There are three electrons out of the nucleus of the lithium atom; and each of them has three freedoms (without considering its spin). So the system is described by a nine-dimensional Schrödinger equation (for fixed-nucleus problem). It is very difficult to solve it by variational methods, finite difference methods and other methods directly. Usual approaches in quantum mechanics are mean-field methods [1]. For them, every electron is considered independently to be in a central electric field formed by the nucleus and other electrons. The original problem is transferred into a system of nonlinear partial differential equations of low-dimension, then solve it iteratively. So the physical model itself is simplified approximately.

The main works of the finite element method (FEM) applied to atomic and molecular problems appeared in 1970's, and in one- or two-dimensional cases [2–4]. In 1975, Askar calculated the energies of hydrogen atom in the ground state and the first excited state [2]. Then Nordholm and Bacsky applied FEM to more general bound state problems [4]. Fridman and Rosenfeld analyzed two model problems of two-dimensional Schrödinger equations with FEM in 1977 [3]. 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 [5]. They calculated the helium in the ground state in 1985. The six-dimensional Schrödinger equation can be transferred into three-dimensional systems of equations rigorously [6]. Most of the works about three-dimensional FEM applied to three-body problems appeared hereafter. They are Braun et al. [7], Scrinzi [8], Ackermann [9], Zheng and Ying [10], and so on. They obtained very precise results.

Shi and Ding [11] solved the Hartree–Fock equation of the ground lithium numerically by one-dimensional piecewise linear finite element method. It is a system of one-dimensional nonlinear partial differential equations(whose Coulomb integral and exchange integral are double). The relative error between their result and the Hartree–Fock limit value is -4.1×10^{-4}. After considering correlative correct, the relative error between their approximate eigenvalue and the experimental value is -4.9×10^{-4}. That is to say, the results by the Hartree–Fock FEM can only be compared with the limit value of the Hartree–Fock method.

To the best of our knowledge, we have not seen any other finite element result for the lithium atom. In this paper, we transfer the nine-dimensional Schrödinger equation into a six-dimensional partial differential eigenvalue equation rigorously for the ground state of the lithium atom. From the variational formulation of the Schrödinger equation, we have also derived an six-dimensional weak form of the eigenvalue problem which is equivalent to the original variational formula for the ground lithium.

We construct a kind of six-dimensional finite element methods to solve the transferred energy equation. With very coarse mesh, the relative error of our approximate eigenvalue and the nonrelativistic limit value is order of 10^{-5} in

atomic unit. Up to now, the finite element methods are only applied to partial differential equations of dimension no more than three. This work is the first try to construct highly dimensional FEM; and it is also valuable in applying FEM to quantum mechanics.

The paper is arranged as follows. The nine-dimensional Schrödinger equation is transferred into a six-dimensional partial differential equation in Section 2. A six-dimensional variational equation is given in Section 3. In Section 4, a kind of six-dimensional finite element methods are described in detail to approximate the obtained variational equation. Numerical results are given in Section 5.

We use atomic unit in this paper, i.e. Bohr Radius a_0 for length, Hartree for energy. We consider the stationary nucleus, nonrelativistic and spin-independent case.

2. Six-dimensional differential equation of the ground lithium

There are three electrons out of the nucleus of the lithium atom. In the Cartesian coordinates, its Schrödinger equation is:

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

where the Hamiltonian operator H is defined as

$$H = -\frac{1}{2}(\Delta_1 + \Delta_2 + \Delta_3) - \frac{3}{r_1} - \frac{3}{r_2} - \frac{3}{r_3} + \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}}, \tag{2.2}$$

$$\Delta_j = \frac{\partial^2}{\partial x_j^2} + \frac{\partial^2}{\partial y_j^2} + \frac{\partial^2}{\partial z_j^2}, \quad 1 \leqslant j \leqslant 3$$

are Laplacian operators. Let

$$\vec{r}_i = (x_i, y_i, z_i) = r_i(\sin\theta_i \cos\phi_i, \sin\theta_i \sin\phi_i, \cos\theta_i) \tag{2.3}$$

be coordinates of the ith electron in the space-fixed system of coordinates $o - xyz$ and spherical coordinates. $r_{jk} = |\vec{r}_j - \vec{r}_k|$ is the distance between the jth electron and the kth electron.

$$\cos\theta_{jk} = \frac{\vec{r}_j \cdot \vec{r}_k}{r_j r_k} = \frac{r_j^2 + r_k^2 - |\vec{r}_j - \vec{r}_k|^2}{2r_j r_k}, \tag{2.4}$$

where θ_{jk} is the inter-electronic angle between radial vectors $\vec{r}_j$ and $\vec{r}_k$, $r_j = |\vec{r}_j|$.

