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Ground-State Energy Calculation of Helium Atom Using Quantum Monte Carlo CASINO-Code

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Abstract
We report an improved variational Monte Carlo (VMC) calculation of the ground-state energy of the helium atom, using quantum Monte Carlo (QMC) CASINO – code. The VMC ground-state energy is studied with a single determinant Slater-Jastrow trial wave-function formed from Hartree-Fock orbitals. The optimization of orbitals improved the agreement between the variational Monte Carlo and recent experiment. The calculated ground-state energy result is –2.903692762 ± 0.000023 a.u., which is in good agreement with the most recent experimental value –2.903693775 a.u. obtained by Bergeson et al. A more accurate trial function for importance sampling and the use of Jastrow–function combine to yield a ground-state energy which is 5 significant figures more accurate than that of previous quantum Monte Carlo calculations.
Keywords: CASINO code, QMC, VMC, Helium atom, Reblocked-standard-error

1. Introduction

Application of quantum mechanics for the investigation of ground-state energies for atomic systems constitutes a reliable problem of interest in theoretical condensed matter physics and chemistry. Quantum-variational methods have proven most suitable for obtaining precise results for the ground-state or low-lying states of two-electron atoms and are superior to perturbative methods (Tanner et al., 2000).

The ground-state energy of helium has for a long time continued to attract the attention of many researchers because, from the early days of quantum mechanics the ground-state ionization energy of the helium atom was set as a benchmark for approximation methods of solving the nonrelativistic Schrödinger equation for a few-body system. We report here calculations of the ground-state energy for the two-electron atoms ―helium― using quantum Monte Carlo (QMC) method in CASINO–code, without the use of Born-Oppenheimer or any other adiabatic approximations.

The history of accurate theoretical calculations of energies for helium atom began with the work of Kellner (in 1927), who was the first to use the Ritz variational principle and obtained a ground-state energy of –2.895 a.u. for helium atom. The variational calculations of Hylleraas, improved upon the work of (Kellner, 1927) by using a trial wave function with 38 variational parameters (Hylleraas, 1928; 1929). The work presented one of the first successes in solving the Schrödinger equation for a two-electron system and obtained ground-state energy of –2.9037 a.u., which was in close agreement with the first experimental result (Lyman, 1924) at the time. In 1959, the method of (Hylleraas, 1929) was again taken up using large-scale variational calculations by (Kinoshita, 1959), who computed the ground-state energy of helium atom with higher-order corrections to be –2.903722 a.u. (see Table 1). The definitive computation by (Pekeris, 1959), gave a nonrelativistic value of –2.903724376 a.u. for the ground-state energy using a 1078-term recursion formula; and according to (Pekeris, 1959), most accurate ground-state energies are achieved by diagonalization of the two-electron Hamiltonian matrix, using large basis sets.

However, according to recent experimental result (Bergeson et al., 1998), the results from the techniques reported above overestimated the helium ground-state energy, (see Table 1). Thus, the discrepancies in the helium ground-state energy calculations have lead theorists to establish the foundation for future theoretical calculations.

In 1993, a relativistic approach was employed for calculating the ground-state energy of helium atom (Drake, 1993); and thereafter a variational method was also employed (Drake, 1998). Earlier Bürgers et al. (1995), also calculated the helium ground-state energy using perimetric coodinates. Both the methods of (Drake, 1998) and (Bürgers et al., 1995) resulted in the same ground-state energy (see Table 1).

In recent days however, with the advent of more computationally powerful computers, some other researchers have tried to calculate the ground-state energy of helium atom by employing various computational techniques and simulation codes. For instance, Martins (in 2007) computed the ground-state energy of helium atom from Green's function Monte Carlo methods using a guiding wave-function and measured the complete ionization energy to be –2.90210 a.u., and this resulted in an underestimation of the ground-state energy of the helium atom when compared to the most recent experiment. Again, Koki (in 2009) employed the algorithm of Hylleraas (1929) to calculate the ground-state energy of helium atom and obtained a value of –2.90420 a.u., which though in close agreement with experiment, resulted in an overestimation of the ground-state energy when

compared to (Bergeson et al., 1998). More recently, a variational method was used by Doma and El-Gamal (2010), while Suleiman and Ewa (2010) employed the path integral Monte Carlo (PIMC) method in the context of Born-Oppenheimer (BO) approximation to calculate the ground-state energy of helium atom. However, from both cases, it is observed that the ground-state energy of helium is still in variance with recent experimental value (see Table 1).

