Finite element calculations for the helium atom*

Weiying Zheng† Lung-an Ying

(School of Mathematical Sciences, Peking University, Beijing, 100871, China)

Abstract

The author gives the explicit form of the Hylleraas-Breit transform (HBT) in the present paper, and applies it to fixed nucleus problems of helium-like ions. Utilizing the relation between the total angular momentum and the Hamilton, the six-dimensional Schrödinger equation is transferred into three-dimensional systems of equations. We use the Lagrange finite element method to obtain their numerical solutions for some low-lying $S$, $1s2p\; ^3P$ and $1s3d\; ^3D$ states of the helium atom. The relative errors of our approximate energies are: $O(10^{-8})\; a.u.$ for $S$ states, $O(10^{-7})\; a.u.$ for $1s2p\; ^3P$ state and $O(10^{-5})\; a.u.$ for $1s3d\; ^3D$ state.

Keywords: finite element method, Hylleraas-Breit transformation, Schrödinger equation, generalized eigenvalue problem.

PACS number: 31. 15. -p

1 Introduction

The three-body Coulomb problem is traditional challenging. The failure of theory to describe precisely the system stimulated many mathematicians and physicists to devote themselves in using various methods to obtain high-precision energies and other expectation values. Helium atom and heliumlike ions are typical models.

Some approaches to the problem include various variational methods, the Hartree-Fock method [1], the finite difference method[2], the correlation-function hyperspherical-harmonic method[3][4] and etc. Variational method is the most powerful among them. As for nonrelativistic energies of low-lying states of the helium, their accuracies have grown very rapidly, with the development of computer power and variational methods. Hylleraas’ work([5], 1929) yields five significant digits and Kinoshita’s work([6], 1957)

---

*Project supported by the China State Major Key project for Basic Researches and the Science Fund of the Ministry of Education of China;
†Email: zhengweiying@yahoo.com
yields seven significant digits, for the ionization energy of the ground helium. Kono and Hattori([7], 1985 and [8], 1986) used two sets of basis functions $r^i_1 r^j_2 r^k_{12} e^{-\xi r_1 - \eta r_2} A(\" \xi \) terms") and $r^i_1 r^j_2 r^k_{12} e^{-\zeta (r_1 + r_2)} A(\" \zeta \) terms") to calculate the energy levels for S, P, D states in He. $A$ is an appropriate angular factor. The former set of functions is expected to describe the whole wave function roughly, while another one is expected to describe the short- and middle-range correlation effect. Their calculations yield 9-10 significant digits for S states. Kleindienst and etc([9], 1994), Drake and Yan([10], 1994) applied the double basis set method to S states of helium. Their basis functions are $r^i_1 r^j_2 r^k_{12} e^{-\xi r_1 - \eta r_2}$ and $r^i_1 r^j_2 r^k_{12} e^{-\xi_2 r_1 - \eta_2 r_2}$. Drake and Yan employed truncations to ensure numerical stability and convergence. By complete optimizations of the exponential scale factors $\alpha_1$, $\beta_1$, $\alpha_2$ and $\beta_2$, they achieved more than 15 significant digits. Recently, Drake and etc([11], 2002) obtained 21 significant digits for the ground helium by the triple basis set method. Korobov([12], 2002) even obtained 25 significant digits for the ground helium. It can be used as a benchmark for other approaches for three-body systems. Their excellent works promote the development of few-body problems.

The finite element method(FEM) is used initially in elastic mechanics and fluid mechanics. It uses local-defined basis functions to approximate unknown functions. The main works of FEM applied to atomic and molecular problems began in 1970’s, and in one- or two-dimensional cases. Askar([13], 1975) calculated the energies of hydrogen atom in the ground state and the first excited state. Then Nordholm and Baesky([14]) applied FEM to more general bound state problems. Fridman and Rosenfeld([15], 1977) analyzed two model problems of two-dimensional Schrödinger equations with FEM. Malik([16], 1980) computed the problem of molecular spectrum with Morse Potential. All these works showed that FEM was simple and efficient for one- and two-dimensional atomic and molecular problems.

The first work of FEM applied to three-dimensional case was due to Levin and Shertzer([17], 1985). They calculated the ionization energy of the ground helium in terms of Hylleraas’ coordinates. M.Braun and etc.([18], 1993), Scrinzi([19], 1995) and etc. calculated the ground state by various finite element scheme. Ackermann and Roitzsch([20], 1993), Ackermann, Erdmann and Roitzsch([21], 1994), J.Ackermann([22], 1995) did good jobs in solving Schrödinger equations by multilevel adaptive FEM. Recently, FEM has been applied to three-body problems in strong external fields. Braun, Schweizer and Elster([23], 1998) developed a method that combines the well known hyperspherical close coupling and FEM to calculate atomic data for the three-body problem in strong magnetic field. Schweizer and etc([24]) presented an effective numerical algorithm by combining discrete variable technique and FEM, applied to hydrogen and helium atom in strong external fields. Garcke and Griebel([25], 2000) computed the eigenproblems of hydrogen and helium in strong magnetic and electric fields with the sparse grid combination technique. They deal with the eigenvalue problems in terms of Cartesian coordinates. For an n-dimensional problem, if we play $M$ grid points on each coordinate direction, the number of unknowns is $O(M^n)$; but the sparse grid approach employs only $O(M (\log M)^{n-1})$ grid points. It is a remarkable advantage for high dimensional problems. Furthermore, the method is feasible on parallel computers. Other references include [26], [27] and the
In this paper, we apply FEM to some low-lying $S, P, D$ states of the helium atom. In terms of accuracies, our results are not comparable with those yielded by high-precision variational calculations mentioned above. But our calculations are valuable in FEM applied to three-body problems and in the development of FEM. We deal with three-dimensional system of partial differential equations which are equivalent to the original six-dimensional Schrödinger equation. The FEM matrices of generalized eigenvalue problems are banded, and the maximal band-width $\ll$ the number of unknowns. The finite element scheme can be applied to other three-dimensional problems directly. We expect to improve our results by improving our numerical schemes and the computer power. As for implementation, we only need to change our software slightly to satisfy new schemes or new problems.