We know from quantum mechanics [12,13], that the ground state of the lithium atom is the stablest and has the lowest energy. It is the most symmetric state under rotations about the vector $\vec{r}_1$ (or equivalently about $\vec{r}_2$ or $\vec{r}_3$); and it depends only on six variables $r_1, r_2, r_3, \theta_{12}, \theta_{13}, \theta_{23}$. So we can suppose that the wave function ψ in (2.1) depends only on them for the ground state, that is, $\psi = \psi(r_1, r_2, r_3, \theta_{12}, \theta_{13}, \theta_{23})$.

In spherical coordinates, the Hamiltonian of the system can be written as

$$H = -\frac{1}{2}\left[\frac{1}{r_1^2}\frac{\partial}{\partial r_1}\left(r_1^2\frac{\partial}{\partial r_1}\right) + \frac{1}{r_2^2}\frac{\partial}{\partial r_2}\left(r_2^2\frac{\partial}{\partial r_2}\right) + \frac{1}{r_3^2}\frac{\partial}{\partial r_3}\left(r_3^2\frac{\partial}{\partial r_3}\right)\right.$$
$$\left. -\frac{L_1^2}{r_1^2} - \frac{L_2^2}{r_2^2} - \frac{L_3^2}{r_3^2}\right] - \frac{3}{r_1} - \frac{3}{r_2} - \frac{3}{r_3} + \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}}, \tag{2.5}$$

where L_i^2 is the square of the angular momentum operator of the ith electron defined as

$$L_i^2 = L_{ix}^2 + L_{iy}^2 + L_{iz}^2$$
$$= -\left(y_1\frac{\partial}{\partial z_1} - z_1\frac{\partial}{\partial y_1}\right)^2 - \left(z_1\frac{\partial}{\partial x_1} - x_1\frac{\partial}{\partial z_1}\right)^2 - \left(x_1\frac{\partial}{\partial y_1} - y_1\frac{\partial}{\partial x_1}\right)^2. \tag{2.6}$$

By (2.3) and (2.4), we have

$$\begin{cases} \dfrac{\partial r_1}{\partial x_1} = \dfrac{x_1}{r_1}, \ \dfrac{\partial r_2}{\partial x_1} = \dfrac{\partial r_3}{\partial x_1} = \dfrac{\partial \theta_{23}}{\partial x_1} = 0, \\[2mm] \dfrac{\partial \theta_{12}}{\partial x_1} = \dfrac{1}{\sin\theta_{12}}\left(\dfrac{x_1\cos\theta_{12}}{r_1^2} - \dfrac{x_2}{r_1 r_2}\right), \\[2mm] \dfrac{\partial \theta_{13}}{\partial x_1} = \dfrac{1}{\sin\theta_{13}}\left(\dfrac{x_1\cos\theta_{13}}{r_1^2} - \dfrac{x_3}{r_1 r_3}\right). \end{cases} \tag{2.7}$$

We can also obtain partial derivatives $\partial r/\partial x$, $r = r_1, r_2, r_3, \theta_{12}, \theta_{23}, \theta_{13}$ and $x = x_i, y_i, z_i$, $i = 1, 2, 3$. But they are left out for briefness. The cross product of any two vectors is defined as

$$\begin{cases} Q_1 = \vec{r}_2 \times \vec{r}_3 = (q_1^1, q_2^1, q_3^1) = (y_2 z_3 - y_3 z_2, z_2 x_3 - z_3 x_2, x_2 y_3 - x_3 y_2), \\ Q_2 = \vec{r}_3 \times \vec{r}_1 = (q_1^2, q_2^2, q_3^2) = (y_3 z_1 - y_1 z_3, z_3 x_1 - z_1 x_3, x_3 y_1 - x_1 y_3), \\ Q_3 = \vec{r}_1 \times \vec{r}_2 = (q_1^3, q_2^3, q_3^3) = (y_1 z_2 - y_2 z_1, z_1 x_2 - z_2 x_1, x_1 y_2 - x_2 y_1). \end{cases} \tag{2.8}$$

By the law of chain, it follows

$$L_{1z}\psi = i\left(x_1\frac{\partial}{\partial y_1} - y_1\frac{\partial}{\partial x_1}\right)\psi = -\frac{iq_3^3}{r_1 r_2 \sin\theta_{12}}\frac{\partial\psi}{\partial\theta_{12}} + \frac{iq_3^2}{r_1 r_3 \sin\theta_{13}}\frac{\partial\psi}{\partial\theta_{13}}. \tag{2.9}$$

