

Numerical calculations of ground state energy of H₂ molecule using quantum Monte Carlo methods

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Abstract

The ground state energy of the hydrogen molecule was numerically analysed using quantum Monte Carlo methods. The QMC methods used in this work are the Variational Quantum Monte Carlo [VQMC] and the Path Integral Monte Carlo [PIMC]. 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 separations $\left(0.4 - 1.0 \text{ \AA}\right)$ are computed using the two different methods mentioned [VQMC and PIMC] and compared with previous numerical and empirical results that are essentially exact. The results from the Path Integral Monte Carlo methods of calculations are found to be precisely approaching the required order of accuracy.

Keywords: Quantum Monte Carlo Methods and Born-Oppenheimer approximation

1.0 Introduction

The determinations of the 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 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

$$\hat{H}\psi(\{r\}) = E\psi(\{r\}) \quad (1.1)$$

Where ψ represents wavefunction for the nth electron, $\{r\} = \{r_1, \dots, r_n\}$ represents the coordinates of the nth electron, E is the eigen-energy and \hat{H} is the Hamiltonian.

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

$$\hat{H} = \left(\sum_{i=1}^n -\frac{\hbar^2}{2m_e} \nabla_i^2 \right) + V(r) \quad (1.2)$$

While the imaginary time-dependant Schrödinger equation has the form

$$i\eta \frac{\partial \psi}{\partial t} = \hat{H} \psi, \quad (1.3)$$

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 ground state energies for H₂ molecule started in 1933 with the work of [1]. 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 by [2] and also by [3], 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 [6]

Before the advent of quantum mechanics all numerical solutions so far obtained made use of 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 numerical analysis that employ mean field approximations necessarily exhibit systemic errors.

As far as the scientific transition is from classical to quantum approaches therefore a remarkable difference is expected in employing the quantum approach. The quantum Monte Carlo techniques are a way of combining the quantum applications in physics and chemistry with Monte Carlo procedures to provide a means to evaluate the electronic properties of a molecular system without making mean-field approximations. A quantum Monte Carlo technique calculates the energies of a molecular system by considering the wavefunctions 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 [4].

The knowledge of refining the Schrödinger equation using Monte Carlo procedures initiated with the work of Fermi. In an attempt to describe that work, [7] 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 for calculating properties of atomic and molecular systems. The random walk methods have been applied to polyatomic ions [6] and molecules [8] using the importance sampling technique of [9]. Importance sampling has also been applied to the Green's function quantum Monte Carlo (GFQMC) method used by [3].

In this work the ground state energy of hydrogen molecule is numerically analysed using the quantum Monte Carlo methods i.e. the variational quantum Monte Carlo (VQMC) and the path integral Monte Carlo (PIMC). We have chosen this case because there is an extensive history 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 [6], [8] and [13] e.t.c.

The Variational Monte Carlo simulates the time-independent Schrödinger equation where as the Path Integral Monte Carlo simulates the time-dependant Schrödinger equation. It thus eliminates the problem of finite time step error, but replaces it by a cut-off of the repulsive potential at small distance necessary for the stability of the algorithm [6].

The QMC methods have been used in different ways for treating several excitonic systems [12] involving coupled nuclear and electronic motion with or without the use of Born-Oppenheimer approximation.

There also have been successful application of QMC technique to the ground state energies in the following areas of research [10];-

- (a) the relativistic electron gas
- (b) cohesive energies of solids
- (c) Static response of electron gas
- (d) Exchange and correlation energies
- (e) Jellium surfaces
- (f) Clusters

- (h) Solid hydrogen
- (i) Formation energies of silicon and self interstitials.