The system of the helium atom is described by the six-dimensional Schrödinger equation. It is unpractical to be solved directly by FEM. By virtue of Hylleraas’ coordinates [5], G.Breit transferred the six-dimensional Schrödinger equation into three-dimensional forms for $S$ states and $P$ states by the Hylleraas-Breit transform (HBT) ([28], 1930). The simplified equation of $S$ states has been widely used in numerical calculations for helium-like ions.

In the present paper, we give an explicit expression of HBT. Expanding wave functions with respect to eigenfunctions of the square of the angular momentum, we obtain three-dimensional energy equations, which are equivalent to the original six-dimensional Schrödinger equation, for all states $S, P, D, F, \cdots$ of helium-like ions. Therefore, most approaches used for the ground state can also be used to solve simplified equations of excited states.

We give a brief introduction to FEM in this paper. As a more general application to the helium atom, we calculate nonrelativistic energies of some low-lying states ($S_\text{-}, 1s2p$- and $1s3d$-states). Since eigenfunctions of the Hamiltonian are not very smooth due to the singular potential, it is more efficient to use the Lagrange FEM than the Hermite FEM. We add no physical assumptions and conditions in the procedure, including the symmetry and anti-symmetry of wave functions. With pure numerical computations for the pure partial differential equations, we can see from the figures of wave functions that our results coincide with known physical properties very well. So we see that FEM is efficient and reflects some intrinsic information of three-body problems.

The paper is organized as follows. HBT and three-dimensional energy equations of all states are derived in §2. The weak equations of $S$, $1s2p$ and $1s3d$ states of the helium are given in §3. FEM approximations of these problems are described in §4. Our computational results and analyses for them are given in §5.

We use atomic unit in this paper, i.e. Bohr Radius $a_0$ for length, Rydberg for energy (we use Hartree from §3 on for convenience). We consider nonrelativistic and spin-independent case.
2 Hylleraas-Breit transform and energy equations

In the Cartesian coordinates, the Schrödinger equation of a helium-like ion is:

$$H\psi = E\psi,$$  \hspace{1cm} (2.1)

where $H$ is the Hamiltonian defined as

$$H = -\Delta_1 - \Delta_2 + V, \quad \Delta_i\psi = \frac{\partial^2\psi}{\partial x_i^2} + \frac{\partial^2\psi}{\partial y_i^2} + \frac{\partial^2\psi}{\partial z_i^2}.$$  

$(x_i, y_i, z_i)$ are coordinates of the $i$-th electron, $(r_i, \theta_i, \phi_i)$ are its spherical coordinates (suppose the nucleus at the origin), $i = 1, 2$. $V = -(2Z)/r_1 - (2Z)/r_2 + 1/r_{12}$ is the Coulomb potential and $Z$ is the nucleus charge. $r_{12} = \sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos \theta}$ is the distance between two electrons, and $\theta$ is the inter-electronic angle.

The eigen-equation of the square of the angular momentum $M^2$ is

$$\left\{ \left[ \sum_{i=1}^{2} \left( y_i \frac{\partial}{\partial z_i} - z_i \frac{\partial}{\partial y_i} \right) \right]^2 + \left[ \sum_{i=1}^{2} \left( z_i \frac{\partial}{\partial x_i} - x_i \frac{\partial}{\partial z_i} \right) \right]^2 + \left[ \sum_{i=1}^{2} \left( x_i \frac{\partial}{\partial y_i} - y_i \frac{\partial}{\partial x_i} \right) \right]^2 + l(l+1) \right\} \psi = 0,$$  \hspace{1cm} (2.2)

where $l = 0, 1, \ldots$. We introduce three Euler angles $(\theta', \phi', \phi)$, such that $(r_1, \theta', \phi')$ are the spherical coordinates of the first electron in the space-fixed coordinate $o$-$xyz$, i.e. $\theta' = \theta_1, \phi' = \phi_1$. $\phi$ is the interfractial angle between the $r_1 - z$ plane and the $r_1 - r_2$ plane. Rotate the system of coordinates, such that $\vec{r}_1$ is the new polar axis $o\vec{z}'$, and the projections of unit vectors $\hat{o}\vec{x}, \hat{o}\vec{y}, \hat{o}\vec{z}$ on $ox', oy', oz'$ are $(-\cos \theta' \cos \phi', \sin \phi')$, $(-\cos \theta' \sin \phi', \cos \phi, \sin \theta' \sin \phi')$, $(\sin \theta', 0, \cos \theta')$ respectively; the spherical coordinates of the second electron in $o - x'y'z'$ are $(r_2, \theta, \pi + \phi)$.

Take $(r_1, r_2, \theta, \theta', \phi, \phi')$ as new variables, then HBT can be defined as follows:

$$\begin{align*}
x_1 &= r_1 \sin \theta' \cos \phi' \
y_1 &= r_1 \sin \theta' \sin \phi' \
z_1 &= r_1 \cos \theta' \\
x_2 &= r_2 (\sin \theta \cos \theta' \cos \phi \cos \phi' - \sin \theta \sin \phi \sin \phi' + \cos \theta \sin \theta' \cos \phi') \
y_2 &= r_2 (\sin \theta \cos \theta' \sin \phi \cos \phi' + \sin \theta \sin \phi \cos \phi' + \cos \theta \sin \theta' \cos \phi') \\
z_2 &= r_2 (\cos \theta \cos \theta' - \sin \theta \sin \theta' \cos \phi).
\end{align*}$$  \hspace{1cm} (2.3)

Take inner products of the unit vector $\vec{r}_2$ with unit vectors $\vec{r}_1$, $\hat{o}\vec{z}$, $\hat{o}\vec{y}$ respectively, we have

$$\begin{align*}
\cos \theta &= \cos \theta' \cos \theta_2 + \sin \theta' \sin \theta_2 \cos (\phi_2 - \phi'), \\
\cos \theta_2 &= \cos \theta \cos \theta' - \sin \theta \sin \theta' \cos \phi, \\
\sin \theta \sin \phi &= \sin \theta_2 \sin (\phi_2 - \phi').
\end{align*}$$  \hspace{1cm} (2.4)

