

Closed-Shell Ground State Energy Calculations of the First Row Diatomic Molecules Using Quantum Monte Carlo CASINO – Code

¹Ekong, S. A., ²Ebomwonyi, O. and ²Idiodi, J. O. A.

¹Department of Physics and Energy Studies, Achievers University, Owo, Nigeria.

²Department of Physics, University of Benin, Benin City, Nigeria.

Abstract

The ground state energies of the first row diatomic molecules have been calculated by applying the quantum Monte Carlo (QMC) CASINO - code simulations to solve the Schrödinger equation, without the use of any adiabatic approximations. By employing the restricted Hartree-Fock (RHF) scheme, two different QMC techniques were used in this work: the variational quantum Monte Carlo (VQMC) and the diffusion quantum Monte Carlo (DQMC) techniques. The ground state energies of hydrogen and helium molecules for different maximum distances from their origins are calculated using the two different methods mentioned (VQMC and DQMC). The simulations require that the configurations must evolve on the time scale of the electronic motion, and after equilibration, the estimated effective time-step be obtained. The ground state energy for hydrogen molecule from VQMC calculation is $[-1.1697(8) \pm 0.00406(7)]a.u.$; and a more accurate result was obtained from the DQMC calculation as $[-1.17456(7) \pm 0.000172(6)]a.u.$ Also, the ground state energy of helium molecule from VQMC calculation is $[-5.8067 \pm 0.0004811]a.u.$, while a more accurate result is obtained from the DQMC calculations as $[-5.808 \pm 0.00005451]a.u.$ The results from the DQMC techniques of the calculations are found to be precisely approaching the required order of accuracies.

Keywords: CASINO code, VQMC, DQMC, RHF, UHF

1.0 Introduction

The hydrogen molecule H_2 is the basic arena for the confirmation of theory and experiment in fundamental molecular Physics [1]; and the determination of the ground state energies for molecular systems constitutes reliable problem of general interest in theoretical condensed matter physics [2]. Hydrogen is the simplest molecular system which exhibits such important effect as electron correlation, the separation of electronic and nuclear motion, and related non-adiabatic effects, as well as relativistic and radiative effects [1].

There is a long history of increasingly accurate theoretical calculations of the energy of hydrogen molecule and increasingly accurate experimental measurements of the ionization potential and dissociation energy. The method of choice for theoretical prediction has most often been analytical variational method, but the quantum Monte Carlo method has recently approached its accuracy for hydrogen molecule. The history of accurate calculations of energies for H_2 begins with one of the first successes in solving the Schrödinger equation for the hydrogen molecules in 1933 with the work of James and Coolidge [3]; when all known corrections were included, the best estimate of the discrepancies was - 1.1744 a.u as established by Kolos and Wolniewicz [4], which has been referred to be the exact value of the ground state energy of the hydrogen molecule [5].

After hydrogen, helium is the most common element in the universe [6]. Hydrogen and helium share some common properties. Both are very light and exhibit rich quantum properties at low temperature. Helium is the second least reactive element and noble gas (after neon). Its low atomic mass, thermal conductivity, specific heat, and sound speed are greatest after hydrogen. The study of stability of bound states for atomic and molecular systems as a function of physical parameters, such as nuclear charges, nuclear distances, is a subject of great interest. Multiple charged anions could be unstable against ionization, and experimental and theoretical search of small stable multiple charged anions is an active research field [7]. On the other hand, in the case of highly ionized molecules, nuclear Coulombic repulsion turns these

Corresponding author: Ekong, S. A. E-mail: -, Tel.: +2348034968173, Ebomwonyi (08058865721)

systems unstable against dissociation. However, even at the present time when we are able to make calculations for many body systems, like extremely large molecules, some properties of small molecules are still being a great subject of study. The ground state of simple molecules like the hydrogen molecule, the helium hydride molecular ion and the helium molecular di-cation was studied with great detail [8–13]. Helium molecule has been a subject of interest for a long time, and continues to attract the attention of many researchers. Davidson [14] discussed the restrictions placed on the ground-state potential energy of a diatomic molecule by the inequality $d^2(R^2 E)/dR^2 < 0$, which leads to rather weak smoothness conditions on $E(R)$. Schiff and Verlet [15] presented a variational calculation of the ground-state energy of liquid helium-3 and liquid helium-4 using, respectively, Jastrow- and Slater-Jastrow-type trial wave functions. Krüger [16] calculated the binding energy of the lowest bound state of three identical particles and predicted a stable tri-atomic helium molecule with a binding energy of 0.4°K using a Morse potential. Ceperley [17], Toennies and Vilesov [18] used the Monte Carlo simulation techniques to simulate boson systems and introduces the picture of a boson super fluid (^4He); and showing the agreement between simulations and experimental measurements on liquid and solid helium for such quantities as pair correlations, the superfluid density, the energy, and the momentum distribution. A more recent research is the work of Ferfon and Serra [19], who studied the ground state behaviour of two-electron diatomic molecules; and obtained the ground state stability diagram for diatomic molecules in the Born–Oppenheimer approximation and the behaviour of the ground state near the stability line.

