Method of Variational Secular Equation for the Ground State of Helium Atom

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METHOD OF VARIATIONAL SECULAR EQUATION
FOR THE GROUND STATE OF HELIUM ATOM

by
Mih-seh Kong

A Thesis
Submitted to the
Faculty of The Graduate College
in partial fulfillment
of the
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Mih-seh Kong
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INTRODUCTION

The theory of one- and two- electron atoms is a fairly completed treated field in quantum mechanics. The dynamic models of the atoms are generally described by the Hamiltonian equation, whose eigenvalues give the allowed energy levels, and whose eigenfunctions are of use in calculating various properties of atoms. For one- electron hydrogen-like atoms, the eigenfunctions are almost exact and give results in good agreement with those obtained from analysis of atomic spectra which is considered the best base for the experimental values of atomic energy levels. The few corrections in hydrogen-like atoms are due to the finite nuclear mass and the structure of heavier nuclei. However, for atoms with more than one electron, the exact analytic eigenfunctions are impossible to construct so far; thus, various approximation method are used. Since the two- electron problem is the simplest and the most essential one among multi-electron-atom problems, a great deal of effort has been focused on looking for the best trial function for the two-electron Hamiltonian equation.

A commonly used method is that of regarding two electrons as moving independently in a central field and then treated the mutual repulsion of the two electrons
by a perturbation method. One method of constructing trial functions is the configuration-mixing method, which superposes the exact eigenfunctions of the hydrogen atom. The other method is the variational method, which is based on the idea of a screening effect: a variable parameter corresponding to the effective nuclear charge is introduced into the wave function. These two methods, and especially the variational method, both give acceptable-theoretical values for the lowest energy state (or "ground" state) of helium.

Our interest here is to combine these two methods, in the hope of getting a lower, and consequently better, theoretical energy level for ground-state Helium. In the first section, we shall discuss the symmetric property of helium which allows us to construct only spin singlet eigenfunctions. Then, we will review briefly the perturbation method, the variational method, and configurational mixing in sections 2 and 3. In sections 4 and 5 we will present the calculations and results of the combined method which is the main purpose of this work.
THE SYMMETRIC PROPERTY OF THE HELIUM ATOM

The Schroedinger equation for atoms having two electrons is:

\[
\frac{-\hbar^2}{2\mu} \left( \frac{1}{2} \left( \frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} \right) - \frac{ze^2}{r_1} - \frac{ze^2}{r_2} + \frac{e^2}{r_{12}} \right) \psi = E \psi, \quad \ldots \ldots (1)
\]

where \( \mu \) is the reduced mass of the system, \( r_1 \) and \( r_2 \) are the distances of the electrons from the nucleus; \( r_{12} \) is their mutual separation. By applying the technique of separation of variables and ignoring the interaction between two particles (we deal with this term as a perturbation later.), the eigenfunction can be written as the product of two independent-particle eigenfunctions:

\[ \psi(r_1, r_2) = \psi(r_1) \psi(r_2). \]

Since electrons are identical particles, the differential equation remains unchanged if the coordinates of two electrons are interchanged, i.e., \( \psi(r_1, r_2) \) and \( \psi(r_2, r_1) \) both satisfy the same Schroedinger equation. Therefore, \( \psi(r_2, r_1) = c \psi(r_1, r_2) \) where \( c \) is a constant, and, interchanging \( r_1 \) and \( r_2 \), \( \psi(r_1, r_2) = c \psi(r_2, r_1) \), therefore,

\[
c^2 = 1, \quad \text{and} \quad c = \pm 1.
\]

\[ \psi(r_2, r_1) = \pm \psi(r_1, r_2). \]

The eigenfunction is either symmetric or antisymmetric. The normalised symmetric and antisymmetric space eigenfunctions have the form:
\[ s = \frac{1}{\sqrt{2}} \left[ \gamma_a(1)\gamma_b(2) + \gamma_b(1)\gamma_a(2) \right], \quad \text{(symmetric)} \]
\[ A = \frac{1}{\sqrt{2}} \left[ \gamma_a(1)\gamma_b(2) - \gamma_b(1)\gamma_a(2) \right]. \quad \text{(antisymmetric)} \]

However, these are not the complete eigenfunctions for the electrons; since electrons possess spin, the complete eigenfunction is a product of the spatial eigenfunction satisfying the Schrödinger Eq.(1), and a function depending on the spin coordinates.

The spin angular momentum \( S \), and \( z \)-component, \( S_z \), of a single electron are related to two quantum numbers \( s \) and \( m_s \), by the quantization relations,

\[ S = s(s+1) \quad ; \quad S_z = m_s , \]

where \( s = \frac{1}{2} \), and \( m_s = \pm \frac{1}{2} \).

The spin wave function of two-electron atoms can be constructed by four possible combinations:

antisymmetric spin eigenfunction:

\[ \frac{1}{\sqrt{2}} [ (+1/2, -1/2) - (-1/2, +1/2) ] \quad \text{(singlet)} \]

symmetric spin eigenfunction:

\[ (+1/2,+1/2) \]

\[ \frac{1}{\sqrt{2}} [ (1/2, -1/2) + (-1/2, +1/2) ] \quad \text{(triplet)} \]

\[ (-1/2,-1/2) \]

When we couple the spatial and spin eigenfunctions to construct a total eigenfunction, Pauli's exclusion principle restrict the total eigenfunction of the system to be antisymmetric. Therefore, if the spatial part is symmetric, the spin part should be antisymmetric, (i.e.
The physical interpretation of the singlet and triplet states can be described by evaluating the magnitude of the total angular momentum $\hat{S}'$ and $\hat{S}_z'$, where $S'$ is defined as $(\hat{S}_1+\hat{S}_2)$, the sum of the spin angular momentum of the two electrons. The total angular momentum and its component are also related to two quantum numbers by the quantization relations,

$$S' = \sqrt{s'(s'+1)} \hat{k}; \quad S_z' = m_{s'} \hat{k}.$$ 

The quantum numbers $s', m_{s'}$ satisfy the relations

$$m_{s'} = -s', -s' + 1, \ldots, \ldots, s' - 1, s' \quad s' = 0, 1.$$ 

The singlet state corresponds to $s' = 0$, $m_{s'} = 0$; whereas the triplet states correspond to $s' = 1$, $m_{s'} = 1, 0, -1$.

The optical transitions between triplet and singlet states have much smaller transition probabilities than those among each set; therefore, the eigenfunction should not mix the two states and we treat helium atom in triplet and singlet states separately. For ground-state helium, $s' = 0$, and so the triplet state does not appear, i.e., the spin eigenfunction is antisymmetric and the spatial eigenfunction is symmetric:

$$\psi_s = \sqrt{2}[\gamma_a(1)\gamma_b(2) + \gamma_a(2)\gamma_b(1)].$$
THE PERTURBATION CALCULATION FOR HELIUM-LIKE ATOMS

We write the Hamiltonian of helium as \( H = H_1 + H_2 + V_{12} \), where \( V_{12} = e^2/r_{12} \) and \( H_1 = -\frac{k}{\mu} \frac{Z^2}{r_1^2} - Ze^2/r_1 \), \( H_2 = -\frac{k}{\mu} \frac{Z^2}{r_2^2} - Ze^2/r_2 \) are hydrogenic Hamiltonian for electrons 1 and 2, respectively. In the zeroth approximation, we neglect \( V_{12} \); thus

\[
(H_1 + H_2) \psi^0(\mathbf{r}_1, \mathbf{r}_2) = E^0 \psi^0(\mathbf{r}_1, \mathbf{r}_2),
\]

where \( E^0 = E_1 + E_2 \), and \( \psi^0(\mathbf{r}_1, \mathbf{r}_2) = \psi_{nm}^0(\mathbf{r}_1) \psi_{n'm'}^0(\mathbf{r}_2) \). \( \psi_{nm}^0 \) and \( \psi_{n'm'}^0 \) are hydrogenic eigenfunctions and \( E_1, E_2 \) are their corresponding energy eigenvalues.

