



## VARIATIONAL QUANTUM MONTE CARLO CALCULATION OF THE GROUND STATE ENERGY OF HYDROGEN MOLECULE

<sup>1</sup>Suleiman\*, A.B. and <sup>2</sup>Ewa, I.O.B.

<sup>1</sup>Department of Physics Kano University of Science and Technology, Wudil P.M.B. 3244 Kano

<sup>2</sup>Center for Energy Research and Training, Ahmadu Bello University, Zaria

\*Correspondence author: Suleiman\_abdussalam@yahoo.com

### ABSTRACT

The ground state energy of the hydrogen molecule was numerically analysed using the quantum Monte Carlo (QMC) method. The type of QMC method used in this work is the Variational Quantum Monte Carlo [VQMC]. This analysis was done under the context of the accuracy of Born-Oppenheimer approximation [fixed nuclei restriction]. The ground state energies of Hydrogen molecule for different interproton separation  $\left(0.4 - 1.0 \text{ \AA}^0\right)$  are computed and compared with previous numerical and empirical results that are essentially exact. It has been found that the ground state energy of the hydrogen molecule obtained in this work approaches the precise value of  $-31.94\text{eV}$ .

**Keywords:** Monte Carlo, Ground, Energy, Hydrogen

### INTRODUCTION

The determinations of ground state energies for a molecular system constitute a reliable problem of interest in theoretical condensed matter physics. The method is based on solving the corresponding time-independent Schrödinger equation (TISE) and the

$$\hat{H}\psi(\{r\}) = E\psi(\{r\}),$$

where  $\psi$  represents wavefunction for the  $n^{\text{th}}$  electron,  $\{r\} = \{r_1, \dots, r_n\}$  represents the coordinates of the  $n^{\text{th}}$  electron,  $E$  is the eigen-energy and  $\hat{H}$  is the Hamiltonian.

The Hamiltonian which is simply represented as the total energy, summing the kinetic and potential energy can be written as

$$\hat{H} = \left( \sum_{i=1}^n -\frac{\hbar^2}{2m_e} \nabla_i^2 \right) + V(r) \tag{2}$$

It is not possible to obtain solutions to the Schrödinger equations analytically in many quantum systems even when the system contains only a few electrons. Instead numerical solutions to the Schrödinger equations are employed.

The numerical evaluation of the energies for  $\text{H}_2$  molecule started in 1933 with the work of James and Coolidge, (1933). Their work represented one of the first successes in solving the Schrödinger equation for molecules. After three decades more accurate results for the hydrogen molecule were obtained, for example by Kolos and Roothaan (1960) and also by Kolos and Wolniewicz (1968), this establishes the basis for further research. They implemented a variational approach in which the wave function is expressed in elliptic coordinates and using a method of Born.

Before the advent of quantum mechanics all numerical solutions so far obtained made use of

time-dependant Schrödinger equation (TDSE), where the fixed nuclear restrictions or the non fixed nuclear restrictions can be considered. In this work the fixed nuclear restrictions is considered. (Born-Oppenheimer Approximation)

The non relativistic TISE has the general form

1

classical approach to arrive at their conclusions which were based mainly on the application of mean field approximations. Calculations based on Hatree-Fock (HF) theory are examples. The fundamental ideology behind the mean field approximations is to consider each electron in isolation and to assume that the effects of its interaction with other electrons can be well approximated by the mean field produced by these other electrons. In a nutshell the electrons in the system are assumed to be uncorrelated. Therefore calculations of total energy that employ mean field approximations necessarily exhibit systemic errors, due to none inclusion of exchange and correlation effects, Ceperley and Mitas (1995). The quantum Monte Carlo techniques are a way of solving high dimensional effects in physics and chemistry without making mean-field approximations.

A quantum Monte Carlo technique calculates the energies of a molecular system by considering the wavefunction as probabilistic distribution and by random sampling them. A comparative analysis between quantum Monte Carlo methods and other mean-field methods can be found in Kent (1999).

