NUMERICAL CALCULATION OF THE GROUND STATE ENERGIES OF THE HYDROGEN MOLECULE AND THE HELIUM ATOM USING QUANTUM MONTE CARLO METHODS

By

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DEDICATION

--to:

My late father, Alhaji Umar Bagudu Suleiman and my Mum Hajia Kareema Umar Suleiman

DECLARATION

I declare that the work in this dissertation titled ***"Numerical calculation of the ground state energies of the hydrogen molecule and the helium atom using Quantum Monte Carlo methods"*** has been performed by me in the Department of Physics Ahmadu Bello University, Zaria under the supervisions of Professor I. O. B. Ewa, Professor S. A. Jonah and Dr. Rabiu Nasiru.

The information derived from the literature has been duly acknowledged in the text and the list of references provided. No part of this dissertation was previously presented for another degree or diploma at any University.

_____	_____	_____
Abdussalam Balarabe Suleiman	Signature	Date

CERTIFICATION

This dissertation titled **"NUMERICAL CALCULATION OF THE GROUND STATE ENERGIES OF THE HYDROGEN MOLECULE AND THE HELIUM ATOM USING QUANTUM MONTE CARLO METHODS"** by Abdussalam Balarabe Suleiman meets the regulations governing the award of the degree of Doctor of Philosophy in Physics of Ahmadu Bello University, Zaria and is approved for its contribution to scientific knowledge and literary presentation.

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ABSTRACT

The ground state energies of Hydrogen molecule and the Helium atom are numerically evaluated using the Variational Quantum Monte Carlo [VQMC] and the Path Integral Monte Carlo [PIMC]. These analysis are done under the context of the accuracy of Born-Oppenhiemer approximation [fixed nuclei restriction]. The ground state energies of hydrogen molecule for different interproton separations (0.4 ï 1.0Å) are computed using the two different methods mentioned [VQMC and PIMC] and compared with previous numerical and empirical results (results obtained by other reviewers in the field) that are essentially exact. The results from the Path Integral Monte Carlo method of calculation were found to be precisely approaching the required order of accuracy i.e. -31.92eV in the case of hydrogen molecule. The VQMC and PIMC were applied to the helium atom at different values of the variational parameter β while the interproton separation was set to zero. The corresponding average values of the ground state energy is found to be -78.94eV and compared with the standard values and also with values obtained from other reviewers in the field. This also shows that results obtained from PIMC are much reliable and approaches the exact values i.e. -78.96eV. The standard errors in both cases were calculated and the effect of time step [PIMC] as per the ground state energies is also observed.

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LIST OF ABBREVIATIONS

QMC	:	Quantum Monte Carlo
QVMC	:	Quantum Variational Monte Carlo
PIMC	:	Path Integral Monte Carlo
DMC	:	Diffusion Monte Carlo
GFMC	:	Green Function Monte Carlo
HF	:	Hartree Fock
PHF	:	Post Hartree Fock
DFT	:	Density Functional Theory
B-O	:	Born Oppenheimer
DFTMD	:	Density Functional Theory Molecular Dynamics
RPIMC	:	Restricted Path Integral Monte Carlo
TDSE	:	Time Dependant Schrödinger Equation
TISE	:	Time Independent Schrödinger Equation
CEIMC	:	Coupled-Electronic Ionic Monte Carlo
PWB	:	Programmers Work Bench
GSE	:	Ground State Energy

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND OF THE STUDY

Hydrogen is the simplest element in the periodic table; it forms a diatomic gas at standard conditions of room temperature and atmospheric pressure. While not yet widely used as an energy carrier, new interest in hydrogen gas revolves around its potential as an alternative energy fuel. The attraction to hydrogen arises partly, because it contains the highest energy content of any common fuel by weight and partly becomes the by-productsô of the combustion which consists of water not the green house emission [Dubravko, 2007].