We present in this paper, quantum Monte Carlo CASINO – code, for the simulation and calculation of the ground-state energy of helium atom from one of QMC methods: variational Monte Carlo (VMC)) method. The reason for the significant difference in the works of the other authors mentioned above could be attributed to the fact that they used variational techniques which goes a long way to limiting the accuracy of the ground-state energy due to the necessity of guessing the trial wave-function. On the basis of this, we have tackled the problem here by using single determinant Slater-Jastrow trial wave-function as a sampling function. In fact, reported studies have shown that trial wave functions based on single Slater configuration can reproduce experimental values with very high accuracy (Grossman, 2002). In addition, the ground-state energy appears highly sensitive to the level of correlation used, especially for problems which require multi-reference treatment. Hence, it is therefore crucial to explore different types of methods to understand the impact of many-body effects more thoroughly.

QMC is in principle exact; and in practice it captures the correlations at a level of 90–95% (Foulkes et al., 2001; Bajdich, M. and L. Mitas, 2009). This is something that is quite difficult to achieve by correlated methods based on expansions in basis sets. The QMC allows a direct representation of many-body effects in the wave function, at the cost of statistical uncertainty that can be reduced with more simulation time; and in addition, use in one way or the other Monte Carlo methods to handle the many-dimensional integrals that arise.

The rest of this paper is structured as follows: In Section 2, the VMC method is briefly introduced with an inclusion of the trial wave functions. Section 3 explains the computational details. In Section 4, the results and discussion are presented. Finally, the paper ends with concluding remarks in Section 5.

2. The Method: Quantum Monte Carlo (QMC)

The term “quantum Monte Carlo” encompasses different techniques based on random sampling, which involves the combination of quantum approach in physics with Monte Carlo procedures as applied to a system. There are many types of QMC techniques but this work focuses mainly on variational Monte Carlo (VMC) which depends on the availability of an appropriate trial wave-function to determine the zero-point energy.

2.1. Variational Monte Carlo method

The variational Monte Carlo (VMC) method is based on the combination of the variational principle and the Monte Carlo evaluation of integrals. The VMC method relies on the availability of a trial wave-function ψ_{T} that is a reasonably good approximation of the true ground-state wave-function. The way to produce good trial wave-function is describe further in this review. The trial wave-function must satisfy some functional conditions. Both ψ_{T} and $\nabla\psi_{\mathrm{T}}$ must be continuous wherever the potential is finite, and the integrals $\int\psi_{\mathrm{T}}^{*}\psi_{\mathrm{T}}$ and $\int\psi_{\mathrm{T}}^{*}\hat{H}\psi_{\mathrm{T}}$ must exist (Foulkes et al., 2001). To keep the variance of the energy finite we also require $\int\psi_{\mathrm{T}}^{*}\hat{H}^{2}\psi_{\mathrm{T}}$ existing. The expectation value of $\hat{H}$ computed with the trial wave-function ψ_{T} provides an upper bound on the exact ground-state energy E_0:

$$E_{\mathrm{V}} = \frac{\int \psi_{\mathrm{T}}^{*}(\mathbf{R})\hat{H}\psi_{\mathrm{T}}(\mathbf{R})d\mathbf{R}}{\int \psi_{\mathrm{T}}^{*}(\mathbf{R})\psi_{\mathrm{T}}(\mathbf{R})d\mathbf{R}} \geq E_0 \tag{2.1}$$