2.0 The methods (Quantum Monte Carlo Methods)

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 but this work focuses mainly on two: Variational quantum Monte Carlo (**VQMC**) which depends on the availability of an appropriate trial wavefunction to determine the ground state energy and the Path integral Monte Carlo (**PIMC**) which basically relies on the principles of superposition, this is because there are much recent researches that could be compared with the result of this work, and specifically considering the case of PIMC which is becoming very authentic nowadays in accurate determination of the ground state energy of a molecular system coupling with the fact that this method (PIMC) does not require a trial wavefunction in determining the ground state energy of a molecular system, instead it is principally based on the techniques of superposition. It has also been recommended by so many reviewers, i.e. [18], [8], [19], [10] e.t.c. that larger extensions would be to implement a Path Integral Monte Carlo method and investigate the difference in the ground state energy of molecular systems in order to arrive at a more precise value which will be approaching the empirical values.

Other QMC methods include the auxiliary-field QMC reviewed by [20], Diffusion Monte Carlo (DMC) reviewed by [13] in demonstrating quantum Monte Carlo methods through the study of hydrogen molecule, Green’s Function Monte Carlo (GFMC) reviewed by Chen and Anderson in Improved Quantum Monte Carlo calculation of the ground state energy of the hydrogen molecule[8], Coupled Electronic Ionic Monte Carlo reviewed by M.D. Dewing in describing Monte Carlo methods as applied to hydrogen gas and hard spheres [16], Trotter Suzuki Monte Carlo reviewed by J. S. Wang in demonstrating quantum Monte Carlo methods [17] etc.

2.1 Variational Monte Carlo method

The Variational Quantum Monte Carlo (VQMC) is the simpler of the two quantum Monte Carlo methods considered in this work. It 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 ψ_T that is a reasonably good approximation of the true ground state wave function.

The way to produce good trial wavefunction is describe further in this review. The trial wavefunction must satisfy some fundamental conditions. Both ψ_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 [5]. 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 ψ_T provides an upper bound on the exact-ground state energy E_0 :

$$E_v = \frac{\int \psi_T^*(R) \hat{H} \psi_T(R) dR}{\int \psi_T^*(R) \psi_T(R) dR} \geq E_0 \quad (2.1)$$

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

$$E_V = \frac{\int |\psi_T(R)|^2 \left[\psi_T(R)^{-1} \hat{H} \psi_T(R) \right] dR}{\int |\psi_T(R)|^2 dR}, \quad (2.2)$$

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

$$\rho(R) = \frac{\int |\psi_T(R)|^2}{\int |\psi_T(R)|^2 dR}. \quad (2.3)$$

At each of these points the “local energy” is evaluated and the average energy accumulated is given by

$$E_V \approx \frac{1}{M} \sum_{m=1}^M E_L(R_m). \quad (2.4)$$

2.2 The Path Integral Monte Carlo method

The path integral method was introduced by Feynman in 1948. It provides an alternative formulation of time-dependant Schrödinger equation. Since its inception the method has found innumerable applications in many areas in physics and chemistry [11], its main attraction can be summarized as follows: the method provides an ideal way of obtaining the classical limit of quantum mechanics: it provides a unified description of quantum dynamics and equilibrium quantum statistical mechanics : it avoids the use of wavefunction and thus is the only viable approach to many-body problems: and it leads to powerful influence functional methods for studying the dynamics of low-dimensional system coupled to a harmonic bath[15].

The path integral formulation is based on the principles of superposition, which leads to celebrated quantum interference observed in the microscopic world. Thus the amplitude for making a transition between two states is given by the sum of amplitudes along all the possible paths that connects these states in a specified time.

For a particle of mass m in one dimension, the amplitude to get from a point x_a at time t_a to point x_b at time t_b is expressed in the path formulations as a sum of contributions from all conceivable paths that connects these two points. The contribution of each path $x(t)$ is proportional to a phase that is given by the action functional $S[x(t)]$ along the path in units of Planck’s constant η :

$$K(x_b, t_b : x_a, t_a) \propto \sum_{\text{all paths } x_t} e^{iS[x(t)]} / \eta \quad (2.5)$$

$$\text{with } x(t_a) = x_a, x(t_b) = x_b$$

For a time-dependant Hamiltonian $H = T + V$, where T and V are kinetic and potential energy operators

$$\text{respectively, thus } K(x_b, t_b : x_a, t_a) \equiv \left\langle x_b \left| \exp\left(-\frac{1}{\eta} H(t_b - t_a)\right) \right| x_a \right\rangle = \left\langle x_b \left| \left(\exp\left(-\frac{1}{\eta} H \Delta t\right) \right)^N \right| x_a \right\rangle$$

