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CALCULATING GROUND STATE ENERGY OF HELIUM BY USING VARIATIONAL MONTE CARLO METHODS

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ABSTRACT

Variational Quantum Monte Carlo (VQMC) is a computational approach that combines the variational principle of quantum mechanics with stochastic Monte Carlo integration to estimate ground-state properties of many-body systems. In this study, the VQMC method is employed to calculate the ground-state energy of the helium atom, a fundamental two-electron system that serves as a benchmark for testing quantum methods. The evaluation of multidimensional integrals arising in the expectation value of the Hamiltonian is performed using importance sampling based on the Metropolis algorithm, which enhances computational efficiency and accuracy. A key advantage of the VQMC approach lies in its flexibility in selecting analytically tractable trial wave functions, enabling systematic improvement of results through parameter optimization. Using an appropriately constructed trial wave function that incorporates electron–electron correlation effects, the calculated ground-state energy of helium is found to be −77.645 eV. This result shows good agreement with the exact reference value, demonstrating that the VQMC method provides reliable and accurate estimations for atomic systems. The findings confirm the effectiveness of VQMC as a powerful tool for solving quantum many-body problems.

Keywords: Monte Carlo; Ground State energy; Helium; Monte Carlo

INTRODUCTION

The accurate determination of ground-state energies in quantum systems remains a fundamental challenge in theoretical physics and quantum chemistry. This problem becomes particularly significant in many-electron systems, where electron–electron interactions introduce correlation effects that cannot be treated exactly using analytical methods. The helium atom, as the simplest two-electron system, serves as a prototypical model for investigating these correlation effects and testing the performance of various computational approaches [1]. Despite its apparent simplicity, the helium atom cannot be solved exactly within the framework of the Schrödinger equation due to the non-separability of the electron–electron interaction term, making it an essential benchmark in computational quantum studies.

Traditional quantum chemistry methods, such as the Hartree–Fock approximation, often fail to accurately capture electron correlation effects, leading to deviations from experimentally observed energies. Although post-Hartree–Fock methods, including configuration interaction and coupled-cluster techniques, can improve accuracy, they typically require substantial computational cost, particularly when extended to larger or more complex systems [2-3].

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Consequently, there is a growing need for alternative computational methods that can provide high accuracy while maintaining computational efficiency.

Quantum Monte Carlo (QMC) methods have emerged as a powerful class of stochastic techniques capable of addressing these challenges. In particular, Variational Quantum Monte Carlo (VQMC) combines the variational principle with stochastic sampling to evaluate multidimensional integrals associated with quantum expectation values [4]. By employing importance sampling through the Metropolis algorithm, VQMC efficiently explores the high-dimensional configuration space and reduces statistical variance, leading to improved numerical stability and convergence [1].

One of the major advantages of VQMC lies in its flexibility in constructing trial wave functions. The incorporation of correlation factors, such as Jastrow functions, enables a more accurate representation of electron–electron interactions and significantly improves the quality of the calculated ground-state energy [5]. Recent advances in wave function optimization and stochastic minimization techniques have further enhanced the reliability and applicability of VQMC in atomic and molecular systems [6].

Despite these advancements, achieving accurate ground-state energy estimations using relatively simple and computationally efficient models remains an important research objective. Therefore, this study applies the Variational Quantum Monte Carlo method to calculate the ground-state energy of the helium atom using an optimized trial wave function that incorporates electron correlation effects. This work not only aims to validate the effectiveness of VQMC in reproducing accurate atomic energies but also contributes to the broader development of stochastic methods for solving quantum many-body problems.

METHOD

This study employs the Variational Quantum Monte Carlo (VQMC) method to calculate the ground-state energy of the helium atom. The method combines the variational principle of quantum mechanics with stochastic Monte Carlo integration, where multidimensional integrals are evaluated using importance sampling based on the Metropolis algorithm [1],[4].

Trial Wave Function

The accuracy of the VQMC method strongly depends on the choice of the trial wave function. In this study, the trial wave function for the helium atom is defined as:

$$\psi_T(r_1, r_2) = exp[-Z(r_1 + r_2)](1 + br_{12}) \quad (1)$$

where r_1 and r_2 represent the distances of the two electrons from the nucleus, r_{12} is the inter-electron distance, Z is the effective nuclear charge, and b is a variational parameter controlling electron–electron correlation. The inclusion of the r_{12} term represents a Jastrow-type correlation factor, which is widely known to improve the accuracy of variational wave functions by capturing short-range electron correlation effects [5].

