Approximate Methods for Calculating Ground-State Energy in Helium Atom

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Abstract. In this paper, several main approximate methods are discussed, including variational principle, Hartree-Fock method, configuration interaction method, quantum Monte Carlo method and parametric perturbation method. These methods solve the complexity of electron-electron correlation and interaction from different angles, and each has its advantages and disadvantages. The variational principle estimates the upper limit of ground state energy by testing the wave function, which effectively captures the electron correlation. Hartree-Fock method uses the mean field approximation to simplify the calculation but ignores the dynamic correlation. The quantum Monte Carlo method provides high-precision results through random sampling where other methods do not perform well, while the configuration interaction method further improves the Hartree-Fock results by considering multiple electron configurations. The parametric perturbation method performs well in iterative approximation, and its calculated results are close to the experimental values. At the end of this paper, the advantages of variational method are analyzed, and how to solve the ground state of helium atom by optimizing the wavefunction and minimizing the energy is shown, which provides theoretical and practical support for the development of materials science and quantum mechanics.

Keywords: Quantum Mechanics, Helium atom, Ground state energy; approximate methods.

1. Introduction

Erwin Schrödinger introduced the concept of the wavefunction in 1926 through his famous Schrödinger equation, which provides a framework for describing quantum systems. Since then, the study of real materials required solving the multi-atom problem. It consists of many interacting particles, such as the massive electrons. Helium atom is an example of interacting particles problem, and it is unsolvable problem till nowadays even there are only two electrons in the atom.

The ground state problem of the helium atom is one of the classical many-body problems in quantum mechanics [1]. Its complexity stems from the fact that there are two electrons and the nucleus in the system, as well as the interaction between electrons, rather than the interaction between a single electron and the nucleus like the hydrogen atom. The motion of two electrons is closely related and cannot be simply regarded as the motion of independent single electrons. By studying these interactions, scientists can predict phenomena such as chemical bonding, electronic structure, and energy levels, which are essential for developing new technologies, materials, and understanding natural processes [2].

At present, the mainstream methods for solving helium atoms are roughly the following: variational principle, independent electron approximation, perturbation method, Hartree-Fock (HF) method, configuration interaction (CI), quantum Monte Carlo (QMC), and parameterized perturbation method. They have their own application scenarios and advantages and disadvantages. For such methods, the parameterized perturbation is used by an article which calculated fourth order approximate energy of the ground state and improves the accuracy of calculation result [3]. Compared with the previous studies of using only zero-order or first-order approximation, the fourth-order approximation can more accurately describe wavefunction and energy of the ground state of helium atoms [4, 5] Another powerful method is variation principle that uses a test function consisting of two ground state wavefunctions of hydrogen atoms and it is used to estimate the ground state energy of helium atoms by the variational principle. The value obtained by the variational principle is closer to the experimental value than the initial estimate.

In this article, the author will introduce the mainstream methods of the solution to the ground state of helium atom and give their respective applicable scenarios. After that, it will talk about each solution method for solving the ground state of helium atom in section 2, then it will give the results of computation in section 3. Furthermore, the author is going to focus on the variational method, introduce the trial wavefunction solution, and apply it to the helium atom. In this sense, the author will explain where it is improved compared with other methods and explain why the variational principal method is chosen. Finally, there is a summary in the last section.

2. Solving Methods

It is very challenging of solving the ground state of helium atom, rather than the hydrogen atom, as it involves a three-body problem. Two electrons interacting with the nucleus and with each other via the Coulomb force. The approximation is the core step for solving the three-body problem, because the Schrödinger equation for helium cannot be solved exactly [6]. Below are the common methods of getting the approximation value.

For the approximation, one needs to guess a function which is called trial wavefunction, and it is used to estimate the properties of a quantum system, particularly the ground state energy. It serves as a starting point for calculations when the exact wavefunction of the system is unknown.

2.1. Variational Principle

In quantum mechanics, this principle offers an approximate method for determining the ground state energy of a quantum system. It relies on the concept that any chosen trial wavefunction will yield an energy value that serves as an upper limit for the actual ground state energy [7]

$$\mathrm{E}[\psi_{\mathrm{trial}}] = \langle \psi_{trial} | H | \psi_{trial} \rangle \geq E_0 \tag{1}$$

If H is the Hamiltonian of the quantum system, ψ_{trial} is a normalized trial wavefunction and it is not necessarily the true wavefunction. The equality holds only if ψ_{trial} is true ground state where E_0 is the exact ground state energy. To guess a reasonable ground state wavefunction, the way is often incorporating parameters to account for electron-electron correlation, for example $\psi(r_1, r_2) = e^{-\alpha(r_1+r_2)}$.

