Finite element calculations for the helium atom*

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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.

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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)

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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 $r_1^i r_2^j r_{12}^k e^{-\xi r_1 - \eta r_2} A$("$\xi$ terms") and $r_1^i r_2^j r_{12}^k e^{-\zeta(r_1+r_2)} A$("$\zeta$ 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 $r_1^i r_2^j r_{12}^k e^{-\xi_1 r_1 - \eta_1 r_2}$ and $r_1^i r_2^j r_{12}^k e^{-\xi_2 r_1 - \eta_2 r_2}$. Drake and Yan employed truncations to ensure numerical stability and convergence. By complete optimizations of the exponential scale factors α_1, β_1, α_2 and β_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 Bacsky([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 a 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

references cited therein.

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-, $1s2p$- 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:

$$H\psi = E\psi, \tag{2.1}$$

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, θ_i, ϕ_i) are its spherical coordinates(suppose the nucleus at the origion), $i = 1, 2$. $V = -(2Z)/r_1 - (2Z)/r_2 + 1/r_{12}$ 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 θ is the inter-electronic angle.

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

$$\begin{aligned}\Big\{\Big[\sum_{i=1}^{2}\Big(y_i\frac{\partial}{\partial z_i} - z_i\frac{\partial}{\partial y_i}\Big)\Big]^2 &+ \Big[\sum_{i=1}^{2}\Big(z_i\frac{\partial}{\partial x_i} - x_i\frac{\partial}{\partial z_i}\Big)\Big]^2 \\ &+ \Big[\sum_{i=1}^{2}\Big(x_i\frac{\partial}{\partial y_i} - y_i\frac{\partial}{\partial x_i}\Big)\Big]^2 + l(l+1)\Big\}\psi = 0,\end{aligned} \tag{2.2}$$

where $l = 0, 1, \cdots$. We introduce three Euler angles (θ', ϕ', ϕ), such that (r_1, θ', ϕ') are the spherical coordinates of the first electron in the space-fixed coordinate o–xyz, i.e. θ'=θ_1,$\phi' = \phi_1$. ϕ 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 $o\vec{x}$, $o\vec{y}$, $o\vec{z}$ on $o\vec{x'}$, $o\vec{y'}$, $o\vec{z'}$ are $(-\cos\theta'\cos\phi',\ \sin\phi',\ \sin\theta'\cos\phi')$, $(-\cos\theta'\sin\phi',\ -\cos\phi',\ \sin\theta'\sin\phi')$, $(\sin\theta',\ 0,\ \cos\theta')$ respectively; the spherical coordinates of the second electron in $o - x'y'z'$ are $(r_2, \theta, \pi + \phi)$.

Take (r_1, r_2, θ, θ', ϕ, ϕ') as new variables, then HBT can be defined as follows:

$$\begin{cases} x_1 = r_1\sin\theta'\cos\phi' \\ y_1 = r_1\sin\theta'\sin\phi' \\ z_1 = r_1\cos\theta' \\ x_2 = r_2(\sin\theta\cos\theta'\cos\phi\cos\phi' - \sin\theta\sin\phi\sin\phi' + \cos\theta\sin\theta'\cos\phi') \\ y_2 = r_2(\sin\theta\cos\phi\cos\theta'\sin\phi' + \sin\theta\sin\phi\cos\phi' + \cos\theta\sin\theta'\sin\phi') \\ z_2 = r_2(\cos\theta\cos\theta' - \sin\theta\sin\theta'\cos\phi). \end{cases} \tag{2.3}$$

Take inner products of the unit vector $\vec{r_2}$ with unit vectors $\vec{r_1}$, $o\vec{z}$, $o\vec{y}$ respectively, we have

$$\begin{cases} \cos\theta = \cos\theta'\cos\theta_2 + \sin\theta'\sin\theta_2\cos(\phi_2 - \phi'), \\ \cos\theta_2 = \cos\theta\cos\theta' - \sin\theta\sin\theta'\cos\phi, \\ \sin\theta\sin\phi = \sin\theta_2\sin(\phi_2 - \phi'). \end{cases} \tag{2.4}$$