(2.6)

Where $\Delta t \equiv (t_b - t_a) / N$ and N is an integer. Inserting complete set of position states one can obtains the identity

$$K(x_b, t_b : x_a, t_a) = \int_{-\infty}^{\infty} dx_1 - \int_{-\infty}^{\infty} dx_{N-1} \prod_{k=1}^N \langle x_k | \exp(-iH\Delta t / \eta) | x_{k-1} \rangle \quad (2.7)$$

where $x_0 \equiv x_a$ and $x_N \equiv x_b$

PIMC is mathematically similar to diffusion Monte Carlo [DMC] and shares many of the same advantages. In fact it goes further since a trial function is not specified and the method generates a quantum distribution directly from the Hamiltonian. Therefore we can define PIMC to be a QMC method which is formulated at a positive temperature. Instead of attempting to calculate the properties of a single quantum state, we sum over all possible states, occupying them according to the Boltzmann distribution. This might sound

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hopeless but, Feynman's imaginary time path integral [15] makes it almost as easy as DMC. The imaginary-time paths, instead of being open-ended as they

are in DMC, close after an imaginary time $\beta = (k_B T)^{-1}$, where T is the temperature. Also, PIMC seems to lead more easily to a physical interpretation of the result of a simulation. The path integral offers an insightful approach to time-dependant quantum mechanics and quantum statistical mechanics.

2.3 Optimizing the wavefunction

The positions of the electrons and protons in fig 1 can be used to define the Hamiltonian and the trial wavefunctions for the hydrogen molecule. Now considering equation (1.2) and setting $\eta = m_e = |e| = 1$, 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:

$$\hat{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) + \left(\frac{1}{S} + \frac{1}{r_{12}} - \frac{1}{r_{1X}} - \frac{1}{r_{1Y}} - \frac{1}{r_{2X}} - \frac{1}{r_{2Y}} \right) \quad (2.8)$$

Where ∇_1^2 and ∇_2^2 are the laplacian with respect to the first and second electron and S is the interproton separation.

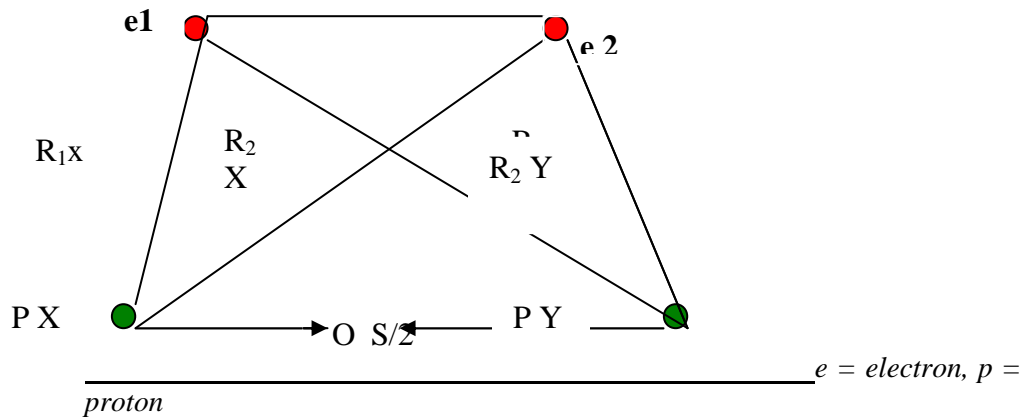


Fig.1 Coordinates used in describing the Hydrogen Molecule

An appropriate trial wavefunction should respect all the symmetries in equation (2.8), therefore the trial wavefunction used in the non fixed nuclei restriction is the product of the four terms:

$$\psi_0 = \psi_1 \psi_2 \psi_3 \psi_4 \quad (2.9)$$

Each of the first two terms is simply the linear combination of atomic orbital of the electron $I = 1, 2$ and for two nuclei $\alpha = X, Y$

$$\psi_1 = \exp(-ar_{1X}) + \exp(-ar_{1Y}) \quad (2.10)$$

$$\psi_2 = \exp(ar_{2X}) + \exp(-ar_{2Y}) \quad (2.11)$$

The term ψ_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 $I = 1$ or 2 and $\alpha = X$ or Y it has the form

$$\psi_3 = \exp \left[\sum_{ij} \frac{a_{ij}^{(0)} r_{ij}}{1 + b_{ij}^{(0)}} + \sum_{ij} \frac{a_{ijkl}^{(1)} r_{ij} r_{kl}}{1 + b_{ijkl}^{(1)} r_{ij} r_{kl}} \right], \quad (2.12)$$

Where i, j and k, l include the interaction, $12, 1X, 1Y, 2X,$ and $2Y$ the wavefunction in (2.12) can be reduced to

$$\psi_3 = \exp\left(\frac{br_{12}}{1+br_{12}}\right) \quad (2.13)$$

The last term ψ_4 is the harmonic oscillator term intended to include in part the effect of nuclear interaction and it is given by

$$\psi_4 = \exp\left[-d(r_{XY} - c)^2\right] \quad (2.14)$$

The parameters $a, b, c,$ and d made use of the following atomic unit respectively; - 1.1750, 0.500, 1.401 and 10.0 [8]

Equations (2.12, 2.13 and 2.14) are only valid when considering the non fixed nuclei restrictions 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 e_1) approaches one of the nuclei say X while the other electron remain fixed, the potential term in e

(electron) 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 e (electron) smooth and have a small variance in the Monte Carlo quadrature. Thus the trial wavefunction should have a "cusp" at $r_{iX} \rightarrow 0$.

This implies that the molecular orbital should satisfy;

$$\lim_{r_{iX} \rightarrow 0} \left[\frac{-\eta^2}{2m} \frac{1}{\psi(r_{iX})} \nabla_1^2 \psi(r_{iX}) - \frac{e^2}{r_{iX}} \right] = \text{finite terms} \quad (2.15)$$

Similar conditions must also be satisfied whenever anyone of the distances $r_{1Y}, r_{2Y,X}$ or r_{12} vanishes. Using the correlated product of the molecular orbit and introducing the factor that expresses the correlation between 2 electrons due to their coulomb repulsion as:

$$f(r) = \exp\left(\frac{r}{\alpha(1+\beta r)}\right) \quad (2.16)$$

Hence forth setting the value of α to satisfy the transcendental equation

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

parameter at our disposal.

Conclusively the ideal way of making a plausible choice of the trial function is the correlated product of molecular orbitals and considering the case of fixed nuclei restriction:

$$\Phi(r_1, r_2) = \psi_1 \psi_2 f(r_{12}) \quad (2.17)$$

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

$$\psi(r_i) = e^{-r_{iX}/\alpha} + e^{-r_{iY}/\alpha}, \quad (2.18)$$

Putting (2.18) and (2.16) in (2.17) a collection of a justifiable trial wavefunction is attained:

$$\psi(r_1, r_2) = \left(e^{-r_{1X}/\alpha} + e^{-r_{1Y}/\alpha} \right) \left(e^{-r_{2X}/\alpha} + e^{-r_{2Y}/\alpha} \right) \exp\left(\frac{r_{12}}{2(1+\beta r_{12})}\right) \quad (2.19)$$

(2.19) 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 α to satisfy the transcendental equation:

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$$\alpha = \frac{1}{1 + e^{-S/a}} \tag{2.20}$$