The zeroth-order eigenfunctions are degenerate with respect to the exchange of \( \mathbf{r}_1 \) and \( \mathbf{r}_2 \). Therefore, the eigenfunction can be written by taking

\[
\psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{nm} \psi_{nm}(\mathbf{r}_1) \psi_{n'm'}(\mathbf{r}_2) = \sum_{nm} \psi_{nm}(\mathbf{r}_1) \psi_{n'm'}(\mathbf{r}_2)
\]

where the "-" sign corresponds to the triplet state and the "+" sign corresponds to the singlet state.

The first-order perturbation energy due to the electron-electron interaction term \( H_{12} \) is

\[
\Delta E = e^2 \int \int \psi^*(\mathbf{r}_1, \mathbf{r}_2) \frac{1}{r_{12}} \psi(\mathbf{r}_1, \mathbf{r}_2) d\tau_1 d\tau_2.
\]

The integrals can be calculated by expanding \( 1/r_{12} \) as

\[
\frac{1}{r_{12}} = \frac{1}{r_1} - \sum_{l=0}^{\infty} \frac{Y_l^0}{r_1^l} \left( \frac{r_2}{r_1} \right)^l P_l(\cos \theta)
\]

where \( r_1 \) and \( r_2 \) are the smaller and the larger, respectively, of \( r_1 \) and \( r_2 \), and the angles are illustrated in Fig.(1).
The ground states of helium-like ions are given by taking \( n = n' = 1 \) and \( l = l' = 0 \). This choice makes \( L = M = 0 \) and \( S = 0 \), and the triplet does not appear.

\[
\psi_{100}(r) = R_{10}(r)Y_{00}(n)
\]

\[
= \left( -\frac{z^3}{\sqrt{\pi}a^3} \right)^{\frac{1}{2}} \exp\left( -\frac{zr}{a} \right) Y_{00}(n)
\]

\[
E_1 = E_2 = -\frac{z^2e^2}{2a}
\]

\[
E = e^2 \int \int |\psi_{100}(r_1)|^2 |\psi_{100}(r_2)|^2 \frac{1}{r_{12}} d\tau_1 d\tau_2
\]

\[
= e^2 \int \int_{0}^{\infty} |R_{10}(r_1)|^2 |R_{10}(r_2)|^2 \frac{1}{r_1^2 r_2^2 r_{12}} dr_1 dr_2
\]
\[ \begin{align*}
&= \int_0^\infty |R_{10}(r_1)|^2 \left[ \int_0^r |R_{10}(r_2)|^2 r_2^2 dr_2 \right] r_1^2 dr_1 \\
&\quad + \int_0^\infty |R_{10}(r_1)|^2 \left[ \int_0^\infty |R_{10}(r_2)|^2 r_2^2 dr_2 \right] r_1^2 dr_1 \\
&= -\frac{5e^2}{8a} z.
\end{align*} \]

The energy of the ground state in this approximation is thus \( E(1s1s;S) = -\frac{2e^2}{a} (z^{-5}) = -74.8 \text{ ev} \).
THE PERTURBATION-VARIATIONAL METHOD

Applying a simple variational method to the perturbation calculation, we replace \( z \) in the eigenfunction of one electron by \( z' = z - \delta \). The physical reason for this is that each electron is partially screened from seeing the full charge of the nucleus by the presence of the other electron. The best trial function \( \psi_t(r_1, r_2) \) is therefore obtained by minimizing \( E(z') \) with respect to the parameter \( z' \).

We first calculate the expectation value of the Hamiltonian with respect to the trial wave function:

\[
\langle \psi_{1s1s} | H' | \psi_{1s1s} \rangle.
\]

\[
\psi_t(r_1, r_2) = (z'/a^3) \exp[-z'(r_1+r_2)/a]
\]

\[
H' = -\frac{\hbar^2}{2\mu} \nabla_1^2 - \frac{ze^2}{r_1} - \frac{\hbar^2}{2\mu} \nabla_2^2 - \frac{ze^2}{r_2} + \frac{e^2}{r_{12}}
\]

\[
= (\frac{-\hbar^2}{2\mu} \nabla_1^2 \frac{e^2}{r_1}) + (\frac{-\hbar^2}{2\mu} \nabla_2^2 \frac{e^2}{r_2}) + \frac{(z'-z)e^2}{r_1} + \frac{(z'-z)e^2}{r_2} + \frac{e^2}{r_{12}}
\]

\[
= H_1' + H_2' + \Delta V_1 + \Delta V_2 + V_{12}
\]

\[
\langle H_1' \rangle = \langle H_2' \rangle = -\frac{e^2}{a}
\]

\[
\langle \Delta V \rangle = \frac{z'^3}{\pi a^3} \int \frac{(z'-z)}{r_1} \exp\left[-\frac{2z'(r_1+r_2)}{a}\right] d\tau_1 d\tau_2
\]
\[
\begin{align*}
\frac{\text{e}^2}{a} &= \left. z' z' \right|_0^\infty = \langle V_2 \rangle \\
\langle V_{12} \rangle &= \left( \frac{z'}{\text{Ta}^3} \right)^2 \frac{\text{e}^2}{2} \int_0^\infty \frac{1}{r_{12}} \exp \left[ -\frac{2z'(r_1 + r_2)}{a} \right] d\tau_1 d\tau_2 \\
\text{where } &\left( \frac{1}{r_{12}} \right) = \sum_{l=1}^\infty \frac{4}{2l+1} \frac{r_1^l}{r_1^{l+1}} \Sigma_{m} Y_{lm}^*(\xi_1) Y_{lm}(\xi_2) \\
\text{so } &\langle V_{12} \rangle = \left( \frac{z'}{\text{Ta}^3} \right)^2 \frac{\text{e}^2}{2} \int_0^\infty \frac{1}{r_{12}} \exp \left[ -\frac{2z'(r_1 + r_2)}{a} \right] \frac{r_1^l}{r_1^{l+1}} \Sigma_{m} Y_{lm}^*(\xi_1) Y_{lm}(\xi_2) r_1^2 r_2^2 d\tau_1 d\tau_2 \\
\text{Since } &\int_0^\infty Y_{lm}^*(\theta, \phi) Y_{lm}(\theta, \phi) \sin \theta d\theta d\phi = s_{ll} S_{mm}, \text{ we can write:} \\
&\int Y_{lm}^*(\xi_1) d\xi_1 = \sqrt{4\pi} \int Y_{lm}(\xi_1) \frac{1}{4\pi} \frac{d\xi_1}{d^n} \\
&\quad = \sqrt{4\pi} \int Y_{lm}^*(\xi_1) Y_{00}(\xi_1) d\xi_1 \\
&\quad = \sqrt{4\pi} s_{10} S_{00}, \\
&\text{and } \int Y_{lm}(\xi_2) d\xi_2 = \sqrt{4\pi} s_{10} S_{m0}, \text{ too.} \\
\text{So, } &\langle V_{12} \rangle = \left( \frac{z'}{\text{Ta}^3} \right)^2 \frac{\text{e}^2}{2} \int_0^\infty \int_0^\infty \exp \left[ -\frac{2z'(r_1 + r_2)}{a} \right] r_1^2 r_2^2 dr_1 dr_2 \\
&\quad = \left( \frac{4\text{e}^2}{a^3} \right)^2 \int_0^\infty \int_0^\infty \exp \left[ -\frac{2z'(r_1 + r_2)}{a} \right] r_1^2 r_2^2 dr_1 dr_2 \\
&\quad = \frac{5\text{e}^2}{8a} = \left. z' \right|_0^\infty.
\end{align*}
\]