Since

$$L_{1z}\frac{q_3^3}{r_1 r_2 \sin\theta_{12}}\frac{\partial\psi}{\partial\theta_{12}} = \frac{i}{r_1 r_2 \sin\theta_{12}}\left\{\left(-x_1 x_2 - y_1 y_2 + \frac{(q_3^3)^2 \cos\theta_{12}}{r_1 r_2 \sin^2\theta_{12}}\right)\frac{\partial\psi}{\partial\theta_{12}}\right.$$
$$\left. -\frac{(q_3^3)^2}{r_1 r_2 \sin\theta_{12}}\frac{\partial^2\psi}{\partial\theta_{12}^2} + \frac{q_3^3 q_3^2}{r_1 r_3 \sin\theta_{13}}\frac{\partial^2\psi}{\partial\theta_{12}\partial\theta_{13}}\right\}, \tag{2.10}$$

$$L_{1z} \frac{q_3^2}{r_1 r_3 \sin \theta_{13}} \frac{\partial \psi}{\partial \theta_{13}} = \frac{i}{r_1 r_3 \sin \theta_{13}} \left\{ \left(x_1 x_3 + y_1 y_3 - \frac{(q_3^2)^2 \cos \theta_{13}}{r_1 r_3 \sin^2 \theta_{13}} \right) \frac{\partial \psi}{\partial \theta_{13}} \right.$$
$$\left. + \frac{(q_3^2)^2}{r_1 r_3 \sin \theta_{13}} \frac{\partial^2 \psi}{\partial \theta_{13}^2} - \frac{q_3^2 q_3^3}{r_1 r_2 \sin \theta_{12}} \frac{\partial^2 \psi}{\partial \theta_{12} \partial \theta_{13}} \right\}, \quad (2.11)$$

So thanks to (2.9)–(2.11), the following is true:

$$L_{1z}^2 \psi = L_{1z}(L_{1z} \psi) = L_{1z} \left(-\frac{i q_3^3}{r_1 r_2 \sin \theta_{12}} \frac{\partial \psi}{\partial \theta_{12}} \right) + L_{1z} \left(\frac{i q_3^2}{r_1 r_3 \sin \theta_{13}} \frac{\partial \psi}{\partial \theta_{13}} \right)$$
$$= -\frac{1}{r_1 r_2 \sin \theta_{12}} \left\{ \left(x_1 x_2 + y_1 y_2 - \frac{(q_3^3)^2 \cos \theta_{12}}{r_1 r_2 \sin^2 \theta_{12}} \right) \frac{\partial \psi}{\partial \theta_{12}} + \frac{(q_3^3)^2}{r_1 r_2 \sin \theta_{12}} \frac{\partial^2 \psi}{\partial \theta_{12}^2} \right\}$$
$$- \frac{1}{r_1 r_3 \sin \theta_{13}} \left\{ \left(x_1 x_3 + y_1 y_3 - \frac{(q_3^3)^2 \cos \theta_{13}}{r_1 r_3 \sin^2 \theta_{13}} \right) \frac{\partial \psi}{\partial \theta_{13}} + \frac{(q_3^2)^2}{r_1 r_3 \sin \theta_{13}} \frac{\partial^2 \psi}{\partial \theta_{13}^2} \right\}$$
$$+ \frac{2 q_3^3 q_3^2}{r_1^2 r_2 r_3 \sin \theta_{12} \sin \theta_{13}} \frac{\partial^2 \psi}{\partial \theta_{12} \partial \theta_{13}}. \quad (2.12)$$

Similarly, we have

$$L_{1y}^2 \psi = -\frac{1}{r_1 r_2 \sin \theta_{12}} \left\{ \left(x_1 x_2 + z_1 z_2 - \frac{(q_2^3)^2 \cos \theta_{12}}{r_1 r_2 \sin^2 \theta_{12}} \right) \frac{\partial \psi}{\partial \theta_{12}} + \frac{(q_2^3)^2}{r_1 r_2 \sin \theta_{12}} \frac{\partial^2 \psi}{\partial \theta_{12}^2} \right\}$$
$$- \frac{1}{r_1 r_3 \sin \theta_{13}} \left\{ \left(x_1 x_3 + z_1 z_3 - \frac{(q_2^2)^2 \cos \theta_{13}}{r_1 r_3 \sin^2 \theta_{13}} \right) \frac{\partial \psi}{\partial \theta_{13}} + \frac{(q_2^2)^2}{r_1 r_3 \sin \theta_{13}} \frac{\partial^2 \psi}{\partial \theta_{13}^2} \right\}$$
$$+ \frac{2 q_2^3 q_2^2}{r_1^2 r_2 r_3 \sin \theta_{12} \sin \theta_{13}} \frac{\partial^2 \psi}{\partial \theta_{12} \partial \theta_{13}}, \quad (2.13)$$

