremin and Frolov and
Table 2: Summary of past results for $H^-$.

<table>
<thead>
<tr>
<th>Author</th>
<th>Year</th>
<th>Method</th>
<th>Energy (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bethe</td>
<td>1957</td>
<td>variational</td>
<td>-0.527 756</td>
</tr>
<tr>
<td>Frolov and Yeremin</td>
<td>1989</td>
<td>variational</td>
<td>-0.527 751 016 52</td>
</tr>
<tr>
<td>Frolov and Bishop</td>
<td>1992</td>
<td>variational</td>
<td>-0.527 751 016 52</td>
</tr>
<tr>
<td>Drake</td>
<td>1996</td>
<td>variational</td>
<td>-0.527 751 016 544 377</td>
</tr>
</tbody>
</table>

**Finite Nuclear Mass Case**

<table>
<thead>
<tr>
<th>Author</th>
<th>Year</th>
<th>Method</th>
<th>Energy (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ackermann and Shertzer</td>
<td>1996</td>
<td>adaptive finite-element</td>
<td>-0.527 445 881 110</td>
</tr>
<tr>
<td>Drake</td>
<td>1996</td>
<td>variational</td>
<td>-0.527 445 881 114 322</td>
</tr>
</tbody>
</table>

$\mu/M = 5.443205668 \times 10^{-4}$

Bishop are for the case of infinite nuclear mass. It must be noted here that the value for the finite mass energy, as calculated in this work, is below their value even with only 376 basis elements, as opposed to the 2333 grid points they used.

In 1996, Drake [23] did a variational calculation with wave functions similar to those introduced by Hylleraas, with the distinction that two sets of nonlinear parameters were used. This doubled basis set consists of terms

$$\{\chi_{ijk}(\alpha_A, \beta_A), \chi_{ijk}(\alpha_B, \beta_B)\}$$

where

$$\chi_{ijk}(\alpha, \beta) = r_1^i r_2^j r_3^k e^{-ar_1 - \beta r_2} \pm \text{exchange}.$$  

His values for the infinite mass case and the finite mass case are $-0.527 751 016 544 377$ and $-0.527 445 881 114 322$.

The results are listed in Table 2.

### 3 Variational Principle

#### 3.1 Stationary States

High precision calculations for the eigenvalues and eigenfunctions of three-body atomic systems often utilize the variational principle. This technique is employed since, for three-body systems, the form of the wave function
includes correlation, and therefore, makes the Schrödinger equation nonseparable.

If $|\Psi\rangle$ is an eigenfunction of $H$ with eigenvalue $E$ we may write

$$H|\Psi\rangle = E|\Psi\rangle.$$  \hspace{1cm} (9)

Multiplying this equation by $\langle \Psi |$ we get

$$\langle \Psi | H | \Psi \rangle = \langle \Psi | E | \Psi \rangle$$  \hspace{1cm} (10)

$$= E \langle \Psi | \Psi \rangle.$$

Solving the above for $E$ gives

$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}.$$ \hspace{1cm} (11)

Since the eigenvalues in the above represent stable atomic states, we know that the eigenfunctions of the Hamiltonian satisfy of the Schrödinger principle

$$\delta E = 0.$$ \hspace{1cm} (12)

### 3.2 Matrix Equivalency

In practice we write our trial wave function in the form

$$\Psi_{tr} = \sum_{i=1}^{N} c_i \phi_i,$$ \hspace{1cm} (13)

where the basis set of functions $\phi_i$ becomes complete only when the summation is carried out over an infinite number of terms. The linear coefficients $c_i$ are determined by Eq. (12), where we want the resultant energy to be a minimum.

The explicit form of Eq. (12), where the energy $E$ depends on a set of linear parameters $c_i$, is

$$\delta E = \sum_{i} \frac{\partial E}{\partial c_i} \delta c_i = 0.$$ \hspace{1cm} (14)

If the $\delta c_i$ are arbitrary, nonzero variations of the linear coefficients then we require that

$$\frac{\partial E}{\partial c_i} = 0$$ \hspace{1cm} (15)
identically for all $i$.

Applying this condition to the energy derived from our trial wave function (13) gives us a system of $N$ homogeneous linear equations

$$\frac{\partial E_{tr}}{\partial c_k} = 0, \quad \text{for all } c_k.$$  \hfill (16)

Using Eq. (13), we may rewrite Eq. (11) as

$$E_{tr} = \frac{\langle \Psi_{tr} | H | \Psi_{tr} \rangle}{\langle \Psi_{tr} | \Psi_{tr} \rangle} = \sum_{ij} \frac{c_i c_j | \phi_i \rangle \langle \phi_j | H | \phi_j \rangle}{\sum_{ij} c_i^* c_j} = \sum_{ij} \frac{c_i^* c_j H_{ij}}{\sum_{ij} c_i^* c_j}.$$  \hfill (17)

This allows us to derive the left-hand side of Eq. (16):

$$\frac{\partial E_{tr}}{\partial c_k} = \frac{(\sum_{ij} c_i^* c_j O_{ij})(\sum_{ij} c_i^* H_{ij} \delta_{jk}) - (\sum_{ij} c_i^* c_j H_{ij})(\sum_{ij} c_i^* O_{ij} \delta_{jk})}{(\sum_{ij} c_i^* c_j O_{ij})^2} \sum_{ij} c_i^* c_j O_{ij} = \frac{\sum_{i} c_i^* H_{ik} - E_{tr} \sum_{i} c_i^* O_{ik}}{\sum_{ij} c_i^* c_j O_{ij}},$$  \hfill (18)

where we have used Eq. (17) in the last line.

Now we have

$$\frac{\partial E_{tr}}{\partial c_k} = 0 \quad \text{and} \quad \sum_{i} c_i^* H_{ik} - E_{tr} \sum_{i} c_i^* O_{ik} = 0 \quad \sum_{ij} c_i^* O_{ij} = 0.$$  \hfill (19)

Taking the complex conjugate of this and noting that $H_{ik}^* = H_{ik}, O_{ik}^* = O_{ik}$, and $E_{tr}^* = E_{tr}$ we have

$$\sum_{i} c_i (H_{ik} - E_{tr} O_{ik}) = 0.$$  \hfill (20)
This is equivalent to the matrix equation

\[ \mathbf{H} \mathbf{c} = \mathbf{E} \mathbf{O} \mathbf{c}, \]  

(21)

where the matrix elements of \( \mathbf{H} \) are \( H_{ij} = \langle \phi_i | H | \phi_j \rangle \), of \( \mathbf{O} \) are \( O_{ij} = \langle \phi_i | \phi_j \rangle \), and \( \mathbf{c} \) is a column matrix of coefficients. Diagonalizing \( \mathbf{H} \) will yield \( N \) eigenvalues \( E_j \) \( (j = 1, 2, 3, \ldots, N) \). The \( j \)th column vector of \( \mathbf{c} \), corresponding to the eigenvalue \( E_j \), represents the optimum values for the components of \( |\Psi_j\rangle \). Thus, the column vector \( \mathbf{c} \) represents \( \Psi_{tr} \) in the chosen basis.