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\[ E(z') = \langle H_1' \rangle + \langle H_2' \rangle + \langle \triangle V_1 \rangle + \langle \triangle V_2 \rangle + \langle V_{12} \rangle \]

\[ = \frac{e^2}{a} - \frac{2}{a} z' \frac{e^2}{a} - \frac{z'^2}{a} \frac{e^2}{a} - z'(z'-z) + z'(z'-z) + z' \]

\[ = -\left( z'^2 - 2zz' + z' \right) a^2. \]

Since \( E(z') \) is an upper limit to the ground state energy, we minimize \( E \) with respect to \( z' \) to obtain the best energy,

\[ \frac{dE(z')}{dz'} = -\left( 2z' - 2z + \right) = 0, \quad z' = \frac{z}{8} \]

The minimum of \( E(z') \) is obtained by setting \( z' = \frac{z}{8} \), and has the value: \( E_{\text{min}} = -77.46 \text{ ev} \). This is closer to the experimental value of -78.86 ev. than the -74.8 ev. obtained by using simple perturbation theory.
CONFIGURATION MIXING AND THE PERTURBATION-VARIATIONAL METHOD

The choice of terms to be used in the foregoing variational method is rather arbitrary. A better result will be reached if we take more terms of the electron configuration to construct our trial function.

We wish to produce an S ground-state wave function of helium by superposing the wave functions of each electron. In order to satisfy $L=0$ and $M=m_1+m_2=0$, $m_1$ and $m_2$ must be of equal magnitude; i.e., $l_1$ and $l_2$ should have the same value. Therefore, we should consider only the configurations like $(ns, n's)$, $(np, n'p)$, $(nd, n'd)$ and so forth. The trial wave function thus has the form:

$$\Psi = C_{1010} \psi(1s,1s) + \sum_{nln'l'n'1} C_{nln'l'n'1} \psi(nln'l'n'1)$$

The coefficients $C_{nln'l'}$ can be determined by the variational method.
Perturbation Method Applied To The Configuration of \((1s,1s)\) And \((1s,2s)\)

\[ \psi(\mathbf{r}_1, \mathbf{r}_2) = \alpha \psi_{1s1s} + \beta \psi_{1s2s} \]

where \( \psi_{1s1s} = \psi_{1s}(r_1)\psi_{1s}(r_2) \)
\[ \psi_{1s2s} = \frac{1}{\sqrt{2}} \left[ \psi_{1s}(r_1)\psi_{2s}(r_2) + \psi_{2s}(r_1)\psi_{1s}(r_2) \right] \]

with the restriction
\[ \alpha^* \alpha + \beta^* \beta = 1 \] \(\text{(a)}\)

The Hamiltonian operator \(H = H_1 + H_2 + V_{12}\) obeys the equation
\[ H\psi = \psi E \psi. \]

Therefore,
\[ H\psi = H(\alpha \psi_{1s1s} + \beta \psi_{1s2s}) = \alpha (H\psi_{1s1s}) + \beta (H\psi_{1s2s}) = E \]
\[ E = \langle \psi | H | \psi \rangle \] \(\text{(b)}\)

From equation (a) and (b):
\[ (\alpha^* \alpha + \beta^* \beta)E = \alpha^* \alpha \langle \psi_{1s1s} | H | \psi_{1s1s} \rangle + \beta^* \beta \langle \psi_{1s2s} | H | \psi_{1s2s} \rangle \]
\[ + \alpha^* \beta \langle \psi_{1s2s} | H | \psi_{1s1s} \rangle + \beta^* \alpha \langle \psi_{1s1s} | H | \psi_{1s2s} \rangle \]

so
\[ (\alpha^* \alpha + \beta^* \beta) \begin{pmatrix} \langle \psi_{1s1s} | H | \psi_{1s1s} \rangle - E \cdot \langle \psi_{1s2s} | H | \psi_{1s2s} \rangle \\ \langle \psi_{1s2s} | H | \psi_{1s1s} \rangle \cdot \langle \psi_{1s2s} | H | \psi_{1s2s} \rangle - E \end{pmatrix} = 0 \]

The determinant of the 2*2 matrix must equal to zero if \((\alpha, \beta)\) has a non-trivial solution.

\[ \begin{vmatrix} \langle \psi_{1s1s} | H | \psi_{1s1s} \rangle - E \cdot \langle \psi_{1s2s} | H | \psi_{1s2s} \rangle \\ \langle \psi_{1s2s} | H | \psi_{1s1s} \rangle \cdot \langle \psi_{1s2s} | H | \psi_{1s2s} \rangle - E \end{vmatrix} = 0 \]

From the previous calculation, we have \(\langle \psi_{1s1s} | H | \psi_{1s1s} \rangle = -74.8\) e.v. We now calculate \(\langle \psi_{1s1s} | H | \psi_{1s2s} \rangle\).
The value of $\langle \psi_1 \psi_2 \rangle$ is the same as $\langle \psi_1 \psi_2 \rangle$.

Finally we must calculate $\langle \psi_1 \psi_2 \rangle$.

$\psi_1 \psi_2 = \int \psi_1^* \psi_2 \, d\tau_1 d\tau_2$.