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

$$L(\psi) - \frac{A_1(\psi)}{r_1^2} - \frac{A_2(\psi)}{r_2^2} = E\psi, \tag{2.5}$$

$$\left[\frac{\partial^2}{\partial\theta'^2}+\mathrm{ctg}\theta'\frac{\partial}{\partial\theta'}+\frac{1}{\sin^2\theta'}\frac{\partial^2}{\partial\phi^2}-2\frac{\cos\theta'}{\sin^2\theta'}\frac{\partial^2}{\partial\phi\partial\phi'}+\frac{1}{\sin^2\theta'}\frac{\partial^2}{\partial\phi'^2}+l(l+1)\right]\psi=0, \quad (2.6)$$

where

$$\begin{aligned}
L(\psi) &= -\sum_{i=1}^{2}\frac{1}{r_i^2}\frac{\partial}{\partial r_i}\left(r_i^2\frac{\partial\psi}{\partial r_i}\right)-\left(\frac{1}{r_1^2}+\frac{1}{r_2^2}\right)\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+V\psi,\\
A_1(\psi) &= M^2(\psi)+2\mathrm{ctg}\theta B_1(\psi)+2\frac{\partial}{\partial\theta}B_2(\psi)-2B_3(\psi)+(\mathrm{ctg}^2\theta-1)\frac{\partial^2\psi}{\partial\phi^2},\\
A_2(\psi) &= \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}, \qquad B_1(\psi)=\mathrm{ctg}\theta'\cos\phi\frac{\partial^2\psi}{\partial\phi^2}+\sin\phi\frac{\partial^2\psi}{\partial\phi\partial\theta'},\\
B_2(\psi) &= \mathrm{ctg}\theta'\sin\phi\frac{\partial\psi}{\partial\phi}-\cos\phi\frac{\partial\psi}{\partial\theta'}, \quad B_3(\psi)=\frac{\sin\phi}{\sin\theta'}\frac{\partial^2\psi}{\partial\theta\partial\phi'}+\frac{\mathrm{ctg}\theta\cos\phi}{\sin\theta'}\frac{\partial^2\psi}{\partial\phi\partial\phi'}.
\end{aligned}$$

By quantum mechanics, all common eigenfunctions of

$$M_z=-\mathsf{i}\sum_{i=1}^{2}(x_i\frac{\partial}{\partial y_i}-y_i\frac{\partial}{\partial x_i})=-\mathsf{i}\frac{\partial}{\partial\phi'} \quad (2.7)$$

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 $\frac{\partial\psi}{\partial\phi'}=0$. They are[29] $D_l^{k\pm}$, $k=0,1,\cdots,l$; $l=0,1,\cdots$; 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

$$\begin{cases}\dfrac{dF_l^k}{d\theta'}=C_{lk}\sin\theta' F_l^{k+1},\\ C_{lk}\sin^2\theta' F_l^{k+1}=2kF_l^{k-1}-2k\cos\theta' F_l^k,\end{cases} \quad (2.8)$$

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:

$$\begin{cases}D_l^{0+}=F_l^0(\theta'), \quad B_2(D_l^{0+})=-C_{l0}D_l^{1+},\\ B_1(D_l^{0+})=B_3(D_l^{0+})=A_2(D_l^{0+})=0,\\ B_1(D_l^{k\pm})=\dfrac{kC_{lk}}{2}D_l^{(k+1)\pm}-k^2D_l^{(k-1)\pm}, \text{ when } k\geq 1;\\ B_2(D_l^{k\pm})=-\dfrac{C_{lk}}{2}D_l^{(k+1)\pm}-kD_l^{(k-1)\pm}, \text{ when } k\geq 1;\\ B_3(D_l^{k\pm})=0, \text{ when } k\geq 1.\end{cases} \quad (2.9)$$