### 3.3 Bounded Solution

Even if \( \Psi \) is not an exact eigenfunction of \( H \), the Schrödinger variational principle is still useful because the corresponding energy eigenvalue is an upper bound to the exact energy eigenvalue. To prove this, an arbitrary trial function can always be expanded in terms of the complete set of exact eigenfunctions according to

\[ \Psi_{tr} = \sum_i c_i \varphi_i. \]  

(22)

The \( \varphi_i \) of Eq. (22) by definition satisfy the Schrödinger equation

\[ H |\varphi_i\rangle = E_i |\varphi_i\rangle, \]  

(23)

where \( E_0, E_1, E_2, \ldots \) are the true eigenvalues in increasing order. It is possible to write Eq. (22), in principle, even though the exact \( \varphi_i \) are not known, since the \( \varphi_i \) span the Hilbert space.

Given the above, the overlap integral may be expressed as

\[
\langle \Psi_{tr} | \Psi_{tr} \rangle = \sum_{ij} c_i^* c_j \langle \varphi_i | \varphi_j \rangle
\]

\[
= \sum_{ij} c_i^* c_j \langle \varphi_i | \varphi_j \rangle
\]

\[
= \sum_{ij} c_i^* c_j \delta_{ij}
\]

\[
= \sum_i c_i^* c_i
\]

\[
= \sum_i |c_i|^2
\]
Now, if $\Psi_{tr}$ normalizes to unity we have

$$\sum_i |c_i|^2 = 1. \quad (25)$$

We know from Eq. (11) that we can write the energy as

$$E_{tr} = \frac{\langle \Psi_{tr}|H|\Psi_{tr} \rangle}{\langle \Psi_{tr}|\Psi_{tr} \rangle} = \langle \Psi_{tr}|H|\Psi_{tr} \rangle,$$  \quad (26)

where we have used the fact that $\langle \Psi_{tr}|\Psi_{tr} \rangle = 1$. This allows us to express the trial energy $E_{tr}$ as

$$E_{tr} = \langle \Psi_{tr}|H|\Psi_{tr} \rangle$$
$$= \sum_{ij} \langle c_i \varphi_i|H|c_j \varphi_j \rangle$$
$$= \sum_i \{ \langle c_i \varphi_i|H|c_0 \varphi_0 \rangle + \langle c_i \varphi_i|H|c_1 \varphi_1 \rangle + \ldots \}$$
$$= \sum_i \{ c_i^* c_0 \langle \varphi_i|E_0|\varphi_0 \rangle + c_i^* c_1 \langle \varphi_i|E_1|\varphi_1 \rangle + \ldots \}$$
$$= \sum_i c_i^* \{ c_0 E_0 \langle \varphi_i|\varphi_0 \rangle + c_1 E_1 \langle \varphi_i|\varphi_1 \rangle + \ldots \}$$
$$= \sum_i c_i^* \{ c_0 E_0 \delta_{i0} + c_1 E_1 \delta_{i1} + \ldots \}$$
$$= c_i^* c_0 E_0 + c_i^* c_1 E_1 + \ldots$$
$$= |c_0|^2 E_0 + |c_1|^2 E_1 + \ldots$$
$$= \{ 1 - |c_1|^2 - |c_2|^2 - \ldots \} E_0 + |c_1|^2 E_1 + |c_2|^2 E_2 + \ldots$$
$$= E_0 + |c_1|^2 (E_1 - E_0) + |c_2|^2 (E_2 - E_0) + \ldots.$$  \quad (27)

since, by Eq. (25),

$$|c_0|^2 = 1 - |c_1|^2 - |c_2|^2 - \ldots \quad (28)$$

It is obvious from the above that

$$E_{tr} \geq E_0 \quad (29)$$

and thus provides an upper bound to the true ground state energy.

### 3.4 Higher Eigenvalues

The result of the above section can be extended to higher eigenvalues via the matrix interleaving theorem. The theorem states that when an extra
column and row are added to a matrix, the \( N \) old eigenvalues lie between the \( N + 1 \) new ones. Since the system is bounded from below and the variational eigenvalues become the exact eigenvalues in the limit \( N \to \infty \), no variational eigenvalue can fall through the corresponding exact eigenvalue. This ensures that the \( N \) variational eigenvalues are upper bounds to the \( N \) true eigenvalues of the system. This is known as the Hylleraas-Undheim [24] theorem in atomic physics. As a result, the \( N \) variational eigenvalues move progressively toward the exact values as \( N \) is increased.

4 General Integral

To determine the Hamiltonian and overlap matrix elements we must evaluate integrals which include both radial and angular parts. These parts are determined by the form of the wave function we choose to describe our physical system. In Hylleraas coordinates (see Fig. 1), the independent variables that specify our system are \( \theta_1, \phi_1, \chi, r_1, \) and \( r_{12} \), where \( \theta_1 \) and \( \phi_1 \) are the spherical polar angles of the vector \( \mathbf{r}_1 \), and \( \chi \) is the angle of rotation of the rigid triangle formed by \( \mathbf{r}_1, \mathbf{r}_2, \) and \( \mathbf{r}_{12} \) about the \( \mathbf{r}_1 \) direction.

General expressions for the reduction of a wide range of two electron matrix elements to finite sums of angular coefficients and radial integrals were developed by Drake in 1978 [25]. His calculations were carried out in the above coordinate system.

4.1 Reduction of Angular Integral

The integrals needed for the present calculations have the general form (for details of the following the reader is referred to Ref. [26, 27])

\[
I = \int \int dr_1 dr_2 R' \mathcal{Y}_{l_1 l_2 L}^{M'}(\hat{r}_1, \hat{r}_2) \mathcal{T}_{k_1 k_2 K}^{Q} \mathcal{Y}_{l_1 l_2 L}^{M}(\hat{r}_1, \hat{r}_2) R, \tag{30}
\]

where \( \mathcal{Y}_{l_1 l_2 L}^{M'}(\hat{r}_1, \hat{r}_2), \mathcal{Y}_{l_1 l_2 L}^{M}(\hat{r}_1, \hat{r}_2), \) and \( \mathcal{T}_{k_1 k_2 K}^{Q} \) are vector coupled products of spherical harmonics given by

\[
\mathcal{Y}_{l_1 l_2 L}^{M}(\hat{r}_1, \hat{r}_2) = \sum_{m_1, m_2} \langle l_1 l_2 m_1 m_2 | LM \rangle Y_{l_1}^{m_1}(\hat{r}_1) Y_{l_2}^{m_2}(\hat{r}_2),
\]
Figure 1: Hylleraas coordinate system.
\[ \mathcal{T}_{k_1k_2K}(\hat{r}_1, \hat{r}_2) = \sum_{q_1q_2} \langle k_1k_2q_1q_2|KQ \rangle Y_{k_1}^{q_1}(\hat{r}_1)Y_{k_2}^{q_2}(\hat{r}_2). \]  

(31)

The function \( R = R(r_1, r_2, r_{12}) \) is the correlated radial part of the integral.