Since it is quite difficult to undertake an experiment in this context, it is of particular urgency to consider a theoretical prediction of some properties of Hydrogen [H_2] molecule. However, there is an extremely restricted choice of non-empirical methods of predicting the properties of hydrogen. Methods based on the Direct Quantum-mechanical computer simulations e.g. the Path Integral Monte Carlo are very demanding for computational resources and have not yet attained the necessary accuracy.

There are certain difficulties in applying to hydrogen the well developed methods of theory of liquids, which make use of model of rigid, impermeable molecules. The absence of closed atomic electronic shells makes hydrogen extremely compressible and stable at once in condensed phase. The softness of intermolecular repulsion in hydrogen becomes very important at high densities. It is just what makes hydrogen different from many other substances, and therefore the well-known and useful

molecular model like hard spheres or dumbbells could not be applied to hydrogen without essential modifications.

The difficulties facing the theoretical prediction of the properties of highly compressed hydrogen are also due to appreciable quantum effects [Yakub, 1999]. Non rigidity effects, which play an important role in highly compressed fluid hydrogen at high temperatures, remain substantial at intermediate temperatures as well, especially near the line of crystallization, where the density of fluid is high. In this region one cannot also neglect quantum effects particularly for the light isotopes of hydrogen. A variety of simulations technique and analytical models have been advanced to describe hydrogen in this particular regime. There are *ab initio* methods such as restricted Path Integral Monte-Carlo [RPIMC] simulations [Orthman, 1999] and Density Functional Theory Molecular Dynamics [DFTMD]. Further there are models that minimises an approximate free energy function constructed from the known theoretical limits with respect to chemical composition.

In this project we will consider Monte-Carlo methods that can be used to evaluate the exact properties of the ground states of quantum many-body systems in both Hydrogen and Helium.

Helium is an element and the next simplest atom to solve after the hydrogen atom. Helium is composed of two electrons in orbit around a nucleus containing two protons along with either one or two neutrons, depending on the isotope. The hydrogen atom is used extensively to aid in solving the helium atom. The Neils Bohr model of atom gave a very accurate explanation of the hydrogen atom but when it came to helium it collapsed. Heisenberg developed a modification of Bohr analysis but it involved half-integral values for the quantum numbers (Bransden and Joachain, 2003). The density

functional theory is also used to obtain the ground state energy levels of the helium atom along with the Hartree-Fock method.

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 (Born-Oppenheimer Approximation) is considered. The non relativistic TISE has the general form

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

Where ψ represents wavefunction for the nth electron, {r} = {r_1---------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

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

While the imaginary time-dependant Schrödinger equation has the form

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi \ , \tag{1.3}$$

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 energies for H_2 molecule started in 1933 with the work of James and Coolidge. 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 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 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 (Kent, 1999).

The knowledge of refining the Schrödinger equation using Monte Carlo procedures initiated with the work of Fermi. In an attempt to describe that work, (Metropolis *et*

al, 1953) 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 demonstrations for 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 (Grimm and Storer,1971). Importance sampling has also been applied to the Greenôs function quantum Monte Carlo (GFQMC) method used by Kolos and Wolniewicz, (1968).

In this work the ground state energy of hydrogen molecule along with that of helium atom were 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 of simple systems 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 Traynor *et al,* (1991), Chen and Anderson (1995), Ko, Wing Ho (2004) Doma and El- Gamal (2010), Koki (2009) and Martin D (2007) 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 Traynor *et al,* (1991).

The QMC methods 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 application 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

e) Static response of electron gas

f) Exchange and correlation energies

g) Jellium surfaces

h) Clusters

i) Solid hydrogen

j) Formation energies of silicon and self interstitials

1.2 RESEARCH PROBLEM

The fundamental problem we did examined is the structure of the H_2 molecule: two protons bound by two electrons and the helium atom which is also consisting of two proton with charge +2Z and two electrons in their electronic structures respectively. This was done within the context of the accuracy of Born-Oppenheimer approximation, which is based on the notion that the heavy protons move slowly compared to the much lighter electrons. The potential governing the protonsô motion

at a separation S, U(S), is the sum of inter-proton electrostatic repulsion and the eigenvalue, $E_0(S)$, of the two-electron Schrödinger equation:

$$U(S) = \frac{e^2}{S} + E_0(S). \tag{1.4}$$

The electronic eigenvalue is determined by the Schrödinger equation:

$$H(S)\psi_0(r_1, r_2; S) \equiv [K + V(S)]\psi_0 = E_0(S)\psi_0(r_1, r_2; S). \tag{1.5}$$