The interest in refining the Schrödinger equation using Monte Carlo procedures was initiated with the work of Fermi (1928). In an attempt to describe that work, Metropolis and Ulam (1949) noted that the Schrödinger equation could be expressed as a diffusion equation and simulated by a system of particles undergoing a random walk in which there is a probability of multiplication of particles. With the subsequent advances in computer technology, Monte Carlo methods have more practical applications in calculating properties of atomic and molecular systems. The random walk methods have been applied to polyatomic ions, Traynor et al (1991) and molecules, Chen and Anderson (1995) using the importance sampling technique of Grimm and Storer (1971). Importance sampling has also been applied to the Green's function quantum Monte Carlo (GFQMC) method used by Kolos and Wolniewicz (1968).

In this work, the ground state energy of hydrogen molecule is numerically investigated using the variational quantum Monte Carlo (VQMC). We have chosen this case because there is an extensive data of accurate theoretical predictions and high quality empirical measurements of the ground state energies that could be compared with our results. Some of the results include the work of Traynor, et al (1991), Chen and Anderson (1995) and Ko, Wing Ho (2004) e.t.c.

The Variational Monte Carlo simulates the time-independent Schrödinger equation. The QMC methods

$$E_V = \frac{\int \psi_T^*(R) \hat{H} \psi_T(R) dR}{\int \psi_T^*(R) \psi_T(R) dR} \geq E_0 \quad 3$$

In a VQMC simulation this bound is calculated using the metropolis Monte Carlo method. Equation (3) can be written as;

$$E_V = \frac{\int |\psi_T(R)|^2 \left[ \psi_T(R)^{-1} \hat{H} \psi_T(R) \right] dR}{\int |\psi_T(R)|^2 dR}, \quad 4$$

and the metropolis is used to sample a set of points  $\{\mathbf{R}_m : m = 1, M\}$  from the configuration-space probability density

$$\rho(R) = \frac{\int |\psi_T(R)|^2}{\int |\psi_T(R)|^2 dR}. \quad 5$$

At each of these points the "local energy" is evaluated and the average energy accumulated is given by Traynor et al as

$$E_V \approx \frac{1}{M} \sum_{m=1}^M E_L(\mathbf{R}_m) \quad 6$$

have been used in different ways for treating several excitonic systems, Ceperley and Mitas (1995) involving coupled nuclear and electronic motion with or without the use of Born-Oppenheimer approximation. There also have been successful applications of QMC technique to the ground state energies in the following areas of research, Foulkes and Mitas (2001).

- a) the relativistic electron gas
- b) cohesive energies of solids
- c) phase of the electron gas
- d) Compton scattering in Si and Li

### The Variational Quantum Monte Carlo

The Variational Quantum Monte Carlo (VQMC) is based on the combination of the Variational principles and Monte Carlo evaluation of integrals. This method relies on the availability of an appropriate trial wavefunction  $\psi_T$  that is a reasonably good approximation of the true ground state wave function, Koonin and Meredith, (1990). The way to produce good trial wavefunction is described further in this review. The trial wavefunction must satisfy some fundamental conditions. Both  $\psi_T$  and  $\nabla \psi_T$  must be continuous wherever the potential is finite, and the

integrals  $\int \psi_T^* \psi_T$  and  $\int \psi_T^* \hat{H} \psi_T$  must exist. To keep the variance of the energy finite we also require

$\int \psi_T^* \hat{H}^2 \psi_T$  existing. The expectation value of  $\hat{H}$  computed with the trial wavefunction  $\psi_T$  provides an upper bound on the exact-ground state energy  $E_0$ , Ho (2004)