We present in this paper, the quantum Monte Carlo CASINO code, for the simulation and calculation of the ground state energy of diatomic molecules of some first row elements (hydrogen and helium) from two QMC methods: variational quantum Monte Carlo (VQMC) and diffusion quantum Monte Carlo (DQMC) methods. The ground state energy of hydrogen molecule was recently calculated by Suleiman and Ewa [2] using the VQMC/Path Integral Monte Carlo (PIMC) method. Their calculated ground state energy was -1.1736 a.u which differs from the exact value [4,5] by 0.0008 a.u. Also recently, Ebomwonyi et al [20] using the VQMC method (CASINO-code) by employing the unrestricted Hartree-Fock (UHF) technique (open shell), had a value of -1.168 a.u. This value differs from the exact value by 0.0064 a.u, which is much more farther from the exact value. The reason for this significant error difference in both results could be attributed to the fact that both authors [2,20] used the VQMC method which limits 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 the DQMC method which requires an optimized trial wave-function as a sampling function.

2.0 Method (Quantum Monte Carlo Methods)

Quantum Monte Carlo method encompasses several different techniques that relies on random sampling or numbers [21], which involves the combination of quantum approach in physics with Monte Carlo procedures as applied to a system [2]. There are many different QMC methods, but this work concentrates only on two: Variational quantum Monte Carlo (VQMC) and fixed-node diffusion quantum Monte Carlo (DQMC). Like all QMC methods, these are closely related to Monte Carlo methods used in classical statistical mechanics [22]. In the VQMC method, expectation values are calculated via the Monte Carlo integration over $3N$ -dimensional space of electron coordinates. The more sophisticated DQMC is a projector approach in which a stochastic imaginary-time evolution is used to improve a starting trial wave-function. QMC has a number of desirable features which, even if the fermion sign problem is not solved, imply the method will still be useful [23].

2.2 Variational Quantum Monte Carlo (VQMC) Technique

The variational QMC technique is implemented in the use of the CASINO-code in this review, for the calculation of the ground state energy of the hydrogen molecule, by employing the RHF (Restricted Hartree-Fock) method over the UHF (Unrestricted Hartree-Fock) method.

The RHF method involves where the atoms or molecules is a closed-shell system with all orbitals (atomic or molecular) doubly occupied. It is a variant of Hartree-Fock theory for open shell molecules. It uses doubly occupied molecular orbitals as far as possible and then singly occupied orbitals for the unpaired electrons. The foundation of the RHF method were first formulated by Roothaan [24] and then extended by other authors [25,26]. The RHF method for closed shell molecules, leads to Roothaan equations written in the form of a generalized eigen value problem.

$$FC = SC\epsilon \quad (2.1)$$

Where F is the Fock matrix (which is a function of C), C is a matrix of coefficient, S is the overlap matrix of the basis functions and ϵ is the matrix of orbital energies.

The UHF method is the most common molecular orbital method for open shell molecules where the numbers of electron of each spin are not equal. It uses different molecular orbitals for the α and β electron. This has been called a different orbitals for different spin (DODS) method. The result is a pair of coupled Roothaan equation known as the Pople-Nesbert-Berthier equation [27, 28]

$$F^\alpha C^\alpha = SC^\alpha \epsilon^\alpha \quad (2.2)$$

$$F^\beta C^\beta = SC^\beta \epsilon^\beta \quad (2.3)$$

where F^α and F^β are the Fock matrices for the α and β orbitals, C^α and C^β are the matrices of coefficients for the α and β orbitals, S is the overlap matrix of the basis function, ϵ^α and ϵ^β are the diagonal matrices of orbital energies for the α

and β orbitals. The pair of equations is coupled because the Fock matrix elements of one spin contain coefficients of both spin as the orbital has to be optimized in the average field of all other electrons. The final result is a set molecular orbitals and orbital energies for the α spin electrons and a set of molecular orbitals and orbital energies for the β electrons. The UHF has one setback. A single Slater determinant of different orbitals for different spins is not a satisfactory eigen function of the total spin operators, S^2 . The ground state is contaminated by excited states. If there is one more electron of α spin than β spin, the ground state is a doublet. The average value of S^2 i.e. $\langle S^2 \rangle = \frac{1}{2} \left(\frac{1}{2} + 1 \right) = 0.75$, but will actually be rather more than this value as the doublet state is contaminated by a quadruplet state. A triplet state with two excess α electrons should have $\langle S^2 \rangle = 1(1 + 1) = 2$, but it will be larger as the triplet state is contaminated by a quintuplet state. When carrying out UHF calculations, it is always necessary to check this contamination. For example, with a doublet state, if $\langle S^2 \rangle = 0.8$ or less, it is probably satisfactory. If it is 1.0 or so, it is certainly not satisfactory and the calculation should be rejected, then a different approach taken.