$$L_{1x}^2 \psi = -\frac{1}{r_1 r_2 \sin \theta_{12}} \left\{ \left(y_1 y_2 + z_1 z_2 - \frac{(q_1^3)^2 \cos \theta_{12}}{r_1 r_2 \sin^2 \theta_{12}} \right) \frac{\partial \psi}{\partial \theta_{12}} + \frac{(q_1^3)^2}{r_1 r_2 \sin \theta_{12}} \frac{\partial^2 \psi}{\partial \theta_{12}^2} \right\}$$
$$- \frac{1}{r_1 r_3 \sin \theta_{13}} \left\{ \left(y_1 y_3 + z_1 z_3 - \frac{(q_2^2)^2 \cos \theta_{13}}{r_1 r_3 \sin^2 \theta_{13}} \right) \frac{\partial \psi}{\partial \theta_{13}} + \frac{(q_1^2)^2}{r_1 r_3 \sin \theta_{13}} \frac{\partial^2 \psi}{\partial \theta_{13}^2} \right\}$$
$$+ \frac{2 q_1^3 q_1^2}{r_1^2 r_2 r_3 \sin \theta_{12} \sin \theta_{13}} \frac{\partial^2 \psi}{\partial \theta_{12} \partial \theta_{13}}. \quad (2.14)$$

Since

$$Q_3 \cdot Q_2 = (\vec{r}_1 \times \vec{r}_2) \cdot (\vec{r}_3 \times \vec{r}_1) = (\vec{r}_1 \cdot \vec{r}_3)(\vec{r}_2 \cdot \vec{r}_1) - (\vec{r}_1 \cdot \vec{r}_1)(\vec{r}_3 \cdot \vec{r}_3)$$
$$= r_1 r_3 \cos \theta_{13} \cdot r_1 r_2 \cos \theta_{12} - r_1^2 r_2 r_3 \cos \theta_{23}$$
$$= r_1^2 r_2 r_3 (\cos \theta_{12} \cos \theta_{13} - \cos \theta_{23}), \quad (2.15)$$

Combining (2.6) with (2.12)–(2.15) gives

$$
\begin{aligned}
L_1^2\psi &= (L_{1x}^2 + L_{1y}^2 + L_{1z}^2)\psi \\
&= -\frac{1}{\sin\theta_{12}}\frac{\partial}{\partial\theta_{12}}\left(\sin\theta_{12}\frac{\partial}{\partial\theta_{12}}\right)\psi - \frac{1}{\sin\theta_{13}}\frac{\partial}{\partial\theta_{13}}\left(\sin\theta_{13}\frac{\partial}{\partial\theta_{13}}\right)\psi \\
&\quad + \frac{2(\cos\theta_{12}\cos\theta_{13} - \cos\theta_{23})}{\sin\theta_{12}\sin\theta_{13}}\frac{\partial^2\psi}{\partial\theta_{12}\partial\theta_{13}}.
\end{aligned}
\tag{2.16}
$$

Similarly, we have

$$
\begin{aligned}
L_2^2\psi &= (L_{2x}^2 + L_{2y}^2 + L_{2z}^2)\psi \\
&= -\frac{1}{\sin\theta_{12}}\frac{\partial}{\partial\theta_{12}}\left(\sin\theta_{12}\frac{\partial}{\partial\theta_{12}}\right)\psi - \frac{1}{\sin\theta_{23}}\frac{\partial}{\partial\theta_{23}}\left(\sin\theta_{23}\frac{\partial}{\partial\theta_{23}}\right)\psi \\
&\quad + \frac{2(\cos\theta_{12}\cos\theta_{23} - \cos\theta_{13})}{\sin\theta_{12}\sin\theta_{13}}\frac{\partial^2\psi}{\partial\theta_{12}\partial\theta_{23}}.
\end{aligned}
\tag{2.17}
$$

$$
\begin{aligned}
L_3^2\psi &= (L_{3x}^2 + L_{3y}^2 + L_{3z}^2)\psi \\
&= -\frac{1}{\sin\theta_{13}}\frac{\partial}{\partial\theta_{13}}\left(\sin\theta_{13}\frac{\partial}{\partial\theta_{13}}\right)\psi - \frac{1}{\sin\theta_{23}}\frac{\partial}{\partial\theta_{23}}\left(\sin\theta_{23}\frac{\partial}{\partial\theta_{23}}\right)\psi \\
&\quad + \frac{2(\cos\theta_{13}\cos\theta_{23} - \cos\theta_{12})}{\sin\theta_{13}\sin\theta_{23}}\frac{\partial^2\psi}{\partial\theta_{13}\partial\theta_{23}}.
\end{aligned}
\tag{2.18}
$$