Optimization of Trial Wavefunction

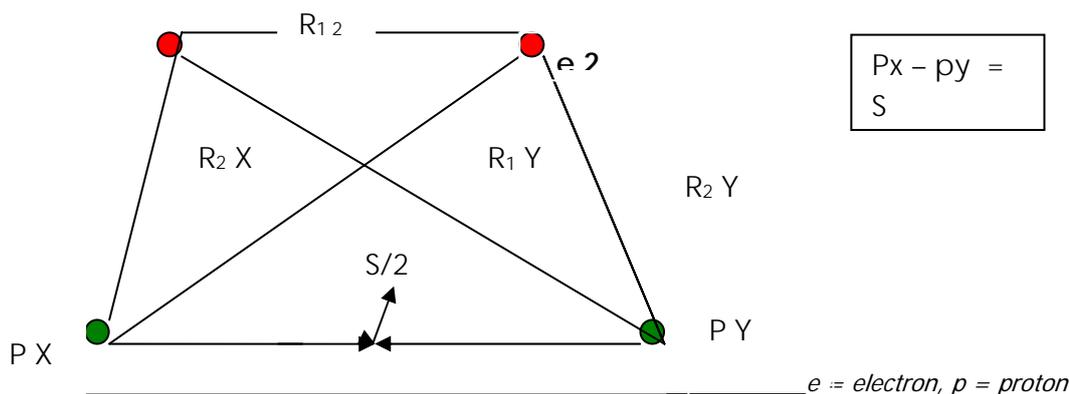


Fig.1 Coordinates used in describing the Hydrogen Molecule

The positions of the electrons and protons in fig 1 can be used to define the Hamiltonian and the trial wavefunction for the hydrogen molecule. Now considering equation (2) and setting  $\hbar = m_e = |e| = 1$ , where  $m_e$  and  $e$  are the mass and charge of electron respectively. The non-relativistic Hamiltonian based on Born-Oppenheimer approximation of the hydrogen molecule can be represented as:

$$\hat{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) + \left( \frac{1}{S} + \frac{1}{r_{12}} - \frac{1}{r_{1X}} - \frac{1}{r_{1Y}} - \frac{1}{r_{2X}} - \frac{1}{r_{2Y}} \right) \tag{7}$$

Where  $\nabla_1^2$  and  $\nabla_2^2$  are the laplacian with respect to the first and second electron and  $S$  is the interproton separation.

An appropriate trial wavefunction should respect all the symmetries in equation (7), therefore the trial wavefunction used in the non fixed nuclei restriction is the product of the four terms Chen and Anderson (1995)

$$\psi_0 = \psi_1 \psi_2 \psi_3 \psi_4 \tag{8}$$

Each of the first two terms is simply the linear combination of atomic orbital of electron

$l = 1, 2$  and for two nuclei  $\alpha = X, Y$

$$\psi_1 = \exp(-ar_{1X}) + \exp(-ar_{1Y}) \tag{9}$$

$$\psi_2 = \exp(ar_{2X}) + \exp(-ar_{2Y}) \tag{10}$$

The term  $\psi_3$  is the Jastrow factor which accounts for both electron-electron and electron-proton correlation such that the cusp condition are satisfied as  $r_{12}, r_{i\alpha} \rightarrow 0$  for  $l = 1$  or  $2$  and  $\alpha = X$  or  $Y$  and has the form

$$\psi_3 = \exp \left[ \sum_{ij} \frac{a_{ij}^{(0)} r_{ij}}{1 + b_{ij}^{(0)}} + \sum_{ijkl} \frac{a_{ijkl}^{(1)} r_{ij} r_{kl}}{1 + b_{ijkl}^{(1)} r_{ij} r_{kl}} \right], \tag{11}$$

where  $ij$  and  $kl$  include the interaction, 12, 1X, 1Y, 2X, and 2Y. Equation 11 can be reduced to

$$\psi_3 = \exp \left( \frac{br_{12}}{1 + br_{12}} \right) \tag{12}$$

The last term  $\psi_4$  in Equation (8) is the harmonic oscillator term intended to include in part the effect of nuclear interaction and it is given by

$$\psi_4 = \exp \left[ -d(r_{XY} - c)^2 \right] \tag{13}$$

The parameters  $a, b, c,$  and  $d$  made use of the following atomic unit respectively; - 1.1750, 0.500, 1.401 and 10.0 Traynor et al (1991). Equations (11, 12, and 13) are only valid when considering the non fixed nuclei restrictions i.e. a situation where the principle of Born-Oppenheimer approximation is not taking in to consideration, therefore taking the 12-D model. In this work the fixed nuclei restriction is

considered therefore the coulomb potential in its singular state at short distances constitutes an additional constraints on the trial wavefunction, if one of the electron (say 1) approaches one of the nuclei say X while the other electron remain fixed, the potential term in  $e_1$  becomes large and negative, since  $r_{iX} \rightarrow 0$ .