Thank to (2.3) and (2.4), (2.1) and (2.2) can be transferred into the following forms:

$$L(\psi) - \frac{A_1(\psi)}{r_1^2} - \frac{A_2(\psi)}{r_2^2} = E\psi,$$  \hspace{1cm} (2.5)
\[
\left[ \frac{\partial^2}{\partial \theta'^2} + \text{ctg} \theta' \frac{\partial}{\partial \theta'} + \frac{1}{\sin^2 \theta'} \frac{\partial^2}{\partial \phi'^2} - 2 \frac{\cos \theta'}{\sin^2 \theta'} \frac{\partial^2}{\partial \phi \partial \phi'} + \frac{1}{\sin^2 \theta'} \frac{\partial^2}{\partial \phi'^2} + l(l+1) \right] \psi = 0, \tag{2.6}
\]

where

\[
L(\psi) = -\sum_{i=1}^{2} \frac{1}{r_{i}^2} \frac{\partial}{\partial r_{i}} \left( r_{i}^2 \frac{\partial \psi}{\partial r_{i}} \right) - \left( \frac{1}{r_{1}^2} + \frac{1}{r_{2}^2} \right) \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + V \psi,
\]

\[
A_{1}(\psi) = M^2(\psi) + 2\text{ctg} \theta B_{1}(\psi) + 2 \frac{\partial}{\partial \theta} B_{2}(\psi) - 2B_{3}(\psi) + (\text{ctg}^2 \theta - 1) \frac{\partial^2 \psi}{\partial \phi'^2},
\]

\[
A_{2}(\psi) = \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi'^2}, \quad B_{1}(\psi) = \text{ctg} \theta \cos \phi \frac{\partial^2 \psi}{\partial \phi'^2} + \sin \phi \frac{\partial^2 \psi}{\partial \phi \partial \phi'},
\]

\[
B_{2}(\psi) = \text{ctg} \theta \sin \phi \frac{\partial^2 \psi}{\partial \phi \partial \phi'} - \cos \phi \frac{\partial^2 \psi}{\partial \theta \partial \phi'}, \quad B_{3}(\psi) = \frac{\sin \phi}{\sin \theta} \frac{\partial^2 \psi}{\partial \theta \partial \phi'} + \frac{\text{ctg} \theta \cos \phi}{\sin \theta} \frac{\partial^2 \psi}{\partial \phi \partial \phi'}.
\]

By quantum mechanics, all common eigenfunctions of

\[
M_{z} = -i \sum_{i=1}^{2} (x_{i} \frac{\partial}{\partial y_{i}} - y_{i} \frac{\partial}{\partial x_{i}}) = -i \frac{\partial}{\partial \phi'} \tag{2.7}
\]

and \(M^{2}\) construct a complete basis of the square integrable function space (\(i\) is the imaginary unit). So any eigenfunction of (2.5) can be expanded with them.

Since eigenvalues of (2.6) are combined with the magnetic quantum number \(m\), we only need to think of the case \(m = 0\), i.e., to find those eigenfunctions of (2.6) satisfying \(\frac{\partial \psi}{\partial \theta'} = 0\). They are[29] \(D_{l}^{k\pm}, k = 0, 1, \ldots; l = 0, 1, \ldots\); where \(D_{l}^{k+} = F_{l}^{k}(\theta') \sin k \theta' \cos k \phi, D_{l}^{k-} = F_{l}^{k}(\theta') \sin k \theta' \sin k \phi\) and \(F_{l}^{k}(\theta') = F(k-l, k+l+1;k+1;\sin^2 \frac{\theta'}{2})\) are the hypergeometric functions[30]. In view of the expression of \(F_{l}^{k}\) and the hypergeometric equation[30], we have

\[
\begin{cases}
\frac{dF_{l}^{k}}{d\theta'} = C_{lk} \sin \theta' F_{l}^{k+1}, \\
C_{lk} \sin^2 \theta' F_{l}^{k+1} = 2k F_{l-1}^{k-1} - 2k \cos \theta' F_{l}^{k},
\end{cases} \tag{2.8}
\]

where \(C_{lk} = \frac{(k-l)(k+l+1)}{2(k+1)}\). Thank to (2.8) and definitions of operators \(L, A_{1}, A_{2}, B_{1}, B_{2}\) and \(B_{3}\), by direct calculations, the following relations are true:

\[
\begin{align*}
D_{l}^{0+} & = F_{l}^{0}(\theta'), & B_{2}(D_{l}^{0+}) & = -C_{l0} D_{l}^{1+}, \\
B_{1}(D_{l}^{0+}) & = B_{3}(D_{l}^{0+}) = A_{2}(D_{l}^{0+}) = 0, \\
B_{1}(D_{l}^{k\pm}) & = \frac{k C_{lk}}{2} D_{l}^{(k+1)\pm} - k^2 D_{l}^{(k-1)\pm}, \text{ when } k \geq 1; \\
B_{2}(D_{l}^{k\pm}) & = -\frac{C_{lk}}{2} D_{l}^{(k+1)\pm} - k D_{l}^{(k-1)\pm}, \text{ when } k \geq 1; \\
B_{3}(D_{l}^{k\pm}) & = 0, \text{ when } k \geq 1.
\end{align*} \tag{2.9}
\]

Clearly, all function spaces \(V_{l}^{\pm} = \text{span}\{D_{l}^{k\pm}, k = 0, 1, \ldots, l\}\) are invariant subspaces under the operator \(H\). For any eigen-state of \(H\) with angular number \(l\), we can construct the
wave function as: \( \psi^\pm_l = \sum_{k=0}^l u^{k\pm}_l (r_1, r_2, \theta) D^{k\pm}_l \). Substitute \( \psi^\pm_l \) into (2.5). Since \( D^{k\pm}_l \) are independent solutions of (2.6), in view of (2.9), we have

\[
L(u^{k\pm}_l) = \left[ \frac{l(l+1) + k^2(\cot^2\theta - 1)}{r^2_1} + \frac{k^2}{r^2_2 \sin^2\theta} \right] u^{k\pm}_l
- \frac{C_{l,-k-1}(k-1)(1-\delta_{k0})\cot\theta}{r^2_1} u^{(k-1)\pm}_l + \frac{2(k+1)^2(1-\delta_{kl})\cot\theta}{r^2_1} u^{(k+1)\pm}_l
+ \frac{C_{l,-k-1}(1-\delta_{k0})(1+\delta_{k1})}{r^2_1} \frac{\partial u^{(k-1)\pm}_l}{\partial \theta} + \frac{2(k+1)(1-\delta_{kl})}{r^2_1} \frac{\partial u^{(k+1)\pm}_l}{\partial \theta}
= Eu^{k\pm}_l, \tag{2.10}
\]

where \( \delta_{ij} = 1 \), if \( i = j \); \( \delta_{ij} = 0 \), if \( i \neq j \).