3.0 Computing the ground state energy of the hydrogen molecule

In hydrogen molecule there are two electrons shared by two nuclei as shown in fig 1, this can be simulated using quantum Monte Carlo methods discussed in this review. In this work the protons are held in a fixed position (B-O approximation) so that the bond made by the electrons can be simulated. The potential regulating the protons' motion at a separation S , is then the sum of the interproton electrostatic repulsion and the eigenvalue, E_0 , of the two-electron Schrödinger equation:

$$U(S) = \frac{e^2}{S} + E_0(S) \tag{3.1}$$

Where e is the coulombic repulsion and E_0 is the ground-state energy eigenvalue of the two electron system. Thus the ground state energy E_0 can be found by solving the corresponding 6-D Schrödinger equation:

$$H(S)\psi_0(r_1, r_2; S) \equiv [K + V(S)]\psi_0 = E_0(S)\psi_0(r_1, r_2; S) \tag{3.2}$$

$$\begin{aligned} &= -\frac{\hbar^2}{2m} \sum_{i=1}^2 \nabla_i^2 \psi(r_1, r_2; S) + V(r_1, r_2; S)\psi(r_1, r_2; S) \\ &= E_0(S)\psi_0(r_1, r_2; S) \end{aligned} \tag{3.3}$$

Where m is the mass of an electron and r_i is the position of the i th electron and $V(r_1, r_2; S)\psi$ is the only Coulomb force in the potential $V(\mathbf{R})$ therefore,

$$V(\mathbf{R}) = V(r_1, r_2; S)\psi = e^2 \left[\frac{1}{r_{12}} - \frac{1}{r_{1L}} - \frac{1}{r_{1R}} - \frac{1}{r_{2L}} - \frac{1}{r_{2R}} \right] \tag{3.4}$$

Where r_{ij} are distances between particles as labelled in fig 1 and \mathbf{R} is the 6-D configuration vector, and encompassing the two 3-D particle position r_1 and r_2 , an appropriate class of trial function evaluated as equation (2.3.12) was used, where $\phi(r_i)$ is an independent particle wavefunction, and $f(r_{12})$ is the term that deals with the correlations between the two electrons due to their Coulomb repulsion, $a, \alpha,$ and β are variational parameters. Because the wavefunction is required to meet the Coulomb 'cusp' conditions, it is found that $\alpha = 2a_0$ (where a_0 is the Bohr radius), and α satisfies the transcendental equation (2.3.13): this can easily be solved numerically, to the required degree of accuracy, using the Newton Raphson method, leaving only a single variational parameter β . After a series of algebra the local energy is found to be:

$$E_L(\mathbf{R}) = -\frac{1}{2} \sum_{i=1}^2 \left[\frac{2}{r_{12}\alpha(1+\beta r_{12})^3} + \frac{1}{a^2} + \frac{1}{\alpha^2(1+\beta r_{12})^4} - \frac{2(e^{-r_{iL}/\alpha}/r_{iL} + e^{-r_{iR}/\alpha}/r_{iR})}{a(e^{-r_{iL}/\alpha} + e^{-r_{iR}/\alpha})} \right] + V(\mathbf{R}) \\ + \frac{(-1)^i . 2(e^{-r_{iL}/\alpha} \hat{r}_i L . \hat{r}_i 2 + e^{-r_{iR}/\alpha} \hat{r}_i R . \hat{r}_i 2)}{a\alpha(1+\beta r_{12})^2 (e^{-r_{iL}/\alpha} + e^{-r_{iR}/\alpha})} \tag{3.5}$$

3.1 The algorithm of the code

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The code is design to operate dual purpose i.e. it can be used to calculate the ground state energy of the hydrogen molecule by either using the variational quantum Monte Carlo techniques or the Path Integral Monte Carlo techniques whenever it is prompted to do so. The flowchart of this algorithm is illustrated overleaf: (figure 2)

