A Quantum Monte Carlo Calculation of the Ground State Energy for the Hydrogen Molecule Using the CASINO Code.

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Abstract—*The quantum Monte Carlo (QMC), CASINO code was run to calculate the ground state energy for the hydrogen molecule. The variational Monte Carlo (VMC) technique was used, employing the unrestricted Hartree-Fock (UHF) method, instead of the restricted Hartree-Fock (RHF) method. By altering the VMC steps in the input parameters of the CASINO code, the best ground state energy for the hydrogen molecule was obtained to be (-1.168 ± 0.000059) a.u. differing by 0.006 a.u from the exact value.*

Keywords: CASINO code, VMC, UHF, RHF.

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1 INTRODUCTION

The calculation of the ground state energy for the hydrogen molecule has generated a lot of interest amongst researchers in the past. These researchers employed various techniques in tackling this problem. However, the history of accurate calculations of the ground state energy for the hydrogen molecule began with the 1993 work of James and Coolidge [1]. Their work represented one of the first successes in solving the Schrodinger equation for molecules. In the 1960's, more accurate results of the ground sate energy for the hydrogen molecules were obtained by Kolos and Roothan [2] and Kolos and Wolniewicz [3], who established the foundation for future calculations. They implemented a variational approach in which the wave function is expressed in elliptic coordinates, and using a method of Born [4], in which the Hamiltonian is separated into two parts viz:

$$H = H^0 + H^1 \qquad (1.1)$$

where H^0 is the electronic Hamiltonian including nuclear repulsion and H^1 is the Hamiltonian for the nuclear motion including coupling between the electrons and the nuclei.

When all known corrections were included, the best estimate of the discrepancies was -1.174 a.u as established by Kolos and Wolniewicz [3], which has been referred to be the exact value of the ground state energy for the hydrogen molecule [5].

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Some other researchers have tried to calculate the ground state energy for the hydrogen molecule by employing various methods. For instance, Traynor et al [6] employed the diffusion quantum Monte Carlo (DQMC)/Green's function quantum Monte Carlo (GFQMC) methods, Chen and Anderson [7] employed the Green's function quantum Monte Carlo (GFQMC) method and Ho [8] employed the variational Monte Carlo (VMC)/diffusion Monte Carlo (DMC) in the Born-Oppenheimer (BO) approximation method.

The QMC is a large class of computer algorithm that simulates quantum systems with the idea of solving the quantum many-body problem. They use in one way or the other the Monte Carlo method to handle the many-dimensional integrals that arise. 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.

In principle, any physical system can be described by the many-body Schrodinger equation;

$$i\hbar \frac{\partial \varphi}{\partial t} = H\varphi \qquad (1.2)$$

as long as the constituent particles are not moving 'too fast', that is, they are not moving near the speed of light. This covers a wide range of electronic problems in condensed matter physics. So, if we can solve the Schrodinger equation for a given system, we could predict its behavior.

Traditionally, theorists have approximated the many-body wave function as an anti-symmetric function of one-body orbital. This kind of formulation either limits the possible wave functions, as in the case of the Hartree-Fock (HF) approximation, or converges slowly, as in the configuration

interaction. One of the reasons for the difficulty with a HF initial estimate (ground state seed, also known as Slater determinant) is that it is very difficult to model the electronic and nuclear cusps in the wave function. However, one does not generally model at this point of the approximation.

QMC is a way around these problems because it allows us to model a many-body wave function of our choice directly. Specifically, we can use a HF approximation as our starting point, but then multiplying it by any symmetric function of which Jastrow functions are typical, designed to enforce the cusp condition.

2. METHOD

2.1 The CASINO Code

The CASINO code is a computer program package originally developed in Cambridge in the group of Needs and Towler [9, 10]. Its purpose is to perform quantum Monte Carlo electronic structure calculations for finite and periodic systems. Its development was inspired by a Fortran 77 development code written in the early 1990s in Cambridge [11]. This was later extended by other authors and various versions of this program were able to treat FCC solids, single atoms and the homogenous electron gas (HEG).

By late 1990s, it was clear that a modern and general code capable of treating arbitrary systems (at least atoms, molecules, polymers, slabs, crystals and electron phases) was required. So beginning in 1999, a new Fortran 90 code-CASINO was gradually developed. Some routines from the old code were retained, translated and reused. The philosophy behind this new code were generality, speed, portability, ease-of-use and transferability over a wide range of computational hard ware. Generality in this sense means that one ought to be able to create a trial wave function for any system, expanded in any of a variety of different basis sets and use it as input to a CASINO QMC calculation [12].

The most important current capabilities of CASINO are as follows:

   i.   It can do VMC calculations (including wave function optimization through minimization of the variance or the energy) and DMC calculations.

   ii.   It may be applied to finite system such as atom and molecules and also to system with periodic boundary conditions in one, two or three dimensions (polymers, slabs/surfaces, crystalline solids) with arbitrary crystal structure.

   iii.   Both ground and excited state energies may be computed.

   iv.   The code can compute expectation values of quantities other than the energy such as density, spin density, spin density matrix, pair-correlation function, localization tensor, structure factors and electric dipole moment etc.