An efficient QMC variant is the variational QMC method (VQMC). Here the Rayleigh-Ritz quotient [29]

$$E = \frac{\langle \psi_T | H | \psi_T \rangle}{\langle \psi_T | \psi_T \rangle} = \frac{\int \psi_T^2 \frac{H\psi_T}{\psi_T} d\tau}{\int \psi_T^2 d\tau} \quad (2.4)$$

is evaluated with Monte Carlo integration. The energy E is variational: $E \geq E_0$. Usually, but not necessarily, ψ_T^2 is sampled with the Metropolis algorithm [30]. In this form, VQMC was first used by Conroy [31] for small molecules and by McMillan [32] for the ground state of liquid helium. In the current VQMC applications, the generalized Metropolis algorithm [33] is used, thereby allowing directed finite time steps such as diffusion step from the importance-sampled DQMC algorithm. This not only increases the efficiency of the VQMC method considerably, but it also makes DQMC and VQMC algorithms very similar, with VQMC being more efficient and less accurate. Because of its efficiency, VQMC is the method used for the largest QMC applications. In electronic-structure calculations, the trial function ψ_T is often of the same form as the guide function ψ_G in DQMC.

2.3 The Diffusion Quantum Monte Carlo (DQMC) Technique

The most widely used QMC method in Chemistry and Physics is the diffusion QMC method DQMC [22,34,35]. It is based on the mathematical equivalence of the time-dependent Schrödinger equation in imaginary time $\tau = it$:

$$\frac{\partial \psi(r, \tau)}{\partial \tau} = \frac{1}{2m} \nabla^2 \psi(r, \tau) - V(r) \psi(r, \tau), \quad (2.5)$$

with a generalized diffusion equation

$$\frac{\partial c(r, \tau)}{\partial \tau} = D \nabla^2 c(r, \tau) - k(r) c(r, \tau), \quad (2.6)$$

Here D is identified as the diffusion constant in Fick's second law and $k(r)$ as the position-dependent rate constant of a first-order rate equation. Fermi not only noticed the equivalence between Schrödinger's equation and the diffusion equation, but suggested also that a random walk in which a particle diffuses and simultaneously multiplies based on the rate constant would eventually give the ground-state wave function [36]. Fermi's conclusion is seen from the formal solution of the Schrödinger equation of (1.1) as follows [29]:

$$\psi(r, \tau) = e^{-\tau H} \psi(r, 0), \quad (2.7)$$

where
$$H = -\frac{1}{2m} \nabla^2 - V(r). \quad (2.8)$$

After expanding the initial wave function in eigen-functions of H ,

$$\psi(r, 0) = \sum_i a_i \Phi_i, \quad (2.9)$$

the time-dependent solution is obtained in terms of eigen-functions

$$\psi(r, \tau) = \sum_i a_i e^{-E_i \tau} \Phi_i, \quad (2.10)$$

The contributions for a positive real τ , from higher states decay exponentially causing the states with the larger eigenvalues to decay away, leaving the state with the smallest eigenvalue (i.e., the ground state) after long τ . When a random walk satisfying the diffusion equation is constructed, the ground-state wave function is obtained exactly after a sufficiently long time, as a distribution of random walkers. Quantum mechanical expectation values can be obtained as

statistical expectation values. The importance sampling here is a technique used to improve the statistical accuracy of the simulation. To implement importance sampling, the exact wave function ψ is multiplied by a trial wave function ϕ_T to obtain a new function f [37,38]

$$f(r, \tau) = \phi_T(r)\psi(r, \tau) \quad (2.11)$$

In this form, the DQMC method can be applied to obtain zero-point energies and ground-state wave functions of vibrational Schrödinger equations. When this method is applied to electronic-structure problems, two difficulties are met; the Coulomb singularities in the electronic Hamiltonian prohibit an efficient simulation of the rate part, and the Pauli principle leads to nodes in the wave function for the ground state of systems with more than two electrons.

The first problem is solved with an importance-sampling transformation of the original Schrödinger equation [37], in which a guide function ψ_G is introduced that guides the random walk towards regions where ψ_G is large. The random walk then consists of a diffusion step as before, a new drift step with a velocity $\nabla \psi_G / \psi_G$, and a reaction term with the rate constant now $E = H\psi_G / \psi_G$ [39].

The second problem, the node structure of the physical ground-state wave function, is a manifestation of the general fermion sign problem. An approximation to the true ground state is obtained when the nodes of a nodal function are imposed on the random walk—the FN-DQMC [40]. Usually, a fixed-node (FN) energy is variational, that is, $E_{FN} \geq E_0$. Typically, the importance-sampling guide function ψ_G serves also to define the nodes. If ψ_G satisfies the Pauli principle, then so too will the FN-DQMC solution ψ_0 . A more accurate, but less efficient solution can be obtained in principle when the nodes are released from their fixed locations in released node QMC [41].