In a VQMC simulation this bound is calculated using the Metropolis Monte Carlo method. Equation (2.1) is rearranged as follows:

$$E_{\mathrm{V}} = \frac{\int |\psi_{\mathrm{T}}(\mathbf{R})|^2 \left[\psi_{\mathrm{T}}(\mathbf{R})^{-1}\hat{H}\psi_{\mathrm{T}}(\mathbf{R})\right]d\mathbf{R}}{\int |\psi_{\mathrm{T}}(\mathbf{R})|^2 \, d\mathbf{R}} \tag{2.2}$$

and the Metropolis algorithm is used to sample a set of points $\{\mathbf{R}_m : m = 1, M\}$ from the configuration-space probability density given in Equation (2.3) as

$$\rho(\mathbf{R}) = \frac{|\psi_{\mathrm{T}}(\mathbf{R})|^2}{\int |\psi_{\mathrm{T}}(\mathbf{R})|^2 \, d\mathbf{R}}. \tag{2.3}$$

Here, the equilibrium walker density $n(\mathbf{R})$ is proportional to $\rho(\mathbf{R})$, and the probability of finding any given walker in $d\mathbf{R}$ is $\rho(\mathbf{R})d\mathbf{R}$. The trial moves are sampled from the current position of the walker, the variance of the Gaussian being chosen such that average acceptance probability is roughly 50% (Needs et al., 2009).

At each of these points the "local energy" $E_L(\mathbf{R}) = \psi_{\mathrm{T}}(\mathbf{R})^{-1} \hat{H} \psi_{\mathrm{T}}(\mathbf{R})$ is evaluated and the average energy accumulated is given by

$$E_{\mathrm{V}} \approx \frac{1}{M} \sum_{m=1}^{M} E_L(\mathbf{R}_m). \tag{2.4}$$

2.2. Trial wave functions

The trial wave functions used in this work are of the Slater–Jastrow type (Jastrow, 1955) written as:

$$\psi_T(\mathbf{R}) = \sum_i d_i D_i^{\alpha}(\mathbf{R}) D_i^{\beta}(\mathbf{R}) e^{J(\mathbf{R})} \tag{2.5}$$

where $D_i^{\alpha(\beta)}(\mathbf{R})$ is a Slater determinant of spin $\alpha(\beta)$ electrons, d_i is the coefficient and $J(\mathbf{R})$ is the Jastrow function. The nodes of a trial wave-function are determined by the antisymmetric Slater component. The Jastrow function containing one-body and two-body explicit correlation terms is given by

$$J(\mathbf{R}) = \sum_{i>j} u(r_{ij}) + \sum_I \sum_i \chi_I(r_{iI}) \tag{2.6}$$

where *i(j)* and *I* are electron and nuclei indices, respectively, and r_{iI} , r_{ij} are the corresponding distances. The u and χ terms describe electron–electron and electron–nucleus correlations respectively. Although the accuracy of the simulation relies on the Slater component, the Jastrow factor is also important for the efficiency of the simulation as it helps to reduce fluctuations and the cost of the computation. Again, though VMC can be quite powerful when applied to the right problem, the necessity of guessing the functional form of the trial function limits its accuracy and there is no known way to systematically improve it all the way to the exact non-relativistic limit. Thus in practice, the main use of VMC is in providing the optimized trial wave function required as an important sampling function by the much more powerful DMC (diffusion Monte Carlo) technique.

3. Computational Details

In this work, our calculation was carried out using the QMC software package, CASINO-code (Needs et al., 2012). The CASINO-code simulation was run for the ground-state energy of helium atom by VMC technique. The VMC steps serves as an input parameter corresponding to the total number of particle configurations for which the simulation depends. The correlated wave-function from VMC is then optimized using the variance-minimization method to obtain an efficient and more accurate convergence of the ground-state energy. Thus, one of the most important steps in our QMC calculation is to obtain suitable trial wave function. Following the generation of the Slater components, the optimization of the Jastrow function containing one-body and two-body explicit correlation terms was carried out. The optimization of the Jastrow function was as important as obtaining the Slater components since inadequacy in the Jastrow can increase the locality approximation bias. In this study, all the Jastrow variational parameters were optimized using a variance–minimization scheme (Umrigar et al., 1988) in the framework of variational Monte Carlo (VMC), a variant of QMC. The CASINO-code used was run on a Linux based operating system (Ubuntu environment) having a working Fortran 90 compiler.