2.2 The VMC Technique

The VMC technique was used in the CASINO code for the calculation of the ground state energy of the hydrogen molecule, by employing the UHF method over the RHF 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 [13] and then extended by other authors [14,15]. The RHF method for closed shell molecules, leads to Roothaan equations written in the form of a generalized eigen value problem.

$$FC = SC \in \qquad (2.1)$$

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 $\in$ is the matrix of orbital energies.

The UHF method is the most common molecular orbital method for open shell molecules where the number 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 [16, 17].

$$F^{\alpha}C^{\alpha} = SC^{\alpha} \in^{\alpha} \qquad (2.2)$$

$$F^{\beta}C^{\beta} = SC^{\beta} \in^{\beta} \qquad (2.3)$$

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, $\in^{\alpha}$ and $\in^{\beta}$ 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, S². 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 S² 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.

Despite this setback, the UHF method is used frequently and in preference to the RHF method because UHF is simple to code, easier to develop post HF methods with and returns unique function unlike RHF where different Fock operators can give the same final wave function [18].

The VMC employs the variational method in which case we must guess an appropriate many-electron wave function which is then used to calculate the energy as the expectation value of the Hamiltonian operator. In general, this wave function will depend on a set of parameters {α} which can be varied to optimized the function and minimize either the energy or the statistical variance. The energy thus obtained is an upper bound to the true ground state energy.

$$\frac{\langle \varphi_T(\{\alpha\}) | \widehat{H} | \varphi_T(\{\alpha\}) \rangle}{\langle \varphi_T(\{\alpha\}) | \varphi_T(\{\alpha\}) \rangle}$$
$$= E(\{\alpha\}) \geq E_0 \qquad (2.4)$$

The expectation value of Hamiltonian $\widehat{H}$ with respect to the trial wave function φ_T can be written as

$$\langle \widehat{H} \rangle = \frac{\int E_L(R)\varphi_T^2(R)dR}{\int \varphi_T^2(R)dR}, \qquad (2.5)$$

Where R is a 3N dimensional vector giving the coordinates $(r_1, r_2, \ldots, r_N)$ of the N particles in the system, and

$$E_L(R) = \frac{\widehat{H}(R)\varphi_T(R)}{\varphi_T(R)} \qquad (2.6)$$

is known as the local energy.

For VMC however, it is clear that the choice of the trial wave function is particularly important as it directly determines the accuracy of the calculation. The answer will approach the true energy as we use better and better wave function. As the trial wave function approaches an exact eigen state, the local energy $\widehat{H}\varphi/\varphi$ approaches a constant, E, everywhere in configuration space and hence the variance approaches zero (zero variance principle). Through its direct influence on the variance of the energy, the accuracy of the trial wave function then determines the amount of computation required to achieve a specified accuracy. When optimizing wave function, one can therefore choose to use energy or variance as the objective function to be minimized.

The fact that arbitrary wave functions can be used is one of the defining characteristics of QMC. We do not need to be able to interpret the wave function analytically as it is done for instance in quantum chemistry methods with Gaussian basis function. We just need to be able to evaluate it at a point in the configuration space, i.e. if the electron and nuclei have certain fixed position in space, what is the value of the wave function? This being the case, we can use correlated wave functions which depend explicitly on the distances between the particles.

The most commonly used functional form is known as the Slater-Jastrow wave function [19]. This consists of a single Slater determinant (or sometimes a linear combination of a small number of them) multiplied by a positive-definite Jastrow correlation function which is symmetric in the electron coordinates and depends on the inter-particle distances. The Jastrow factor allows efficient inclusion of both long and short range correlation effects.

The basic functional form of the Slater-Jastrow function is

$$\varphi(X) = e^{J(X)} \sum_n c_n D_n(X) \qquad (2.7)$$

Where $X = (x_1, x_2 \ldots, x_N)$ and $x_i = \{r_i, \sigma_i\}$ denotes the space-spin coordinates of electron i, $e^{J(x)}$ is the Jastrow factor, c_n are coefficients, and $D_n(X)$ are Slater determinants of single particles orbitals,

$$D(X) = \begin{vmatrix} \varphi_1(x_1) & \varphi_1(x_2) & ... & \varphi_1(x_N) \\ \varphi_2(x_1) & \varphi_2(x_2) & ... & \varphi_2(x_N) \\ \vdots & & & \\ \varphi_N(x_1) & \varphi_N(x_2) & ... & \varphi_N(x_N) \end{vmatrix} \qquad (2.8)$$

The orbitals in the determinants are often obtained from self-consistent density functional theory (DFT) or HF calculations and are assumed to be products of spatial and spin factors,

$$\varphi_\alpha(x) = \varphi_\alpha(r)\delta_{\sigma,\sigma_\alpha} \qquad (2.9)$$

Where $\delta_{\sigma,\sigma_\alpha} = 1$ if $\sigma = \sigma_\alpha$ and zero otherwise.