The error caused by the fixed-node approximation is smaller when the guidefunction is closer to the exact ground-state function. In many DQMC calculations, ψ_G is of the form

$$\psi_G = e^U \sum_k c_k \det(\phi_k), \quad (2.12)$$

where $\det(\phi_k)$ is a Slater determinant of HF or local density approximation (LDA) orbitals and U is a “Jastrow” term, depending explicitly on the electron-electron distances

$$U = U \left[(r_{ij}) \right], \quad (2.13)$$

with $r_{ij} = |r_i - r_j|$, to satisfy the electron cusp condition. Because the dynamic electron correlation is accounted for by e^U , one or only a few determinants in ψ_G are used. The parameters of U are optimized by variance minimization with Monte Carlo methods [31]. With guide functions of this type, >90% of the correlation energy is routinely obtained with FN-DQMC.

3.0 Computational Procedures

The CASINO code used in this work was run on a Linux based operating system (Ubuntu environment) having a working Fortran 90 compiler.

In this work, the CASINO code simulations was generated for a dual purpose, and thereby used for calculating the ground state energies of hydrogen and helium molecules by either VQMC or DQMC, or both at once, with the time step (for dtmc) set at 0.003. The VQMC step is an input parameter to the DQMC, corresponding to the total number of particle configurations for which the energy is calculated. The correlated wave-function from VQMC is then optimized by DQMC using the variance minimization method to obtain an efficient and more accurate convergence of the energy.

4.0 Results and Discussion

4.1 Hydrogen Molecule

The DQMC steps generated from the optimized VQMC steps (which serve as an input to the DQMC simulation) give rise to new configurations of electrons and nuclei at each move and because of the difference in inter-particle separation, the energy value of each of these configurations will be different. The correct expectation value of the energy (for each of the molecules in this work) is the average energy of thousands of these configurations.

Figure 1, Figure 2 and Figure 3, show the graphical results of a DQMC run for a hydrogen molecule, generated from 100,000 configurations. The number of equilibration steps underwent is 2000 moves, at an imaginary time-step set to 0.003. The simulation took 10000 line of data between accepted configurations, and gave the best estimate of effective

time-step to be 0.00299903. The ground state energy from the output file is obtained at 8.30688737a.u. (which is the maximum distance from origin), with an acceptance ratio of 99.973% which is in good agreement as predicted by Equation (2.12) and Equation (2.13).

The results presented in Figure 1 and Figure 3 show that the more the DQMC steps simulated, the smaller the error bar, and the more likely that the calculated energy will be closer to the exact ground state value, and this value obtained was in close agreement with the exact value [4]. The corresponding ground state energy is obtained with an error-bar as $[-1.17456(7) \pm 0.000172(6)]a.u.$ for Hydrogen molecule using DQMC method.

Again at the same time-step of 0.003, a VQMC run was done for the hydrogen molecule and the ground state energy obtained with an error – bar is $[-1.1697(8) \pm 0.00406(7)]a.u.$ and with an acceptance ratio of 60.867%.

Nevertheless, the energy convergence in both cases was reached at a point when the continual increase in the DQMC steps and VQMC steps did not result in any significant further increase in the energy of the hydrogen molecule as shown in Figure 1 and Figure 2. The CASINO simulations from the DQMC method show a significant improvement towards the exact value over the VQMC method in Figure 2; and this could be attributed to the stochastic gradient approximation method used in DQMC. The energy difference between the calculated VQMC / DQMC method (from CASINO code) and the exact ground state energy obtained from Green’s Function Monte Carlo (GFMC) [42] and diffusion Monte Carlo by applying the non-restricted method is 0.0116 Hartree. Another observation from the graphs is that the ground state energy was obtained at a maximum distance of 8.31a.u. from the origin, which falls within the limits of the theoretically obtained values; this indicates greater intensity of the lowest energy levels from configuration to equilibration at a small inter-particle distances.

The results of the ground state energy calculated here for both DQMC and VQMC techniques are in agreement with the work of other researchers shown in Table 1.