Results and Discussion

4.1 Results

The lowest eigenvalue of the hydrogen H_2 molecule (E_0) for different interproton separations were computed using the variational quantum Monte Carlo [VQMC] and the Path Integral Monte Carlo [PIMC] methods with respect to Born-Oppenhiemer approximations. The results were presented graphically in Fig 3 and Fig 4 respectively. These two results were further accumulated in Fig 5 and compared with the exact values obtained

by [3] which were considered as the values obtained from the first analytical principle calculations. The results from fig 3 and 4 were obtained with the correlated sample of the trial wavefunction in equation (2.19). The numerical calculations from the PIMC method show a significant improvement towards the exact values over the VQMC, this could be attributed to the stochastic gradient approximation method used in PIMC.

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

$$\begin{aligned} 1 \text{ Bohr radius} &= 0.529177249 \text{\AA} \\ 1 \text{ Hatree} &= 27.2\text{eV} \end{aligned}$$

For every interproton separation input depending on the group of ensembles provided the group average ground state energy was calculated.

4.2 Discussions

The results obtained in this work are in agreement with the results obtained from the work of [13] where a comparison of the ground state energy of hydrogen molecule between Variational Quantum Monte Carlo and Diffusion Monte Carlo under the context of Born-Oppenhiemer approximation was analysed. The DMC calculation almost gives the exact ground state energy of about -1.16 Hatree at about 1.4 Bohr radius of interproton separation. The result also agrees with [6] 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 0.75\AA 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.

Table of comparative analysis of ground state energies of Hydrogen molecule calculated by other researchers at an interproton separation of 1.4 Bohr is shown in Table 1.

Table 1

S/N	AUTHOR/REFERENCE	DATE	TYPE	GSE (a.u)
1	Koloz & Wolniewicz [3]	1968	Exact (theory) BO Variational;	-1.1744
2	Traynor, Anderson & Boghosian [6]	1991	DQMC/GFQMC (Non Restricted)	-1.163
3	Chen & Anderson [8]	1995	GFQMC (Non restricted)	-1.1728
4	Ko, Wing Ho [13]	2004	VMC/DMC (BO)	-1.1750
5	This work	2010	VQMC/PIMC (BO)	-1.1736