4. Results and Discussion of Results

Every VMC step generates a new configuration of electrons and nuclei, and because of the difference in inter-particle separation, each of these will have different ground-state energy. The correct expectation value of the ground-state energy is the average energy of thousands of these configurations. Figure 1 presents the result of the VMC simulation for the helium atom generated from 150,000 configurations. The number of equilibration steps underwent is 2000 moves, at an optimized time-step of 0.17634 with the number of VMC block as 1, and having a target weight of 1000. The simulation took 35,000 lines of data between accepted configurations.

The calculated ground-state energy from the output file is obtained at $6.758348757024 a.u.$ (which is the maximum distance from origin), with an acceptance ratio of 50.8803% which is in good agreement as predicted by (Needs et al., 2009). The result presented in Figure 1 indicates that the more the VMC steps

simulated the more likely that the calculated value of the ground-state energy is closer to the experimental value (Bergeson, 1998). However, it can be seen in Figure 1 that it got to a point where as the numbers of VMC – step were further increased, convergence was reached with a minimized error (see Figure 2) corresponding to a ground-state energy value of $-2.903692762 a.u.$ as shown in table 1. Again, from table 1 it is observed that the relative difference between our work and the most recent experiment is $-0.000001013 a.u$. Thus, the result of our VMC calculation (black-line-with-star) in this work using CASINO-code is in perfect agreement with the most resent experimental result by Bergeson et al., compared to other theoretical works in the literature which either underestimate or overestimate the helium ground-state energy (see Table 1); and the interpolation of our result is shown with the green-line as in Figure 1. However, we observed from the graph of Figure 1 that, the standout points may be due to inclusion of unequilibrated data in the final average data which will give a systematic bias to the averages obtained. Also, from the output file, an acceptance ratio of 50.8803% obtained, implies an improved stability in the ground-state energy from the use of VMC method in the CASINO – code which is in conformity with the prediction of Foulkes et al. (Foulkes et al., 2001). This indicates that the optimized time-step does not limit the number of accepted Monte Carlo moves. Hence, as more configurations are included, the sampling is improved.

In addition, the reblocking analysis to calculate an estimate of the standard error in the mean energy as a function of the length of blocks into which the data are gathered resulted in a plateau as shown in the reblocked standard-error in mean energy against block-length (reblocking transformation number) curve in Figure 2. For low values of the block length the error bar gradually appears too small, and then increases upward with a roughly constant value for larger block lengths which is in good agreement as predicted by Needs et al. (2012). According to them, for very large block lengths the estimated error bar will oscillate as the error bar becomes large and the constant value in the middle (i.e. the plateau) is the accurate error bar. The VMC calculation in our study gives this plateau within the optimized time-step and therefore indicating that the serial correlation in the data is less in the result of Figure 2 obtained. Thus, the standard error in the mean ground-state energy is 0.0000227578 a.u. as shown in Figure 2.

Table 1 presents the comparative analysis of the work of other researchers with respect to our calculated ground-state energy result.

5. Conclusion

The ground-state energy for helium atom was numerically calculated by running the QMC CASINO code, under the principles of the VMC techniques. The results in this work demonstrated that VMC is capable of accurately calculating the précised ground-state energy of the system as it falls inside the error bars of previous experimental and numerical calculations. The wave-function was been optimized to suit the cusp condition of the electron-electron and the electron-proton conditions. Thus, the higher the VMC steps, the more the values of the energies get closer to the exact value. The CASINO code reached a convergence at –2.903692762 ± 0.000023 a.u., which is the point taken as the value of the ground-state energy for the helium atom.

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References

Bajdich, M. and L. Mitas, (2009), Acta Physica Slovaca, **59**: 81.
Bergeson, S. D., et al., (1998), Phys. Rev. Lett. **80**, 3475.
Bürgers, A., D. Wintgen, and J.-M. Rost, (1995), J. Phys. B **28**, 3163.
Doma, S. B. and F. El-Gamal, (2010), Monte Carlo variational method and the ground state of helium atom. The Open Applied Mathematics Journal 11: 15
Drake, G. W. F., (1988), Nucl. Instrum. Methods Phys. Res. B **31**, 7.
Drake, G. W. F., (1993), in Long-Range Casimir Forces: Theory and Recent Experiments on Atomic Systems, edited by F. S. Levin and D. A. Micha (Plenum, New York), Pp. 107.
Foulkes, W. M. C., L. Mitas, R. J. Needs, and G. Rajagopal, (2001). Rev. Mod. Phys. **73**: 33.
Grossman, J. C., (2002), Benchmark quantum Monte Carlo calculations, Journal of Chemical Physics, Volume 117, Number 4, 1434.
Hylleraas, E. A., (1928), Z. Phys. **48**, 469.
Hylleraas, E. A., (1929), Z. Phys. **54**, 347.
Jastrow, R.J., (1955), Many- Body Problem with Strong Forces, Phys. Rev. 98, 1479.