Table 1: Comparative analysis of the ground state energies for the hydrogen molecule calculated by different researchers

S / No	Author / Reference	Technique/ Method	GSE (a.u.)
1	Kolos & Wolniewicz [4]	Exact value (BO Approx.)	-1.1744
2	Traynor, Anderson & Boghosian [42]	DQMC / GFQMC (Non-Restricted)	-1.1630
3	Chen & Anderson [1]	GFQMC (Non-Restricted)	-1.1728
4	K. W. Ho [43]	VMC / DMC (BO)	-1.1750
5	D. Martin [21]	VMC / GFMC	-1.1660
6	Suleiman & Ewa [2]	VQMC / PIMC (BO)	-1.1736
7	Ebomwonyi et al [20]	VMC CASINO code (UHF)	-1.1680
8	This work	VQMC (CASINO-code)	-1.1697
9	This work	DQMC (CASINO-code)	-1.1746

GSE = Ground State Energy
1 a.u. = 27.2eV

From the output file the results of the acceptance ratios of 99.97% (for DQMC) and 60.87% (for VQMC) implies an improved stability in the ground state energy in the use of DQMC over VQMC methods. This indicates that the chosen time-step does not limit the number of accepted Monte Carlo moves.

Figure 3 presents the reduction in the reblocked error-bar as the reblocking transformation number (RTN) is increased. However, the standout points in the graph may be due to inclusion of unequilibrated data in the final averaged data which will give a systematic bias to the averages obtained [44].

Figure 4 is a graphical representation of a plateau showing the statistical accuracy of the standard deviation of error-bar at an increased block length. This result indicates that, for large enough blocks, there should be a distributed constant value, which is the true standard error in the mean. It also indicates that the absence of a plateau would be a result of insufficient data to estimate the standard error in the energy estimate [45]. Hence, as more configurations are included, the sampling is improved.

4.2 Helium Molecule

A VQMC CASINO code simulation was done for helium molecule with 40000 configuration steps, and a move of 500 equilibration steps at a time-step of 0.1 second. The number of attempts before accepted move is 3. The VQMC output file gives an acceptance ratio of 53.3% with a variance of local energy $(0.00573 \pm 0.000045)a.u.$ The local energy is discontinuous at cutoff, and the ground state energy was obtained at a maximum distance of 11.338a.u. from the origin.

DQMC run for a helium molecule was again generated from 100,000 configurations at an imaginary time-step set to 0.01 second. The number of attempts before accepted move is 4. The best estimated effective time-step from the output is 0.009949 second. The ground state energy from the output file is obtained at 10.94a.u. which is the maximum distance from origin, with an acceptance ratio of 99.64% which is in good agreement as predicted by Equation (2.12) and Equation (2.13). The ground state energies are calculated with an error-bar for DQMC method as $[-5.808 \pm 0.00005451]a.u.$ and VQMC method as $[-5.8067 \pm 0.0004811]a.u.$ for Helium molecule and compared with other results as shown in Table 2.

Table 2: Comparative analysis of the ground state energies for the diatomic helium molecule calculated by different researchers

S / No	Author / Reference	Technique/ Method	GSE (a.u.)
1	Atkins [46]	Experiment	-7.1400
2	Schiff & Verlet [15]	Variational wave-function	-5.9500
3	Østgaard [47]	Brueckner theory	-5.9000
4	Pokrant [48]	Molecular-dynamics	-6.6300
5	This work	VQMC (CASINO-code)	-5.8067
6	This work	DQMC (CASINO-code)	-5.8080

Figure 5 and Figure 6 present the graphs of the ground state energy of the helium molecule calculated using CASINO code at maximum distances from their origin. The results from the graphs obtained show a fast convergence of the configuration moves to the ground state energy in using the DQMC method over the VQMC method. This indicates that when the number of configuration is few, the equilibration stage will take longer than usual. The observations from the graphs show that the energy in Figure 5 converges at a maximum distance of 10.94 a.u. for DQMC at an effective time of 0.009949 seconds, while in Figure 6; it converges at a maximum distance of 11.34a.u. from the origin for the VQMC method at a VQMC_time-step optimization of 1 second. Just like in the case of the hydrogen molecule discussed above, this is an indication that in DQMC calculations, a systematic time-step error which is always present may be due to the approximation used for the Green's function. Another observation is that the possible changes in wave-function quality as the system size and geometry changes may be causality to the systematic error.

Figure 7 is the combination of Figures 5 and 6, showing significant improvement in calculation from DQMC method towards the exact energy value over the VQMC method. The observed energy difference from Figure 7 is 0.0013 a.u., and it could be attributed to the stochastic method used in DQMC.

The diffusion quantum Monte Carlo (DQMC) method simulates the time-dependent Schrödinger equation, and thus eliminates the problem of finite time step error, by replacing it with a small cutoff of the repulsive potential at small distances necessary for the stability of the algorithm. Just as the DQMC method converges to the exact answer only in the limit of small time step, it has also been used for treating several excitonic systems involving coupled nuclear and electronic motion without the Born-Oppenheimer approximation [23,25,50].