Using the fact that the spherical polar coordinates \( \theta_2 \) and \( \phi_2 \) of \( \mathbf{r}_2 \) are not independent, but can be expressed in terms of the independent variables \( \mathbf{r}_1, \mathbf{r}_{12}, \theta_1, \phi_1, \) and \( \chi \) using rotation matrices, one can arrive at the basic angular integral algorithm

\[ I(l_1m_1, l_2m_2; R'R) = 2\pi\delta_{m_1m_2}\delta_{l_1l_2}I_{l_1}(R'R), \]

(32)

where

\[ I_{l}(R'R) = \int_{0}^{\infty} r_1 dr_1 \int_{0}^{\infty} r_2 dr_2 \int_{r_{12}-r_2}^{r_1+r_2} r dr \, R'R P_l(\cos \theta). \]

(33)

The radial integral \( I_{l}(R'R) \) will be considered in the next section. For now, it is important to note that \( \cos \theta \) is a purely radial function, defined by

\[ \cos \theta = \frac{r_1^2 + r_2^2 - r^2}{2r_1r_2}, \]

(34)

and \( P_l(\cos \theta) \) is the ordinary Legendre polynomial.

The above, in conjunction with standard angular-momentum coupling techniques, allows one to write the general integral in terms of 3-\( j \), 6-\( j \), and 9-\( j \) symbols as

\[ I = (-)^{L'-M'} \left( \begin{array}{ccc} \frac{L'}{2} & K & L \\ -M' & Q & M \end{array} \right) \sum_{\lambda_1, \lambda_2, \lambda} X_{\lambda_1, \lambda_2, \lambda} D_{\lambda_1, \lambda_2, \lambda} I_{\lambda}(R'R), \]

(35)

where \((a, b, \ldots) = (2a + 1)(2b + 1) \ldots,\)

\[ X_{\lambda_1, \lambda_2, \lambda} = \frac{(-)^{l_1' + l_2 + L + \lambda}}{8\pi} (\lambda_1, \lambda_2, \lambda)(l_1, k_1, l_1', k_1', l_2, k_2, L, L', K)^{1/2} \]

\[ \times \begin{pmatrix} l_1 & k_1 & \lambda_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1' & \lambda_1 & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & k_2 & \lambda_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2' & \lambda_2 & \Lambda \end{pmatrix}, \]

(36)

and

\[ D_{\lambda_1, \lambda_2, \lambda} = \left\{ \begin{array}{ccc} L' & l_2' & l_1' \\ \Lambda & \lambda_1 & \lambda_2 \end{array} \right\} \left\{ \begin{array}{ccc} l_1 & l_2 & L \\ k_1 & k_2 & K \end{array} \right\}. \]

(37)

The general integral can thus be expressed in the simple form

\[ I = \sum_{\Lambda} C_{\Lambda} I_{\Lambda}(R'R), \]

(38)
where
\[ C_{\Lambda} = \sum_{\lambda_1, \lambda_2} C_{\lambda_1, \lambda_2, \Lambda} \] (39)
are the angular coefficients, and
\[ C_{\lambda_1, \lambda_2, \Lambda} = (-)^{L-M'} \begin{pmatrix} L' & K & L \\ -M' & Q & M \end{pmatrix} X_{\lambda_1, \lambda_2, \Lambda} D_{\lambda_1, \lambda_2, \Lambda}. \] (40)

For the the case of \( K = 0 \) the angular coefficients have the simpler form
\[ C_{\Lambda}(1) = \frac{(-1)^{L+\Lambda}}{8\pi} (2\Lambda + 1)(l_1, l_1', l_2, l_2')^{1/2} \begin{pmatrix} l_1' & l_1 & \Lambda \\ 0 & 0 & 0 \end{pmatrix} \]
\[ \times \begin{pmatrix} l_2' & l_2 & \Lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L & l_1 & l_2 \\ \Lambda & l_2' & l_1' \end{pmatrix}. \] (41)

4.2 Radial Integral

In the present calculation, the correlated radial part of the wave function has the form
\[ R(r_1, r_2, r_{12}) = r_1^i r_2^j r_{12}^k e^{-\alpha r_1 - \beta r_2 - \gamma r_{12}}. \] (42)

The basic radial integral that we need to evaluate is
\[ I(i, j, k) = \int_0^\infty r_1^{i+1} e^{-\alpha r_1} dr_1 \int_0^\infty r_2^{j+1} e^{-\beta r_2} dr_2 \int_{|r_1-r_2|}^{r_1+r_2} r_{12}^{k+1} e^{-\gamma r_{12}} dr_{12}. \] (43)

For the specific case of \( i = j = k = -1 \), the integral reduces to the following:
\[ I(-1, -1, -1) = \int_0^\infty dr_1 \int_0^\infty dr_2 \int_{|r_1-r_2|}^{r_1+r_2} dr_{12} e^{-\alpha r_1 - \beta r_2 - \gamma r_{12}} \] (44)

In order to deal with the absolute value in the limit of this integral we can split it up into two parts:
\[ I(-1, -1, -1) = \int_0^\infty dr_1 \int_0^\infty dr_2 \int_{r_1-r_2}^{r_1+r_2} dr_{12} e^{-\alpha r_1 - \beta r_2 - \gamma r_{12}} \]
\[ + \int_0^\infty dr_2 \int_0^\infty dr_1 \int_{r_1-r_2}^{r_1+r_2} dr_{12} e^{-\alpha r_1 - \beta r_2 - \gamma r_{12}} \] (45)

Carrying out the integration we are left with the result
\[ I(-1, -1, -1) = \frac{2}{(\alpha + \beta)(\alpha + \gamma)(\beta + \gamma)}. \] (46)

From this equation we can generate all higher-power integrals through the relation
\[ I(i, j, k) = (-1)^{i+j+k+3} \frac{\partial^{i+1}}{\partial \alpha^{i+1}} \frac{\partial^{j+1}}{\partial \beta^{j+1}} \frac{\partial^{k+1}}{\partial \gamma^{k+1}} \left[ \frac{2}{(\alpha + \beta)(\alpha + \gamma)(\beta + \gamma)} \right]. \] (47)
Using Leibnitz’s notation [28] we can write

$$D^p_a \equiv \frac{\partial^{i+1}}{\partial \alpha^{i+1}}; \quad D^m_\beta \equiv \frac{\partial^{j+1}}{\partial \beta^{j+1}}; \quad D^n_\gamma \equiv \frac{\partial^{k+1}}{\partial \gamma^{k+1}},$$

where $p = i + 1$, $m = j + 1$, $n = k + 1$. This implies that

$$D^p_a D^m_\beta D^n_\gamma (uv) = D^p_a D^m_\beta (u'v') = D^p_a (u''v'') = \frac{I(i, j, k)}{(-1)^{p+m+n}}.$$  \hspace{1cm} (49)

where

$$u = \frac{1}{(\alpha + \beta)(\alpha + \gamma)},$$

$$v = \frac{2}{(\beta + \gamma)}.$$

$$D^N(uv) = uD^Nv + \binom{N}{1} (Du)(D^{N-1}v)$$

$$+ \binom{N}{2} (D^2u)(D^{N-2}v) + \ldots + vD^Nu,$$ \hspace{1cm} (50)

and $\binom{N}{1}, \binom{N}{2}, \ldots$ are the binomial coefficients.