Combining (2.5) with (2.16)–(2.18), we can transfer the Hamiltonian into the following form:

$$
\begin{aligned}
H = &-\frac{1}{2}\left[\frac{1}{r_1^2}\frac{\partial}{\partial r_1}\left(r_1^2\frac{\partial}{\partial r_1}\right) + \frac{1}{r_2^2}\frac{\partial}{\partial r_2}\left(r_2^2\frac{\partial}{\partial r_2}\right) + \frac{1}{r_3^2}\frac{\partial}{\partial r_3}\left(r_3^2\frac{\partial}{\partial r_3}\right)\right. \\
&+ \left(\frac{1}{r_1^2}+\frac{1}{r_2^2}\right)\frac{1}{\sin\theta_{12}}\frac{\partial}{\partial\theta_{12}}\left(\sin\theta_{12}\frac{\partial}{\partial\theta_{12}}\right) + \left(\frac{1}{r_1^2}+\frac{1}{r_3^2}\right)\frac{1}{\sin\theta_{13}} \\
&\times\frac{\partial}{\partial\theta_{13}}\left(\sin\theta_{13}\frac{\partial}{\partial\theta_{13}}\right) + \left(\frac{1}{r_2^2}+\frac{1}{r_3^2}\right)\frac{1}{\sin\theta_{23}}\frac{\partial}{\partial\theta_{23}}\left(\sin\theta_{23}\frac{\partial}{\partial\theta_{23}}\right) \\
&- \frac{2(\cos\theta_{12}\cos\theta_{13}-\cos\theta_{23})}{r_1^2\sin\theta_{12}\sin\theta_{13}}\frac{\partial^2}{\partial\theta_{12}\partial\theta_{13}} - \frac{2(\cos\theta_{12}\cos\theta_{23}-\cos\theta_{13})}{r_2^2\sin\theta_{12}\sin\theta_{13}} \\
&\left.\times\frac{\partial^2}{\partial\theta_{12}\partial\theta_{23}} - \frac{2(\cos\theta_{13}\cos\theta_{23}-\cos\theta_{12})}{r_3^2\sin\theta_{13}\sin\theta_{23}}\frac{\partial^2}{\partial\theta_{13}\partial\theta_{23}}\right] \\
&- \frac{3}{r_1} - \frac{3}{r_2} - \frac{3}{r_3} + \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}}.
\end{aligned}
\tag{2.19}
$$

The partial differential equation (2.19) is six-dimensional and can be solved by finite difference methods, variational methods or finite element methods.

3. Six-dimensional variational equation

In order to obtain finite element approximations to the energy of the ground lithium, we look for the six-dimensional weak formula of the Schrödinger equation. The expected formula will be derived from the original equation (2.1) instead of (2.19).

Let $R > 0$ and define domains in R^6 and R^9 as follows:

$$\Omega = [0, R] \times [0, R] \times [0, R] \times [0, \pi] \times [0, \pi] \times [0, \pi], \tag{3.1}$$

$$\widehat{\Omega} = \left\{ (x_1, y_1, \ldots, z_3) \in R^9 \,\middle|\, \sqrt{x_i^2 + y_i^2 + z_i^2} \leqslant R, \quad i = 1, 2, 3 \right\}. \tag{3.2}$$

We consider the approximate problem of (2.1) in the bounded domain $\widehat{\Omega}$

$$\begin{cases} H\psi = E\psi, & \text{in } \widehat{\Omega}, \\ \psi = 0, & \text{on } \partial\widehat{\Omega}, \end{cases} \tag{3.3}$$

where $\partial\widehat{\Omega}$ is the boundary of $\widehat{\Omega}$. The equivalent variational formula of (3.3) is find $(E, \psi) \in R^1 \times H_0^1(\widehat{\Omega})$ and $\psi \neq 0$, such that

$$a(\psi, \varphi) = E(\psi, \varphi), \quad \forall \varphi \in H_0^1(\widehat{\Omega}), \tag{3.4}$$

where

$$
\begin{aligned}
a(\psi, \varphi) = {} & \frac{1}{2} \int_{\widehat{\Omega}} \sum_{i=1}^{3} \left(\frac{\partial \psi}{\partial x_i} \frac{\partial \varphi}{\partial x_i} + \frac{\partial \psi}{\partial y_i} \frac{\partial \varphi}{\partial y_i} + \frac{\partial \psi}{\partial z_i} \frac{\partial \varphi}{\partial z_i} \right) d\mathbf{x} \\
& + \int_{\widehat{\Omega}} \left(\frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}} - \frac{3}{r_1} - \frac{3}{r_2} - \frac{3}{r_3} \right) \psi \varphi \, d\mathbf{x},
\end{aligned}
\tag{3.5}
$$