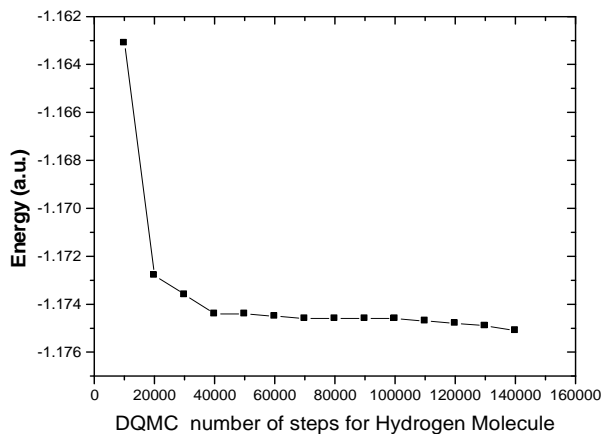


Fig. 1: Graph of Ground State Energy versus DQMC number of steps for H₂ molecule.

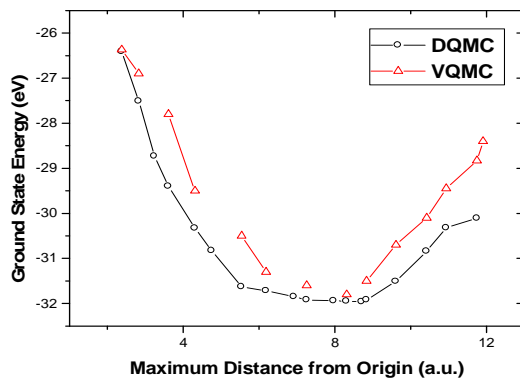


Fig. 2: Graph of Ground State Energy versus Maximum Distance from Origin for VQMC and DQMC for H₂ molecule.

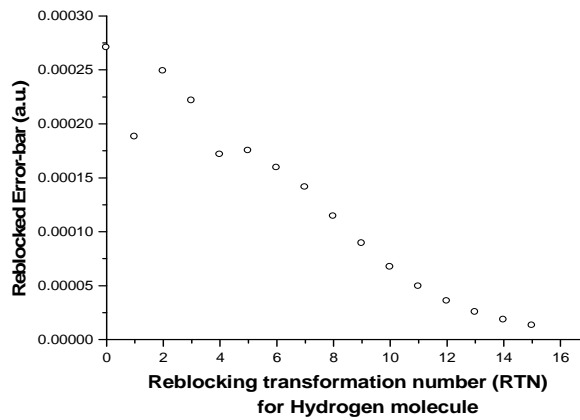


Fig. 3: Graph of Reblocked Error – bar versus Reblocking transformation number (DQMC) for H₂ molecule.

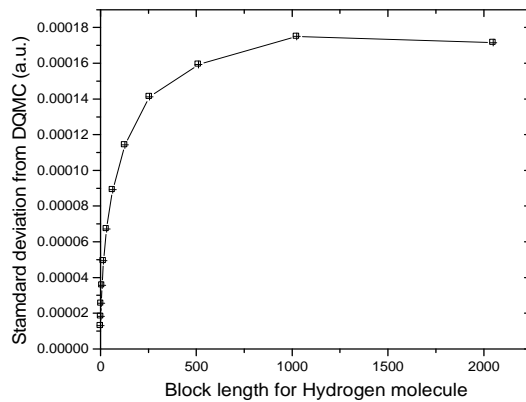


Fig. 4: Graph of Standard Deviation (DQMC) versus Block Length for H₂ molecule.

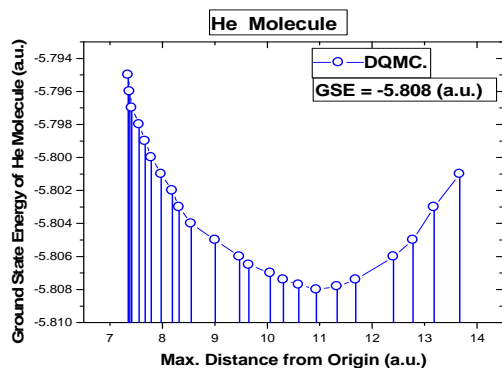


Fig. 5: Graph of Ground State Energy versus DQMC Maximum Distance from Origin for He molecule.

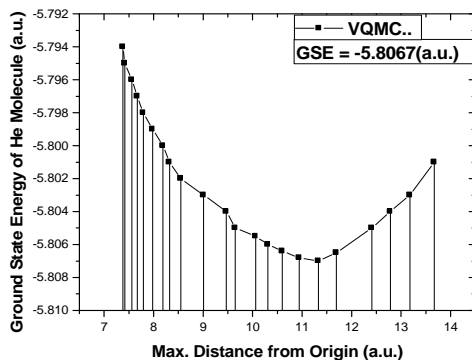


Fig. 6: Graph of Ground State Energy versus VQMC Maximum Distance from Origin for He molecule.

