Solutions of the Schrödinger equation for the ground helium by finite element method

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1. Introduction

Multi-body Coulomb problems are traditional challenging problems [1]. The failure of theory to describe precisely the system stimulated many mathematicians and physicists to devote themselves in using various methods to obtain the energies and other expectation values. Few-electron systems like helium are typical models.

There are two electrons out of the nucleus of the helium atom; and each of them has three freedoms (without considering its spin). So the system is described by a six-dimensional Schrödinger equation (for fixed-nucleus problem). One usual approach in quantum mechanics is mean-field method [2]. Each 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. The other usual approach, named variational method [3-4], searches the status function to find the minimum energy value, which has been proved to be close to the precise value.

A common feature of these calculations is a higher error in the non-Hamiltonian expectation values than in the energy, an indication that the approximate wave functions are less accurate than one might originally assume from the well-converged energies [5]. This behavior provides the motivation for applying a new method to the problem.

The finite element method (FEM) is a numerical algorithm that uses local interpolation methods to solve second-order differential equations describing boundary-value problems. A local interpolation scheme should be superior to global variational approaches in yielding an accurate wave function because of the ease by which local improvements to the approximate wave function can be introduced in the FEM. In principle, therefore, it is expected that this algorithm may provide new insights into the structure of molecules and atoms [5].

The main works of the finite element method applied to atomic and molecular problems appeared in 1970's, in one- and two-dimensional cases [6-7], where simplicity and efficiency of FEM was shown. The first work of FEM applied to

three-dimensional case was done by Levin and Shertzer [5]. They calculated the helium in the ground state and the six-dimensional Schrödinger equation was transferred into three-dimensional systems of equations rigorously [8]. Works about three-dimensional FEM applied to three-body problems appeared hereafter [9-11]. They all obtained very precise results.

2. Governing Equations

In Cartesian coordinates, the spin-independent, nonrelativistic Schrödinger equation for the two electrons in the helium atom is [5]:

$$\left[-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} \right]\psi = E\psi$$

$$H = \left[-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} \right],$$

where H is called Hamiltonian operator, ψ stands for the wave function and operator ∇^2 calculates the kinetic energy of electron 1 and electron 2 (all the expressions are in the atomic units). Also we have:

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

$$r_{12} = (r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_{12})^{1/2}$$

In spherical coordinates, the Hamiltonian of the system can be written as [1]:

$$H = -\frac{1}{2}\left[\frac{1}{r_1^2}\frac{\partial}{\partial r_1}\left(r_1^2 \frac{\partial}{\partial r_1} \right) + \frac{1}{r_2^2}\frac{\partial}{\partial r_2}\left(r_2^2 \frac{\partial}{\partial r_2} \right) - \frac{L_1^2}{r_1^2} - \frac{L_2^2}{r_2^2} \right] - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}},$$

Where L_i^2 is the square of the angular momentum operator of the i th electron:

$$L_i^2 = L_{ix}^2 + L_{iy}^2 + L_{iz}^2 = -\left(y_i \frac{\partial}{\partial z_i} - z_i \frac{\partial}{\partial y_i} \right)^2 - \left(z_i \frac{\partial}{\partial x_i} - x_i \frac{\partial}{\partial z_i} \right)^2 - \left(x_i \frac{\partial}{\partial y_i} - y_i \frac{\partial}{\partial x_i} \right)^2$$

By the law of chain for the differential calculations:

$$L_{1z}\psi = i\left(x_1 \frac{\partial}{\partial y_1} - y_1 \frac{\partial}{\partial x_1} \right)\psi = \frac{i(x_2 y_1 - x_1 y_2)}{r_1 r_2 \sin\theta_{12}}\frac{\partial\psi}{\partial\theta_{12}}$$

$$L_{1z}^2\psi = -\frac{1}{r_1 r_2 \sin\theta_{12}}\left\{ \left(x_1 x_2 + y_1 y_2 - \frac{(x_1 y_2 - x_2 y_1)^2 \cos\theta_{12}}{r_1 r_2 \sin^2\theta_{12}} \right)\frac{\partial\psi}{\partial\theta_{12}} + \frac{(x_1 y_2 - x_2 y_1)^2}{r_1 r_2 \sin\theta_{12}}\frac{\partial^2\psi}{\partial\theta_{12}^2} \right\}$$