Here, the electronic wave function, ψ_0, is a function of space coordinates of the two electrons, $r_{1,2}$ and depends parametrically upon the inter-proton separation. Since we are interested in the electronic ground state energies of the hydrogen molecule and helium atom and we are willing to neglect small interactions involving the electronsô spin, then we can assume that the electrons are in antisymmetric spin-singlet state; the Pauli principles requires that ψ_0 be symmetric under the interchange of r_1 and r_2. Thus, even though the electrons are two fermions, the spatial equation satisfied by their wave function is analogous to that for two bosons; ground state wave function ψ_0 will therefore have no nodes, and can be chosen to be positive everywhere.

In the case of helium atom, a nucleus with charge Z and infinite mass the Hamiltonian in atomic unitsô a.u. can be interpreted as:

$$H = H_0 + H_1 \tag{1.6}$$

Where the term H_0 represents the columbic interaction between the particles where as the term H_1 is due to relativistic correction to the kinetic energy and it represents the dependence of the mass of the electron on the velocity.

1.3 JUSTIFICATION OF THE STUDY

There are various importanceôs and justifications that led to the implementation of Quantum Monte Carlo [QMC] methods in the determination of the ground state energy of the Hydrogen [H_2] molecule and Helium atom in this work over the traditional approaches (Hartree- Fock [HF], post Hartree-Fock [PHF] and the Density Functional Theory [DFT] (Mitas, 2006). This includes the following;

1. The methods make use of stochastic approach to map the many-body problem on to a sampling/simulation problem.
2. It focuses on many-body effects and efficiency of their description.
3. It has many ideas applicable to other system/model.
4. In many ways it is complementary to the traditional approaches.

The traditional approaches are based on the following;

I. The Hartree-Fock and post Hartree-Fock methods relies on the following.
   - Wave functions as Slater determinants (anti-symmetry) of one particle orbital

$$\psi_{HF}\left(r_{1,}\, r_2 \ldots\ldots\right) = Det\left[\phi_i\{\left(r_j\right)\}\right]. \tag{1.7}$$

   - In the post Hartree-Fock there is expansion in excitation

$$\psi_{corr}\left(r_{1,} r_2 \ldots\ldots\right) = \sum d_n Det_n\left[\{\phi_i\left(r_j\right)\}\right]. \tag{1.8}$$

Problem: Accurate but inefficient

The post Hartree-Fock method converges in one-particle basis and the set is slow, inefficient description of many-body effects. Therefore needs to explicitly evaluate the integrals restrict functional forms which can be used.

II. Density Functional Theory [DFT]

- Based on one-particle density

$E_{TOT} = \int F[\rho(r)]dr$.

- Exact Functional F is unknown

- Various approximations for F:

LDA (Local Density Approximation)

GGA (Generalised Gradient Approximation)

Problem: Efficient but inaccurate.

The density functional theory is difficult and having a symmetrical improvement (the fundamental proof is not constructive).

Alternative therefore is the Quantum Monte Carlo methods (QMC).

In this research particularly and among the known quantum Monte Carlo methods, the path integral Monte Carlo will be the method of experimentation, due to the fact that it is one of the quantum Monte Carlo method that had not been implemented on these kinds of systems by most reviewers.

1.4 SIGNIFICANCE OF THE CHOICE OF HYDROGEN MOLECULE AND THE HELIUM ATOM

The underlining reason for choosing these two simple elements of the periodic table in this work include the following:-

Hydrogen and helium belong to the simple systems groups of the periodic table, in such a way that their analytical first principles calculation are very possible, thereby providing an extensive history of accurate theoretical predictions and high quality empirical measurements of their ground state energies that could be referred for further comparative analysis.