$$(\psi, \varphi) = \int_{\widehat{\Omega}} \psi \varphi \, d\mathbf{x}, \tag{3.6}$$

where $d\mathbf{x} = dx_1 dy_1 \cdots dz_3$ is the volume element of $\widehat{\Omega}$. Thanks to [14], the spectrum of H in (3.3) is discrete and bounded below and approximates the discrete spectrum of H in (2.1) as $R \to \infty$. If ψ is an eigenfunction of (3.3) or (3.4), then $\psi \in H^2(\widehat{\Omega}) \bigcap H_0^1(\widehat{\Omega})$.

Denote $\Omega = [0, R] \times [0, R] \times [0, R] \times [-1, 1] \times [-1, 1] \times [-1, 1]$ without confusion. Let

$$\mu_{12} = \cos\theta_{12}, \quad \mu_{13} = \cos\theta_{13}, \quad \mu_{23} = \cos\theta_{23}. \tag{3.7}$$

Like in Section 2, we also suppose that the wave function of the ground lithium depending only on six variables,

$$\psi = \psi(r_1, r_2, r_3, \mu_{12}, \mu_{23}, \mu_{13}), \quad \varphi = \varphi(r_1, r_2, r_3, \mu_{12}, \mu_{23}, \mu_{13}) \tag{3.8}$$

Substituting ψ, φ into (3.5) and (3.6), in view of (2.3), (2.4) and (2.7), we can transfer (3.4) into the following form: Find $(E, \psi) \in R^1 \times V$ and $\psi \neq 0$, such that

$$a_r(\psi, \varphi) = E(\psi, \varphi)_r, \quad \forall \varphi \in V, \tag{3.9}$$

where

$$(\psi, \varphi)_r = \int_\Omega \psi\varphi r_1^2 r_2^2 r_3^2 \mathrm{d}r_1 \, \mathrm{d}r_2 \, \mathrm{d}r_3 \, \mathrm{d}\mu_{12} \, \mathrm{d}\mu_{23} \, \mathrm{d}\mu_{13}. \tag{3.10}$$

$$\begin{aligned}
a_r(\psi, \varphi) = \frac{1}{2} \int_\Omega \Bigg[&\left(\frac{\partial\psi}{\partial r_1}\frac{\partial\varphi}{\partial r_1} + \frac{\partial\psi}{\partial r_2}\frac{\partial\varphi}{\partial r_2} + \frac{\partial\psi}{\partial r_3}\frac{\partial\varphi}{\partial r_3} \right) r_1^2 r_2^2 r_3^2 \\
&+ \frac{\partial\psi}{\partial\mu_{12}}\frac{\partial\varphi}{\partial\mu_{12}}(r_1^2 + r_2^2)r_3^2(1 - \mu_{12}^2) + \frac{\partial\psi}{\partial\mu_{13}}\frac{\partial\varphi}{\partial\mu_{13}}(r_1^2 + r_3^2)r_2^2(1 - \mu_{13}^2) \\
&+ \frac{\partial\psi}{\partial\mu_{23}}\frac{\partial\varphi}{\partial\mu_{23}}(r_2^2 + r_3^2)r_1^2(1 - \mu_{23}^2) \\
&+ \left(\frac{\partial\psi}{\partial\mu_{12}}\frac{\partial\varphi}{\partial\mu_{13}} + \frac{\partial\psi}{\partial\mu_{13}}\frac{\partial\varphi}{\partial\mu_{12}} \right) r_2^2 r_3^2 (\mu_{23} - \mu_{12}\mu_{13}) \\
&+ \left(\frac{\partial\psi}{\partial\mu_{12}}\frac{\partial\varphi}{\partial\mu_{23}} + \frac{\partial\psi}{\partial\mu_{23}}\frac{\partial\varphi}{\partial\mu_{12}} \right) r_1^2 r_3^2 (\mu_{13} - \mu_{12}\mu_{23}) \\
&+ \left(\frac{\partial\psi}{\partial\mu_{13}}\frac{\partial\varphi}{\partial\mu_{23}} + \frac{\partial\psi}{\partial\mu_{23}}\frac{\partial\varphi}{\partial\mu_{13}} \right) r_1^2 r_2^2 (\mu_{12} - \mu_{13}\mu_{23}) \\
&+ \left(\frac{2r_1^2 r_2^2 r_3^2}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \mu_{12}}} + \frac{2r_1^2 r_2^2 r_3^2}{\sqrt{r_1^2 + r_3^2 - 2r_1 r_3 \mu_{13}}} \right. \\
&\left. + \frac{2r_1^2 r_2^2 r_3^2}{\sqrt{r_2^2 + r_3^2 - 2r_2 r_3 \mu_{23}}} - 6r_1^2 r_2^2 r_3 - 6r_1^2 r_2 r_3^2 - 6r_1 r_2^2 r_3^2 \right) \psi\varphi \Bigg] \\
&\times \mathrm{d}r_1 \, \mathrm{d}r_2 \, \mathrm{d}r_3 \, \mathrm{d}\mu_{12} \, \mathrm{d}\mu_{23} \, \mathrm{d}\mu_{13}. \tag{3.11}
\end{aligned}$$