Performing the required differentiation, we get

$$D^p_a (u''v'') = \sum_{a=0}^{p} \sum_{b=0}^{m} \sum_{c=0}^{n} 2 (-1)^{p+m+n} \binom{p}{a} \binom{m}{b} \binom{n}{c}$$

$$\times \frac{(a+b)!(c+p-a)!(n+m-b-c)!}{(\alpha + \beta)^{a+b+1}(\alpha + \gamma)^{c+p-a+1}(\beta + \gamma)^{n+m-b-c+1}}$$

$$= \sum_{a=0}^{p} \sum_{b=0}^{m} \sum_{c=0}^{n} 2 (-1)^{p+m+n} \frac{a! b! c! (p-a)! (m-b)! (n-c)!}{m! n!}$$

$$\times \frac{(a+b)!(c+p-a)!(n+m-b-c)!}{(\alpha + \beta)^{a+b+1}(\alpha + \gamma)^{c+p-a+1}(\beta + \gamma)^{n+m-b-c+1}}.$$ \hspace{1cm} (51)

So now the general radial integral is

$$I(p, m, n) = (-1)^{p+m+n} D^p_a (u''v'')$$

$$= \sum_{a=0}^{p} \sum_{b=0}^{m} \sum_{c=0}^{n} \frac{2 p! m! n!}{a! b! c! (p-a)! (m-b)! (n-c)!}$$

$$\times \frac{(a+b)!(c+p-a)!(n+m-b-c)!}{(\alpha + \beta)^{a+b+1}(\alpha + \gamma)^{c+p-a+1}(\beta + \gamma)^{n+m-b-c+1}}.$$ \hspace{1cm} (52)

since the factor $(-1)^{2(p+m+n)} = +1$ for all integer $p$, $m$, $n$. 

\hspace{1cm} 24
It is possible to write this expression in a more compact form if we extract all terms that depend explicitly upon $a$. Upon doing so, we may write

$$I(p, m, n) = \sum_{b=0}^{m} \sum_{c=0}^{n} \frac{2p! m! n! (n + m - b - c)! T(b, c, p)}{b! c! (m - b)! (n - c)! (\alpha + \beta)^{b+1} (\alpha + \gamma)^{c+p+1} (\beta + \gamma)^{n+m-b-c+1}}.$$

where

$$T(b, c, p) = \sum_{a=0}^{p} \frac{(a + b)! (c + p - a)! (\alpha + \gamma)^{a}}{a! (p - a)! (\alpha + \beta)}.$$

It is useful, for computational purposes, to note two special cases of this three-dimensional array:

$$T(0, 0, p) = \sum_{a=0}^{p} \left( \frac{\alpha + \gamma}{\alpha + \beta} \right)^{a}$$

and

$$T(b, c, 0) = bc!.$$

### 4.3 Hamiltonian Matrix Elements.

The infinite nuclear mass Hamiltonian, in $Z$-scaled atomic units, is given by

$$H = -\frac{1}{2} \nabla_{1}^{2} - \frac{1}{2} \nabla_{2}^{2} - \frac{1}{r_{1}} - \frac{1}{r_{2}} + \frac{Z^{-1}}{r_{12}}.$$

Let us first consider how the operator $\nabla_{1}^{2}$ acts on the wave function

$$\Psi(r_{1}, r_{2}) = \sum_{i,j,k} a_{ijk} r_{1}^{i} r_{2}^{j} \frac{e^{-a r_{1} - b r_{2} - c r_{12}}}{r_{12}} \mathcal{Y}_{l_{1}l_{2}l_{3}}^{m}(\hat{r}_{1}, \hat{r}_{2}).$$

The operator $\nabla_{1}^{2}$ has the form

$$\nabla_{1}^{2} = \frac{1}{r_{1}^{2}} \frac{\partial}{\partial r_{1}} \left( \frac{r_{1}^{2}}{r_{1}^{2}} \frac{\partial}{\partial r_{1}} \right) + \frac{1}{r_{12}^{2}} \frac{\partial}{\partial r_{12}} \left( \frac{r_{12}^{2}}{r_{12}^{2}} \frac{\partial}{\partial r_{12}} \right) - \frac{(1^{m})^{2}}{r_{1}^{2}}$$

$$+ \frac{2(r_{1} - r_{2} \cos \theta_{12})}{r_{12}} \frac{\partial^{2}}{\partial r_{1} \partial r_{12}} - 2(\nabla_{1}^{m} \cdot r_{2}) \frac{1}{r_{12}} \frac{\partial}{\partial r_{12}},$$

where $\mathcal{Y}^{m}$ is defined to act only on the angular part of the wave function; and $\nabla_{2}^{2}$ is of the same form except with the index change $1 \rightarrow 2$. Thus, letting (59) act upon (58), we may write

$$\nabla_{1}^{2} \Psi(r_{1}, r_{2}) = \left\{ \frac{1}{r_{1}^{2}} [i(i + 1) - l_{1}(l_{1} + 1)] + \frac{k(k + 1)}{r_{12}^{2}} \right\} \Psi(r_{1}, r_{2}) + \left\{ \frac{1}{r_{2}^{2}} [i(i + 1) - l_{2}(l_{2} + 1)] + \frac{k(k + 1)}{r_{12}^{2}} \right\} \Psi(r_{2}, r_{1}).$$
\[-2 \left( \frac{\alpha(i + 1)}{r_1} + \frac{\gamma(k + 1)}{r_{12}} \right) + \frac{2(r_1 - r_2 \cos \theta_{12})}{r_1r_{12}^2} \left((k - \gamma r_{12})(i - \alpha r_1)\right) - \frac{2(\hat{\nabla}_1^2 \cdot \hat{r}_2)r_2}{r_1^2 r_{12}^2} \left[k - \gamma r_{12} + \alpha^2 + \gamma^2\right] \Psi(r_1, r_2). \quad (60)\]

We may write the complete Hamiltonian as

\[H' = H + H_1, \quad (61)\]

where \(H_1\) is the mass polarization term, given by

\[-\frac{\mu}{M} \nabla_1 \cdot \nabla_2. \quad (62)\]