These two elements merely consist of two electrons they still contain rich physical content, and lastly their composition of the two electrons make it clear that the sign problem introduce by the Fermi statistics can be avoided.

1.5 PRINCIPAL AND SPECIFIC OBJECTIVES OF THE RESEARCH

The principal objectives in this work incude:-

- The study of the structure of Hydrogen molecule and Helium atom.
- Finding a much precise among Quantum Monte Carlo methods to evaluate their respective properties, thus the path integral Monte Carlo which is considered to be more precise than other methods and which has not been implemented on these type of systems will be applied to the systems to evaluate their ground states energies respectively.

The specific objectives of this research are as follows;-

- Solving the 6-D partial differential eigenvalue equation (1.5) for the lowest eigenvalue E_0 at some interproton separations S and variational parameter β

- Tracing out the potential U(S) via equation (1.4) for the two physical systems mentioned above.
- Applying the Path Integral Monte Carlo [PIMC] and Variational Quantum Monte Carlo [VQMC] techniques to determine their respective ground state energies.
- Comparing the results obtained with the experimental and empirical results that were essentially exact and available.
- Determining the relationship between the variational parameter and the ground state energies of the physical systems, and make appropriate comparism.
- Correlating the ground state energy using both methods mentioned above.

Within the code to be used the variational Monte Carlo code will be applied as preliminary test to solve for the ground state energy of both the hydrogen molecule and helium atom at some specified interproton lengths and some values of variational parameter. The algorithm employed in this work is the Metropolis algorithm by the variational Monte Carlo code and the time step by the Path integral Monte Carlo code.

1.6 SCOPE AND LIMITAIONS

The scope of this study will be limited to H_2 molecule [two protons and two electrons] and the helium atom [two protons with charge +2Z and two electrons] because the QVMC and PIMC techniques through the metropolis algorithm and time step will be applied to evaluate the ground state energy at every given interproton separation and some values of variational parameters β , hence the energy and the correlation in energy will also be evaluated.

For every interproton separation both the Quantum Variational Monte Carlo [QVMC] and the Path Integral Monte Carlo [PIMC] will be applied to calculate the ground state energies of the hydrogen molecule, in the case of the helium atom only the variational parameter β will be varied at static position when the two protons are matched together i.e. S= 0, therefore there is an expectation of four different outputs of both the ground state energy and the correlations in the energy in each case. From the above views it could be observed that introducing another element will require the attention of considering the case of higher shells in the electronic structure in which each shell will generate its level ionisation energy and therefore will accumulate huge amount of data by the Monte Carlo procedure employed.

1.7 FOUNDATIONS OF QUANTUM PHYSICS

The theory of quantum physics was developed in the first half of the 20th century by Planck, Einstein, Bohr, Schrödinger, Born, Heisenberg, Pauli, Dirac and others. It replaced Newtonian mechanics and classical electromagnetism, as it can explain observations at atomic and subatomic levels which cannot be explained by these classical theories (Bethe and Jackiw, 1968).

Although the beginning of the quantum mechanics, as well as the whole of modern physics is related to the discoveries of Max Planck that gave the first evidence of radiated energy quantization, as its real birth and that of its entire comprehensibilityôs one would better mean the hydrogen atom model proposed by Niels Bohr in 1913. On the other hand, it is known that under ordinary conditions on Earth, elemental hydrogen exists as the diatomic gas H_2 and that the most elements aside from the

noble gases form diatomic molecules when heated, but high temperatures - sometimes thousands of degrees - are often required

From the exposed above one can conclude that:

- The Balmer-Rydberg formula $v = cR_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ used by Bohr as a foundation for creating the hydrogen atom model as relating not to the hydrogen atom H but to its molecule H_2 cannot serve as a foundation for the hydrogen atom model construction;
- Photons being formed in hydrogen molecules, the above formula can serve to construct a model of such kind of molecules (Dunaev, 2009).