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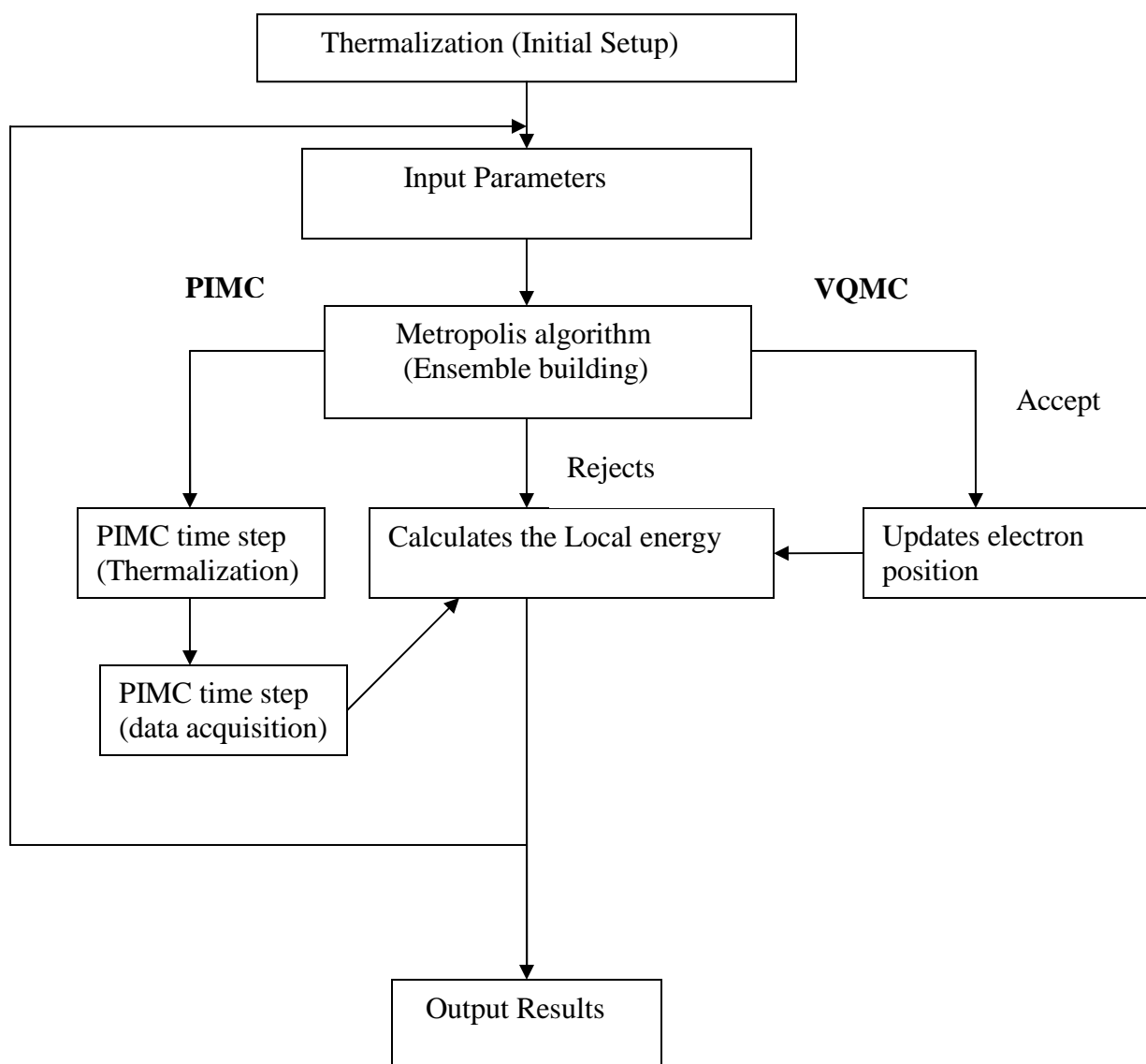


Figure 2

Intuitively the collection of the ground state wavefunction used in this work is expected to have a higher electron density in between the protons when the proton-proton separation is small as compared to the case

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when the proton-proton separation is large. This is due to the fact that when the proton-proton separation is small, it is energetically favourable for this class of wavefunction to locate both electrons in between the two protons as exhibited by the wavefunction.

Graph of Ground State Energy Vs Interproton Separation (VQMC) for H₂ Molecule

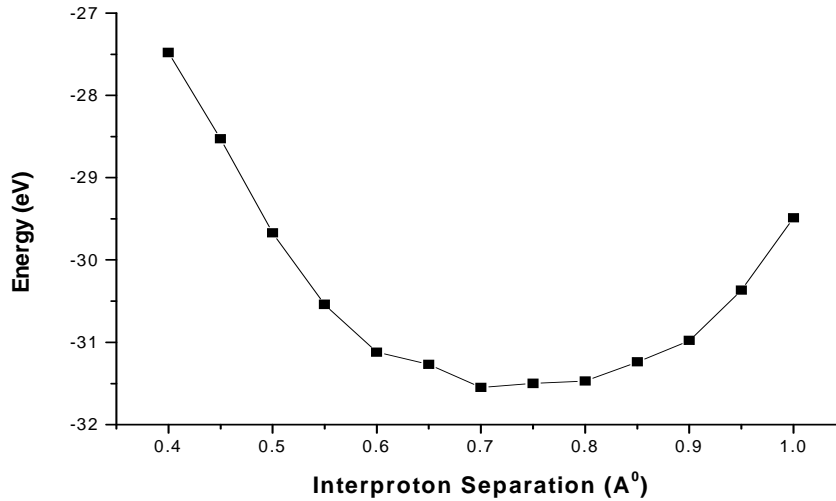


Fig. 3: Graph of Ground state Energy Vs Interproton Separation (VQMC) for H₂ Molecule