Similarly, we have L_{1x}^2 and L_{1y}^2:

$$L_{1x}^2 \psi = -\frac{1}{r_1 r_2 \sin \theta_{12}} \left\{ \left(y_1 y_2 + z_1 z_2 - \frac{(y_1 z_2 - y_2 z_1)^2 \cos \theta_{12}}{r_1 r_2 \sin^2 \theta_{12}} \right) \frac{\partial \psi}{\partial \theta_{12}} + \frac{(y_1 z_2 - y_2 z_1)^2}{r_1 r_2 \sin \theta_{12}} \frac{\partial^2 \psi}{\partial \theta_{12}^2} \right\}$$

$$L_{1y}^2 \psi = -\frac{1}{r_1 r_2 \sin \theta_{12}} \left\{ \left(z_1 z_2 + x_1 x_2 - \frac{(z_1 x_2 - z_2 x_1)^2 \cos \theta_{12}}{r_1 r_2 \sin^2 \theta_{12}} \right) \frac{\partial \psi}{\partial \theta_{12}} + \frac{(z_1 x_2 - z_2 x_1)^2}{r_1 r_2 \sin \theta_{12}} \frac{\partial^2 \psi}{\partial \theta_{12}^2} \right\}$$

Since:

$$\vec{r}_1 \cdot \vec{r}_2 = r_1 r_2 \cos \theta_{12} = x_1 x_2 + y_1 y_2 + z_1 z_2$$

$$\vec{r}_1 \times \vec{r}_2 = (y_1 z_2 - y_2 z_1, z_1 x_2 - z_2 x_1, x_1 y_2 - x_2 y_1), \quad \left| \vec{r}_1 \times \vec{r}_2 \right| = r_1 r_2 \sin \theta_{12}$$

Thus:

$$L_1^2 \psi = (L_{ix}^2 + L_{iy}^2 + L_{iz}^2) \psi = -\frac{1}{\sin \theta_{12}} \frac{\partial}{\partial \theta_{12}} \left(\sin \theta_{12} \frac{\partial}{\partial \theta_{12}} \right) \psi$$

Therefore, the Hamiltonian can be transferred to an operator with three variables:

$$H = -\frac{1}{2} \left[\frac{1}{r_1^2} \frac{\partial}{\partial r_1} \left(r_1^2 \frac{\partial}{\partial r_1} \right) + \frac{1}{r_2^2} \frac{\partial}{\partial r_2} \left(r_2^2 \frac{\partial}{\partial r_2} \right) + \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \frac{1}{\sin \theta_{12}} \frac{\partial}{\partial \theta_{12}} \left(\sin \theta_{12} \frac{\partial}{\partial \theta_{12}} \right) \right] - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$

where r_{12} can be expressed by r_1, r_2, and θ_{12}.

2.1. Boundary conditions

In order to perform FEM, the infinite volume of coordinate space spanned by r_1, r_2, and θ_{12} was made finite by truncation, i.e., r_1 and r_2 were each limited to the domain $[0, r_c]$. The wave function ψ was set equal to zero for $r < 0$ and $r > r_c$. Similarly, $\theta_{12} \in [0, \pi]$, and $\psi = 0$ when $\theta_{12} < 0$ and $\theta_{12} > \pi$

2.2. Formulation

COMSOL Multiphysics describes the coefficient form of eigenvalue PDE as:

$$-\nabla \cdot (c \nabla u + \alpha u) + \beta \nabla u + au = d_a \lambda u$$

In order to match the equation form, the Hamiltonian should be formulated as:

$$H = -\frac{1}{r_1} \frac{\partial}{\partial r_1} - \frac{\partial^2}{2 \partial r_1^2} - \frac{1}{r_2} \frac{\partial}{\partial r_2} - \frac{\partial^2}{2 \partial r_2^2} - \frac{ctg \theta_{12}}{2} \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \frac{\partial}{\partial \theta_{12}} - \frac{1}{2} \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \frac{\partial^2}{\partial \theta_{12}^2} - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$

Then the following coefficient values are used:

$$c = \begin{pmatrix} 0.5 & - & - \\ - & 0.5 & - \\ - & - & \dfrac{1}{2}\left(\dfrac{1}{r_1^2} + \dfrac{1}{r_2^2}\right) \end{pmatrix}$$

$$\beta = \left(-\dfrac{1}{r_1} \quad -\dfrac{1}{r_2} \quad -\dfrac{ctg\,\theta_{12}}{2}\left(\dfrac{1}{r_1^2} + \dfrac{1}{r_2^2}\right) \right)$$

$$a = -\dfrac{2}{r_1} - \dfrac{2}{r_2} + \dfrac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_{12}}}$$

3. Solution

The solution provides a number of the lowest eigenvalues. The ground state energy is solved as: E = -2.7285 hartree = -74.22 eV, close to the experimental value -78.98eV. Fig. 1 shows the calculation results, plotting with the value of the wave function u, which is interpreted as the probability density. Therefore, the red area should stand for the most possible distribution of electrons when at the ground state energy. According to Fig. 1, when E = -2.7285 hartree, one electron should be very close to the helium nuclei, with another electron far from it.