$E_1 = \int \psi_1^* \psi_2 \, d\tau_1 d\tau_2 + \int \psi_2^* \psi_1 \, d\tau_1 d\tau_2$

$E_2 = \frac{1}{2} \int \psi_1^2 \psi_2 \, d\tau_1 d\tau_2 + \frac{1}{2} \int \psi_2^2 \psi_1 \, d\tau_1 d\tau_2$

$E_3 = \frac{1}{2} \int \psi_1 \psi_2 \, d\tau_1 d\tau_2 + \frac{1}{2} \int \psi_2 \psi_1 \, d\tau_1 d\tau_2$

$E_4 = \frac{1}{2} \int \psi_1 \psi_2 \, d\tau_1 d\tau_2 + \frac{1}{2} \int \psi_2 \psi_1 \, d\tau_1 d\tau_2$

$E_5 = \frac{1}{2} \int \psi_1 \psi_2 \, d\tau_1 d\tau_2 + \frac{1}{2} \int \psi_2 \psi_1 \, d\tau_1 d\tau_2$

$E_6 = \frac{1}{2} \int \psi_1 \psi_2 \, d\tau_1 d\tau_2 + \frac{1}{2} \int \psi_2 \psi_1 \, d\tau_1 d\tau_2$

$E_7 = \frac{1}{2} \int \psi_1 \psi_2 \, d\tau_1 d\tau_2 + \frac{1}{2} \int \psi_2 \psi_1 \, d\tau_1 d\tau_2$

Similarly:

$E_2 = \frac{1}{2} \left[ -e^2 z / 2a - e^2 z / 8a \right]$
\[ \langle \psi_{1s2s} \hat{H} \psi_{1s2s} \rangle = -55.38875 \text{ev}. \]

When these values are substituted into the secular equation,

\[
\begin{vmatrix}
\langle \psi_{1s1s} \hat{H} \psi_{1s1s} \rangle - E & \langle \psi_{1s1s} \hat{H} \psi_{1s2s} \rangle \\
\langle \psi_{1s2s} \hat{H} \psi_{1s1s} \rangle & \langle \psi_{1s2s} \hat{H} \psi_{1s2s} \rangle - E
\end{vmatrix} = 0
\]

the lower solution is \( E_{\text{min}} = -76.9879 \text{ev} \).
Perturbation-Variational Method Applied To
The (1s1s) And (1s2s) Configuration

While using \( \psi_1 = \psi_{1s1s} + \psi_{1s2s} \) as the trial
function, we now replace \( z \) by variational variable \( z' \).
We then carry out the calculations of \( \langle \psi_{1s1s} H' \psi_{1s1s} \rangle \),
\( \langle \psi_{1s1s} H' \psi_{1s2s} \rangle \), and \( \langle \psi_{1s2s} H' \psi_{1s2s} \rangle \) with the same
technique we have used in calculating \( \langle \psi_{1s1s} H \psi_{1s1s} \rangle \),
\( \langle \psi_{1s1s} H \psi_{1s2s} \rangle \), and \( \langle \psi_{1s2s} H \psi_{1s2s} \rangle \), where \( H' \) is the
modified Hamiltonian operator:

\[ H' = H_1' + H_2' + \alpha V_1 + \alpha V_2 + V_{12}. \]

The results are:

\( \langle \psi_{1s1s} H' \psi_{1s1s} \rangle = \frac{e^2}{a} (z'^2 - 2z'z + \frac{5}{8} z') \),

\( \langle \psi_{1s1s} H' \psi_{1s2s} \rangle = \frac{e^2}{a} \left( \frac{8}{27} z'(z' - z) + \frac{213}{74} z' \right) \),

\( \langle \psi_{1s2s} H' \psi_{1s2s} \rangle = \frac{e^2}{a} \left( \frac{5}{8} z'^2 - \frac{5}{4} z' + \frac{169}{36} z' \right) \).

With a similar argument to that used in the previous
section, we get a matrix form:

\[
\begin{pmatrix}
\langle \psi_{1s1s} H' \psi_{1s1s} \rangle & \langle \psi_{1s1s} H' \psi_{1s2s} \rangle \\
\langle \psi_{1s1s} H' \psi_{1s2s} \rangle & \langle \psi_{1s2s} H' \psi_{1s2s} \rangle
\end{pmatrix}
\begin{pmatrix}
\alpha \\
\beta
\end{pmatrix}
= \begin{pmatrix}
\lambda \\
\mu
\end{pmatrix}
\begin{pmatrix}
\alpha \\
\beta
\end{pmatrix}
\]

In order to find \( \lambda \), we try to diagonalize the matrix,
because if it is diagonalized, then, the diagonal elements
are the eigenvalue we want.

We change the parameter \( z' \), and use a computer pro-
gram to compute the value of \( \lambda(z') \). We find the minimum

ground energy \( E_{\text{min}}(z') = -77.6355 \text{ev.} \), corresponds to

\( z' = 1.76 \).

Compared to the (1s1s) configuration, \( (z' = 1.69) \),
the increased value of \( z' \) is physically expected. Since

a 2s electron is usually farther away from the nucleus

than a 1s electron, the repulsive interaction between

the two electrons is not as strong as in the case of the

(1s1s) configuration; the screening effect is decreased,

and we have a larger value of effective nuclear charge \( z' \).

Solving for \( x \) and \( \beta \) with the above \( z' = 1.76 \), we get

the eigenfunction:

\[
\psi(r_1, r_2) = 0.99266 \gamma_{1s}(r_1) \gamma_{1s}(r_2) - 0.1209 \frac{1}{\sqrt{2}} \left[ \gamma_{1s}(r_1) \gamma_{2s}(r_2) + \gamma_{1s}(r_2) \gamma_{2s}(r_1) \right]
\]
Application Of The Method To A Configuration Including (2s2s)

According to the previous discussion, we may write our trial function as
\[ \psi_{t}(\vec{r}_1, \vec{r}_2) = \alpha \psi_{1s1s} + \beta \psi_{1s2s} + \gamma \psi_{2s2s}, \]
where
\[ \psi_{1s1s} = \psi_{1s}(r_1) \psi_{1s}(r_2), \]
\[ \psi_{1s2s} = \frac{1}{\sqrt{2}} \left[ \psi_{1s}(r_1) \psi_{2s}(r_2) + \psi_{1s}(r_2) \psi_{2s}(r_1) \right], \]
and \[ \psi_{2s2s} = \psi_{2s}(r_1) \psi_{2s}(r_2). \]

Let \[ \langle \psi_{1s1s} | H | \psi_{1s1s} \rangle = A_{11}, \langle \psi_{1s1s} | H | \psi_{1s2s} \rangle = A_{12}, \]
\[ \langle \psi_{1s1s} | H | \psi_{2s2s} \rangle = A_{13}, \langle \psi_{1s2s} | H | \psi_{1s1s} \rangle = A_{21}, \]
\[ \langle \psi_{1s2s} | H | \psi_{1s2s} \rangle = A_{22}, \langle \psi_{1s1s} | H | \psi_{2s2s} \rangle = A_{23}, \]
\[ \langle \psi_{2s2s} | H | \psi_{1s1s} \rangle = A_{31}, \langle \psi_{2s2s} | H | \psi_{1s2s} \rangle = A_{32}, \]
and \[ \langle \psi_{2s2s} | H | \psi_{2s2s} \rangle = A_{33}. \]