Graph of Ground State Energy Vs Interproton Separation (PIMC) for H₂ Molecule

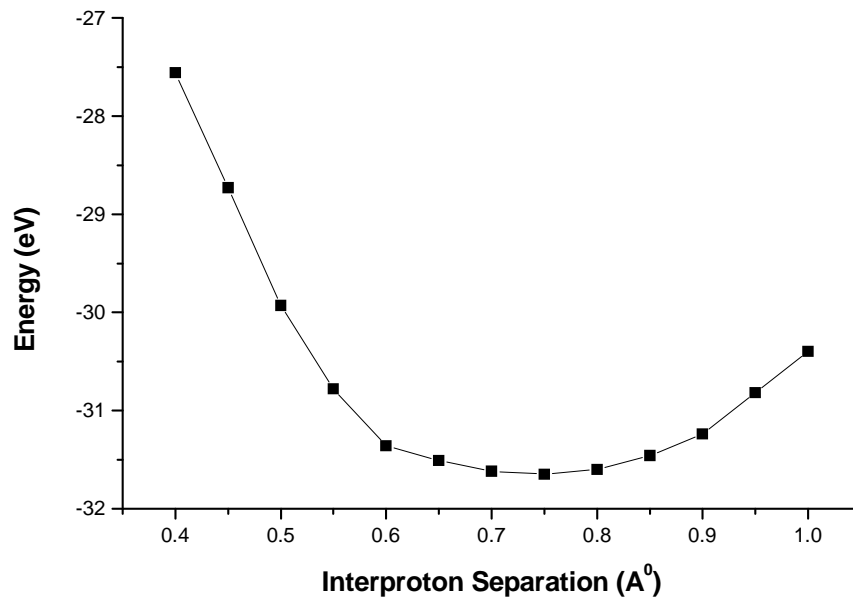


Fig. 4: Graph of Ground state Energy Vs Interproton Separation (PIMC) for H₂ Molecule

Graph of ground State Energy Vs Interproton Separation for VQMC and PIMC (H_2) Molecule

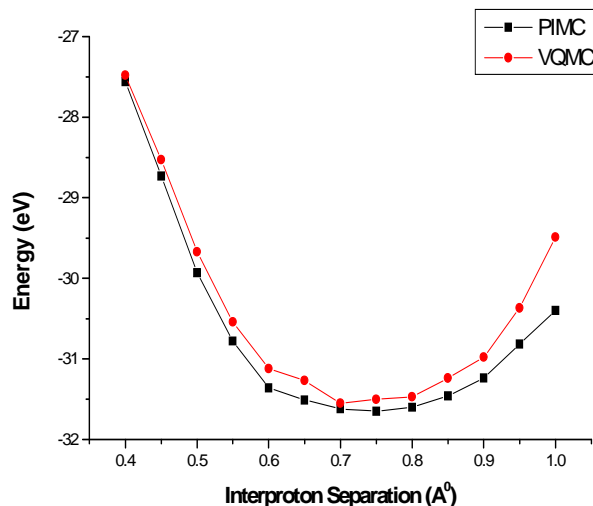


Fig. 5: Graph of Ground state Energy Vs Interproton Separation for VQMC and PIMC (H_2) Molecule

Conclusions

The ground state energy of hydrogen molecule at different interproton separation was numerically calculated under the principles of Born-Oppenheimer approximation using two different quantum Monte Carlo techniques i.e. the Variational Quantum Monte Carlo [VQMC] and Path Integral Monte Carlo [PIMC]. The results in this work demonstrated that PIMC is capable of accurately calculating the precise ground state energy of the system as it falls inside the error bars of previous empirical and numerical calculations.

The trial wavefunction have been optimised to suite the cusp condition of the electron-electron and electron-proton conditions.

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