Since \( D^{0\pm}_l = 0 \), we set \( u^{0\pm}_l = 0 \). For any given \( l \geq 0 \), (2.10) are two independent systems of equations. The unknown functions of one are \( u^{0\pm}_l, u^{1\pm}_l, \ldots, u^{l\pm}_l \) satisfying \( l+1 \) equations (the index \( k \) varies from 0 to \( l \) in (2.10)). Those of another are \( u^{l-}_l, u^{l-}_l, \ldots, u^{l-}_l \) satisfying \( l \) equations (\( k = 1, 2, \ldots, l \)). They are used for different stationary state problems.

\section{3 Weak forms of energy equations}

By the discussion in section 2, the magnetic number \( m = 0 \) means that the \( z \)-component \( M_z \) of the angular momentum \( M \) is zero, so \( \partial \psi / \partial \phi' = 0 \) by (2.7). If \( l = 0 \) (\( S \)-state), (2.6) has only constant solutions, so \( V^+_0 \) consists of all square integrable functions depending on \( r_1, r_2, \theta \). If \( l = 1 \) (\( P \)-state), all independent solutions of (2.6) are

\[
\cos \theta', \sin \theta' \cos \phi, \sin \theta' \sin \phi, \tag{3.1}
\]

so \( V^+_1 = \text{span}\{\cos \theta', \sin \theta' \cos \phi\} \) and \( V^-_1 = \text{span}\{\sin \theta' \sin \phi\} \). If \( l = 2 \) (\( D \)-state), all independent solutions of (2.6) are

\[
3 \cos^2 \theta' - 1, \sin^2 \theta' \sin 2\phi, \sin^2 \theta' \cos 2\phi, \sin 2\theta' \sin \phi, \sin 2\theta' \cos \phi, \tag{3.2}
\]

so \( V^+_2 = \text{span}\{3 \cos^2 \theta' - 1, \sin 2\theta' \cos \phi, \sin^2 \theta' \cos 2\phi\} \) and \( V^-_2 = \text{span}\{\sin^2 \theta' \sin 2\phi, \sin 2\theta' \cos \phi\} \). Since each of the five spaces is invariant under the Hamiltonian \( H \), any eigenfunction \( \psi_p \) of \( P \) states must be in \( V^+_1 \) or \( V^-_1 \). Similar results hold for \( S \) and \( D \) states. Now we show that the wave functions \( \psi_p \) and \( \psi_d \) of \( 1s2p \) and \( 1s3d \) states belong to \( V^+_1 \) and \( V^+_2 \) respectively.

If we assume one electron is in a \( s \)-state and neglect the interaction between two electrons, the angular part of any wave function is a linear combination of the following functions:

\[
\text{const. (S states)}, \ \cos \theta_1, \cos \theta_2 \ (P \text{ states}), \ \frac{3 \cos^2 \theta_1 - 1}{2}, \frac{3 \cos^2 \theta_2 - 1}{2} \ (D \text{ states}). \tag{3.3}
\]
So the conclusion is true in view of the following relations:

\[
\begin{align*}
\cos \theta_1 &= \cos \theta', \\
\cos \theta_2 &= \cos \theta \cos \theta' - \sin \theta \sin \theta' \cos \phi \\
\frac{1}{2} (3 \cos^2 \theta_1 - 1) &= \frac{1}{2} (3 \cos^2 \theta' - 1) \\
\frac{1}{2} (3 \cos^2 \theta_2 - 1) &= \frac{3 \cos^2 \theta - 1}{4} (3 \cos^2 \theta' - 1) + \frac{3 \sin^2 \theta}{4} \sin^2 \theta' \cos 2\phi - \frac{3 \sin^2 \theta}{4} \sin 2\theta' \cos \phi.
\end{align*}
\tag{3.4}
\]

We construct the wave functions of the $S$, $1s2p$ and $1s3d$ states as follows:

\[
\begin{align*}
\psi_s &= u_s(r_1, r_2, \theta) \\
\psi_p &= u_{1p} \cos \theta_1 - u_{2p} \cos \theta_2 = (u_{1p} - u_{2p} \cos \theta) \cos \theta' + u_{2p} \sin 2\theta \sin \theta' \cos \phi \\
\psi_d &= u_{1d}(3 \cos^2 \theta' - 1) + u_{2d} \sin 2\theta \sin 2\theta' \cos \phi + u_{3d} \sin^2 \theta \sin^2 \theta' \cos 2\phi,
\end{align*}
\tag{3.5}
\]

where all coefficient functions $u$ depend only on three variables $r_1, r_2, \theta$.