In the energy eigenvalue equation,
\[ H \psi = \lambda \psi, \]
suppose that we have three eigenfunctions \( U_1, U_2, U_3 \), corresponding to the eigenvalues \( \lambda_1, \lambda_2, \lambda_3 \), where
\[ U_1 = \alpha_1 \psi_{1s1s} + \alpha_2 \psi_{1s2s} + \alpha_3 \psi_{2s2s}, \]
\[ U_2 = \beta_1 \psi_{1s1s} + \beta_2 \psi_{1s2s} + \beta_3 \psi_{2s2s}, \]
and \[ U_3 = \gamma_1 \psi_{1s1s} + \gamma_2 \psi_{1s2s} + \gamma_3 \psi_{2s2s}. \]
Then we can write the three equations in the matrix form:

\[
\begin{pmatrix}
U_1 \\
U_2 \\
U_3
\end{pmatrix} =
\begin{pmatrix}
X_{11} & X_{12} & X_{13} \\
X_{21} & X_{22} & X_{23} \\
X_{31} & X_{32} & X_{33}
\end{pmatrix}
\begin{pmatrix}
\gamma_{1s1s} \\
\gamma_{1s2s} \\
\gamma_{2s2s}
\end{pmatrix}
\]

............(c)

The transpose of a matrix product \((AB)\)' is \(B'A'\); therefore

\[
(U_1, U_2, U_3) = (\gamma_{1s1s}, \gamma_{1s2s}, \gamma_{2s2s})
\]

\[
\begin{pmatrix}
X_{11} & X_{12} & X_{13} \\
X_{21} & X_{22} & X_{23} \\
X_{31} & X_{32} & X_{33}
\end{pmatrix}
\]

\[
\begin{pmatrix}
X_{11} & X_{21} & X_{31} \\
X_{12} & X_{22} & X_{32} \\
X_{13} & X_{23} & X_{33}
\end{pmatrix}
\]

Operating on both sides of the equation with \(H\) and multiplying by the complex conjugate of Eq.(c), we obtain:

\[
\begin{pmatrix}
U_1^* \\
U_2 \\
U_3
\end{pmatrix}
H(U_1, U_2, U_3) =
\begin{pmatrix}
X_{11} & X_{12} & X_{13} \\
X_{21} & X_{22} & X_{23} \\
X_{31} & X_{32} & X_{33}
\end{pmatrix}
\begin{pmatrix}
\gamma_{1s1s} \\
\gamma_{1s2s} \\
\gamma_{2s2s}
\end{pmatrix}
\]

\[
\begin{pmatrix}
X_{11} & X_{21} & X_{31} \\
X_{12} & X_{22} & X_{32} \\
X_{13} & X_{23} & X_{33}
\end{pmatrix}
\]

The left side of the equation equals:

\[
\begin{pmatrix}
\langle U_1^* H U_1 \rangle, \langle U_2^* H U_2 \rangle, \langle U_3^* H U_3 \rangle
\end{pmatrix}
\]

\[
\begin{pmatrix}
X_1 & 0 & 0 \\
0 & \lambda_2 & 0 \\
0 & 0 & \lambda_3
\end{pmatrix}
\]

The equation therefore can be written as:

\[
\begin{pmatrix}
X_{11} & X_{12} & X_{13} \\
X_{21} & X_{22} & X_{23} \\
X_{31} & X_{32} & X_{33}
\end{pmatrix}
\begin{pmatrix}
A_{11} & A_{12} & A_{13} \\
A_{21} & A_{22} & A_{23} \\
A_{31} & A_{32} & A_{33}
\end{pmatrix}
\begin{pmatrix}
X_{11} & X_{21} & X_{31} \\
X_{12} & X_{22} & X_{32} \\
X_{13} & X_{23} & X_{33}
\end{pmatrix}
\]

\[
\begin{pmatrix}
\lambda_1 & 0 & 0 \\
0 & \lambda_2 & 0 \\
0 & 0 & \lambda_3
\end{pmatrix}
\]
when \( X \) is unitary, \([(X^*)^*]^{-1} = X\), and when \( X \) is real, \( X^* = x^{-1} \), so, \((X')^{-1} = X\), and \( x' = x^{-1} \). This result applies to our case, which has the form:

\[
XAX^{-1} = \begin{pmatrix}
\lambda_1 & 0 & 0 \\
0 & \lambda_2 & 0 \\
0 & 0 & \lambda_3
\end{pmatrix}.
\]

Multiplying both sides with \( X^{-1} = x' \), we obtain

\[
AX' = \begin{pmatrix}
\lambda_1 & 0 & 0 \\
0 & \lambda_2 & 0 \\
0 & 0 & \lambda_3
\end{pmatrix} X'.
\]

from which it follows that

\[
(A_{11} - \lambda_1)X_{11} + A_{12}X_{12} + A_{13}X_{13} = 0,
\]
\[
A_{21}X_{21} + (A_{22} - \lambda)X_{22} + A_{23}X_{23} = 0,
\]
and
\[
A_{31}X_{31} + A_{32}X_{32} + (A_{33} - \lambda)X_{33} = 0.
\]

If \( X \) has a non-trivial solution, the determinant of the matrix of the coefficients must equal zero:

\[
\begin{vmatrix}
A_{11} - \lambda_1 & A_{12} & A_{13} \\
A_{21} & A_{22} - \lambda & A_{23} \\
A_{31} & A_{32} & A_{33} - \lambda
\end{vmatrix} = 0.
\]

Diagonalizing the matrix, we have:

\[
\begin{vmatrix}
A_{11} - \lambda_1 & 0 & 0 \\
0 & A_{22} - \lambda_2 & 0 \\
0 & 0 & A_{33} - \lambda_3
\end{vmatrix} = 0.
\]

\( \lambda_1, \lambda_2, \lambda_3 \) are eigenvalues. From the eigenvalues, we can easily get eigenfunctions \( \psi_1, \psi_2, \psi_3 \).
We now compute \( A_{13} = \langle \psi_{1s1s} | H | \psi_{2s2s} \rangle \). We had

\[
H' = H_1' + H_2' + \Delta V_1 + \Delta V_2 + V_{12},
\]

\[
\psi_{1s1s} = \frac{z'^3}{\Omega a^3} \exp \left[ -\frac{z'(r_1 + r_2)}{a} \right],
\]

and \( \psi_{2s2s} = \frac{z'^3}{32\pi a^3} \left( \frac{z'r_1}{a} \right) \left( \frac{z'r_2}{a} \right) \)

\* \exp \left[ -\frac{z'(r_1 + r_2)}{2a} \right].

Now, \( E_1 = \int \psi_{1s1s} H'_1 \psi_{2s2s} d\tau_1 d\tau_2 \)

\[
= \int \psi_{1s}(r_1) \psi_{1s}(r_2) H'_1 \psi_{2s}(r_1) \psi_{2s}(r_2) d\tau_1 d\tau_2
\]

\[
= \int \psi_{1s}(r_2) \psi_{2s}(r_2) d\tau_2 \int \psi_{1s}(r_1) H'_1 \psi_{2s}(r_1) d\tau_1.
\]

Since the wavefunctions \( \psi_{1s} \) and \( \psi_{2s} \) are orthonormalized, we have

\[
\int \psi_{1s}(r_2) \psi_{2s}(r_2) d\tau_2 = 0,
\]

so that

\( E_1 = 0 \).