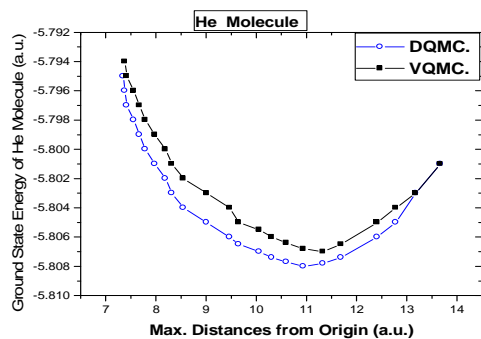


Fig. 7: Graph of Ground State Energy versus (VQMC and DQMC) Maximum Distance from Origin for He molecule.

5.0 Conclusion

We have combined in this work, variational and diffusion quantum Monte Carlo techniques under the restricted Hartree–Fock (RHF) scheme using quantum Monte Carlo CASINO-code simulations to calculate the ground state energies of hydrogen and helium molecules taking into account their maximum distances from origin. These calculations yield the total energies for the ground state of the two molecules including their coulomb interaction and local electron-ion energy. The result for the ground state energy of the hydrogen molecule using the DQMC method was in good agreement with the exact value. However, the result for that of the helium molecule, though close to the results of other authors has a significant difference from the experimental value. This could be as a result of the instability of the diatomic molecular helium.

Acknowledgements

We have benefited from the exchange of ideas, materials and results with other colleagues, to all of whom we offer our thanks. We thank Richard Needs, Mike Towler, Neil Drummond and Pablo López Ríos, of the Theory of Condensed Matter Group, Cavendish Laboratory, J. J. Thomson Avenue, Cambridge, UK, for the release of the CASINO-code. Acknowledgement goes also to Dr. Silas N. Umoh, of the University of Leeds, UK, for his constructive criticisms.

References

- [1] B. Chen and J. B. Anderson, "Improved quantum Monte Carlo calculation of the ground-state energy of the hydrogen molecule", *J. Chem. Phys.* **102** (7), 2802–2805, (1995).
- [2] A. B. Suleiman and I. O. B. Ewa, "Numerical calculations of ground state energy of H₂ molecule using quantum Monte Carlo methods", *Journal of the Nigerian Association of Mathematical Physics*, Volume 16, Pp. 1, 45 – 49, (2010).
- [3] H. M. James and A. S. Coolidge, *Journal of Chem. Phys.* **1**, 825 (1933).
- [4] W. Kolos and L. Wolniewicz, "Improved Theoretical Ground State Energy of the Hydrogen Molecule", *Journal of Chem. Phys.* **49**, 404, (1968).
- [5] K. Hong, Y. Kawazoe, and H. Yasuhara, "Diffusion Monte Carlo Study of Correlation in the Hydrogen Molecule", *Int. Journal of Quantum Chem.* Vol. 107, 1459 – 1467, (2007).
- [6] B. Militzer, Path integral Monte Carlo and density functional molecular dynamics simulations of hot, dense helium. *Physical Review B* **79**, Pp. 155105, (2009).
- [7] A. Drew and L. S. Cederbaum, *Chem. Rev.* **102**, 181 (2002).
- [8] W. Kolos and C. C. Roothaan, *J. Rev. Mod. Phys.* **32**, 219 (1960).
- [9] W. Kolos, *J. Chem. Phys.* **101**, 1330 (1994).
- [10] L. Wolniewicz, *J. Phys. B: At. Mol. Opt. Phys.* **32**, 2257 (1999).
- [11] H. H. Michels, *J. Chem. Phys.* **44**, 3834 (1966).
- [12] C. Urdaneta, A. Largo-Cabrerizo, G. C. Lie, and E. Clementi, *J. Chem. Phys.* **88**, 2091 (1987).
- [13] H. Yagisawa, H. Sato, and T. Watanabe, *Phys. Rev. A* **16**, 1352 (1977).
- [14] Ernest R. Davidson, Ground-State Potential Energy of Diatomic Molecules. *Journal of Chem. Phys.* **36**, 2527 (1962).
- [15] D. Schiff and L. Verlet, - Ground State of Liquid Helium-4 and Helium-3, *Phys. Rev.* **160**, 208 (1967).
- [16] H. Krüger, Ground-State Binding Energies of Three Identical Particles which interact via Three Mutual Morse Potentials, *Phys. Rev. Letts.* **28**, 71 (1972).
- [17] D. M. Ceperley: Path integrals in the theory of condensed helium. *Rev Mod Phys* **67**: 279 – 355 (1995).
- [18] J. P. Toennies, and A. F. Vilesov, Spectroscopy of Atoms and Molecules in Liquid Helium. *Annual Review of Physical Chemistry*, Vol. 49: 1 – 41 (1998).
- [19] A. Ferfon and P. Serra, Stability of two-electron diatomic molecules. *Journal of Physics B: Atomic, Molecular and Optical Physics*, **40**, Pp. 995–1002, (2007).
- [20] O. Ebomwonyi, E.E. Erukpere and O.E. Osunkwor: A Quantum Monte Carlo Calculation of the Ground State Energy for the Hydrogen Molecule Using the CASINO Code, *Int. Journal of Scientific and Engineering Research*, Vol. 4, Issue 6, 890-895 (2013).
- [21] D. Martin, "Computing the ground state energy of helium", M.Sc. Thesis, University of Manchester, (2007).
- [22] M. P. Nightingale, "in Quantum Monte Carlo Methods in Physics and Chemistry", Vol. **525** of NATO Advanced-Study Institute, Series C: Mathematical and Physical Sciences, (1999).
- [23] D. M. Ceperley and L. Mitas, "Quantum Monte Carlo Methods in Chemistry", University of Illinois at Urbana-Champaign, IL 61801, Pp. 1–8, 23–28, (1995).
- [24] C. C. J. Roothaan, Self Consistent Field Theory for Open Shell of Electronic Systems, *Rev. Mod. Phys.* **32** (2): 179 – 185 (1960).
- [25] M. A. Lee, P. Vashista, and R. K. Kalia, *Phys. Rev. Lett.* **129**, 2422, (1983).
- [26] V. Mohan and J. B. Anderson, *Chem. Phys. Lett.* **156**, 520 (1989).
- [27] J. A. Pople and R. K. Nesbitt, Self consistent orbitals for radicals, *The Journal of Chem. Phys.* **22** (3) 571 (1954).
- [28] G. Berthier, *Comptes rendus hebdomadaires des séances de l'Académie des sciences.* **238**: 91 – 93 (1954).
- [29] A. Lüchow and J. B. Anderson, Monte Carlo Methods in Electronic Structures for Large Systems. *Annual Review of Physical Chemistry*, Vol. **51**: 501 – 526 (2000).
- [30] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. M. Teller, and E. Teller, *J. Chem. Phys.* **21**: 1087 – 1092 (1953).
- [31] H. Conroy, *J. Chem. Phys.* **41**: 1331 – 1335 (1964).
- [32] W. L. McMillan, *Phys. Rev.* **138**: 442 – 451 (1965).
- [33] M. H. Kalos, and P. A. Whitlock, In *Monte Carlo Methods*, New York: Wiley, Pp. 73–86 (1986).
- [34] W. M. C. Foulkes, L. Mitas, R. J. Needs, and G. Rajagopal, Quantum Monte Carlo simulations of solids, *Review of Modern Physics*, Vol. **73**, No. 1, Pp. 33 – 42, (2001).
- [35] J. B. Anderson, *J. Chem. Phys.* **63**: 1499– 1503 (1975).