2.2. Hartree-Fock Method

Solving the Schrödinger equation for many-electron systems, the HF method is another tool that gives a more accurate value. It simplifies the problem by approximating the wavefunction as a single Slater determinant, capturing the antisymmetry of the wavefunction while neglecting explicit electron-electron correlation.

The total wavefunction of a system N interacting electrons is approximated as a single determinant of one-electron orbitals (spin-orbitals). Each electron interacts with the average field created by the others. The goal is to find the best set of one-electron orbitals that minimize the total energy of the system.

2.3. Quantum Monte Carlo method

The QMC methods use stochastic sampling to approximate the ground state energy. It mainly has two techniques for the approximation such as variational Monte Carlo (VMC). It combines the variational principle with Monte Carlo integration to compute the energy for a trial wavefunction. And diffusion Monte Carlo (DMC) which Improves upon VMC by using imaginary-time propagation to project out the ground state of the system. These techniques of QMC are computationally intensive but highly accurate when other methods fail to capture strong electron correlations.

2.4. Configuration Interaction

The CI method is a method by the quantum chemistry. It improves upon Hartree-Fock by including electron correlation explicitly to solve the Schrödinger equation also for many-electron systems. This method achieves this by expanding the wavefunction as a linear combination of multiple Slater determinants, representing different electronic configurations.

The exact wavefunction Ψ of a many-electron system is expressed as a linear combination of determinants $\Psi = \sum_I c_I \Phi_I$, where Φ_I are Slater determinants formed by distributing electrons among molecular orbitals, c_I are coefficients to be determined by solving the Schrödinger equation [8].

2.5. Parametric Perturbation Method

This method involves treating the electron-electron interaction as a small perturbation to the unperturbed Hamiltonian. The Hamiltonian for the helium atom includes $\mathrm{H} = H_0 + H_{int}$ where the unperturbed Hamiltonian $H_0 = \frac{\hbar}{2m} - \left(\nabla_1{}^2 + \nabla_2{}^2\right) - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2}$ and describes two electrons independently moving in the Coulomb field of the nucleus (ignoring electron-electron interaction). The perturbation Hamiltonian $H_{\text{int}} = \frac{e^2}{4\pi\varepsilon_0}\frac{1}{|r_1 - r_2|}$ and represents the Coulomb repulsion between the two electrons [9].

3. Computation and Comparison

3.1. Result of Parametric Perturbation Method

Lu presented a method of calculating the ground state energy of helium atom and considers the radial repulsion of two electrons in a helium atom is considered [1]. Here, the wave functions of two hydrogen-like atoms with an effective nuclear charge Z^* = 2-σ are chosen as zeroth and first to fourth order approximations of the ground state wave functions of helium atoms. By applying the parametric perturbation method, they calculated the fourth approximation of the ground state energy of helium atoms and found that the error between the calculated and experimental values is $\Delta E = 0.004922028\frac{e^2}{a_0}$.

The total Hamiltonian is expressed as $\hat{H} = \hat{\hat{H}}^{(0)}(r_1, r_2, \sigma) + \hat{H}'(r_1, r_2, \sigma)$, where $\hat{\hat{H}}^{(0)}$ represents the unperturbed Hamiltonian of two hydrogen-like atoms with effective nuclear charge Z^*, and $\hat{H}'$ includes the Coulomb repulsion and corrections due to electron interactions. The unperturbed Hamiltonian is given by

$$\hat{\hat{H}}^{(0)}(r_1, r_2, \sigma) = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{(2-\sigma)e^2}{r_1} - \frac{(2-\sigma)e^2}{r_2} \tag{2}$$

The perturbation term $\hat{H}'(r_1, r_2, \sigma)$ accounts for the Coulomb repulsion between the two electrons and the corrections to their potential energy due to the screening effect. Using the effective nuclear charge Z^* = 2-σ, the wave function approximations for the helium atom's ground state were constructed. The zeroth-order approximation $\psi^{(0)}(r_1, r_2, \sigma)$ represents both electrons in the 1s state of a hydrogen-like atom, while higher-order approximations incorporate excited states (e.g., 2s, 3s).