Substituting (3.5) into (2.5) gives

\[
L(u_s) = E_s \cdot u_s, \tag{3.6}
\]

\[
\begin{align*}
L(u_{1p}) + \frac{1}{r_1^2} \left( u_{1p} - \ctg \theta \frac{\partial u_{1p}}{\partial \theta} \right) - \frac{1}{r_2^2} \frac{\partial u_{2p}}{\partial \theta} &= E_p \cdot u_{1p}, \\
L(u_{2p}) + \frac{1}{r_2^2} \left( u_{2p} - \ctg \theta \frac{\partial u_{2p}}{\partial \theta} \right) - \frac{1}{r_1^2} \frac{\partial u_{1p}}{\partial \theta} &= E_p \cdot u_{2p}, \\
L(u_{1d}) + \frac{3 u_{1d}}{r_1^2} + \frac{(6 \cos^2 \theta - 2) u_{2d}}{r_2^2} + \frac{\sin 2\theta}{r_1^2} \frac{\partial u_{2d}}{\partial \theta} &= E_d \cdot u_{1d} \\
L(u_{2d}) - 2 \left( \frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \ctg 2\theta \frac{\partial u_{2d}}{\partial \theta} - \frac{3}{r_1^2} \frac{\partial u_{1d}}{\partial \theta} + \frac{\ctg \theta}{2r_1^2} \frac{\partial u_{3d}}{\partial \theta} \\
&\quad + \left( \frac{5}{r_1^2} + \frac{3}{r_2^2} \right) u_{2d} + \frac{2 u_{3d}}{r_1^2} &= E_d \cdot u_{2d} \\
L(u_{3d}) - 2 \left( \frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \ctg \theta \frac{\partial u_{3d}}{\partial \theta} - \frac{2 \ctg \theta}{r_1^2} \frac{\partial u_{2d}}{\partial \theta} + \frac{2 u_{2d}}{r_1^2} \\
&\quad + \left( \frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \frac{u_{3d}}{\sin^2 \theta} + \frac{u_{3d}}{r_2^2} &= E_d \cdot u_{3d}
\end{align*}
\tag{3.7}
\]

**Remark:** Systems of equations (3.6)-(3.8) are equivalent to (2.10) and to (2.1). With (3.6)-(3.8), it is convenient to find proper trial spaces for variational equations of the $S$, $1s2p$ and $1s3d$ states respectively.
Let $\mu = \cos \theta$ and $R > 0$ large enough, denote $\vec{v}_p = (v_{1p}, v_{2p})^T$, $\vec{v}_d = (v_{1d}, v_{2d}, v_{3d})^T$, $\Omega = \{(r_1, r_2, \mu)|0 \leq r_1, r_2 \leq R, -1 \leq \mu \leq 1\}$. Define

$$(u_s, v_s) = \int_{\Omega} u_s v_s r_1^2 r_2^2 dr_1 dr_2 d\mu, \quad (\vec{u}_p, \vec{v}_p) = \int_{\Omega} (u_{1p} v_{1p} + u_{2p} v_{2p}) r_1^2 r_2^2 dr_1 dr_2 d\mu,$$

$$(u_d, \vec{v}_d) = \int_{\Omega} (u_{1d} v_{1d} + \mu u_{2d} v_{2d} + u_{3d} v_{3d}) r_1^2 r_2^2 dr_1 dr_2 d\mu;$$

$$\|\vec{v}_t\|_0^2 = (\vec{v}_t, \vec{v}_t), \quad t = s, p, d; \quad \|\vec{v}_p\|_s^2 = \|v_{1p}\|_s^2 + \|v_{2p}\|_s^2,$$

$$\|v_s\|_s^2 = \|v_s\|_0^2 + \int_{\Omega} \left[ \sum_{i=1}^{2} \left( \frac{\partial v_s}{\partial r_i} \right)^2 r_1^2 r_2^2 + (r_1^2 + r_2^2)(1 - \mu^2) \left( \frac{\partial v_s}{\partial \mu} \right)^2 \right] dr_1 dr_2 d\mu,$$

$$\|\vec{v}_d\|_d^2 = \|v_{1d}\|_s^2 + \|v_{3d}\|_s^2 + \int_{\Omega} \left[ r_1^2 r_2^2 \mu u_{2d} + r_1^2 r_2^2 \mu \left( \frac{\partial u_{2d}}{\partial r_1} \right)^2 + (r_1^2 + r_2^2)(\mu - \mu^3) \left( \frac{\partial u_{2d}}{\partial \mu} \right)^2 \right] dr_1 dr_2 d\mu,$$

where $\vec{v}_s = v_s$. Define

$$U_t = \{\vec{v}_t(r_1, r_2, \mu)||\vec{v}_t||_t < +\infty, \vec{v}_t|_{r_1=R} = \vec{v}_t|_{r_2=R} = \vec{0}\}, \quad t = s, p, d. \quad (3.9)$$

The weak forms of eigenvalue problems (3.6)–(3.8) are: Find $(E_t, \vec{u}_t) \in R \times U_t$ and $\vec{u}_t \neq 0$, such that

$$a_t(\vec{u}_t, \vec{v}_t) = E_t \cdot (\vec{u}_t, \vec{v}_t), \quad \forall \vec{v}_t \in U_t, \quad t = s, p, d; \quad (3.10)$$

where

$$a_s(u_s, v_s) = \int_{\Omega} \left[ \frac{1}{2} r_1^2 r_2^2 \left( \frac{\partial u_s}{\partial r_1} \frac{\partial v_s}{\partial r_1} + \frac{\partial u_s}{\partial r_2} \frac{\partial v_s}{\partial r_2} \right) + \frac{1}{2} (r_1^2 + r_2^2)(1 - \mu^2) \frac{\partial u_s}{\partial \mu} \frac{\partial v_s}{\partial \mu} \right] dr_1 dr_2 d\mu,$$

$$a_p(u_p, \vec{v}_p) = \int_{\Omega} \left[ \frac{1}{2} r_1^2 r_2^2 \left( \frac{\partial u_{1p}}{\partial r_1} \frac{\partial v_{1p}}{\partial r_1} + \frac{\partial u_{1p}}{\partial r_2} \frac{\partial v_{1p}}{\partial r_2} + \frac{\partial u_{2p}}{\partial r_1} \frac{\partial v_{2p}}{\partial r_1} + \frac{\partial u_{2p}}{\partial r_2} \frac{\partial v_{2p}}{\partial r_2} \right) \right]$$

$$\frac{1}{2} (r_1^2 + r_2^2)(1 - \mu^2) \left( \frac{\partial u_{1p}}{\partial \mu} \frac{\partial v_{1p}}{\partial \mu} + \frac{\partial u_{2p}}{\partial \mu} \frac{\partial v_{2p}}{\partial \mu} \right)$$

$$+ \left( \frac{r_1^2 r_2^2}{r_1^2 + r_2^2 - 2r_1 r_2} \right) u_{1p} v_{1p} + u_{2p} v_{2p}$$