Clearly, all function spaces $V_l^{\pm}$=span$\{D_l^{k\pm}, k=0,1,\cdots,l\}$ are invariant subspaces under the operator H. For any eigen-state of H with angular number l, we can construct the

wave function as: $\psi_l^{\pm} = \sum_{k=0}^{l} u_l^{k\pm}(r_1, r_2, \theta) D_l^{k\pm}$. Substitute $\psi_l^{\pm}$ into (2.5). Since $D_l^{k\pm}$ are independent solutions of (2.6), in view of (2.9), we have

$$\begin{aligned} L(u_l^{k\pm}) &+ \left[\frac{l(l+1)+k^2(\mathrm{ctg}^2\theta-1)}{r_1^2} + \frac{k^2}{r_2^2\sin^2\theta}\right] u_l^{k\pm} \\ &- \frac{C_{l,k-1}(k-1)(1-\delta_{k0})\mathrm{ctg}\theta}{r_1^2} u_l^{(k-1)\pm} + \frac{2(k+1)^2(1-\delta_{kl})\mathrm{ctg}\theta}{r_1^2} u_l^{(k+1)\pm} \\ &+ \frac{C_{l,k-1}(1-\delta_{k0})(1+\delta_{k1})}{r_1^2}\frac{\partial u_l^{(k-1)\pm}}{\partial\theta} + \frac{2(k+1)(1-\delta_{kl})}{r_1^2}\frac{\partial u_l^{(k+1)\pm}}{\partial\theta} \\ &= E u_l^{k\pm}, \end{aligned} \tag{2.10}$$

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

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

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, θ. If $l = 1$ (P-state), all independent solutions of (2.6) are

$$\cos\theta', \quad \sin\theta'\cos\phi, \quad \sin\theta'\sin\phi, \tag{3.1}$$

so $V_1^+ = \mathrm{span}\{\cos\theta',\ \sin\theta'\cos\phi\}$ and $V_1^- = \mathrm{span}\{\sin\theta'\sin\phi\}$. 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 $V_2^+ = \mathrm{span}\{3\cos^2\theta' - 1,\ \sin 2\theta'\cos\phi,\ \sin^2\theta'\cos 2\phi\}$ and $V_2^- = \mathrm{span}\{\sin^2\theta'\sin 2\phi,\ \sin 2\theta'\cos\phi\}$. Since each of the five spaces is invariant under the Hamiltonian H, any eigenfunction ψ_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 ψ_p and ψ_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:

$$const.\ (S\ \text{states}),\ \cos\theta_1, \cos\theta_2\ (P\ \text{states}),\ \frac{3\cos^2\theta_1 - 1}{2}, \frac{3\cos^2\theta_2 - 1}{2}\ (D\ \text{states}). \tag{3.3}$$

So the conclusion is true in view of the following relations:

$$\begin{cases} \cos\theta_1 = \cos\theta' \\ \cos\theta_2 = \cos\theta\cos\theta' - \sin\theta\sin\theta'\cos\phi \\ \dfrac{1}{2}(3\cos^2\theta_1 - 1) = \dfrac{1}{2}(3\cos^2\theta' - 1) \\ \dfrac{1}{2}(3\cos^2\theta_2 - 1) = \dfrac{3\cos^2\theta - 1}{4}(3\cos^2\theta' - 1) + \dfrac{3\sin^2\theta}{4}\sin^2\theta'\cos 2\phi \\ \qquad\qquad\qquad\qquad\qquad\qquad -\dfrac{3\sin^2\theta}{4}\sin 2\theta'\cos\phi. \end{cases} \tag{3.4}$$

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

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

where all coefficient functions u depend only on three variables r_1, r_2, θ.

Substituting (3.5) into (2.5) gives

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

$$\begin{cases} L(u_{1p}) + \dfrac{1}{r_1^2}\left(u_{1p} - \mathrm{ctg}\theta\dfrac{\partial u_{1p}}{\partial\theta}\right) - \dfrac{1}{r_2^2\sin\theta}\dfrac{\partial u_{2p}}{\partial\theta} = E_p \cdot u_{1p} \\ L(u_{2p}) + \dfrac{1}{r_2^2}\left(u_{2p} - \mathrm{ctg}\theta\dfrac{\partial u_{2p}}{\partial\theta}\right) - \dfrac{1}{r_1^2\sin\theta}\dfrac{\partial u_{1p}}{\partial\theta} = E_p \cdot u_{2p}, \end{cases} \tag{3.7}$$