The differential operator \(\nabla_2\) has the form

\[\nabla_2 = \hat{r}_2 \frac{\partial}{\partial r_2} + \frac{(r_2 - r_1)}{r_{12}} \frac{\partial}{\partial r_{12}} + \frac{\hat{\nabla}_2^\gamma}{r_2}; \quad (63)\]

and \(\nabla_1\) is of the same form with subscripts 1 and 2 interchanged. Thus, the matrix elements of the mass polarization operator are

\[H_1 = -\frac{\mu}{M} \left\{ \frac{1}{r_1r_2} \left[i j \cos \theta + i(\hat{\nabla}_1^\gamma \cdot \hat{\nabla}_2^\gamma) + j(\hat{r}_2 \cdot \hat{\nabla}_1^\gamma) + \hat{\nabla}_1^\gamma \cdot \hat{\nabla}_2^\gamma \right] \right. \]
\[+ \frac{1}{r_1} \left[ -\beta(i \cos \theta + \hat{r}_2 \cdot \hat{\nabla}_2^\gamma) \right] + \frac{1}{r_2} \left[ -\alpha(i \cos \theta + \hat{r}_1 \cdot \hat{\nabla}_1^\gamma) \right] \]
\[+ \frac{1}{r_{12}} \left[ \gamma(i + j + 2k + 2) \right] - \frac{1}{r_{12}^2} \left[k(k + 1) + jk + ik\right] \]
\[+ \frac{r_1}{r_{12}} \left[ \gamma(\beta \cos \theta - \alpha) \right] + \frac{r_2}{r_{12}} \left[ \gamma(\alpha \cos \theta - \beta) \right] \]
\[+ \frac{r_2}{r_{12}^2} \left[ \beta k - \alpha k \cos \theta \right] + \frac{r_1}{r_{12}^2} \left[ \alpha k - \beta k \cos \theta \right] \]
\[+ \frac{r_1}{r_{21}r_{12}} \left[ -\gamma(i \cos \theta + \hat{r}_1 \cdot \hat{\nabla}_1^\gamma) \right] + \frac{r_2}{r_{12}r_{12}} \left[ -\gamma(i \cos \theta + \hat{r}_2 \cdot \hat{\nabla}_2^\gamma) \right] \]
\[+ \frac{r_2}{r_{12}r_{12}^2} \left[k(i \cos \theta + \hat{r}_2 \cdot \hat{\nabla}_1^\gamma) \right] + \frac{r_1}{r_{21}r_{12}^2} \left[k(i \cos \theta + \hat{r}_1 \cdot \hat{\nabla}_2^\gamma) \right] \]
\[+ \alpha \beta \cos \theta - \gamma^2 \right\}. \quad (64)\]

5 Description of the Calculations

For our variational calculation, we expand the trial wave function in a doubled basis set [29] (in Hylleraas coordinates)

\[\{ R_{ijk}(\alpha_A, \beta_A, \gamma_A), R_{ijk}(\alpha_B, \beta_B, \gamma_B) \}, \quad (65)\]

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where
\[ R_{ijk}(\alpha, \beta, \gamma) = r_1^i r_2^j r_{12}^k e^{-\alpha r_1 - \beta r_2 - \gamma r_{12}}. \] (66)

The completeness of the radial part of the basis set has been proven by Klahn and Bingel [30]. Our wave function, thus, has the form (for S states)
\[ \Psi(r_1, r_2) = (1 + P_{1 \rightarrow 2}) \sum_{ijk} a_{ijk} [R_{ijk}(\alpha_A, \beta_A, \gamma_A) + R_{ijk}(\alpha_B, \beta_B, \gamma_B)]. \] (67)

Since our basis set is nonorthogonal, the overlap integral must be carried throughout the calculation in order to obtain the correct eigenvalues:
\[ E(\Psi) = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \] (68)

In contrast to previous three-body atomic calculations done by Drake [31], our basis set contains three, instead of two, nonlinear parameters. The reason for the introduction of this new parameter is to be able to extend the accuracy obtained by Drake for helium into the molecular region. Introducing the new nonlinear parameter allows distance scales in the wave function to be chosen independently for all radial coordinates, \( r_1, r_2, r_{12} \). (The older basis sets exhibit such an independence for only the ‘electron-nuclear’ coordinates \( r_1 \) and \( r_2 \).) The need for this independent scale-setting becomes more important as the atomic mass ratio gets closer to unity. Without the new parameter the basis set starts to produce large linear coefficients that cancel; this seems to be a sort of mimicking of an exponential decay of the wave function along the \( r_{12} \) coordinate. This is justified by the fact that when the two \( \gamma \)'s are introduced the \( \alpha \)'s and \( \beta \)'s can be reduced, i.e. the larger \( \alpha \)'s and \( \beta \)'s are compensated for by allowing for exponential decay along the \( r_{12} \) direction through the new \( \gamma \)-dependence.

A given basis set is defined by including all terms such that the powers satisfy
\begin{align*}
i + j + k & \leq \omega, \\
i & \leq j, \\
i + j + k + |i - j| & \leq \omega + 1 + M. \end{align*} (69)
The value of $M$ is adjusted downward as much as possible without significantly disrupting the convergence of the largest basis sets; and then the convergence is studied as $\omega$ is increased. These truncations of the basis set are introduced to avoid near linear dependence and redundancy. Although the basis set is, in a strict mathematical sense, linearly independent, the calculations are carried out using finite computer precision; and so, problems of linear dependence may arise. This can occur even though the difference in the values between members of the basis set are well above the internal accuracy of the computer; it is a result of the collective effect of the basis set members taken all together becoming linearly dependent.

The above basis set was used to determine the nonrelativistic $1s^2 \ 1S$ ground state energies for $H^-$ and $Ps^-$. The accuracy of the calculations for these states is determined by both the numerical stability of the method used and by the extent of convergence. The numerical stability of the method employed ensures that round-off error is kept below the level of convergence. And since, by the variational principle, the variational eigenvalues approach the exact eigenvalues with increasing basis set size, we may take the level of convergence as a measure of the accuracy of the calculations.

Another element that must be considered when speaking of accuracy is the effect of small adjustments in the nonlinear parameters. Since we have optimized the energy with respect to these nonlinear parameters, we are in essence saying that our value for the energy is at a minimum with respect to all the nonlinear parameters. Therefore, our answers should be independent of small adjustments of the parameters.

Thus the degree of convergence determines the accuracy of these calculations.

All calculations were carried out in quadruple precision (about 32 decimal digits on an RS/6000 workstation).
5.1 Solution of the Eigenvalue Problem

To obtain energies for our system we must solve the eigenvalue problem

\[ \mathbf{H} \tilde{\Psi} = E \mathbf{O} \tilde{\Psi}, \]  

(70)

where \( H_{mn} = \langle \Psi_m | H | \Psi_n \rangle \), \( O_{mn} = \langle \Psi_m | \Psi_n \rangle \), \( \Psi \) is that of Eq. (67), \( m, n \) denote distinct combinations of the powers \( i, j, k \) and \( \tilde{\Psi} \) is a column vector of linear coefficients. There are many of ways of solving the above problem; but since we are primarily interested in just the single eigenvalue of the Hamiltonian for the state being optimized, we may utilize what is known as the power method [32].