$$+ \left( \frac{r_1^2 r_2^2}{r_1^2 + r_2^2 - 2r_1 r_2} \right) (u_{1p} v_{1p} + u_{2p} v_{2p})$$

$$+ r_1^2 u_{1p} v_{1p} + r_2^2 u_{2p} v_{2p} + \left( \mu r_1^2 \frac{\partial u_{1p}}{\partial \mu} + r_1^2 \frac{\partial u_{2p}}{\partial \mu} \right) v_{1p}$$

$$+ \left( \mu r_1^2 \frac{\partial u_{2p}}{\partial \mu} + r_2^2 \frac{\partial u_{1p}}{\partial \mu} \right) v_{2p} \right] dr_1 dr_2 d\mu,$$
\[ a_d(u_d, v_d) = \int_{\Omega} \left\{ \frac{1}{2} r_1^2 r_2^2 \left( \frac{\partial u_{1d}}{\partial r_1} \frac{\partial v_{1d}}{\partial r_1} + \frac{\partial u_{1d}}{\partial r_2} \frac{\partial v_{1d}}{\partial r_2} + \mu \frac{\partial u_{2d}}{\partial r_1} \frac{\partial v_{2d}}{\partial r_1} \right. \right. \\
\left. \left. + \mu \frac{\partial u_{2d}}{\partial r_2} \frac{\partial v_{2d}}{\partial r_2} + \frac{\partial u_{3d}}{\partial r_1} \frac{\partial v_{3d}}{\partial r_1} + \frac{\partial u_{3d}}{\partial r_2} \frac{\partial v_{3d}}{\partial r_2} \right) \right. \\
\left. + \frac{1}{2} (r_1^2 + r_2^2)(1 - \mu^2) \left( \frac{\partial u_{1d}}{\partial \mu} \frac{\partial v_{1d}}{\partial \mu} + \mu \frac{\partial u_{2d}}{\partial \mu} \frac{\partial v_{2d}}{\partial \mu} + \frac{\partial u_{3d}}{\partial \mu} \frac{\partial v_{3d}}{\partial \mu} \right) \right. \\
\left. + \left( \frac{r_1^2 r_2^2}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \mu}} - 2r_1^2 r_2 - 2r_1 r_2^2 \right) \left( u_{1d} v_{1d} + \mu u_{2d} v_{2d} + u_{3d} v_{3d} \right) \right. \\
\left. + \left[ 3r_2^2 u_{1d} + r_2^2 (6 \mu^2 - 2) u_{2d} + 2r_2^2 (\mu^3 - \mu) \frac{\partial u_{2d}}{\partial \mu} \right] v_{1d} \right. \\
\left. + \left[ \frac{r_1^2 + r_2^2}{2} (3 \mu^2 - 1) \frac{\partial u_{2d}}{\partial \mu} + 3r_2^2 \frac{\partial u_{1d}}{\partial \mu} + \frac{r_2^2}{2} (\mu^2 - 1) \frac{\partial u_{3d}}{\partial \mu} \right. \right. \\
\left. \left. + 2r_2^2 \mu u_{3d} + (3r_1^2 + 5r_2^2) \mu u_{2d} \right] v_{2d} + \left[ 2r_2^2 \mu \frac{\partial u_{2d}}{\partial \mu} + 2(r_1^2 + r_2^2) \mu \frac{\partial u_{3d}}{\partial \mu} \right. \right. \\
\left. \left. + 2r_2^2 \mu u_{2d} + \left( r_1^2 + \frac{r_1^2 + r_2^2}{1 - \mu^2} \right) u_{3d} \right] v_{3d} \right\} \, dr_1 dr_2 d\mu. \]

\section{Finite-element approximations}

FEM is a numerical algorithm that uses local interpolation functions to solve partial differential equations describing boundary-value problems\cite{31}. It is a generalization of traditional variational methods and finite difference methods. For a variational problem on a function space $V$: Find $u \in V$ such that

\[ a(u, v) = (f, v) \quad \forall v \in V, \]

where $a(\cdot, \cdot)$ is a continuous bilinear form on $V \times V$ and $f$ is a continuous linear form on $V$. The approximate problem called discrete problem is: Find $u_h \in V_h$ such that

\[ a_h(u_h, v_h) = (f, v_h) \quad \forall v_h \in V_h, \]

where $V_h$ is a finite dimensional space which is included in $V$ (conforming FEM) or not (nonconforming FEM). Then FEM is characterized by three basic aspects in the construction of $V_h$ and the finite-element interpolation operator $\pi_h$ defined over $V$. First, a subdivision $T_h$ of the set $\overline{\Omega}$, i.e. the set $\overline{\Omega}$ is written as a finite union of finite elements $K \in T_h$. Secondly, the function of $v_h \in V_h$ are piecewise polynomials, in the sense that for each $K \in V_h$, the spaces $P_K = \{ v_h|_K : v_h \in V_h \}$ consist of polynomials. Thirdly, there should exist a basis of $V_h$ whose functions have small support. $\pi_h$ is characterized as: (1), $\forall v \in V$, $\pi_h v \in V_h$; (2), $\forall K \in T_h$, let $\Sigma_K = \{ l_1^K, \ldots, l_l^K \}$ whose elements are defined for
$v$ be a basis of $(P_K)'$, then operator $\pi_K$ is defined by: $\pi_Kv \in P_K, l_i^K(\pi_Kv) = l_i^K(v)$; (3), $\pi_hv|_K = \pi_Kv$.