The proposed planetary model of the hydrogen molecule has much in common with the model of atom proposed by Rutherford and at that time considered inoperative, for the reason that charged electrons turning around a nucleus and meeting no resistance at all would continuously accelerate, whereas all accelerated charges according to the classic theory of electromagnetism emit electromagnetic energy, in this case at the expenses of the kinetic energy of their own, whose losses would very soon enforce the electrons to fall on the nucleus.

1.8 GROUND STATE ENERGY CALCULATIONS

The ground state energy is the lowest energy levels which electrons can occupy in an atom, molecule or ion. For hydrogen molecule and the helium atom, it is referred to as the energy level closest to the nucleus. However this energy level can accommodate only two electrons, so for the next heaviest element i.e. lithium, the ground state has two electrons in the lowest energy level and one in the second level. The second energy level can contain a maximum of eight electrons, the third level a maximum of

eighteen electrons, and so on ($2n^2$ electron in the nth level). The ground state for the heavier element may therefore have some of their electrons in quite high energy levels.

During the past few decades there had been procedures of determining the lowest energy value of a specific quantum system which were based mainly on solving the Schrödinger equations, though it has transited from so many empirical approaches to the present most reliable quantum Monte Carlo techniques. It has become quite impossible to generate analytical solutions to Schrödinger equations in many quantum systems and as such computational techniques solutions are preferred.

The main objective in calculating the ground state energy of a quantum system is to minimize the total energy with respect to the wave function $|\psi_{i,k}\rangle$ starting with a trial wave function $|\psi^{o}_{i,k}\rangle$. The energy minimization scheme is formulated in terms of an equation of motion for the wave function $|\psi^{(t)}_{i,k}\rangle$ in the fictitious time variable *t*. Some of the pre-quantum Monte Carlo approaches include those carried out in the density functional approach such as;

1.8.1 **The steepest descent**

The simplest scheme to iterate the wave functions is the steepest descent approach (Parr and Yang, 1989). It can be derived from a first-order equation of motion,

$$\frac{d}{dt}|\psi^{(t)}_{i,k}\rangle = \left(\tilde{\in}_{i,k} - \hat{H}_{KS}\right)|\psi^{(t)}_{i,k}\rangle, \qquad (1.9)$$

Imposing the ortho-normality constraint $\langle\psi^{(t)}_{i,k}|\psi^{(t)}_{j,i}\rangle = \delta_{i,j}$, where $\hat{H}_{KS}$ is the Kohn-Sham Hamiltonian and $\tilde{\in}_{i,k}$ are the Lagrange parameters introduced to account for the

ortho-normality constraint. In the simplest possible discretization of this differential equation, only information from the last step is used,

$$\left\langle G+k\middle|\psi_{i,k}^{(t-1)}\right\rangle=\left\langle G+k\middle|\psi_{i,k}^{(t)}\right\rangle+\beta\left\langle G+k\middle|\psi_{i,k}^{(t)}\right\rangle-\eta\left\langle G+k\middle|\hat{H}_{KS}\middle|\psi_{i,k}^{(t)}\right\rangle, \tag{1.10}$$

where $\beta=\tilde{\varepsilon}_{i,k}\delta t$ and $\eta=\delta t$. However, it turns out that this discretization scheme is not very efficient

1.8.2 **Damped Joannopoulos:**

A more efficient scheme based on a second order equation of motion might also be used

$$\frac{d^2}{dt^2}\left|\psi_{i,k}^{(t)}\right\rangle+2\gamma\frac{d}{d\tau}\left|\psi_{i,k}^{(t)}\right\rangle=\left(\tilde{\varepsilon}_{i,k}-\hat{H}_{KS}\right)\left|\psi_{i,k}^{(t)}\right\rangle, \tag{1.11}$$

where γ is a damping parameter. The equation of motion is integrated for a step length δt by the Joannopoulos approach (Miltzer, 2008), which iteratively improves the initial wave functions. In this algorithm the new wave functions $\left|\psi_{i,k}^{(t-1)}\right\rangle$ is constructed from the wave functions of the last two iteration steps t and (t-1),