One thing is left to be puzzled that since exchanging the positions of the two electrons should not change the system, the figure should have been symmetric. (Actually I am not able to well understand this figure, but the eigenvalue is close to the experimental result.)
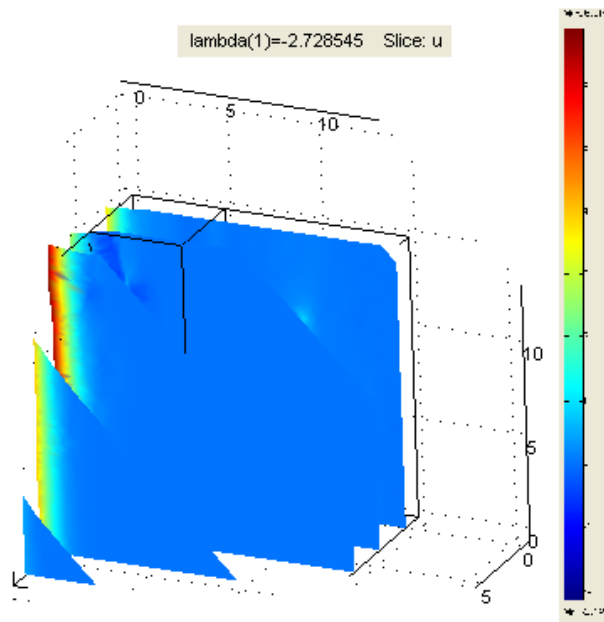

Fig. 1 The slice scheme of the wave function with the lowest eigenvalue.

4. Validation

In chemistry, an atomic orbit is a region in which an electron may be found. One specific region corresponds to one eigenvalue, which is the value of one energy level. Since the atomic orbits and energy levels of hydrogen atom have been well documented than any other atoms, the same model and solution process will be applied to hydrogen atom to validate the correction of our results for helium.

4.1. Energy levels

According to Bohr model, the energy levels of hydrogen atom can be solve as:

$$E_n = -\frac{1}{n^2} E_0, n = 1,2,3...., $$

where E_0 is the lowest energy level, about -0.5 hartree, viz. -13.6eV. The following

table compares the energy values got from FemLab and the values calculated from Bohr model.

Energy level	Energy value based on Bohr model (hartree)	Energy value calculated by FemLab (hartree)	Error
n=1	-0.5000	-0.5014	0.28%
n=2	-0.1250	-0.1247	0.24%

Moreover, as mentioned above, the energy eigenvalue of helium atom is calculated as -2.7285 hartree, close to the experimental result -2.9037 hartree.

4.2. Atomic orbits

Similar to the energy levels, the atomic orbits of hydrogen atom are also well known. The following figures validate our calculations by comparing the isosurfaces of wave functions plotted by FemLab and the known atomic orbits of hydrogen.

$2p_z$
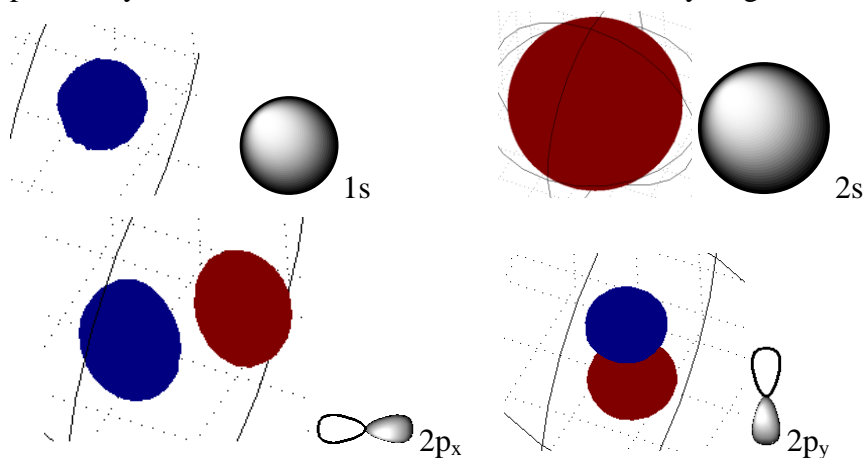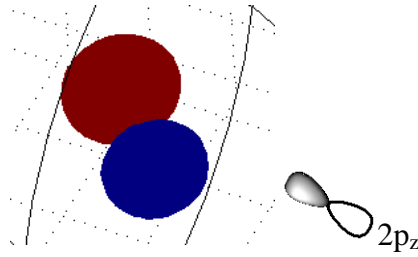
5. Conclusion

Based on the discussions above, it can be concluded that:

1. Schrödinger equation can be simplified by decreasing some variables, making it an equation with fewer dimensions.
2. FEMlab is a good tool when trying to find out the eigenvalues of energy of some three-dimensional systems (e.g. hydrogen and helium atoms). However, it can't deal with a complicated many-body Schrödinger equation.

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