The ground-state energy is calculated iteratively as the sum of the zeroth-order energy $E^{(0)}$ and corrections from higher-order terms ($E^{(1)}$,$E^{(2)}$, etc.). The total energy expression is optimized with respect to the screening parameterσ, resulting in the value σ=0.618422517, corresponding to an effective nuclear charge of Z^* = 1.381577483. The calculated ground-state energy using this method is

$$E = -2.89846445\,\frac{e^2}{a_0} \tag{3}$$

This method demonstrates the effectiveness of introducing a physically meaningful screening parameter, achieving high accuracy without requiring extensive computational resources. As the approximation order increases, the results approach the experimental value more closely, validating the parameter perturbation approach for multi-electron systems.

3.2. Use of Approximate Method

It is reported in Ref. [2] that the author discusses the helium atom and the challenge of solving its Schrodinger equation due to the 3-body problem. It outlines the independent electron approximation, where the electron-electron repulsion force is ignored, and compares the predicted ionization potential and ground state energy with the experimental values, showing significant errors. The paper then introduces perturbation theory to go beyond the independent electron model and consider electron-electron repulsion. It provides details to the first-order perturbation theory and with how it can be used to obtain improved energy levels and wave functions for helium atoms.

Firstly, the independent electron approximation is adopted, ignoring the electron-electron interaction, and the helium atom is reduced to two independent hydrogen atoms. In this approximation method, the total wavefunction of a helium atom can be written as the product of the wave functions of two single electrons, and the total energy can also be expressed as the sum of the energies of two single electrons. However, the independent electron approximation cannot accurately describe the ionization potential and ground state energy of helium atoms, and there are large deviations from the experimental values. This is because the effects of electron-electron interactions are ignored.

To improve the independent electron model, the method of perturbation theory can be used to treat the electron-electron interaction be the perturbation term of the one-electron Hamiltonian. First-order perturbation theory can be used to calculate improved energy levels and wave functions of helium atoms to better describe the effects of electron-electron interactions. For more general multi-electron atoms, orbital approximation can be used to express the total wavefunction to be product of the single-electron orbital wavefunction. In this way, the n-body problem will be simplified into N numbers of one-body problems and solved by self-consistent computation. In this method, it is still necessary to ignore the electron correlation effect, which is an approximation. More accurate electronic correlation methods have also been widely developed and applied.

3.3. Result in Hatree-Fock Method

The main challenge in the helium atom lies in the electron-electron interaction term, which complicates the exact result of the Schrödinger equation. The HF method addresses this by treating each electron in the system as moving independently in an effective potential created by the nucleus and the averaged influence of the other electrons.

The Hamiltonian for the helium atom in atomic units is given by

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{|r_1 - r_2|} \tag{4}$$

The terms correspond to the kinetic energy of the two electrons, the potential energy from the Coulomb attraction between the electrons and the nucleus, and the repulsion between the two electrons. The last term$\frac{1}{|r_1-r_2|}$, which accounts for the interaction between the two electrons, makes the Schrödinger equation unsolvable analytically.

To simplify the problem, the HF method approximates the total wavefunction of the helium atom as a product of two single-electron wave functions $\Psi(r_1, r_2) = \phi_{HF}(r_1)\phi_{HF}(r_2)$. Each single-electron wavefunction, $\phi_{HF}(r)$, satisfies a single-electron Schrödinger equation with an effective Hamiltonian. The effective Hamiltonian for one electron, say electron 1, is given by

$$\hat{H}\mathrm{eff}, 1 = -\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} + U_{\mathrm{eff}}(r_1) \tag{5}$$

Where $U\mathrm{eff}(r_1)$ is the effective potential that represents the averaged interaction of electron 1 with electron 2. This effective potential is calculated as

$$\mathrm{U_{eff}(r_1)} = \int |\phi_{\mathrm{HF}}(\mathrm{r}_2)|^2 \frac{1}{|\mathrm{r}_1 - \mathrm{r}_2|} \ \mathrm{d}^3\mathrm{r}_2 \tag{6}$$

The HF method proceeds iteratively. An initial guess for the wavefunction $\phi_{HF}(r_2)$ is used to calculate $U_{\mathrm{eff}}(\mathrm{r}_1)$, which is then substituted into the Schrödinger equation to solve for an updated$\phi_{HF}(r_1)$. This updated wavefunction is used to recompute $U_{\mathrm{eff}}(\mathrm{r}_1)$, and the process is repeated until convergence is achieved, meaning the wavefunctions no longer change significantly between iterations.