5.1.1 The Power Method

If \( \mathbf{H} \) is a diagonalizable, \( n \times n \) matrix with eigenvalues \( \lambda_1, \lambda_2, \ldots, \lambda_n \) corresponding to the eigenvectors \( \Psi^{(1)}, \Psi^{(2)}, \ldots, \Psi^{(n)} \) with ordering \( |\lambda_1| < |\lambda_2| < \cdots < |\lambda_n| \) (i.e. \( \mathbf{H} \) has a largest eigenvalue \( |\lambda_n| > |\lambda_i|, i \neq n \)) we may choose an arbitrary starting vector

\[ \chi_0 = a_1 \Psi^{(1)} + a_2 \Psi^{(2)} + \ldots + a_n \Psi^{(n)}, \]  

(71)

and then form the sequence

\[ \mathbf{H} \chi_0 = a_1 \lambda_1 \Psi^{(1)} + a_2 \lambda_2 \Psi^{(2)} + \ldots + a_n \lambda_n \Psi^{(n)} = \chi_1 \]
\[ \mathbf{H} \chi_1 = a_1 \lambda_1^2 \Psi^{(1)} + a_2 \lambda_2^2 \Psi^{(2)} + \ldots + a_n \lambda_n^2 \Psi^{(n)} = \chi_2 \]
\[ \vdots \]
\[ \mathbf{H} \chi_{k-1} = a_1 \lambda_1^k \Psi^{(1)} + a_2 \lambda_2^k \Psi^{(2)} + \ldots + a_n \lambda_n^k \Psi^{(n)} = \chi_k \]  

(72)

As \( k \) becomes large \( \chi_k \) becomes the eigenvector of \( \mathbf{H} \) with the largest eigenvalue:

\[ \chi_k = a_1 \lambda_1^k \Psi^{(1)} + a_2 \lambda_2^k \Psi^{(2)} + \ldots + a_n \lambda_n^k \Psi^{(n)} \]  

(73)

\[ \frac{\chi_k}{\lambda_n^k} = a_1 \left( \frac{\lambda_1}{\lambda_n} \right)^k \Psi^{(1)} + a_2 \left( \frac{\lambda_2}{\lambda_n} \right)^k \Psi^{(2)} + \ldots + a_n \Psi^{(n)} \]

Thus, since \( |\lambda_n| > |\lambda_i|, i \neq n \), and as \( k \to \infty \) we are left with

\[ \chi_k = a_n \lambda_n^k \Psi^{(n)}, \quad a_n \neq 0. \]  

(74)
From this we may infer that

\[ \chi_{k+1} = a_n \lambda_k^{k+1} \Psi^{(n)} = \lambda_n \chi_k \]  

(75)

and since

\[ \chi_{k+1} = H \chi_k \]  

(76)

we have

\[ H \chi_k = \lambda_n \chi_k . \]  

(77)

In order for us to be able to pick out any one of the \( n \) eigenvalues of \( H \)
we transform the above in the following way:

\[ H \chi = \lambda_n O \chi \]

\[ (H - \lambda_g O) \chi = (\lambda_n - \lambda_g) O \chi \]

\[ (H - \lambda_g O)^{-1} O \chi = \frac{1}{(\lambda_n - \lambda_g)} \chi \]  

(78)

\[ G \chi = \lambda' \chi \]

where \( G = (H - \lambda_g O)^{-1} O \) and \( \lambda' = \frac{1}{(\lambda_n - \lambda_g)} \). By choosing \( \lambda_g \) close to any
one of the eigenvalues \( \lambda_n \) will make \( \lambda' \) much larger for that \( \lambda_n \) than for any
other. We thus form the sequence

\[ \chi_1 = G \chi_0 \]

\[ \chi_2 = G \chi_1 \]  

(79)

\[ \chi_3 = G \chi_2 \]

\[ \vdots \]  

(80)

until the ratios of the components of two successive \( \chi \)'s stop changing.

The drawback to the above method is that it requires the inversion of a
matrix with \( \frac{1}{2} (n^2 + 1) \) elements (\( H \) is symmetric). To avoid this we do the
following:

\[ \chi_n = G \chi_{n-1} \]

\[ \chi_n = (H - \lambda_g O)^{-1} O \chi_{n-1} \]  

(81)

\[ (H - \lambda_g O) \chi_n = O \chi_{n-1} \]

\[ F \chi_n = O \chi_{n-1} \]

30
where \( F = (H - \lambda \rho O) \) and \( \lambda_n = \langle \chi_n | H | \chi_n \rangle / \langle \chi_n | \chi_n \rangle \). This requires us to solve a set of \( n \) inhomogeneous equations.

To solve this set of equations we use the square-root method [33]. To do this we write

\[
F = S^T S
\]

(82)

where \( S \) is an upper triangular matrix and \( S^T \) its transpose. Now we have

\[
S^T S \chi_n = O \chi_{n-1}
\]

(83)

or, equivalently,

\[
S^T K = O \chi_{n-1} \quad \text{and} \quad S \chi_n = K
\]

(84)

Knowing the elements of \( F \) allows us to find the elements of \( S \) and \( S^T \), which allow us to determine \( K \) (we know \( O \chi_n \)), and ultimately leads us to the elements of \( \chi_n \).

6 Optimization of Nonlinear Parameters

The values for the \( \alpha \)'s and \( \beta \)'s were originally taken from data compiled by Drake. These data were optimized using Newton's method, applied to the derivatives of the wave functions with respect to the nonlinear parameters, for the case of basis sets with only two nonlinear parameters. (Analytical expressions for the derivatives were used for this optimization process.) Optimization of the six nonlinear parameters used for the present calculations were carried out using a trial-and-error method.

7 Results and Discussion

Nonrelativistic energy eigenvalues were calculated for the \( 1s^2 \, ^1S \) state of \( Ps^- \) and \( H^- \). (The coding for the calculation of the radial integral is listed in the Appendix.) Detailed studies of the convergence patterns for the variational energies for these two atomic systems are presented in Tables 3 and 5. In addition, studies of the improvement over basis functions containing only two nonlinear parameters are given in Tables 4 and 6.
Figure 2: Behaviour of the nonlinear parameters in sector 1 for $P_s^-$. 

Ps- (Sector 1) 

Nonlinear Parameters 

$\alpha$, $\beta$, $\gamma$ 

Basis Set Size 

135 182 236 302 376 464 561 674 797
Figure 3: Behaviour of the nonlinear parameters in sector 2 for Ps⁻.
Figure 4: Behaviour of the nonlinear parameters in sector 1 for $H^-$. 
Figure 5: Behaviour of the nonlinear parameters in sector 2 for $H^-$. 
Tables 4 and 6 clearly show that an improvement of approximately 40% over the same calculations with only two nonlinear parameters has been obtained for the ground state of Ps\(^-\), while an improvement of about 30% has been obtained for H\(^-\). These improvements seem to be consistently better for larger basis set sizes.