Similarly, we have \( E_2 = 0 \) and \( \langle \Delta V_1 \rangle = \langle \Delta V_2 \rangle = 0 \). Next,

\[
\langle V_{12} \rangle = \int \int \psi_{1s}(r_1) \psi_{1s}(r_2) \frac{e^2}{r_{12}} \psi_{2s}(r_1) \psi_{2s}(r_2) d\tau_1 d\tau_2,
\]

We can make the expansion.
\[
\frac{1}{r_{12}} = \sum_{l=1}^{2l+1} \frac{r_{\leq l+1}}{r_{>l+1}} \sum_{m} Y_{lm}^{*}(\Omega_1)Y_{lm}(\Omega_2).
\]

Since we are considering the 1s and 2s configurations, \(l=m=0\). Therefore:

\[
\int \int \frac{4\pi e^2}{l_{2l+1}} \frac{r_{l}}{r_{>l+1}} \sum_{m} Y_{lm}^{*}(\Omega_1)Y_{lm}(\Omega_2) d\Omega_1 d\Omega_2 = \frac{(4\pi)^2 e^2}{r_{>l}}.
\]

Thus we have:

\[
<V_{12}> = 16\pi^2 e^2 \frac{1}{32(\pi a^3)} \int \int \left(1 - \frac{z' r_1}{a} - \frac{z' r_2}{a}\right)
\]

*exp\left[\frac{-3z'(r_1 + r_2)}{2a}\right] \frac{1}{r_{>l}} \frac{r_1^2 r_2^2 dr_1 dr_2}{r_{>l}}

\[
= \frac{e^2 z' 6}{2a^6} \int_{0}^{\infty} (2 - \frac{z' r_2}{a}) \exp\left(-\frac{3z' r_2}{2a}\right) \int_{0}^{r_2} \exp\left(-\frac{3z' r_1}{2a}\right) \frac{1}{r_2} dr_2
\]

*exp\left(-\frac{3z' r_1}{2a}\right) \frac{z' r_1}{a} r_1^2 dr_1 + \int_{r_2}^{\infty} \exp\left(-\frac{3z' r_1}{2a}\right) \frac{z' r_1}{a} r_1^2 dr_1
\]

*exp\left(-\frac{3z' r_1}{2a}\right) \frac{z' r_1}{a} r_1^2 dr_2

\[
= 16 e^2 \frac{z'}{3^6 a}.
\]

So, \(A_{13} = \langle \psi_{1s1s}^* | H | \psi_{2s2s} \rangle = \frac{16 e^2}{3^6 a} z'\).

Furthermore, since \(\psi_{1s1s}, \psi_{2s2s}\) and \(\psi_{1s2s}\) are all real functions, we have \(A_{31} = A_{13}\).

Similar arguments and calculations apply for \(A_{23}\) and
A_{32}, we have \(<H_1^2>=<H_2^2>=0,\\n\\n\langle \Delta V_1 \rangle = \langle \Delta V_2 \rangle = \frac{4 e^2}{27 a} z'(z'-z),\\n
\langle V_{12} \rangle = \frac{210}{33*55} z',\\n
and A_{23}=A_{32}=\frac{e^2}{a} \left( 8 \frac{z'^2}{27} - \frac{8 z' z}{27} + \frac{210}{33*55} z' \right).\\n
For A_{33}, we get\\n
\langle H_1^2>=\langle H_2^2>=-\frac{e^2}{8a} z',\\n
\langle \Delta V_1 \rangle = \langle \Delta V_2 \rangle = -\frac{1 e^2}{4 a} (z'-z) z',\\n
\langle V_{12} \rangle = \frac{77 e^2}{29 a} z',\\n
and A_{33}=\frac{e^2}{4a} z'^2 + \left( \frac{77}{29} - 1 \right) \frac{e^2}{a} z'.\\n
Our result for E_{min}(z') is -77.66874 ev. which corresponds to z'=1.76. Solving for \(\alpha\), \(\beta\), and \(\gamma\), we get\\n
\(\alpha = 0.9920196,\\n\beta = -0.1237841,\\nand \gamma = -0.02397215.\\n
When z' of the variational method equals two, the values are those obtained from the simple perturbational
calculation which are:

\[ A_{13} = A_{31} = \frac{16 e^2}{36 a} z \]
\[ A_{23} = A_{32} = \frac{e^2}{a} \frac{210}{33 \times 55} (\frac{e}{z}) \]
\[ \text{and } A_{33} = \frac{e^2}{a} \frac{z^2}{4} + \frac{77}{29} z \]

In this case, we get \( E_{\min}(z) = -77.003 \text{ ev} \).

and \( \chi = 0.9948547 \),
\( \xi = -0.315895 \),
and \( \gamma = -0.016888 \).
Application Of The Methods To A Configuration Of \( \gamma_{1s1s} \), \( \gamma_{1s2s} \), \( \gamma_{2s2s} \) And \( \gamma_{2p2p} \)

We now use as a trial function

\[
|t\rangle = \gamma_{1s1s} + \gamma_{1s2s} + \gamma_{2s2s} + \gamma_{2p2p}
\]

Using the same linear algebra technique, we first let

\[
A_{14} = A_{41} = \langle \gamma_{1s1s}, \gamma_{2p2p} | H | \gamma_{2p2p} \rangle
\]

\[
A_{24} = A_{42} = \langle \gamma_{2s1s}, \gamma_{2p2p} | H | \gamma_{2p2p} \rangle
\]

\[
A_{34} = A_{43} = \langle \gamma_{2s2s}, \gamma_{2p2p} | H | \gamma_{2p2p} \rangle
\]

and \( A_{44} = \langle \gamma_{2p2p}, \gamma_{2p2p} | H | \gamma_{2p2p} \rangle \)

First we calculate \( \langle \gamma_{1s1s}, \gamma_{2p2p} | H | \gamma_{2p2p} \rangle \). We had

\[
\gamma_{1s1s} = \frac{z^3}{a^3} \exp \left[ -\frac{z'(r_1 + r_2)}{a} \right]
\]

For the 2p configuration, the \( l_1 = l_2 = 1 \), i.e. \( m_1 \) and \( m_2 \) can have the values -1, 0, 1. Since we are constructing a ground-state helium eigenfunction, \( L = 0, M = 0 \). So \( m_1 \) and \( m_2 \) must be of equal value but opposite sign. Therefore, the trial function \( \gamma_{2p2p} \) can be written as:

\[
\gamma_{2p2p} = \frac{z''5}{24a^5} r_1 r_2 \exp \left[ \frac{-z''(r_1 + r_2)}{2a} \right] \sum_m (l_1 m_1 l_2 m_2 | LM) \quad *Y_{l_1 m_1}^{(n_1)} Y_{l_2 m_2}^{(n_2)}
\]
The following expressions have been determined:

\[(1,1,1,-1,0,0)^* = \frac{(j_1+m+1)(j_1+m)}{2j_1(2j_1+1)} = \frac{2*1}{2*3} = \frac{1}{3}, \]

\[(1,-1,1,1,0,0)^* = \frac{(j_1-m)(j_1-m+1)}{2j_1(2j_1+1)} = \frac{1*2}{2*3} = \frac{1}{3}, \]

and \((1,0,1,0,0,0)^* = \frac{(j_1-m)(j_1+m)}{j_1(2j_1+1)} = \frac{1}{3}, \]

thus \[\psi_{2p2p} = \frac{z''^5}{24a^5}r_1r_2\exp\left[-\frac{z''(r_1+r_2)}{2a}\right] \left[-\frac{1}{\sqrt{3}} \sum_{m} (-1)^m Y_{1m}(\alpha_1 Y_{1m}(\alpha_2) \right],\]

Here, we use another parameter \(z''\) instead of \(z'\), since, because of the very different electron configuration of a 2p state compared to an s state, we do not expect the same screening effect. In addition, the angular part of the wave function in a 2p state is orthogonal to that of 1s and 2s state, and introducing a different parameter \(z''\) does not spoil the orthogonality of wavefunctions.