The trial wave function must satisfy important physical constraints, including the cusp condition arising from Coulomb interactions, as well as appropriate asymptotic boundary conditions. These conditions ensure the correct physical behavior of the wave function when particles approach each other and at large distances [1],[7].

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Hamiltonian and Variational Principle

The Hamiltonian operator for the helium atom is given by:

$$\hat{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \quad (2)$$

The ground-state energy is obtained using the variational principle, where the expectation value of the Hamiltonian is minimized:

$$E = \frac{\int \psi_T^*(r)\hat{H}\psi_T(r)dr}{\int |\psi_T(r)|^2 dr} \quad (3)$$

This expression can be reformulated using a probability distribution and local energy as:

$$E = \int P(r)E_L(r)dr \quad (4)$$

where $P(r) = |\psi_T(r)|^2 / \int |\psi_T|^2 dr$ and the local energy is defined as $E_L = \hat{H}\psi_T/\psi_T$. This formulation enables efficient stochastic evaluation of the energy expectation value [8].

Monte Carlo Sampling Procedure

The multidimensional integral is evaluated using importance sampling via the Metropolis-Hastings algorithm [9-10]. The computational procedure involves:

- Generating random electron configurations using the Metropolis-Hastings algorithm
- Sampling configurations according to the probability distribution $|\psi_T|^2$
- Computing the local energy for each sampled configuration
- Estimating the ground-state energy as the average of local energies:

$$E \approx \frac{1}{N}\sum_{i=1}^{N} E_L(r_i) \quad (5)$$

In this study, a total of $N = 2\times10^6$ samples are used to ensure statistical reliability and convergence of the results [1].

Convergence Criteria

The convergence of the VQMC simulation is assessed based on two main criteria:

1. **Energy Stabilization**
   The calculated average energy is monitored as a function of the number of Monte Carlo samples. Convergence is achieved when the energy fluctuates around a stable mean without systematic drift.
2. **Variance Minimization**
   According to the variational principle, the optimal trial wave function not only minimizes the energy but also minimizes the variance of the local energy. In the exact limit, the variance approaches zero, making it a key indicator of wave function quality [4, 6].

Statistical Uncertainty and Error Estimation

The statistical uncertainty in the Monte Carlo calculation arises from the stochastic nature of sampling. The standard deviation of the energy is calculated as:

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$$\sigma = \sqrt{\frac{\langle E_T^2 \rangle - \langle E_T \rangle^2}{N(N-1)}} \quad (6)$$

This measure quantifies the spread of sampled energy values and provides an estimate of the statistical error. However, this formulation assumes statistically independent samples. In practice, Monte Carlo samples generated using the Metropolis algorithm may exhibit autocorrelation, which can lead to underestimation of uncertainty. To address this issue, a data blocking technique is employed to obtain more reliable error estimates [11-12].

Computational Algorithm

The computational procedure follows these steps:

1. Initialize system parameters and trial wave function
2. Generate random numbers for sampling
3. Apply the Metropolis algorithm to accept or reject new configurations
4. Compute the local energy for each accepted configuration
5. Accumulate energy values and calculate averages
6. Evaluate statistical uncertainty and convergence

RESULT AND DISCUSSION

The ground-state energy of the helium atom was calculated using the Variational Quantum Monte Carlo (VQMC) method with a trial wave function containing two variational parameters, namely the effective nuclear charge Z and the electron–electron correlation parameter b. The Monte Carlo sampling employed $N = 2\times10^6$ configurations, ensuring statistically meaningful estimates of the energy expectation value.

Figures 1–3 illustrate the dependence of the ground-state energy on the variational parameter Z. The observed minimum at $Z\approx1.67$ reflects the effective nuclear charge experienced by each electron after accounting for electron–electron repulsion (screening effect). This value is lower than the actual nuclear charge $Z = 2$, indicating that each electron partially shields the other from the nucleus.

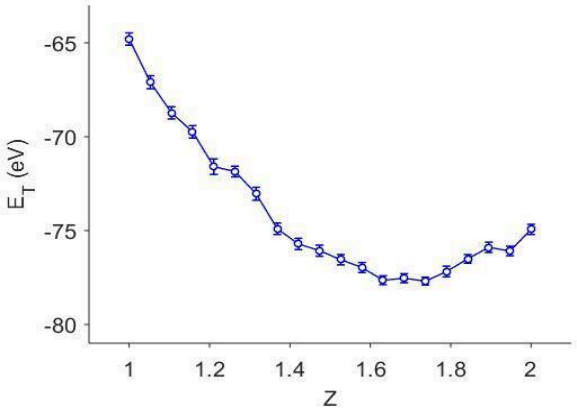


Figure 1. Ground State versus the variational parameter Z, b=2.