We define the function space V as

$$V = \{\psi | \psi|_{\partial\Omega} = 0, \; \|\psi\|_V < \infty\}, \tag{3.12}$$

where $\partial\Omega$ is the boundary of Ω defined as

$$\partial\Omega := \{(r_1, r_2, r_3, \mu_{12}, \mu_{23}, \mu_{13}) \in \Omega | r_1 = R \text{ or } r_2 = R \text{ or } r_3 = R\},$$

$$\begin{aligned}
\|\psi\|_V^2 := \int_\Omega \Bigg[&\left(\frac{\partial\psi}{\partial r_1} \right)^2 + \left(\frac{\partial\psi}{\partial r_2} \right)^2 + \left(\frac{\partial\psi}{\partial r_3} \right)^2 + (1 - \mu_{12}^2)\left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right)\left(\frac{\partial\psi}{\partial\mu_{12}} \right)^2 \\
&+ (1 - \mu_{13}^2)\left(\frac{1}{r_1^2} + \frac{1}{r_3^2} \right)\left(\frac{\partial\psi}{\partial\mu_{13}} \right)^2 + (1 - \mu_{23}^2)\left(\frac{1}{r_2^2} + \frac{1}{r_3^2} \right)\left(\frac{\partial\psi}{\partial\mu_{23}} \right)^2 \\
&+ \frac{2(\mu_{23} - \mu_{12}\mu_{13})}{r_1^2}\frac{\partial\psi}{\partial\mu_{12}}\frac{\partial\psi}{\partial\mu_{13}} + \frac{2(\mu_{13} - \mu_{12}\mu_{23})}{r_2^2}\frac{\partial\psi}{\partial\mu_{12}}\frac{\partial\psi}{\partial\mu_{23}} \\
&+ \frac{2(\mu_{12} - \mu_{13}\mu_{23})}{r_3^2}\frac{\partial\psi}{\partial\mu_{13}}\frac{\partial\psi}{\partial\mu_{23}} \Bigg] \\
&\times r_1^2 r_2^2 r_3^2 \mathrm{d}r_1 \, \mathrm{d}r_2 \, \mathrm{d}r_3 \, \mathrm{d}\mu_{12} \, \mathrm{d}\mu_{13} \, \mathrm{d}\mu_{23} + (\psi, \psi)_r. \tag{3.13}
\end{aligned}$$

4. Finite element approximations

Let $\{\mathscr{T}_h\}$ be the family of subdivisions of the domain $\Omega \subset R^6$ (defined as in Section 3). Each K in $\mathscr{T}_h$ is a rectangle in R^6. Use notations similar to those in [15], the finite element triple is defined as:

$$K = [r_{1,0}, r_{1,0} + h_1] \times [r_{2,0}, r_{2,0} + h_2] \times [r_{3,0}, r_{3,0} + h_3] \times [\mu_{12,0}, \mu_{12,0} + h_4]$$
$$\times [\mu_{13,0}, \mu_{13,0} + h_5] \times [\mu_{23,0}, \mu_{23,0} + h_6] \text{—six-dimensional rectangle},$$

$$\Sigma_K = \{a_{ijklmn} = (r_{1,0} + ih_1/2, r_{2,0} + jh_2/2, r_{3,0} + kh_3/2, \quad \mu_{12,0} + lh_4/2,$$
$$\mu_{13,0} + mh_5/2, \mu_{23,0} + nh_6/2)|i,j,k,l,m,n = 0,1,2\},$$

$$P_K = \left\{ p = \sum_{i,j,k,l,m,n=0}^{2} \alpha_{ijklmn} r_1^i r_2^j r_3^k \mu_{12}^l \mu_{13}^m \mu_{23}^n \mid \alpha_{ijklmn} \in R^1 \right\}, \tag{4.1}$$

where $(r_{1,0}, r_{2,0}, r_{3,0}, \mu_{12,0}, \mu_{13,0}, \mu_{23,0})$ are coordinates of some vertex of K. Choose a basis of P_K as