Next we evaluate

\[<H_1> = \int \psi_{1s1s} H_1 \psi_{2p2p} d\tau_1 d\tau_2.\]

The angular part of the integration involves
\[
\int \frac{1}{\sqrt{3}} \sum (-1)^m y_{1m}(\ell_1) y_{1-m}(\ell_2) d\Omega_1 d\Omega_2 \\
= -\frac{1}{\sqrt{3}} \left[ \int y_{10}(\ell_1) d\Omega_1 \int y_{10}(\ell_2) d\Omega_2 - \int y_{1-1}(\ell_1) d\Omega_1 \int y_{1+1}(\ell_2) d\Omega_2 \\
+ \int y_{1+1}(\ell_1) d\Omega_1 \int y_{1-1}(\ell_2) d\Omega_2 \right] = 0.
\]

For the same reason \( <H_2>, <\Delta V_1> \) and \( <\Delta V_2> \) equal to zero; the only nonzero contribution is \( <V_{12}> \).

\[
< V_{12} > = \int \frac{e^2}{r_{12}} \frac{4 \pi e^2}{a^3} \frac{z^4 z^*}{2a^5} \left[ \int_0^\infty r_2 \exp \left[ -\frac{(2z^*+z^n)}{2a} r_2 \right] \right] \text{(Angular part)} \\
\times \left\{ \int_0^\infty r_1 \exp \left[ -\frac{(2z^*+z^n)}{2a} r_1 \right] r_1^2 dr_1 + \int_{\nu_2}^\infty r_1 \exp \left[ -\frac{(2z^*+z^n)}{2a} r_1 \right] \right\} r_2^2 dr_2 ,
\]
where, (Angular part)

\[
= \sum_{l} \frac{1}{2^{l+1}} \sum_{m} \left[ \sum_{\ell_1} \frac{1}{\sqrt{3}} (-1)^m y_{1m}(\ell_1) y_{1m}(\ell_2) y_{1m}(\ell_1) \right] \\
\times y_{1-m}(\ell_2) d\Omega_1 d\Omega_2 \\
= \sum_{l} \frac{1}{2^{l+1}} \sum_{\ell_1} \left[ \sum_{\ell_2} (-1)^m y_{1m}(\ell_1) y_{1m}(\ell_2) d\Omega_1 \right] \\
\times \int y_{1m}(\ell_2) y_{1-m}(\ell_2) d\Omega_2 .
\]
\[
\begin{align*}
\xi &= \frac{1}{3} \frac{21+1}{21+1} \frac{r_2^1}{r_2^1 + 1} \left[ \frac{1}{\sqrt{3}} (-1)^m (-1)^m \sum_{m=0}^{\infty} S_{11} S_{11} S_{mm} S_{mm} \right] \\
&= \frac{1}{3} \frac{r_2^1}{\sqrt{3} r_2^1} (-1)^m (3) \\
&= \frac{1}{\sqrt{3} r_2^1}.
\end{align*}
\]

So, \( \langle \nu_{12} \rangle = \frac{e^2}{6} \left( \frac{z'}{a} \right)^3 \left( \frac{z''}{a} \right)^5 \frac{\infty}{\int_0^\infty} \frac{r_2 \exp \left( -\frac{2z'+z''}{2a} r_2 \right) \left\{ \frac{1}{r_2^2} \int_0^{2a} r_1^r \exp \left( -\frac{2z'+z''}{2a} r_1 \right) \right\} dr_1}{r_2^2} \int_0^\infty \right\} dr_2 \\
= \frac{112 e^2 z' z''^5}{3a (2z'+z'')}.
\]

Combining these results we have

\[
\langle \Psi_{1s1s} | H | \Psi_{2p2p} \rangle = \frac{112 e^2 z' z''^5}{3a (2z'+z'')}.
\]

\[
\langle \Psi_{1s1s} | H | \Psi_{2p2p} \rangle \quad \text{and} \quad \langle \Psi_{2s2s} | H | \Psi_{2p2p} \rangle \quad \text{can be}
\]

obtained by similar calculations; the results are:

\[
\langle \Psi_{2s2s} | H | \Psi_{2p2p} \rangle = \frac{14 e^2 z' z''^5}{3a (z'+z'')} \left[ \frac{1-7z'}{z'+z''} + \frac{185 z''^2}{14(z'+z'')^2} \right].
\]
and \( \langle 1s2s | H | 2p2p \rangle = - \frac{z^5 e^2}{\sqrt[3]{3 a}} \frac{15e^*}{(2z^*+z^*)^2(3z^*+2z^*)^6} \)

\[
+ \frac{3(z^* - z^*)}{(2z^*+z^*)^3(3z^*+2z^*)^5} - \frac{3z^*}{(2z^*+z^*)^4(3z^*+2z^*)^4} \\
- \frac{2(z^*+z^*)}{(2z^*+z^*)^5(3z^*+2z^*)^3} - \frac{1}{(2z^*+z^*)^5(3z^*+2z^*)^2} \\
+ \frac{1}{(2z^*+z^*)^5(z^*+z^*)^2} - \frac{2z^*}{(2z^*+z^*)^5(z^*+z^*)^3} \]

The calculation of \( \langle \Psi_{2p2p} | H | \Psi_{2p2p} \rangle \), which follows, is slightly different and tedious, because the angular parts of \( \Psi_{2p2p} \) from each electron interact with each other.

The wave function under consideration is

\[
\Psi_{2p2p} = \left( \frac{z^5}{24a^5} \right) r_1 r_2 \exp \left[ - \frac{z^*(r_1+r_2)}{2a} \right] \left[ \frac{1}{\sqrt{3} m} \sum (-1)^m Y_{lm}(\tau_1) Y_{lm}(\tau_2) \right]
\]

and we first wish to calculate

\[
\langle H_1 \rangle = \int \Psi_{2p2p}^* H_1 \Psi_{2p2p} d\tau_1 d\tau_2 .
\]

The radical and angular parts of integration can be done separately; if we express the wave function as

\[
\Psi_{2p2p} (r) = \Psi_{2p2p} (r) Y_{2p2p} (\alpha),
\]

the results of the radical and angular parts of the integration are...
\[
\int R_2^*p_2p^*H_1R_2p_2p^*r_1^2dr_1r_2^2dr_2 = \frac{z^ne^2}{8a},
\]

and
\[
\int \frac{1}{3m'} \sum (\Delta m)^* Y_{lm'}(\Omega_1)Y_{l-m'}(\Omega_2) \sum Y_{lm}(\Omega_1)Y_{l-m}(\Omega_2) d\Omega_1 d\Omega_2 = 1,
\]

the last result comes from the normalization property of the spherical harmonic functions \(Y_{lm}(\Omega)\).