$$\begin{cases} L(u_{1d}) + \dfrac{3u_{1d}}{r_1^2} + \dfrac{(6\cos^2\theta - 2)u_{2d}}{r_2^2} + \dfrac{\sin 2\theta}{r_1^2}\dfrac{\partial u_{2d}}{\partial\theta} = E_d \cdot u_{1d} \\ L(u_{2d}) - 2\left(\dfrac{1}{r_1^2} + \dfrac{1}{r_2^2}\right)\mathrm{ctg}2\theta\dfrac{\partial u_{2d}}{\partial\theta} - \dfrac{3}{r_1^2\sin 2\theta}\dfrac{\partial u_{1d}}{\partial\theta} + \dfrac{\mathrm{tg}\theta}{2r_1^2}\dfrac{\partial u_{3d}}{\partial\theta} \\ \qquad\qquad + \left(\dfrac{5}{r_1^2} + \dfrac{3}{r_2^2}\right)u_{2d} + \dfrac{2u_{3d}}{r_1^2} = E_d \cdot u_{2d} \\ L(u_{3d}) - 2\left(\dfrac{1}{r_1^2} + \dfrac{1}{r_2^2}\right)\mathrm{ctg}\theta\dfrac{\partial u_{3d}}{\partial\theta} - \dfrac{2\mathrm{ctg}\theta}{r_1^2}\dfrac{\partial u_{2d}}{\partial\theta} + \dfrac{2u_{2d}}{r_1^2} \\ \qquad\qquad + \left(\dfrac{1}{r_1^2} + \dfrac{1}{r_2^2}\right)\dfrac{u_{3d}}{\sin^2\theta} + \dfrac{u_{3d}}{r_2^2} = E_d \cdot u_{3d} \end{cases} \tag{3.8}$$

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 $\vec{v_p} = (v_{1p}, v_{2p})^T$, $\vec{v_d} = (v_{1d}, v_{2d}, v_{3d})^T$, $\Omega = \{(r_1, r_2, \mu) | 0 \le r_1, r_2 \le R, -1 \le \mu \le 1\}$. Define

$$
\begin{aligned}
&(u_s, v_s) = \int_\Omega u_s v_s r_1^2 r_2^2 dr_1 dr_2 d\mu, \quad (\vec{u_p}, \vec{v_p}) = \int_\Omega (u_{1p}v_{1p} + u_{2p}v_{2p}) r_1^2 r_2^2 dr_1 dr_2 d\mu, \\
&(\vec{u_d}, \vec{v_d}) = \int_\Omega (u_{1d}v_{1d} + \mu u_{2d}v_{2d} + u_{3d}v_{3d}) r_1^2 r_2^2 dr_1 dr_2 d\mu; \\
&\|\vec{v_t}\|_0^2 = (\vec{v_t}, \vec{v_t}), \quad t = s, p, d; \qquad \|\vec{v_p}\|_p^2 = \|v_{1p}\|_s^2 + \|v_{2p}\|_s^2, \\
&\|v_s\|_s^2 = \|v_s\|_0^2 + \int_\Omega \Big[\sum_{i=1}^{2} \left(\frac{\partial v_s}{\partial r_i}\right)^2 r_1^2 r_2^2 + (r_1^2 + r_2^2)(1-\mu^2) \left(\frac{\partial v_s}{\partial \mu}\right)^2 \Big] dr_1 dr_2 d\mu, \\
&\|\vec{v_d}\|_d^2 = \|v_{1d}\|_s^2 + \|v_{3d}\|_s^2 + \int_\Omega \Big[r_1^2 r_2^2 \mu u_{2d}^2 + r_1^2 r_2^2 \mu \left(\frac{\partial u_{2d}}{\partial r_1}\right)^2 \\
&\qquad + r_1^2 r_2^2 \mu \left(\frac{\partial u_{2d}}{\partial r_2}\right)^2 + (r_1^2 + r_2^2)(\mu - \mu^3) \left(\frac{\partial u_{2d}}{\partial \mu}\right)^2 \Big] dr_1 dr_2 d\mu \ ,
\end{aligned}
$$