The variational energies calculated in this work are true upper bounds to the exact energy levels; the result for H\(^-\) is the lowest value and the result for Ps\(^-\) is comparable to the lowest value in the literature to date. An extra decimal place or two of precision could be obtained by extrapolation.

The inclusion of two sets of nonlinear parameters provides a detailed description of the physical nature of the problem: the first set of nonlinear parameters (sector 1) in the wave function dominates at large distances, while the second set (sector 2) dominates for small radial distances. The values of the nonlinear parameters in sector 1 are relatively independent of basis set size while those in sector 2 increase. With reference to Figs. 2-5 we see that the necessity of a third nonlinear parameter decreases in sector 1 and increases in sector 2 for increasing basis set size. The stable behaviour of the nonlinear parameters – at the same time incorporating a completely automated optimization scheme – could be used to quickly predict new values for the parameters of larger basis sets.

The results obtained through this work, as a pilot project, clearly point to the success of utilizing this method for further calculations. Definitive calculations can now be made for the Ps\(^-\) and H\(^-\) systems as well as for other systems usually cast into the framework of a molecular problem, in particular H\(_2\)^+.

### 7.1 Suggestions for Future Work

The first step to be taken to try to increase the amount of improvement over the basis sets with only two nonlinear parameters is to completely automate the optimization process. In order to do this, we would calculate the first derivatives of the wave function with respect to all nonlinear parameters (the
linear parameters have already been optimized by diagonalizing the Hamiltonian) analytically, and then apply Newton's method to these derivatives until the change in energy is below a set minimum. This method has been employed by Drake and provides, in general, a rapid location of the minima (i.e. within a few iterations). This method, applied to the calculations done in this thesis, would ensure finding a lower and more stable energy; and, as the case may be, allow the possible study of multiple minima on the energy surface.

Another improvement, in the area of computer time, would be possible if recursion relations were used to calculate the integrals. As the program stands now, a three dimensional array is necessary to store values needed for the calculation of the radial integrals. As well, the calculation of the radial integrals involves a double summation, which is carried out for every integral. In this thesis this implies anywhere from 2 to $15^2$ runs through the integral subroutine. By applying a recursion relation this would involve storing at most the penultimate and last integrals and then performing a simple addition and multiplication for each new integral. This would allow for much quicker calculations and for basis sets of higher $N$ than found in this thesis.

Once this is done definitive calculations could be made for the $H^- \text{ and } Ps^-$ atomic systems; and new calculations could be made for heavier and more exotic systems like $H_2^+$ and muonic atoms, respectively. The interest in muonic atoms, besides various other reasons, lies in the phenomenon of muon-catalyzed fusion ($\mu$CF). These muonic atoms allow fusion to occur at room temperature. The lifetime of the muon ($\approx 2.197 \mu s$ [34]) is amply long for most experiments to be carried out.

The systems of concern in $\mu$CF [34] are of the form $xymu$, where $x, y = p, d, t$. In this notation, $p$ is a proton, $d$ is a deuteron (a proton plus a neutron), and $t$ triton (a proton plus two neutrons). The process of $\mu$CF is subject to both atomic and molecular as well as to nuclear physics. Calculations such as the expectation value of delta functions, the interparticle distances,
Table 3: Convergence pattern for the 1s² 1S state of Ps⁻, where Ratio = \[\frac{\text{Energy}(\Omega - 1) - \text{Energy}(\Omega)}{\text{Energy}(\Omega) - \text{Energy}(\Omega + 1)}\].

<table>
<thead>
<tr>
<th>Basis Set Size</th>
<th>Energy</th>
<th>Difference</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>135</td>
<td>-.262 005 066 102 130</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>182</td>
<td>-.262 005 069 552 908</td>
<td>.000000003450778</td>
<td>-</td>
</tr>
<tr>
<td>236</td>
<td>-.262 005 070 052 952</td>
<td>.00000000500044</td>
<td>6.9009</td>
</tr>
<tr>
<td>302</td>
<td>-.262 005 070 209 939</td>
<td>.00000000147987</td>
<td>3.3790</td>
</tr>
<tr>
<td>376</td>
<td>-.262 005 070 227 150</td>
<td>.0000000026211</td>
<td>5.6460</td>
</tr>
<tr>
<td>446</td>
<td>-.262 005 070 231 106</td>
<td>.000000003956</td>
<td>6.6260</td>
</tr>
<tr>
<td>561</td>
<td>-.262 005 070 232 600</td>
<td>.000000001494</td>
<td>2.6480</td>
</tr>
<tr>
<td>674</td>
<td>-.262 005 070 232 856</td>
<td>.000000000256</td>
<td>5.8360</td>
</tr>
<tr>
<td>797</td>
<td>-.262 005 070 232 950</td>
<td>.0000000000094</td>
<td>2.7234</td>
</tr>
</tbody>
</table>

Table 4: Study of the improvement in energies with the addition of a third nonlinear parameter for the 1s² 1S state of Ps⁻, where \( R = \frac{\gamma(\Omega) - E_0(\Omega)}{E_0(\Omega) - E_0(\Omega + 1)} \).

<table>
<thead>
<tr>
<th>Ω</th>
<th>Basis Size</th>
<th>( E_0 )</th>
<th>( E_\gamma )</th>
<th>( R )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>135</td>
<td>-.262 005 064 775 562</td>
<td>-.262 005 066 102 130</td>
<td>.2930</td>
</tr>
<tr>
<td>2</td>
<td>182</td>
<td>-.262 005 069 303 468</td>
<td>-.262 005 069 552 908</td>
<td>.3483</td>
</tr>
<tr>
<td>3</td>
<td>236</td>
<td>-.262 005 070 019 330</td>
<td>-.262 005 070 052 952</td>
<td>.2085</td>
</tr>
<tr>
<td>4</td>
<td>302</td>
<td>-.262 005 070 179 798</td>
<td>-.262 005 070 209 939</td>
<td>.4815</td>
</tr>
<tr>
<td>5</td>
<td>376</td>
<td>-.262 005 070 223 700</td>
<td>-.262 005 070 227 150</td>
<td>.5336</td>
</tr>
<tr>
<td>6</td>
<td>446</td>
<td>-.262 005 070 230 466</td>
<td>-.262 005 070 231 106</td>
<td>.3548</td>
</tr>
<tr>
<td>7</td>
<td>561</td>
<td>-.262 005 070 232 270</td>
<td>-.262 005 070 232 600</td>
<td>.6574</td>
</tr>
<tr>
<td>8</td>
<td>674</td>
<td>-.262 005 070 232 772</td>
<td>-.262 005 070 232 856</td>
<td>.5753</td>
</tr>
<tr>
<td>9</td>
<td>797</td>
<td>-.262 005 070 232 918</td>
<td>-.262 005 070 232 950</td>
<td>-</td>
</tr>
</tbody>
</table>

distances squared, and sticking fractions have, even to the present day have been restricted in accuracy due to the choice of basis set used [35, 36]. It is our opinion that using basis sets of the type used in this thesis will increase the accuracy of some, if not all, these calculations.
Table 5: Convergence pattern for the 1s² 1S state of H⁻, where Ratio = [Energy(Ω) - Energy(Ω + 1)]/Energy(Ω) - Energy(Ω + 1)].