This must be cancelled by a corresponding positive divergence in the kinetic energy term if there is need to keep the wavefunction smooth and have a small variance in the Monte Carlo quadrature. Thus the trial

$$\lim_{r_{1X} \rightarrow 0} \left[ \frac{-\hbar^2}{2m} \frac{1}{\psi(r_{1X})} \nabla_1^2 \psi(r_{1X}) - \frac{e^2}{r_{1X}} \right] = \text{finite terms} \tag{14}$$

Similar conditions must also be satisfied whenever anyone of the distances  $r_{1Y}$ ,  $r_{2Y,X}$  or  $r_{1,2}$  vanishes. Using the correlated product of the molecular orbit and employing the Born-Oppenheimer approximation

$$f(r) = \exp\left(\frac{r}{\alpha(1 + \beta r)}\right) \tag{15}$$

Hence forth setting the value of  $\alpha$  to satisfy the transcendental equation

$$\alpha = \frac{1}{1 + e^{-S/a}}, \text{ and that } \alpha = 2a_0 \text{ where } a_0 = \frac{\hbar^2}{me^2} \text{ is the Bohr radius. Thus } \beta \text{ is the only variational parameter at our disposal.}$$

Conclusively the ideal way of making a plausible choice of the trial function is the correlated product of  $\Phi(r_1, r_2) = \psi_1 \psi_2 f(r_{12})$ .

The first two factors are an independent-particle wavefunction placing each electron in a molecular orbital in which it is shared equally between the two

$$\psi(r_i) = e^{-r_{iX}/\alpha} + e^{-r_{iY}/\alpha} \tag{17}$$

Putting (9), (10) and (15) in (16) a collection of a justifiable trial wavefunction is attained:

$$\psi(r_1, r_2) = \left( e^{-r_{1X}/\alpha} + e^{-r_{1Y}/\alpha} \right) \left( e^{-r_{2X}/\alpha} + e^{-r_{2Y}/\alpha} \right) \exp\left(\frac{r_{12}}{2(1 + \beta r_{12})}\right) \tag{18}$$

(18) is the collection of the trial wavefunction in which the **electron-electron cusp condition** is satisfied automatically by the factor  $\exp\left(\frac{r_{12}}{2(1 + \beta r_{12})}\right)$ , while the **electron-proton cusp condition** is satisfied by the

factor  $e^{-r_i/\alpha}$  and also by setting  $\alpha$  to satisfy the transcendental equation:

$$\alpha = \frac{1}{1 + e^{-S/a}} \tag{19}$$

**Algorithm of Metropolis**

One of the most effective and prominent way of producing random variables with a given probability distribution of arbitrary form is the algorithm of metropolis. Metropolis and Ulam, (1949)

Therefore Monte Carlo Methods described in the previous section utilizes the metropolis algorithm to evaluate multidimensional integrals. In high-dimensional spaces it is necessary to sample

- a) Start the walker at random position  $\mathbf{R}$ .
- b) Make a trial move to a new position  $\mathbf{R}'$  chosen from some probability density function  $T(\mathbf{R}' \leftarrow \mathbf{R})$ . after the trial move the probability that the walker initially at  $\mathbf{R}$  is now in the volume element  $d\mathbf{R}'$  is  $d\mathbf{R}' \times T(\mathbf{R}' \leftarrow \mathbf{R})$ .
- c) Accept the trial move to  $\mathbf{R}'$  with probability

$$A(\mathbf{R}' \leftarrow \mathbf{R}) = \text{Min}\left(1, \frac{T(\mathbf{R} \leftarrow \mathbf{R}')\rho(\mathbf{R}')}{T(\mathbf{R}' \leftarrow \mathbf{R})\rho(\mathbf{R})}\right)$$

wavefunction should have a "cusp" at  $r_{iX} \rightarrow 0$ . This implies that the molecular orbital should satisfy;

coupling with the factor that expresses the correlation between 2 electrons due to their coulomb repulsion as:

molecular orbitals and considering the case of fixed nuclei restriction:

protons. A simple choice for the molecular orbital is the symmetric linear combination of atomic orbitals centered about each proton,

complicated probability distribution. The normalization of these distributions is unknown and they cannot be sampled directly. The metropolis algorithm has the great advantage that it allows an arbitrary complex distribution to be sampled in a straight forward way without knowledge of its normalization. The metropolis algorithm works this way by moving a single walker according to the following steps:

If the trial move is accepted the point  $R'$  becomes the next point on the walk; if the trial move is rejected, the point  $R$  becomes the next point on the walk. If probability distribution  $\rho(R)$  is high, most trial moves away from  $R$  will be rejected and the point  $R$  may occur many times in the set of points making up the random walks.

d) Return to step b and repeat.

### The VQMC Code Procedure

The program in the above named code (Koonin and Meredith, 1990) is written in Fortran 77 and implements VMC to solve the two-center, two electron problem of the hydrogen molecule using the trial wavefunction specified by equation (18). The program calculates either the electronic eigenvalue (energy of the electrons) or the correlations in the energy of the electrons. As soon as the compilation and the execution are successful, equation (15) is solved for  $\alpha$  (subroutine **PARAM**) and the initial configuration (for VMC, subroutine **INTCFG**) is generated. The program commences by thermalizing the "walker" generated by the metropolis algorithm. The metropolis step for the Variational calculations are taken in the subroutine **METROP**, the method use functions **ELOCAL** to find the local energy and **Real Function PHI** to calculate the wavefunction for a given configurations. The users are required to input the variable factor of the interproton separation thereby setting the Variational parameters in the trial wavefunction. It also requires the user to input the metropolis step size. When thermalization is completed, it returns the percentage of accepted steps, which is useful in determining if the step size has to be modified. The next step after thermalization (initialization) is to generate an initial ensemble; therefore the metropolis algorithm already evaluated in the initialization is applied. After the generation of the ensemble the energy and the standard error in energy of that ensemble is calculated. This ensemble can also be written in to a separate file as requested in the program.

### RESULTS AND DISCUSSION

The lowest eigenvalue of the hydrogen molecule ( $E_0$ ) for different interproton separations were computed using the variational quantum Monte Carlo [VQMC] with respect to Born-Oppenheimer approximations. The results were presented graphically in Fig 1. These results were further compared with the exact values obtained by Kolos and Wolniewicz, (1968) which were

considered as the values obtained from the first principle analytical calculations. The results from fig 1 were obtained with the correlated sample of the trial wavefunction in equation (18). The numerical calculations from VQMC show some significant improvement towards the exact numerical results but a more improved method may be applied, this could involve the Path integral method that uses the stochastic gradient approximation approach which may yield a more accurate result.

Furthermore the results obtained in this work were already programmed to have the following units; the interproton separation is measured in Angstroms

$\left( \overset{0}{\text{A}} \right)$  and the ground state energy is measured in

electron volt (eV). Therefore during the course of comparison between other theoretical and empirical methods the following standard conversion rates were applied;

$$1 \text{ Bohr radius} = 0.529177249 \overset{0}{\text{A}}$$

$$1 \text{ Hartree} = -27.2 \text{ eV}$$

For every interproton separation input depending on the group of ensembles provided the group average ground state energy was calculated. The results obtained in this work are in agreement with the results obtained from the work of Ko, Wing Ho (2004) where a comparison of the ground state energy of hydrogen molecule between Variational Quantum Monte Carlo and Diffusion Monte Carlo (DMC) under the context of Born-Oppenheimer approximation was analysed. The DMC calculation almost gives the exact ground state energy of about -1.16 Hartree at about 1.4 Bohr radius of interproton separation. The result also approaches the accuracy of the work of Traynor, Anderson and Boghosian (1991) where they compare results obtained from Green's Function Monte Carlo and Diffusion Monte Carlo in calculating the ground state energy of the Hydrogen molecule without considering the fixed nuclei restriction.