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

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

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

$$
a_t(\vec{u_t}, \vec{v_t}) = E_t \cdot (\vec{u_t}, \vec{v_t}), \quad \forall \vec{v_t} \in U_t, \quad t = s, p, d; \tag{3.10}
$$

where

$$
\begin{aligned}
a_s(u_s, v_s) \ = \ & \int_\Omega \Big[\frac{1}{2} r_1^2 r_2^2 \left(\frac{\partial u_s}{\partial r_1}\frac{\partial v_s}{\partial r_1} + \frac{\partial u_s}{\partial r_2}\frac{\partial v_s}{\partial r_2} \right) + \frac{1}{2}(r_1^2 + r_2^2)(1-\mu^2) \frac{\partial u_s}{\partial \mu}\frac{\partial v_s}{\partial \mu} \\
& + \left(\frac{r_1^2 r_2^2}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \mu}} - 2r_1^2 r_2 - 2r_1 r_2^2 \right) u_s v_s \Big] dr_1 dr_2 d\mu, \\
a_p(\vec{u_p}, \vec{v_p}) \ = \ & \int_\Omega \Big[\frac{1}{2} r_1^2 r_2^2 \left(\frac{\partial u_{1p}}{\partial r_1}\frac{\partial v_{1p}}{\partial r_1} + \frac{\partial u_{1p}}{\partial r_2}\frac{\partial v_{1p}}{\partial r_2} + \frac{\partial u_{2p}}{\partial r_1}\frac{\partial v_{2p}}{\partial r_1} + \frac{\partial u_{2p}}{\partial r_2}\frac{\partial v_{2p}}{\partial r_2} \right) \\
& + \frac{1}{2}(r_1^2 + r_2^2)(1-\mu^2) \left(\frac{\partial u_{1p}}{\partial \mu}\frac{\partial v_{1p}}{\partial \mu} + \frac{\partial u_{2p}}{\partial \mu}\frac{\partial v_{2p}}{\partial \mu} \right) \\
& + \left(\frac{r_1^2 r_2^2}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \mu}} - 2r_1^2 r_2 - 2r_1 r_2^2 \right) (u_{1p}v_{1p} + u_{2p}v_{2p}) \\
& + r_2^2 u_{1p} v_{1p} + r_1^2 u_{2p} v_{2p} + \left(\mu r_2^2 \frac{\partial u_{1p}}{\partial \mu} + r_1^2 \frac{\partial u_{2p}}{\partial \mu} \right) v_{1p} \\
& + \left(\mu r_1^2 \frac{\partial u_{2p}}{\partial \mu} + r_2^2 \frac{\partial u_{1p}}{\partial \mu} \right) v_{2p} \Big] dr_1 dr_2 d\mu,
\end{aligned}
$$

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

4 Finite-element approximations

FEM is a numerical algorithm that uses local interpolation functions to solve partial differential equations describing boundary-value problems[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 π_h defined over V. First, a subdivision $\mathcal{T}_h$ of the set $\overline{\Omega}$, i.e. the set $\overline{\Omega}$ is written as a finite union of *finite elements* $K \in \mathcal{T}_h$. 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*. π_h is characterized as: (1), $\forall v \in V$, $\pi_h v \in V_h$; (2), $\forall K \in \mathcal{T}_h$, let $\Sigma_K = \{l_1^K, \ldots, l_d^K\}$ whose elements are defined for

v be a basis of $(P_K)'$, then operator π_K is defined by: $\pi_K v \in P_K, l_i^K(\pi_K v) = l_i^K(v)$; (3), $\pi_h v|_K = \pi_K v$.