Similarly, for \(\langle H_2 \rangle, \langle \Delta V_1 \rangle\) and \(\langle \Delta V_2 \rangle\), we have
\[
\langle H_2 \rangle = \langle H_1 \rangle = \frac{z^ne^2}{8a},
\]

and
\[
\langle \Delta V_1 \rangle = \langle \Delta V_2 \rangle = \frac{z^n(z^n - z) e^2}{4a}.
\]

Next we consider
\[
\langle V_{12} \rangle = \int \frac{e^2}{r_{12}^2} \frac{1}{r_{12}} \sum \tau_{2p2p} d\tau_1 d\tau_2.
\]

\(1/r_{12}\) can be expanded as
\[
\frac{1}{r_{12}} = \sum_{l=0}^{\infty} \frac{1}{2l+1} \sum_{m} Y_{lm}^*(\Omega_1)Y_{lm}^*(\Omega_2),
\]

as before.

The angular part of the integration is
\[
X = \int \frac{1}{3} \sum_{m,m,m''} \sum (\Delta m)^* (\Delta m') Y_{lm'}(\Omega_1)Y_{l-m'}(\Omega_2) Y_{lm}(\Omega_1)Y_{l-m}(\Omega_2) Y_{lm''}(\Omega_1)Y_{l-m''}(\Omega_2).
\]
\[
Y_{1-m^*}^{(\ell_2)} d\alpha_1 d\alpha_2
= \sum_{nm} \sum_{m''} \frac{1}{3} \left[ \int Y_{1m}^{*} (\ell_1) Y_{1m}^{*} (\ell_1) Y_{1m}^{*} (\ell_1) d\alpha_1 \right] \nonumber \\
\left[ \int Y_{1-m}^{*} (\ell_2) Y_{1m}^{*} (\ell_2) Y_{1-m}^{*} (\ell_2) d\alpha_2 \right].
\]

But
\[
\int Y_{1m_3}^{*} (\ell) Y_{1m_2}^{*} (\ell) Y_{1m_1} (\ell) d\alpha = \frac{(2l+1)(2l_2+1)}{4\pi(2l_3+1)} \langle l_1 l_2 00 | l_1 l_2 l_3 0 | l_1 l_2 m_1 m_2 l_1 l_2 l_3 \rangle.
\]

(cf. Merzbacher: Quantum Mechanics, P. 396)

so that
\[
X = \sum_{nm} \sum_{m''} \frac{1}{3} \left[ \frac{(2l+1)^*3}{4\pi^*3} (1010 10) (1m_1 m' 1m'') \right] \nonumber \\
\left[ \frac{(2l+1)^*3}{4 * 3} (1011 11) (1m_1-m' 1-m') \right].
\]

\[
= \frac{2l+1}{4\pi^*3} - (1010 10) \sum_{nm} \sum_{m''} (1m_1 m' 1m'')^* (1m_1-m' 1-m').
\]

When \(l=1\), \(1010 10\)=0, so, we only have the terms with \(l=0\) and \(l=2\). Therefore

\[
X = \sum_{1,0} \frac{1}{4\pi^*3} (0010 10) \sum_{m} \sum_{m''} (001m' |1m'\rangle (001-m'' |1-m\rangle)
\]

\[
+ \sum_{1,2} \frac{5}{4\pi^*3} (2010 10) \sum_{m} \sum_{m''} (2m_1 m' |1m'\rangle (2m_1-m'' |1-m'\rangle)
\]
Thus, \[ V_{12} = \frac{z'^5}{2a^5} \int r_1^2 \exp\left(-\frac{z' r_1}{a}\right) r_2^2 \exp\left(-\frac{z'' r_2}{a}\right) \frac{1}{4\pi} e^2 \]

\[ = \frac{111 e^2}{1536 a} z''. \]

Combining these results we obtain

\[ \left< \hat{\chi}_{2p2p}^{\dagger} \hat{\chi}_{2p2p} \right> = \left< H \right> + \left< \Delta V_1 \right> + \left< \Delta V_2 \right> + \left< V_{12} \right> \]

\[ = \frac{e^2}{a} \left( \frac{z'^2}{4} - \frac{zz''}{2} + \frac{111}{1536} \right). \]

We vary both \( z' \) and \( z'' \) to find \( E_{\text{min}}(z', z'') \), which is -78.3243370 ev., corresponding to \( z'=1.755 \), and \( z''=4.890 \).

The expansion coefficients are

\( \alpha = 0.9814025 \),

\( \beta = -0.1108672 \),

\( \gamma = -0.0224294 \),

and \( \delta = 0.0738727 \).

Here \( z'=1.755 \) is the effect of screening the nuclear charge, as we mentioned earlier, but \( z''=4.890 \) can only be interpreted as a pure mathematical parameter, because the effective charge cannot exceed \( z=2 \).
Furthermore, when z' = 2 and z'' = 2, the values correspond to the pure perturbational-method values which are

\[ A_{14} = A_{41} = \frac{112 e^2}{3\sqrt{3} a} z, \]

\[ A_{24} = A_{42} = \frac{e^2 29}{a 3 3^5 z}, \]

\[ A_{34} = A_{43} = \frac{e^2 45}{a 13 2^9 z}, \]

\[ A_{44} = \frac{e^2 z^2 111}{a 4 1536} \left( z + \frac{111}{4} \right), \]

\[ E_{\text{min}}(z) = -77.078224 \text{ ev}, \]

\[ \alpha = 0.951772, \]

\[ \beta = -0.30418, \]

\[ \gamma = -0.014335, \]

and \[ \delta = 0.0374112. \]
CONCLUSION

The summary of the above calculations, (Table I) shows that by applying the perturbation-variational method, the $E_{\text{min}}$ value we get is much closer to the exact value than the result obtained using the configuration mixing and simple perturbation method. Even when we only consider the (1s1s) configuration, the perturbation-variational result is better than the value of the pure perturbational calculation using four terms.

<table>
<thead>
<tr>
<th>method</th>
<th>perturbation method</th>
<th>perturbation-variational method</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1s1s)</td>
<td>-74.8</td>
<td>-77.46 ($z' = 1.69$)</td>
</tr>
<tr>
<td>(1s1s)+(1s2s)</td>
<td>-76.99</td>
<td>-77.63 ($z' = 1.76$)</td>
</tr>
<tr>
<td>(1s1s)+(1s2s)+ (2s2s)</td>
<td>-77.003</td>
<td>-77.67 ($z' = 1.76$)</td>
</tr>
<tr>
<td>(1s1s)+(1s2s) +(2s2s)+(2p2p)</td>
<td>-77.078</td>
<td>-78.32 ($z' = 1.755$)  ($z'' = 4.890$)</td>
</tr>
</tbody>
</table>

Table I, the minimum ground energy of helium expressed in ev. The experimental value is -78.86 ev.

In the configuration method, we assume that using only a relatively small number of terms in

$$\psi(r_1,r_2) = c_{1010}\psi(1s1s) + \sum_{nln'l} c_{nln'l} \psi(nln'l)$$

can give a good approximation to the exact eigenfunction of the ground state. A better result is expected when
the number of terms is increased and when more adjustable parameters such as \( z' \) and \( z'' \) are used.
BIBLIOGRAPHY