Another observation from the graphs is that the ground state energy was obtained at an interproton

separation of about  $0.8 \overset{0}{\text{A}}$  which also falls in the range of the theoretically obtained values; this indicates a greater intensity of the lowest energies levels at very small interproton separations.

Graph of Ground State Energy Vs Interproton Separation (VQMC) for H<sub>2</sub> Molecule

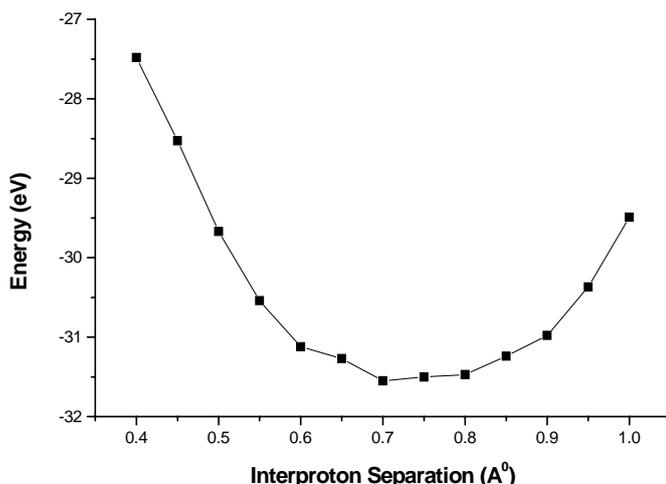


Fig 2: Ground state energy Vs Interproton Separation (VQMC) for H<sub>2</sub> molecule

### CONCLUSION

The ground state energy of hydrogen molecule at different interproton separation was numerically calculated under the principles of Born-Oppenheimer approximation using Monte Carlo technique i.e. the Variational Quantum Monte Carlo [VQMC] technique. The results in this work demonstrated that VQMC is capable of approaching the precise ground state

energy of the hydrogen molecule as it falls inside the error bars of previous empirical and numerical calculations obtained by Kolos and Wolniewicz (1968) which were considered as the values obtained from the first analytical principle calculations. The trial wavefunction have been optimized to suite the cusp condition of the electron-electron and electron-proton conditions.

### REFERENCES

- Ceperley D. M. and L. Mitas, (1995) "Quantum Monte Carlo Methods in chemistry" University of Illinois at Urbana-Champaign IL 61801. Chapter2 pp 6
- Chen, B. and J.B. Anderson (1995) "Improved Quantum Monte Carlo calculation of the ground state energy of the hydrogen molecule" J. Chem. Phys. 102, 7.
- E. Fermi, Z. Physik, **48**, 73 (1928)
- Foulkes, W. M. C and L. Mitas, (2001). "Quantum Monte Carlo simulations of solids" Rev. Mod. Phys. 73,
- Grimm, R. C. and R. G. Storer. (1971). J. Comp. Phys. 7, 134
- Ho, K. W. (2004) "Demonstrating quantum Monte Carlo methods through the study of hydrogen molecule" University of Illinois at Urbana-Champaign IL 61801
- James H. A. and A. S. Coolidge, (1933) J. Chem. Phys. **1**, 825
- Kent, P.R.C. "Techniques and application of Quantum Monte Carlo", PhD thesis, University of Cambridge, (1999)
- Kolos, W. and C.C J. Roothan, (1960) "Accurate electronic wavefunction for the hydrogen molecule" Rev. Mod. Phys.32. 219
- Kolos, W. and L. Wolniewicz, (1968) "Improved Theoretical Ground State energy of the Hydrogen Molecule," J. Chem. Phys. 49 404
- Koonin, S. E. and D. C. Meredith, (1990) "Computational physics Fortran version" Benjamin, Reading Revised Edition chapter 8 pp 221-230
- Metropolis, N. and S. Ulam (1949). J. Am. Stat Assoc 44, 335
- Miltzer, B. (2008) "Path Integral Monte Carlo and DF molecular dynamics simulations of hot dense Helium" Phys. Rev. B
- Traynor, C. A ,J. B. Anderson and B. M. Boghosian (1991) "A Quantum Monte Carlo calculations of the ground state energy of the hydrogen molecule" J. Chem. Phys. 94, 3657