Once the self-consistent wavefunctions are obtained, the total energy of the system in the HF approximation is computed as

$$E_{\mathrm{HF}} = \int \phi_{HF}(r_2)\,\phi_{HF}(r_1)\left(-\frac{1}{2}(\nabla_1^2+\nabla_2^2)-\frac{2}{r_1}-\frac{2}{r_2}+\frac{1}{|r_1-r_2|}\right)\phi_{\mathrm{HF}}(r_1)\phi_{\mathrm{HF}}(r_2)\,d^3r_1d^3r_2 \quad (7)$$

This can be expressed in terms of individual contributions $E_{\mathrm{HF}} = I_1 + I_2 + J_{12}$, where$I_1$ and I_2 are the one-electron integrals accounting for the kinetic energy and the electron-nucleus attraction, while J_{12} is the Coulomb integral representing the averaged electron-electron repulsion. These terms are defined as

$$I_1 = \int \phi_{\mathrm{HF}}^*(r_1)\left(-\frac{1}{2}\nabla_1^2-\frac{2}{r_1}\right)\phi_{\mathrm{HF}}(r_1)\ d^3r_1 \quad (8)$$

And

$$J_{12} = \int |\phi_{H\mathrm{F}}(r_1)|^2|\phi_{H\mathrm{F}}(r_2)|^2\frac{1}{|r_1-r_2|}\ d^3r_1d^3r_2 \quad (9)$$

For the helium atom, the HF ground-state energy is calculated as approximately -77.87 eV, which is very close to the experimental value of $-79.0\ eV$. This demonstrates that the HF method effectively captures the essential physics of the system, even though it neglects electron correlation.

Despite its accuracy, the HF method has limitations. It does not account for the instantaneous correlation between the motions of electrons, which can further lower the total energy. This correlation can be addressed by more advanced methods, such as Configuration Interaction or Coupled-Cluster Theory, which build on the HF wavefunctions as a starting point. Nevertheless, the HF method remains a cornerstone of quantum chemistry and is foundational for understanding the electronic structure of multi-electron atoms.

3.4. Comprehensive Optimization Process

Based on the results of each references summarized above, by constructing a trial wavefunction, one can more intuitively and easily understand the solution of the internal ground state energy of helium atom from the methods that the author has mentioned in section 2.

When applying the variational method to calculate the ground state energy of helium, the critical step is selecting an appropriate trial wavefunction. This function should closely approximate the true ground-state wavefunction, incorporating electron correlation effects and respecting physical symmetry. Electron correlation describes how interactions between electrons influence their motion and distribution in multi-electron systems. By carefully designing trial wavefunctions, more detailed electron correlation information can be captured in the ground state solution for helium.

In the helium atom, two electrons have inseparable relations to each other, which means there are correlations cause the motion such as radial correlation, angular correlation, electron shielding effect, higher order association, exchange correlation etc. At this optimization process, this paper will choose the radial correlation, angular correlation and the electron shielding effect as the elementaries.

Without considering the electron interaction, the wavefunction can be expressed in terms of two independent $1s$ wavefunctions

$$\phi_{1s}(r) = \frac{Z^3}{\pi a_0^3}e^{-Zr/a_0} \quad (10)$$

Where $Z$the number of the charges in the nucleus is, r is the distance from the electron to nucleus, and a_0 is the Bohr radius. The initial wavefunction is

$$\psi_0(r_1,r_2) = \phi_{1s}(r_1)\phi_{1s}(r_2) \quad (11)$$

When two electrons are too close together, the coulomb repulsion makes them tend to move apart, the radial correlation describes the effect of the distance distribution between electrons on each other's motion. This effect is captured by introducing an explicit $r_{12} = |r_1 - r_2|$ dependency, so the trial wavefunction with this correlation is

$$\psi(r_1, r_2) = \phi_{1s}(r_1)\phi_{1s}(r_2)f(r_{12}) \tag{12}$$

Where the form of $f(r_{12})$ is equal to $e^{-\lambda r_{12}}$, and $\lambda > 0$ is a variational parameter used to optimize the effect of electron spacing on the wavefunction. Then one can get the wavefunction of including the radial correlation

$$\psi_1(r_1, r_2) = \phi_{1s}(r_1)\phi_{1s}(r_2)e^{-\lambda|r_1 - r_2|} \tag{13}$$