$$p_{ijklmn} = \frac{(r_1 - r_{1,i+1})(r_1 - r_{1,i-1})(r_2 - r_{2,j+1})(r_2 - r_{2,j-1})(r_3 - r_{3,k+1})}{(r_{1,i} - r_{1,i+1})(r_{1,i} - r_{1,i-1})(r_{2,j} - r_{2,j+1})(r_{2,j} - r_{2,j-1})(r_{3,k} - r_{3,k+1})}$$

$$\times \frac{(r_3 - r_{3,k-1})(\mu_{12} - \mu_{12,l+1})(\mu_{12} - \mu_{12,l-1})(\mu_{13} - \mu_{13,m+1})}{(r_{3,k} - r_{3,k-1})(\mu_{12,l} - \mu_{12,l+1})(\mu_{12,l} - \mu_{12,l-1})(\mu_{13,m} - \mu_{13,m+1})}$$

$$\times \frac{(\mu_{13} - \mu_{13,m-1})(\mu_{23} - \mu_{23,n+1})(\mu_{23} - \mu_{23,n-1})}{(\mu_{13,m} - \mu_{13,m-1})(\mu_{23,n} - \mu_{23,n+1})(\mu_{23,n} - \mu_{23,n-1})}, \tag{4.2}$$

where all subscripts and superscripts recur in turn according to 0, 1, 2. Denote $r_{1,i} = r_{1,0} + ih_1/2$ and define other notations similarly. Obviously, the following relations are true:

$$p_{ijklmn}(a_{IJKLMN}) = \delta_{ijklmn,IJKLMN}$$
$$= \begin{cases} 1, & (i,j,k,l,m,n) = (I,J,K,L,M,N), \\ 0, & (i,j,k,l,m,n) \neq (I,J,K,L,M,N). \end{cases} \tag{4.3}$$

Define the finite element space as

$$V_h = \{\psi \in C^0(\Omega)|\psi|_{\partial\Omega} = 0, \ \psi|_K \in P_K, \quad \forall K \in \mathscr{T}_h\}, \tag{4.4}$$

where $\partial\Omega$ is the boundary of Ω. Clearly, $V_h \subset H^1(\Omega) \subset V$. So the conforming finite element approximation of (3.9) is: Find $(E_h, \psi_h) \in R^1 \times V_h$ and $\psi_h \neq 0$, such that

$$a_r(\psi_h, \varphi_h) = E_h(\psi_h, \varphi_h)_r, \quad \forall \varphi_h \in V_h. \tag{4.5}$$

Since the dimension of V_h is finite, (4.5) is equivalent to the following generalized algebraic eigenvalue problem:

$$AX = E_h MX, \tag{4.6}$$

where A is the global stiffness matrix and M is global mass matrix. Their orders are equal to the dimension of V_h. Furthermore, both of them are large and banded matrices. In real computations, we only need to calculate all element stiffness matrices A^K and element mass matrices M^K and assemble them to A and M [16]. The number of freedoms in each inner element equals to 729.

Remark. The convergence and error estimates of the finite element scheme will be our future work.

5. Numerical results

We use inverse iteration method [16] to solve the generalized eigenvalue problems (4.6), and use the standard Gaussian integral formula to obtain all matrix elements. We carry out our computation on PC: Intel PIII750 with 1G SDRAM. Since the dimension of the domain is six, the number of freedoms grows very quickly as the mesh is refined. We can not get very small meshes, nor can we choose very big R for the domain Ω because of the limit of our computer. Although the number of grid points for each variable is very small, the relative error of our result is order of 10^{-5}. So our result can be improved as capabilities of computers are improved.

We place same grid points along three radial directions and also along three angular directions. The subdivisions and computational results are listed in the Table 1 (NGPs means number of Gaussian points).

   Nonrelativistic limit value [11]: -7.47807 a.u.

Subdivisions (grid points):

1. Radial directions (unit a_0): 0.0, 1.0, 3.0,
  Angular directions: -1.0, 1.0.
2. Radial directions (unit a_0): 0.0, 0.8, 2.0, 4.0,
  Angular directions: -1.0, 1.0.
3. Radial directions (unit a_0): 0.0, 0.4, 1.0, 2.5, 5.0,
  Angular directions: -1.0, 1.0.

Table 1
Approximate energies of the ground lithium by FEM (*a.u.*)

Subdivisions of the domain	Approximate energies	Cutoff radiuses $R(a_0)$	Numbers of freedoms	NGPs in each direction
1	−7.450617	3	1620	3
2	−7.47699138	4	5319	5
3	−7.47794341	5	13 149	6

Acknowledgements

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