$$\left\langle G+k\middle|\psi_{i,k}^{(t+1)}\right\rangle=\left\langle G+k\middle|\psi_{i,k}^{(t)}\right\rangle+\beta_G\left\langle G+k\middle|\psi_{i,k}^{(t)}\right\rangle-\gamma_G\left\langle G+k\middle|\psi_{i,k}^{(t-1)}\right\rangle-\eta_G\left\langle G+k\middle|\hat{H}_{KS}\middle|\psi_{i,k}^{(t)}\right\rangle, \tag{1.12}$$

where the coefficients are

$$\begin{aligned}\beta_G &= \frac{\tilde{\varepsilon}_{i,k}\,(h_G(\delta t)-1)-\left\langle G+k\middle|\hat{H}_{KS}\middle|G+k\right\rangle e^{-\gamma\delta t}}{\tilde{\varepsilon}_{i,k}-\left\langle G+k\middle|\hat{H}_{KS}\middle|G+k\right\rangle},\\ \gamma_G &= e^{-\gamma\delta t},\\ \eta_G &= \frac{(h_G(\delta t)-e^{-\gamma\delta t}-1}{\tilde{\varepsilon}_{i,k}-\left\langle G+k\middle|\hat{H}_{KS}\middle|G+k\right\rangle},\end{aligned}$$

with $\tilde{\epsilon}_{i,k} = \left\langle \psi^t_{i,k} \middle| \check{\tilde{H}}_{KS} \middle| \psi^t_{i,k} \right\rangle$. The function $h(\delta t)$ is defined by

$$h_G(\delta t) = \begin{cases} 2e^{-\frac{\gamma}{2}\delta t} \cos(\omega_G \delta t) & if \quad \omega_G^2 \geq 0 \\ 2e^{-\frac{\gamma}{2}\delta t} \cosh\left(\sqrt{|\omega_G^2|}\delta t\right) & if \quad \omega_G^2 < 0 \end{cases}$$

with $\omega_G^2 = \left\langle G+k \middle| \check{\tilde{H}}_{KS} \middle| G+k \right\rangle - \tilde{\varepsilon}_{i,k} - \frac{\gamma^2}{4}$.

1.9 DEFNATION OF TERMS

i.) NUMERICAL ANALYSIS: This is computational physics method which is designed to provide experience in the computer modeling of physical problems, it scope includes the essential numerical techniques needed to do physics on a computer, each of these are developed heuristically in the text with the aid of simple mathematical illustrations [Konin and Meredith, 1990]. Thus it really simplifies methods for solving large arrays of system within a define range of inputs.

ii). PATH INTEGRAL MONTE CARLO: This is one of the many quantum Monte Carlo techniques that are used to simulate quantum systems using pseudorandom number generators, instead of calculating the properties of a single quantum states it summed over all possible states occupying them according to the Boltzmann distribution (principles of super position).

iii). VARIATIONAL MONTE CARLO: This is also a quantum Monte Carlo technique of simulating the solutions of eigenvalue problem. In this technique any trial wave function is chosen to be real not orthogonal to the exact ground state Ψ_0, therefore an upper bound to the electronic eigenvalue is the variational energy.

iv). ELECTRONIC EIGEN VALUE: This is the exact ground state energy value of the electron which is based upon the evolution of the imaginary-time dependent and independent Schrödinger equations that refines the trial wave function.

v). ENERGY CORRELATIONS: The degree to which two or more energy variables are related and changed together.

1.10 OUTLINE OF THE RESEARCH

The main objectives of this research is to numerically calculate the ground state energy of hydrogen molecule and the helium atom using Quantum Monte Carlo methods i.e. Variational quantum Monte Carlo [VQMC] and the Path Integral Monte Carlo method [PIMC] and comparing the values of the lowest energy level obtained in each case with previous numerical and empirical results that are essentially exact. The correlation in energy with respect to each method while considering the case of hydrogen molecule is evaluated and compared. The standard error in each case is then computed to find the actual ground state energy deviations from the exact results.