In order to reduce the repulsion between the electrons, the two electrons tend to be distributed in symmetrical positions in the nucleus. This effect can be captured by the distribution of relative angles θ_{12} which is $\cos\theta_{12} = \frac{r_1 \cdot r_2}{r_1 r_2}$. When adding an Angle association, this paper selects an item of the following form

$$g(\cos\theta_{12}) = 1 + \gamma\cos\theta_{12} \tag{14}$$

Where γ is a variational parameter that controls the degree to which electrons tend to be distributed in the opposite direction (when $\gamma < 0$, electrons tend to be distributed in the opposite position). Combining the radial and angular correlation, so the wavefunction is going to be

$$\psi_2(r_1, r_2) = \phi_{1s}(r_1)\phi_{1s}(r_2)e^{-\lambda r_{12}}(1 + \gamma\cos\theta_{12}) \tag{15}$$

In the helium atom, there is also an interaction between electron-electron, due to the interaction between electrons, one electron partially blocks the nucleus's attraction to the other electron. This makes the perceived effective nuclear charge of the electron smaller than the true nuclear charge. Modify the radial distribution of the wave function by adjusting the nuclear charge Z to the effective nuclear charge Z_{eff} will get

$$\phi'_{1s}(\boldsymbol{r}) = \frac{Z_{\text{eff}}^3}{\pi a_0^3} e^{-Z_{\text{eff}} r/a_0} \tag{16}$$

Effective nuclear charge Z_{eff} as a variational parameter which can be obtained by optimization. Make $\phi_{1s}(r)$ replaced by$\phi'_{1s}(r)$, then the wavefunction after adding the shielding effect is

$$\psi_3(r_1, r_2) = \phi'_{1s}(r_1)\phi'_{1s}(r_2)e^{-\lambda r_{12}(1 + \gamma\cos\theta_{12})} \tag{17}$$

Combining the above three correlations, the final trial wave function is

$$\psi(r1, r2) = \frac{Z\text{eff}^3}{\pi a_0^3} e^{-Z\text{eff} r_1/a_0} \cdot \frac{Z_{\text{eff}}^3}{\pi a_0^3} e^{-Z_{\text{eff}} r_2/a_0} \cdot e^{-\lambda r_{12}}(1 + \gamma\cos\theta_{12}) \tag{18}$$

Z_{eff} Captures the masking effect; λ captures radial correlation; γ captures angular correlations. Optimizing the process by define a Hamiltonian of

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}, \tag{19}$$

And the expectation value $E = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}$. In the end, this paper optimizes Z_{eff}, λ γ to minimize the total energy E to get the ground state energy of helium atom.

4. Conclusion

The ground state of the helium atom poses a significant challenge in quantum mechanics due to the complexities of the three-body problem involving two electrons and a nucleus. Unlike the hydrogen atom, where a single electron interacts with the nucleus, the helium atom requires a detailed account of electron-electron interactions, making its Schrödinger equation unsolvable exactly. To address this, approximation methods such as the variational principle, Hartree-Fock, quantum Monte Carlo, configuration interaction, and parametric perturbation methods have been developed. Each method has its unique strengths and limitations. The variational principle uses trial wavefunctions to provide the upper bounds for ground state energy, incorporating electron correlation to improve accuracy. The Hartree-Fock method simplifies the problem by averaging electron interactions but neglects instantaneous correlations. Quantum Monte Carlo methods rely on stochastic sampling for high accuracy, particularly where other approaches fail. The configuration interaction explicitly includes electron correlations by combining multiple electronic configurations, refining results beyond Hartree-Fock approximation. Lastly, parametric perturbation methods treat electron-electron interactions as perturbations, achieving high accuracy through iterative approximations. These methods collectively enhance people’s understanding of helium’s energy levels and wavefunctions, with approaches like the variational principle and parametric perturbation standing out for their ability to describe electron correlations more precisely. Their applications advance not only quantum mechanics but also material science and technological innovation.

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