Journal of the Nigerian Association of Mathematical Physics Volume 28 No. 1, (November, 2014), 317 – 326

- [36] N. Metropolis and S. Ulam, *J. Am. Stat. Assoc.* **44**:335– 341 (1949).
- [37] R. C. Grimm, and R. G. Storer, *J. Comput. Phys.* **7**:134– 156 (1971).
- [38] M. H. Kalos, D. Levesque, and L. Verlet, *Phys. Rev. A* **9**,2178 (1974).
- [39] P. J. Reynolds, D. M. Ceperley, B. J. Alder, and W. A. Jr. Lester, *J. Chem. Phys.* **77**:5593– 5603 (1982).
- [40] J. B. Anderson, *J. Chem. Phys.* **65**:4121– 4127 (1976).
- [41] D. M. Ceperley, and B. J. Alder, *J. Chem. Phys.* **81**: 5833 – 5844 (1984).
- [42] C. A. Traynor, J. B. Anderson, and B. M. Boghosian, “A quantum Monte Carlo calculation of the ground state energy of the hydrogen molecule”, *J. Chem. Phys.* Vol. 94, **No 5**, Pp. 3657 – 3663, (1991).
- [43] Ko, Wing Ho, *Demonstrating quantum Monte Carlo methods in chemistry*, University of Illinois at Urbana-Champaign IL 61801 (2004).
- [44] P. R. C. Kent: *Techniques and Applications of Quantum Monte Carlo*, Ph.D – Dissertation at the University of Cambridge (1999).
- [45] R. J. Needs, M. D. Towler, N. D. Drummond, and L. P. Rios, *Theory of Condensed Matter Group*, Cavendish Laboratory, Cambridge, KU, CASINO User’s Guide Version 2.11.0. (2012).
- [46] K.R. Atkins: *Liquid Helium*, Cambridge University Press, Cambridge, England (1959).
- [47] E. Østgaard, *Solid helium. I. Ground-state energy and compressibility*, *Journal of Low Temperature Physics*, Volume **5**, Issue 2, Pp. 237 – 259 (1971).
- [48] M. A. Pokrant, *Ground-State Energy of Liquid He⁴*, *Phys. Rev. A* **6**, 1588 (1972).