We construct the Lagrange finite-element approximation[31] of (3.12), i.e. for any $p \in P_K$, the linear functional $l_i^K$ defined as: $l_i^K(p) = p(a_i^K)$, where $a_i^K$ is some point in $K$ called node. Let $\{T_h\}$ be a non-degenerate family of subdivisions of $\Omega$. $\forall K \in T_h$, $K$ is a cube. Let $\hat{K} = [0, 1]^3$ be the reference element. $F_K$ is an affine transformation from $\hat{K}$ to $K$ defined as:

$$\begin{align*}
\begin{cases}
r_1 = r_1^K + h_1^K \xi, \\
r_2 = r_2^K + h_2^K \eta, \\
\mu = \mu^K + h_3^K \zeta,
\end{cases}
(\xi, \eta, \zeta) \in \hat{K},
\end{align*}
(4.1)
$$

where $(r_1^K, r_2^K, \mu^K)$ is some vertex of $K$, and $h_1^K, h_2^K, h_3^K$ are edge lengths of $K$. Let $\hat{a}_{ijk} = (\xi_j, \eta_i, \zeta_k)$ be the nodes in $\hat{K}$, $\xi_j, \eta_i, \zeta_k \in \{0, 1/3, 2/3, 1\}$.

$$p_{ijk} = \prod_{l \neq i, m \neq j, n \neq k} (\xi - \xi_m)(\eta - \eta_l)(\zeta - \zeta_n) / (\xi_j - \xi_m)(\eta_i - \eta_l)(\zeta_k - \zeta_n) \quad 1 \leq i, j, k \leq 4.$$ Obviously we have

$$p_{ijk}(\hat{a}_{lmn}) = \delta_{ijk, lmn} = \begin{cases} 1, & (i, j, k) = (l, m, n), \\
0, & \text{else}.
\end{cases}$$

We define the interpolation function on $K$ as:

$$\forall v, \ \pi_Kv(x) = \sum_{i,j,k=1}^4 v(a_{i,j,k}^K)p_{ijk}(F_K^{-1}(x)), \ \forall x \in K.$$ where $a_{i,j,k}^K = F_K(\hat{a}_{i,j,k})$ are nodes on $K$. Define $\Sigma_K = \{a_{i,j,k}^K : 1 \leq i, j, k \leq 4\}$, $P_K = \{p_{i,j,k} \circ F_K^{-1} : 1 \leq i, j, k \leq 4\}$. $\pi_Kv_p = (\pi_Kv_{1p}, \pi_Kv_{2p})^T$, $\pi_Kv_d = (\pi_Kv_{1d}, \pi_Kv_{2d}, \pi_Kv_{3d})^T$. Clearly, $(\pi_K\tilde{v}_i)(a_{i,j,k}^K) = \tilde{v}_i(a_{i,j,k}^K), 1 \leq i, j, k \leq 4$. The global interpolation operator $\pi_h$ on $\Omega$ is defined as: $(\pi_h\tilde{v}_i)|_K = \pi_K\tilde{v}_i$. The finite element spaces are

$$U_t^h = \{\tilde{v}_t \in C^0(\Omega) : \tilde{v}_t|_K \in P_K; \tilde{v}_t|_{r_1=R} = \tilde{v}_t|_{r_2=R} = 0\}.$$ $	ilde{v} \in P_K$ means that all components of $\tilde{v}$ are in $P_K$, $t = s, p, d$; and so does $\tilde{v} \in C^0(\Omega)$.

The approximations of (3.12) are: Find $(E_t^h, \overline{u}_t^h) \in R^3 \times U_t^h$ and $\overline{u}_t^h \neq \vec{0}$, such that

$$a_t(\overline{u}_t^h, \overline{v}_t^h) = E_t^h : (\overline{u}_t^h, \overline{v}_t^h), \quad \forall \overline{v}_t^h \in U_t^h, \quad t = s, p, d.$$ (4.2)

Since $U_t^h$ are finite dimensional spaces, let $N_t = \text{dim}(U_t^h)$. We can choose the basis $\{\Phi_1, \ldots, \Phi_{N_t}\}$ of $U_t^h$ such that $\text{supp} \Phi_i = \bigcup_{K \in T_h, a_i \in \Sigma_K} K$ where $a_i$ is a node of $\Omega$. Let $\overline{u}_t^h = \sum_{i=1}^{N_t} a_i^h \Phi_i$, and $\overline{v}_t^h = \Phi_i^t$, $1 \leq i \leq N_t$. Then we obtain the equivalent generalized eigenvalue problem:

$$A_t \overline{X}_t = E_t^h M_t \overline{X}_t, \quad t = s, p, d.$$ (4.3)
where $X_t = (a_1^t, \cdots, a_{N_r}^t)^T$, $A_t = (a_t(\Phi_i^t, \Phi_j^t))_{N_t \times N_t}$, $M_t = ((\Phi_i^t, \Phi_j^t))_{N_t \times N_t}$.

In practice, we calculate all element stiffness matrices $A^K_t$, $M^K_t$ first, then assemble them into $A_t$, $M_t$ according to some rules\[32][33]. For example,

$$
(A^K_{s})_{ijk,lmn} = \frac{h^2_{1}h^2_{2}h^2_{3}}{2h^2_{3}} \int_K \frac{\partial p_{ijk}}{\partial \xi} \frac{\partial p_{lmn}}{\partial \xi} r_1^2 r_2^2 d\xi d\eta d\zeta + \frac{h^2_{1}h^2_{3}}{2h^2_{3}} \int_K \frac{\partial p_{ijk}}{\partial \eta} \frac{\partial p_{lmn}}{\partial \eta} r_1^2 r_2^2 d\xi d\eta d\zeta \\
+ \frac{h^2_{1}h^2_{2}}{2h^2_{3}} \int_K \frac{\partial p_{ijk}}{\partial \zeta} \frac{\partial p_{lmn}}{\partial \zeta} (1 - \mu^2)(r_1^2 + r_2^2) d\xi d\eta d\zeta \\
+ \frac{h^2_{1}h^2_{2}}{h^2_{3}} \int_K p_{ijk}p_{lmn} \left( \frac{r_1^2 r_2^2}{\sqrt{r_1^2 + r_2^2} - 2r_1^2 r_2^2} - 2r_1^2 r_2^2 - 2r_1^2 r_2 \right) d\xi d\eta d\zeta,
$$

$$(M^K_{s})_{ijk,lmn} = h^2_{1}h^2_{2}h^2_{3} \int_K p_{ijk}p_{lmn} r_1^2 r_2^2 d\xi d\eta d\zeta, \quad 1 \leq i, j, k, l, m, n \leq 4.$$

Since all $\Phi_i^t$ have small support, all global stiffness matrices $A_t$ and mass matrices $M_t$ are large and banded. $A_s$, $M_t$ are symmetric, $t = s, p, d$; but $A_p$, $A_d$ are unsymmetrical. For symmetric matrices, we only need to store up the nonzero elements of their lower triangular part. But for unsymmetrical matrices, we need extra storage spaces for the upper part. Furthermore, $1s2p$-state doubles and $1s3d$-state triples the number of unknowns (or degree of freedoms) of $S$ states for the same nodes. So we will get higher precision for $S$ states with the same number of nodes. We use inverse iteration method\[32] to solve the generalized eigenvalue problems (4.3).