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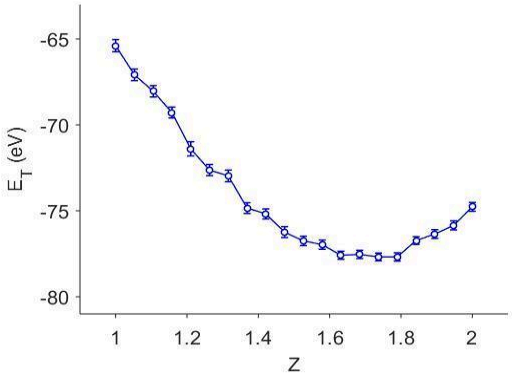


Figure 2. The ground state energy versus the variational parameter Z, for b = 2.5.

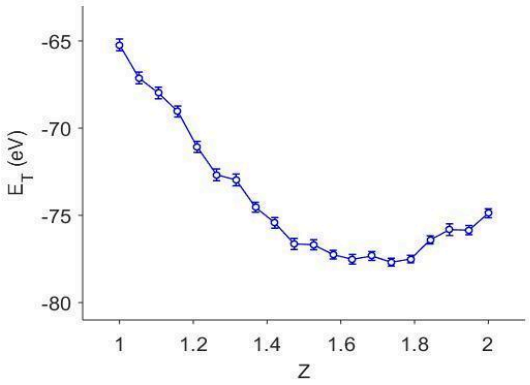


Figure 3. The ground state energy versus the variational parameter Z, for b = 2.8

From a physical standpoint, this behavior is consistent with the concept of **electron correlation**, where the instantaneous positions of electrons are not independent. The variational optimization effectively adjusts Z to minimize the total energy by balancing electron–nucleus attraction and electron–electron repulsion. Similar trends have been reported in QMC studies, where effective charge parameters emerge naturally from variational optimization [1],[4].

Table 1. Ground-state energy of helium for b various value

No.	N	B	E (eV)	Stddev
1.	2.000.000	0,25	-77,4384	0.0179
2.	2.000.000	1,5	-77,5138	0.0179
3.	2.000.000	1,8	-77,66172	0.0179
4.	2.000.000	2	-77.6172	0.0179
5.	2.000.000	2,5	-77,6748	0.0179
6	2.000.000	2,8	-77,1950	0.0179
7	2.000.000	3	-77,1950	0.0179

Table 1 shows that the lowest energy (-77.6748 eV) is obtained at $b = 2.5$. The parameter b governs the strength of electron–electron correlation in the trial wave function. Physically, it can be interpreted as controlling the **correlation hole**, i.e., the reduced probability of finding two electrons close to each other due to Coulomb repulsion.

For small values of b (e.g., $b = 0.25$), the correlation effect between electrons is still weak, resulting in an overestimation of electron–electron repulsion and consequently a higher total

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energy. Conversely, for larger values of b(e.g., $b = 2.8$ or $b = 3$), the correlation is overemphasized, which distorts the trial wave function and leads to an increase in kinetic energy due to excessive electron localization. An optimal condition is achieved at $b = 2.5$, where a balance is established between minimizing Coulomb repulsion and maintaining a physically realistic spatial distribution of electrons. This behavior is consistent with the role of Jastrow correlation factors, which are known to significantly improve variational energies by effectively capturing short-range electron correlation [5-6].

The exact non-relativistic ground-state energy of helium is approximately:

$$E_{exact} = -\ 78.975\ eV \tag{7}$$

The present result:

$$E_{VMC} = -\ 77.6748\ eV \tag{8}$$

gives a relative error:

$$Error = \frac{|E_{exact} - E_{VMC}|}{|E_{exact}|} \approx 1.65\% \tag{9}$$

This level of accuracy is consistent with typical VMC calculations using relatively simple trial wave functions. More advanced methods such as Diffusion Monte Carlo (DMC) can reduce this error to below 0.1% by systematically projecting out higher-energy components [1],[8].