The full Jastrow function that is typically used in CASINO, contained one and two electron terms and may be inhomogenous, i.e. depend on the distances of the electrons from the nuclei.

The CASINO code allows optimization of the coefficients of the determinants of multi-determinant wave function, various parameters in specialized wave functions used e.g. in electron-hole phases, and even the orbitals in the Slater determinant themselves.

Although 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. In practice therefore, 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 technique.

2.3 General Computational Requirements

(2.7)

The CASINO code works in a system that has;

- ❖ A LINUX based operating system or environment like the UBUNTU, which was used in this work
- ❖ A working Fortran 90 compiler

In this work, various runs were carried out for different values of VMC step, in order to determine the true ground state energy of the hydrogen molecule. This VMC step is an input parameter corresponding to the total number of particle configurations for which the energy is calculated.

3.0 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 a different energy. The correct expectation value of the energy is the average energy of thousands of these configurations.

The more VMC steps we do, the smaller the error bar, which is always associated with the energy and the more likely the energy calculated will be closer to the exact value. However, it got to a point where as the numbers of VMC steps were increased further; energy convergence was obtained, corresponding to (-1.1683 ± 0.000059)a.u. This is illustrated in the graph of Energy against VMC steps in Fig. 3.1. This value is in close agreement with the work of other researchers as presented in Table 3.1.
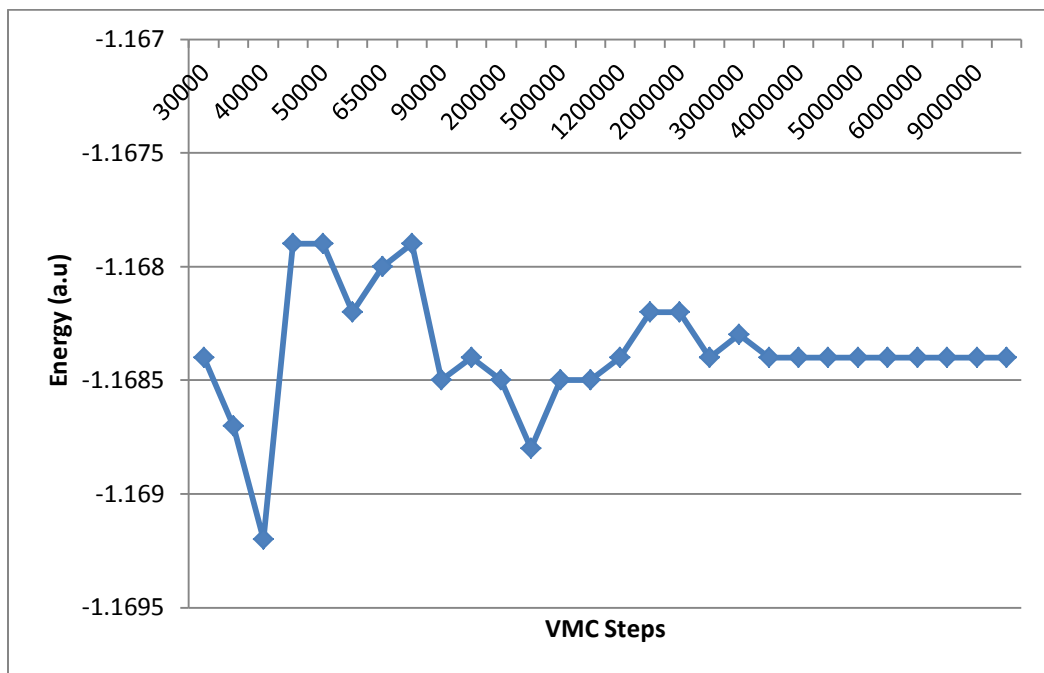
Fig. 3.1 Graph of Energy against VMC Steps

Table 3.1: Comparative analysis of the ground state energies for the hydrogen molecule by different researchers

S/N	Author/Reference	Technique/Method	GSE (a.u)
1	Kolos & Wolniewicz [2]	BO approximation	-1.174
2	Trgynor, Anderson & Boghosian [6]	DQMC/GFQMC	-1.163
3	Chen & Anderson [7]	GFQMC	-1.173
4	Ho [8]	VMC/DMC (BO)	-1.175
5	Suleiman & Ewa [20]	VQMC/PIMC (BO)	-1.174
6	This work	CASINO code	-1.168

GSE=Ground State Energy

1 a.u. = 27.2eV

3.0 CONCLUSION

The ground state energy for the hydrogen molecule was numerically calculated by running the QMC CASINO code, employing the VMC technique.

The higher the VMC steps that was run, the more the values of the energies get closer to the exact value. Convergence was reached at the point where the energy was   -1.1683a.u ± 0.00059. This is taken as the value of the ground state energy for the hydrogen molecule using the CASINO code.

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