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 $\{\mathcal{T}_h\}$ be a non-degenerate family of subdivisions of $\overline{\Omega}$. $\forall K \in \mathcal{T}_h$, 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:

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

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

$$p_{ijk} = \prod_{\substack{l,m,n=1 \\ l\neq i, m\neq j, n\neq k}}^{4} \frac{(\xi - \xi_m)(\eta - \eta_l)(\zeta - \zeta_n)}{(\xi_j - \xi_m)(\eta_i - \eta_l)(\zeta_k - \zeta_n)} \qquad 1 \le i, j, k \le 4.$$

Obviously we have

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

We define the interpolation function on K as:

$$\forall v,\ \pi_K v(x) = \sum_{i,j,k=1}^{4} v(a_{i,j,k}^K) p_{ijk}(F_K^{-1}(x)),\ \forall x \in K.$$

where $a_{i,j,k}^K = F_K(\hat{a}_{i,j,k})$ are nodes on K. Define $\Sigma_K = \{a_{i,j,k}^K : 1 \le i,j,k \le 4\}$, $P_K = \{p_{i,j,k} \circ F_K^{-1} : 1 \le i,j,k \le 4\}$. $\pi_K \vec{v}_p = (\pi_K v_{1p}, \pi_K v_{2p})^T$, $\pi_K \vec{v}_d = (\pi_K v_{1d}, \pi_K v_{2d}, \pi_K v_{3d})^T$. Clearly, $(\pi_K \vec{v}_t)(a_{i,j,k}^K) = \vec{v}_t(a_{i,j,k}^K)$, $1 \le i,j,k \le 4$. The global interpolation operator π_h on Ω is defined as: $(\pi_h \vec{v}_t)|_K = \pi_K \vec{v}_t$. The finite element spaces are

$$U_t^h = \{\vec{v}_t \in C^0(\Omega) :\ \vec{v}_t|_K \in P_K;\ \vec{v}_t|_{r_1=R} = \vec{v}_t|_{r_2=R} = 0\}.$$

$\vec{v} \in P_K$ means that all components of $\vec{v}$ are in P_K, $t = s, p, d$; and so does $\vec{v} \in C^0(\Omega)$.

The approximations of (3.12) are: Find $(E_t^h, \vec{u}_t^h) \in R^1 \times U_t^h$ and $\vec{u}_t^h \neq \vec{0}$, such that

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

Since U_t^h are finite dimensional spaces, let N_t=dim(U_t^h). We can choose the basis $\{\vec{\Phi}_1^t, \cdots, \vec{\Phi}_{N_t}^t\}$ of U_t^h such that supp$\vec{\Phi}_i^t = \bigcup_{K \in \mathcal{T}_h, a_i \in \Sigma_K} K$ where a_i is a node of Ω. Let $\vec{u}_t^h = \sum_{i=1}^{N_t} \alpha_i^t \vec{\Phi}_i^t$, and $\vec{v}_t^h = \vec{\Phi}_i^t$, $1 \le i \le N_t$ in (4.2). Then we obtain the equivalent generalized eigenvalue problems:

$$A_t X_t = E_t^h M_t X_t, \qquad t = s, p, d, \tag{4.3}$$

where $X_t = (\alpha_1^t, \cdots, \alpha_{N_t}^t)^T$, $A_t = (a_t(\vec{\Phi}_i^t, \vec{\Phi}_j^t))_{N_t \times N_t}$, $M_t = ((\vec{\Phi}_i^t, \vec{\Phi}_j^t))_{N_t \times N_t}$.

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

$$\begin{aligned}(A_s^K)_{ijk,lmn} &= \frac{h_2^K h_3^K}{2h_1^K}\int_{\hat{K}} \frac{\partial p_{ijk}}{\partial \xi}\frac{\partial p_{lmn}}{\partial \xi} r_1^2 r_2^2 d\xi d\eta d\zeta + \frac{h_1^K h_3^K}{2h_2^K}\int_{\hat{K}} \frac{\partial p_{ijk}}{\partial \eta}\frac{\partial p_{lmn}}{\partial \eta} r_1^2 r_2^2 d\xi d\eta d\zeta \\ &+ \frac{h_1^K h_2^K}{2h_3^K}\int_{\hat{K}} \frac{\partial p_{ijk}}{\partial \zeta}\frac{\partial p_{lmn}}{\partial \zeta}(1-\mu^2)(r_1^2+r_2^2) d\xi d\eta d\zeta \\ &+ h_1^K h_2^K h_3^K \int_{\hat{K}} p_{ijk} p_{lmn}\left(\frac{r_1^2 r_2^2}{\sqrt{r_1^2+r_2^2-2r_1 r_2\mu}} - 2r_1^2 r_2 - 2r_1 r_2^2\right) d\xi d\eta d\zeta,\end{aligned}$$