Table 2. Wave functions, methods, and research results from previous and current researchers [13-15]

Wave Function Experiment	Method	Result
$\psi_T = \exp\left(Z\,(r_1 + r_2)/a_0\right)$	Analytically variational	-77.5 eV
$\psi_T = (R_c - r\ )\exp\ (-\alpha r)\sum_{i=0}^{15} c_i r^i$	Variational perturbation	-2.903 a.u
$\psi_T = \exp\left(Z\,(r_1 + r_2)/a_0\right)\exp\left(\alpha r_{12}\right)$ $\psi_{ion} = \exp\left(\alpha r\right)$	Variational Monte Carlo Born-Oppenheimer	-78.9 eV
$\psi_T = \exp\left(-\left(Z + b\right)(r_1 + r_2)/a_0\right)$	Variational Monte Carlo	The present result -77.6748 eV.

The reported standard deviation of the energy is approximately 0.0179 eV for all parameter variations, indicating that the Monte Carlo sampling is statistically stable and that the variance of the local energy is relatively low. This suggests that the chosen trial wave function provides a reasonably good approximation of the system. However, it is important to distinguish between statistical error, which arises from finite sampling, and systematic error, which originates from the limitations of the trial wave function. Although the statistical error in this study is small, the dominant source of inaccuracy is attributed to the systematic bias introduced by the imperfect form of the trial wave function, which is a well-known limitation of Variational Monte Carlo methods [16].

The curves in Figures 1–3 show a characteristic **U-shaped behavior**, confirming the existence of an optimal variational parameter. The smoothness of the curves indicates good convergence of the Monte Carlo sampling. Table 1 demonstrates that energy variations with

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respect to $b$are relatively small (~0.2–0.4 eV range), suggesting that the system is moderately sensitive to correlation effects. The variation (~0.2–0.4 eV) is an order of magnitude larger than the statistical uncertainty (0.0179 eV), indicating that the dependence on $b$is physically significant rather than a statistical artifact. However, even small differences are physically significant in quantum systems, as they reflect improvements in capturing electron correlation.

Despite the reasonable accuracy achieved in this study, several limitations of the present approach must be acknowledged. First, the simplicity of the chosen trial wave function may not fully capture dynamic electron correlation effects, leading to residual errors in the calculated energy. More sophisticated wave function forms, such as multi-determinant expansions or neural-network-based approaches, have been shown to significantly improve accuracy [17-18]. Second, the absence of Diffusion Monte Carlo (DMC) limits the method's capability, as VMC inherently provides only an upper bound to the ground-state energy and cannot systematically approach the exact solution without projection techniques. Third, although a large number of samples (2×10^6) were employed, increasing the sampling size could further reduce statistical fluctuations and improve precision. Additionally, Monte Carlo simulations may suffer from autocorrelation between successive samples, which can lead to an underestimation of statistical uncertainties if not properly addressed [12]. Finally, relativistic effects and finite nuclear mass corrections were neglected in this study; while these contributions are generally small, they become increasingly important when targeting high-precision results.

From a broader perspective, the findings demonstrate that the Variational Quantum Monte Carlo method is capable of providing accurate and physically meaningful estimates of ground-state energies with relatively modest computational cost. The method effectively captures essential electron correlation effects and offers valuable insight into the relationship between variational parameters and physical observables. Furthermore, this study highlights the critical role of wave function design and parameter optimization, which remain central challenges in quantum Monte Carlo research. Recent advances integrating machine learning techniques into QMC frameworks present promising opportunities for achieving near-exact accuracy in solving many-body quantum systems [17-18].

CONCLUSION

This study has demonstrated that the Variational Quantum Monte Carlo (VQMC) method is an effective numerical approach for calculating the ground-state energy of the helium atom. By combining the variational principle with stochastic Monte Carlo integration, the method enables accurate evaluation of multidimensional integrals that arise in quantum many-body systems. The accuracy of the results is strongly influenced by the choice of the trial wave function, which must satisfy physical requirements such as cusp conditions and appropriate boundary behavior, as well as incorporate electron–electron correlation effects.

The results show that the optimized trial wave function yields a minimum ground-state energy of $E = -77.6748$eV at the variational parameter $b = 2.5$. This value is in good agreement with theoretical reference values and demonstrates an improvement compared to simpler variational approaches reported in previous studies. The findings confirm that incorporating correlation effects into the trial wave function significantly enhances the accuracy of the calculated energy.

Overall, this study highlights the importance of wave function design and parameter optimization in achieving reliable results using VQMC. Despite some limitations, such as

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dependence on the trial wave function and the absence of projection methods, the VQMC approach provides a good balance between computational efficiency and accuracy, making it a valuable tool for investigating ground-state properties of quantum systems.

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