## 5 Numerical results

We carried out our computations on PC: Intel PIII750 with 1G SDRAM. The experiment shows that: (1) the energy errors decrease with $R$ or the number of nodes increasing; (2) with excited states becoming higher, $R$ should be larger; and more nodes far from the nucleus be needed; (3) very large $R$ has not remarkable improvement to the precision.

The main error is concerning about the potential $V = -\frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$. For triplets, their wave functions are antisymmetric; so two electrons can not be very close to each other. That is to say, when $r_{12}$ is very small, the wave functions $u$ tend to zero. When we calculate $\int_{\Omega} \frac{u^2}{r_{12}} dr_1 dr_2 d\mu$ with Gaussian integration formulas\[34], the errors for triplets are much smaller than those for singlets with same number of Gaussian points. Furthermore, from the figures below, we can see that the wave function $|u|$ for the ground state is much larger than those for excited states when $r_{12}$ is small and in the neighborhood of the nucleus where the singularities are. So we use more and more Gaussian points and grid points along $\mu$ when the states varies from triplets, singlets to the ground state. But with the number of Gaussian points increasing, the computing time increases.

All matrix elements are computed by standard Gaussian integration formulas. The numbers of Gaussian points are: $9 \times 9 \times 9$ for triplets, $21 \times 21 \times 21$ for singlets, and $27 \times 27 \times 27$ for the ground state. We place grid points symmetrically along $r_1$ and $r_2$ for
all states. The grid points are:

\begin{align*}
1s1s^1S & : \quad 0.0, 0.05, 0.1, 0.15, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 1.0, 1.2, 1.6, \\
         & \quad 2.0, 2.6, 3.2, 4.2, 6.0, 9.0, 15.0; \\
         & \quad -1.0, -0.6, -0.2, 0.2, 0.6, 1.0; \\
1s2s^1S & : \quad 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, \\
         & \quad 2.2, 2.4, 2.6, 3.0, 3.4, 3.8, 4.2, 4.8, 5.6, 8.0, 11.5, 15.0, 20.0; \\
         & \quad -1.0, -0.5, 0.5, 1.0; \\
1s2s^3S & : \quad 0.0, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.2, 1.4, 1.6, \\
         & \quad 1.8, 2.0, 2.2, 2.4, 2.6, 2.8, 3.0, 3.2, 3.4, 3.6, 4.0, 4.5, 5.5, 7.0, 10.0, 13.0, \\
         & \quad 16.0, 20.0, 25.0; \\
         & \quad -1.0, 0.0, 1.0; \\
1s2p^3P & : \quad 0.0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.2, 2.6, 3.0, 3.6, 5.0, 7.0, \\
         & \quad 10.0, 15.0, 20.0, 25.0; \\
         & \quad -1.0, 0.0, 1.0; \\
1s3d^3D & : \quad 0.0, 0.2, 0.4, 0.6, 1.0, 1.6, 2.2, 3.0, 4.0, 6.0, 9.0, 13.0, 18.0, 24.0, 30.0; \\
         & \quad -1.0, 0.0, 1.0;
\end{align*}

\begin{table}[h]
\centering
\caption{Computational efforts.}
\begin{tabular}{|c|c|c|c|c|c|}
\hline
state & \multicolumn{5}{c|}{number of unknowns} \\
\cline{2-6}
 & 1s1s^1S & 1s2s^1S & 1s2s^3S & 1s2p^3P & 1s3d^3D \\
\hline
\multicolumn{5}{|c|}{-2.90372437703411959} \\
\multicolumn{5}{|c|}{-2.1459740460544} \\
\multicolumn{5}{|c|}{-2.1752293782367} \\
\multicolumn{5}{|c|}{-2.133164190} \\
\hline
\multicolumn{5}{|c|}{83111594(4) [12]} \\
\multicolumn{5}{|c|}{188(21) [10]} \\
\multicolumn{5}{|c|}{913037(13) [10]} \\
\multicolumn{5}{|c|}{77927(1) [35]} \\
\hline
\multicolumn{5}{|c|}{-2.903724106} \\
\multicolumn{5}{|c|}{-2.1459740042} \\
\multicolumn{5}{|c|}{-2.1752293277} \\
\multicolumn{5}{|c|}{-2.1331638324} \\
\multicolumn{5}{|c|}{-2.05558078} \\
\hline
\end{tabular}
\end{table}

Now, we show the behaviors of wave functions in a special case $\mu = 1(\theta = 0^\circ)$. From Figure 1-5, we can see that the domain where electrons appear frequently is considerably small, so it is reasonable to solve the Schrödinger equation in bounded domains. Furthermore, we can see that the figures of wave functions $\psi_s, \psi_p$ constructed in (3.6) are symmetric or antisymmetric according to singlets or triplets respectively. We didn’t add this assumption a priori.

\textbf{Acknowledgements:} The authors are grateful to the anonymous referees for their valuable comments and advices for our paper. The authors also thank professor Peizhu Ding of Jilin University for discussing the problem with us and reading this paper.

\section*{References}


Figure 1: Wave function of the $1s1s \,^1S$ state($\mu = 1$).

Figure 2: Wave function of the $1s2s \,^1S$ state($\mu = 1$).

Figure 3: Wave function of the $1s2s \,^3S$ state($\mu = 1$).
Figure 4: Radial function $u_{1p}$ for $1s2p\,^3P$ state($\mu = 1$). Figure 5: Radial function $u_{2p}$ for $1s2p\,^3P$ state($\mu = 1$).