<table>
<thead>
<tr>
<th>Basis Set Size</th>
<th>Energy</th>
<th>Difference</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>135</td>
<td>-0.527 445 879 902 832</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>182</td>
<td>-0.527 445 880 911 032</td>
<td>0.000000001008200</td>
<td>–</td>
</tr>
<tr>
<td>236</td>
<td>-0.527 445 881 075 780</td>
<td>0.000000000164748</td>
<td>6.1196</td>
</tr>
<tr>
<td>302</td>
<td>-0.527 445 881 105 889</td>
<td>0.000000000030109</td>
<td>5.4717</td>
</tr>
<tr>
<td>376</td>
<td>-0.527 445 881 112 222</td>
<td>0.00000000006333</td>
<td>4.7543</td>
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<tr>
<td>446</td>
<td>-0.527 445 881 113 825</td>
<td>0.0000000001603</td>
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<tr>
<td>561</td>
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<tr>
<td>674</td>
<td>-0.527 445 881 114 286</td>
<td>0.0000000000103</td>
<td>3.4757</td>
</tr>
<tr>
<td>797</td>
<td>-0.527 445 881 114 316</td>
<td>0.0000000000030</td>
<td>3.4333</td>
</tr>
</tbody>
</table>

Table 6: Study of the improvement in energies with the addition of a third nonlinear parameter for the 1s² 1S state of H⁻, where $R = [E₀(Ω) - E_γ(Ω)]/[E₀(Ω) - E₀(Ω + 1)]$.

<table>
<thead>
<tr>
<th>Ω</th>
<th>Basis Size</th>
<th>$E₀$</th>
<th>$E_γ$</th>
<th>$R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>135</td>
<td>-0.527 445 879 754 766</td>
<td>-0.527 445 879 902 832</td>
<td>0.1329</td>
</tr>
<tr>
<td>2</td>
<td>182</td>
<td>-0.527 445 880 869 141</td>
<td>-0.527 445 880 911 032</td>
<td>0.2144</td>
</tr>
<tr>
<td>3</td>
<td>236</td>
<td>-0.527 445 881 064 558</td>
<td>-0.527 445 881 075 780</td>
<td>0.2942</td>
</tr>
<tr>
<td>4</td>
<td>302</td>
<td>-0.527 445 881 102 701</td>
<td>-0.527 445 881 105 889</td>
<td>0.3574</td>
</tr>
<tr>
<td>5</td>
<td>376</td>
<td>-0.527 445 881 111 621</td>
<td>-0.527 445 881 112 222</td>
<td>0.3034</td>
</tr>
<tr>
<td>6</td>
<td>446</td>
<td>-0.527 445 881 113 602</td>
<td>-0.527 445 881 113 825</td>
<td>0.4208</td>
</tr>
<tr>
<td>7</td>
<td>561</td>
<td>-0.527 445 881 114 132</td>
<td>-0.527 445 881 114 183</td>
<td>0.3566</td>
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<td>8</td>
<td>674</td>
<td>-0.527 445 881 114 275</td>
<td>-0.527 445 881 114 286</td>
<td>0.3056</td>
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<tr>
<td>9</td>
<td>797</td>
<td>-0.527 445 881 114 311</td>
<td>-0.527 445 881 114 316</td>
<td>–</td>
</tr>
</tbody>
</table>
References


[7] See, for example, G. Herzberg


8 Appendix

What follows is the computer coding used to calculate the radial integrals involved in this thesis:

```plaintext
SUBROUTINE CAS1
IMPLICIT REAL*8 (A-H,O-Z)
COMMON/CS1CS/TCS(150,150,150)
COMMON/F1F/Y1G,Y2G,Y3G,MP1,MP2,MQ1,MQ2,MS1,MS2,ISUM
COMMON/A1A/FAC(51),Y(64),YP(64),Y1X(64),Y2X(64),Z1X(64)
DIMENSION YK(100)
ISUM = ISUM + 3
DO 2 K=0,ISUM
   Y13 = Y1G + Y3G
   Y12 = Y1G + Y2G
   Y123 = Y13/Y12
   Y123K = Y123**K
   YFAC = Y123K/FAC(K+1)
   YK(K+1) = YFAC
2 CONTINUE
DO 6 IPI=0,ISUM
DO 5 I=0,ISUM
   DO 4 J=0,ISUM
      SUM = 0
      DO 3 K=0,IPI
         S1 = FAC(J+K+1)*FAC(I+IPI-K+1)
         S2 = FAC(IPI-K+1)
         SUM = SUM + S1*YK(K+1)/S2
      3 CONTINUE
   TCS(I+1,J+1,IPI+1) = SUM
4 CONTINUE
5 CONTINUE
6 CONTINUE
```
FUNCTION CASSAR(IP,IM,IN)
IMPLICIT REAL*8 (A-H,O-Z)
COMMON/F1F/Y1G,Y2G,Y3G,MP1,MP2,MQ1,MQ2,MS1,MS2,ISUM
COMMON/CS1CS/TCS(150,150,150)
COMMON HB(1523385),AT(25000),JAT0(40),JAT(40,40),JCS(40,40)
1 ,ZSUM(50*50),BIN(50*50),X(50,9),AT0(50,50),JATD(28,28),
2 JCSD(28,28),ATD(12000),OVB(1523385)
COMMON/A1A/FAC(51),Y(64),YP(64),Y1X(64),Y2X(64),Z1X(64)
RAD = 0
Y12 = Y1G + Y2G
Y13 = Y1G + Y3G
Y23 = Y2G + Y3G
FPMN2 = 2*FAC(IP+1)*FAC(IM+1)*FAC(IN+1)
    DO 20 J=0,IM
        FJ12 = FAC(J+1)*FAC(IM-J+1)*(Y12**(J+1))
    DO 10 I=0,IN
        RAD= RAD + FPMN2*FAC(IN+IM-I-J+1)
+ *TCS(I+1,J+1,IP+1)/
+ (FJ12
+ *FAC(I+1)*FAC(IN-I+1)*(Y23)**(IN+IM-I-J+1)
+ *(Y13)**(I+IP+1))
10 CONTINUE
20 CONTINUE
CASSAR = RAD
RETURN
END
VITA AUCTORIS

Mark Michael Cassar was born in Windsor, Ontario on October 29, 1971. He graduated with Honours from Essex District High School in 1989. In the spring of 1994 he received his Honours Bachelor of Arts in English Language and Literature and Physics, and in the spring of 1995 he graduated with a Bachelor of Education with qualifications in the Intermediate/Senior Physics/Math area. In the summer of 1995 he was granted an Ontario Teacher’s Certificate. He entered into the Master of Science program at the University of Windsor in the fall of 1995 and expects to graduate in 1998.