Kellner, G. W., (1927), Z. Phys. **44**, 91.
Kinoshita, T., (1959), Phys. Rev. **115**, 366.
Koki, F. S., (2009), Numerical calculation of the ground state energy of helium using Hylleraas algorithm, Journal of Nigerian Association of Mathematical physics, Vol. 15, 305 – 310.
Lyman, T., (1924), Astrophys. J. **60**, 1.
Martin, D., (2007), Computing the ground state energy of Helium. Fourth year M. Phys. Project Report, The University of Manchester [Unpublished].
Needs, R. J., M. D. Towler, N. D. Drummond, and P. López Ríos, (2009), CASINO User's Guide, version 3.0.0, University of Cambridge, UK, 2009.
Needs, R. J., M. D. Towler, N. D. Drummond, and P. López Ríos, (2012), CASINO User's Guide, version 2.11, Theory of Condensed Matter Group, Cavendish Laboratory, J .J. Thomson Avenue, Cambridge CB3 0HE, United Kingdom, 2012.
Pekeris, C. L., (1959), Phys. Rev. **115**, 1216.
Suleiman, A.B. and I.O.B. Ewa, (2010), Numerical Calculations of ground state energy of H_2 Molecule using quantum Monte Carlo method, Journal of the Nigerian Association of Mathematical Physics, Volume 16, Pp. 39–50.
Tanner, G., K. Richter and J.-M. Rost, (2000), Reviews of Modern Physics, Vol. 72, No. 2, Pp. 505.
Umrigar, C.J., J.G. Wilson, K.W. Wilkins, (1988), Optimized trial wave functions for quantum Monte Carlo calculations, Phys. Rev. Lett., 60, 1719–1722.

Table 1: Comparative analysis of the ground-state energy of helium atom calculated by different researchers

S/N	Authors/Reference	Year	Techniques/Methods	GSE (a.u.)
1	Bergeson et al.	1998	Experimental value	–2.903693775
2	Lyman	1924	Experimental	–2.9035
3	Kellner	1927	Ritz Variational	–2.873
4	Hylleraas	1928	Variational	–2.895
5	Hylleraas	1929	Variational (with 38 parameters)	–2.9037
6	Kinoshita	1959	Variational (with 38 parameters)	–2.903722
7	Pekeris	1959	Non–relativistic	–2.903724376
8	Drake	1993	Relativistic	–2.903700023
9	Bürgers et al.	1995	Perimetric coordinates	–2.903724377
10	Drake	1998	Variational	–2.903724377
11	Martin	2007	GFQMC	–2.90210
12	Koki	2009	Hylleraas Algorithm	–2.90420
13	Doma & El-Gamal	2010	Variational	–2.89810
14	Suleiman & Ewa	2011	PIMC (BO)	–2.90230
15	This Work		VMC (CASINO - Code)	–2.903692762