$$(M_s^K)_{ijk,lmn} = h_1^K h_2^K h_3^K \int_{\hat{K}} p_{ijk} p_{lmn} r_1^2 r_2^2 d\xi d\eta d\zeta, \qquad 1 \le i,j,k,l,m,n \le 4.$$

Since all $\vec{\Phi}_i^t$ 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 μ 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:

$1s1s\ ^1S$: 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, 2.0, 2.6, 3.2, 4.2, 6.0, 9.0, 15.0;
$-1.0, -0.6, -0.2, 0.2, 0.6, 1.0$;

$1s2s\ ^1S$: 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, 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;
$-1.0, -0.5, 0.5, 1.0$;

$1s2s\ ^3S$: 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, 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, 16.0, 20.0, 25.0;
$-1.0, 0.0, 1.0$;

$1s2p\ ^3P$: 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, 10.0, 15.0, 20.0, 25.0;
$-1.0, 0.0, 1.0$;

$1s3d\ ^3D$: 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;
$-1.0, 0.0, 1.0$;

Table 1: Computational efforts.

state	$1s1s\ ^1S$	$1s2s\ ^1S$	$1s2s\ ^3S$	$1s2p\ ^3P$	$1s3d\ ^3D$
number of unknowns	57472	65320	68243	44954	36246

Table 2: FEM results for the helium atom($a.u.$).

state	$1s1s\ ^1S$	$1s2s\ ^1S$	$1s2s\ ^3S$	$1s2p\ ^3P$	$1s3d\ ^3D$
results in references	-2.90372437703411959 83111594(4) [12]	-2.1459740460544 188(21) [10]	-2.1752293782367 913037(13) [10]	-2.133164190 77927(1) [35]	-2.055636309453 261(4) [35]
this work	-2.903724106	-2.1459740042	-2.1752293277	-2.1331633824	-2.05558078

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 ψ_s, ψ_p constructed in (3.6) are symmetric or antisymmetric according to singlets or triplets respectively. We didn't add this assumption a priori.

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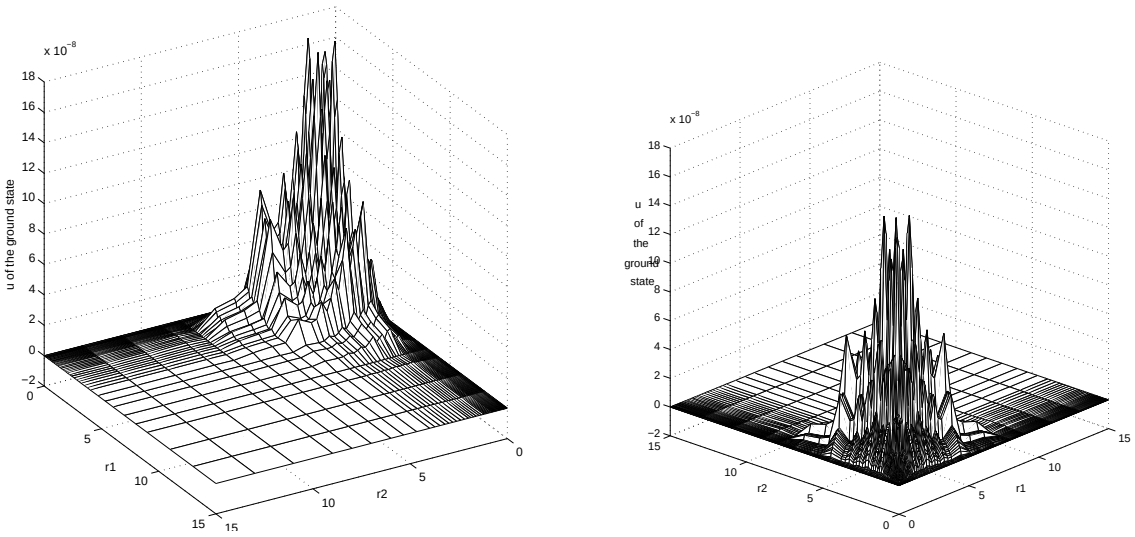

Figure 1: Wave function of the $1s1s\ ^1S$ state($\mu = 1$).