GSE = Ground-state Energy
1 a.u. = 27.2eV

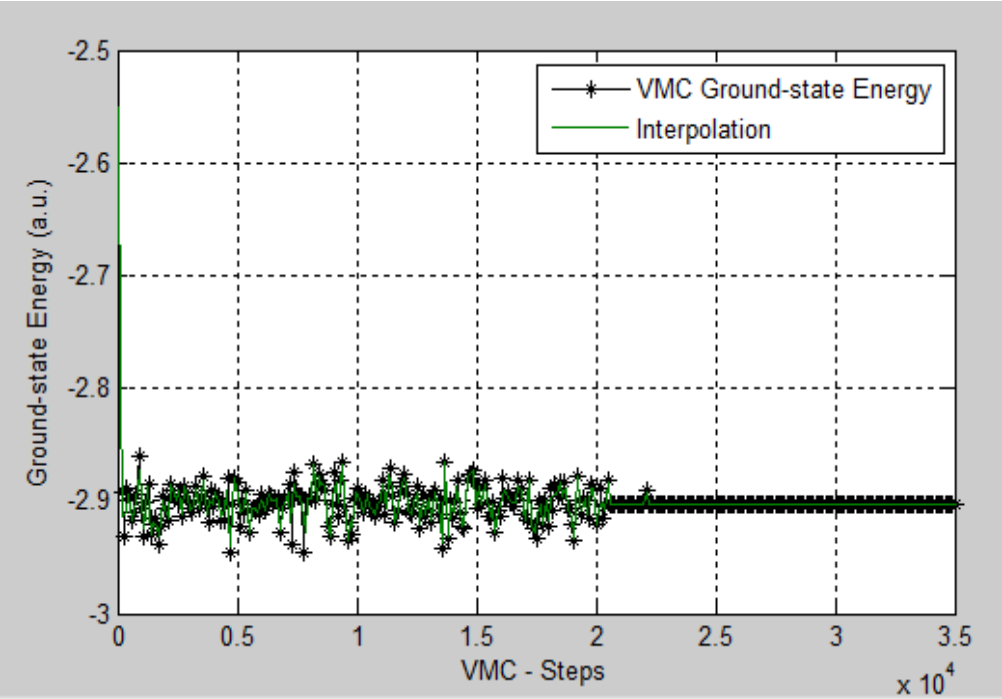

Figure 1: Graph of Ground-state Energy against VMC Steps.

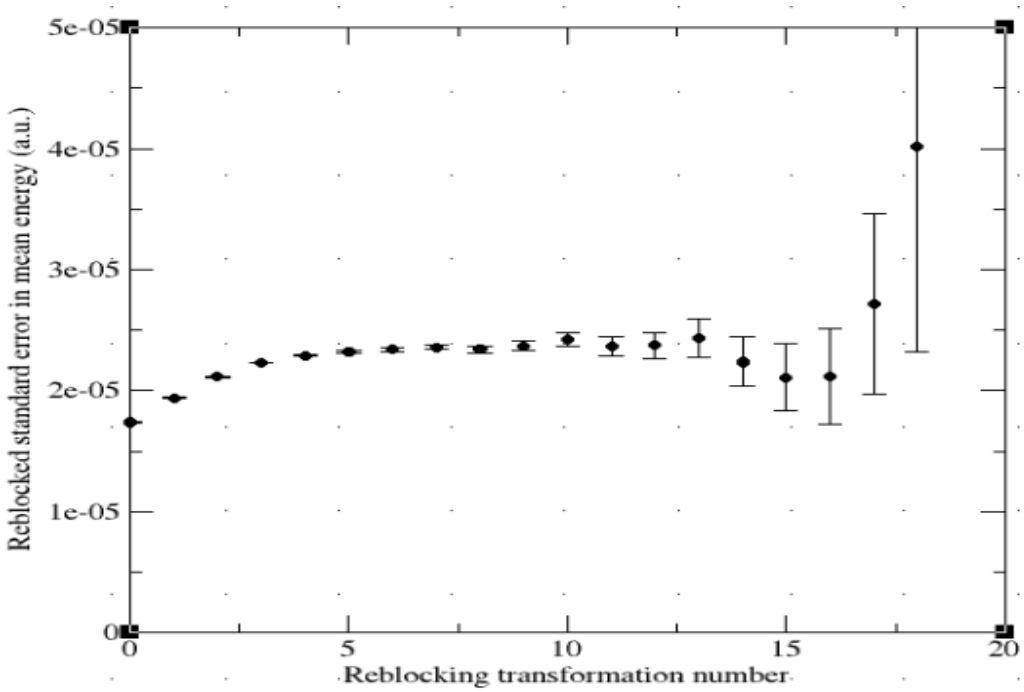

Figure 2: Graph of Reblocked standard error in mean energy against Reblocking transformation number (RTN).

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