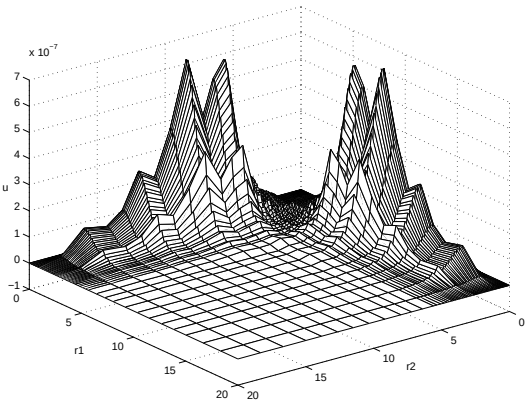

Figure 2: Wave function of the $1s2s\ ^1S$ state($\mu = 1$).

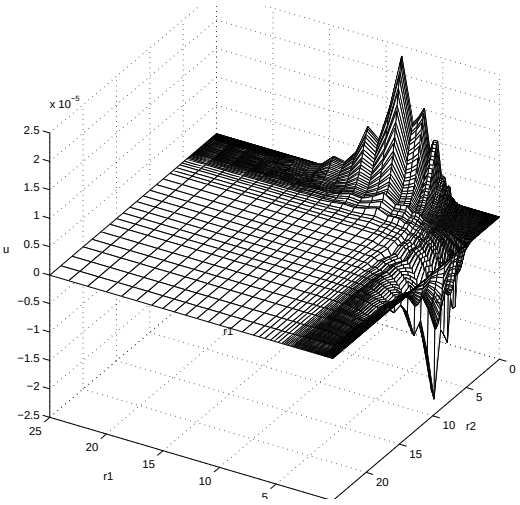

Figure 3: Wave function of the $1s2s\ ^3S$ state($\mu = 1$).

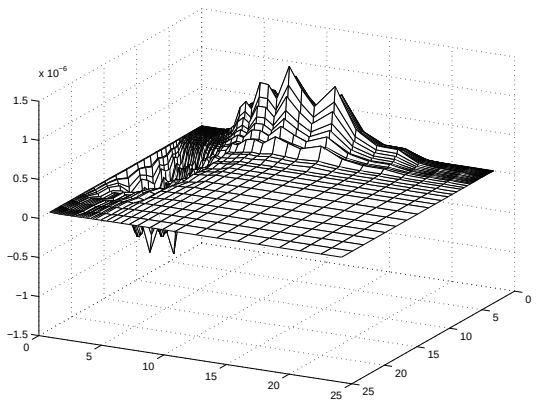

Figure 4: Radial function u_{1p} for $1s2p\ ^3P$ state($\mu = 1$).

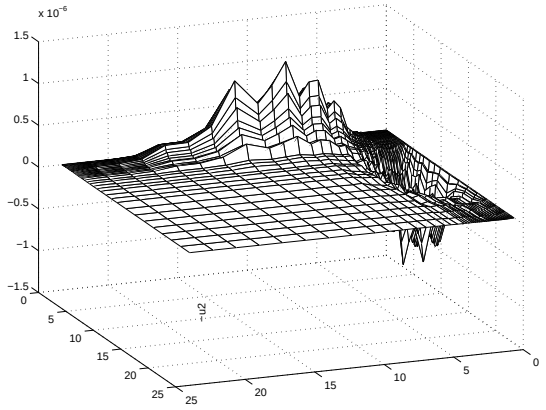

Figure 5: Radial function u_{2p} for $1s2p\ ^3P$ state($\mu = 1$).

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