Chapter 1 of this research contains the introductory aspect of the research, aims and objectives, scope and limitations, justifications on the choice of elements and the method employed.

Chapter two of this review contains the related literature on the subject matter and on which the research was based on, the theoretical input of the methods employed in the research was also presented.

Chapter three contains the computational procedure of the work and the description of the package being used; the algorithm of the code will also be described.

Chapter four present the analysis of the results obtained from the two methods employed in each case, some samples of the results obtained will be presented either graphically or in a tabular form. Furthermore discussions and analysis of the results will also be presented.

Chapter five concludes and summarizes the research findings and suggests some further works on the research.

CHAPTER TWO

LITERATURE REVIEW

2.1 ELECTRONIC STRUCTURE METHOD

Different methods have been in existence for the determination of the electronic structure of molecules ranging from classical to quantum approaches; these constitute the great challenges of condensed matter physics to obtain accurate approximate solutions of the many-electron Schrödinger equation. Because the mass of an electron is much smaller than that of a nucleus $\left(M_e / M \approx 10^{-3} - 10^{-5}\right)$ therefore the dynamics of electrons and nuclei can to a good approximation, be made to reduce interdependence.

Some of the electronic structure methods would be reviewed here. The main goal in electronic structure method is to solve the many-electron Schrödinger equation to obtain the ground state energy and distribution of electrons for a given arrangement of nuclei in a molecule. Quantum Monte Carlo method is at high-accuracy, high-cost end of the spectrum of the available methods for studying material properties (Kent, 1999).

2.2 THE HAMILTONIAN

The Hamiltonian is an important quantity that characterizes a physical body or a system in classical and quantum mechanics. The Hamiltonian is useful in obtaining powerful equations of motion for a system in classical mechanics, the so called canonical equation, and is an essential quantity in the Schrödinger equations in non relativistic quantum mechanics. In many physical situations, it is equal to the total kinetic energy plus the potential energy.

$$[H = T + U] \qquad (2.1)$$

In general, the Hamiltonian is expressed as a function of the generalised coordinates, the generalised coordinates, the generalised momenta, and the time.

$$H = H(q_x, p_x, t) \tag{2.2}$$

So in the case that the generalised coordinates are scleronomic (the equations that transform them from ordinary Cartesian do not explicitly contain the time), and of course that the potential energy is not an explicit function of the generalised velocities then the Hamiltonian is equal to the total energy as represented in (2.1)

In this case where the Hamiltonian is equal to the total energy and working in Cartesian coordinates, it can by elementary mechanics, be expressed (in the non-relativistic case) as $H = \frac{p^2}{m} + U(x)$ (2.3)

Where *p* is the ordinary momentum

The Hamiltonian enters the Schrödinger equation of quantum mechanics as an operator which states that $H\psi = i\hbar \frac{\partial \psi}{\partial t}$ (2.4)

The physical significance of the Hamiltonian is rather mystical and subtle, but extremely important. It can be seen as the generator of system evolution in time. It can also be seen as the conjugate of momentum to time, meaning that if time is thought of a generalised coordinate, the momentum corresponding to that coordinate will be the Hamiltonian, just as the momentum corresponding to a Cartesian coordinate is the familiar linear momentum.

Most physical problems consist of a number of interacting electrons and ions. The total number of particles N is usually adequate and large that an exact solution cannot be obtained. Therefore there is need to introduce a well perceived approximations to reduce the complexity to a tractable level. Once the equations are solved, a large no of properties may be calculated from the wavefunction.

2.3 BORN OPPENHEIMER APPROXIMATION

As for atoms, all information about a molecule is contained in the wavefunction ψ, which is the solution of the time-independent Schrödinger equation:

$$H\psi(\vec{x},\vec{r}) = E\psi(\vec{x},\vec{r}) \tag{2.5}$$

where $\vec{x}$ stands collectively for the spatial and spin coordinates of the n electrons in the molecule, and $\vec{r}$ denotes collectively the positions of all N nuclei in the molecule. In the non-relativistic limit, the total Hamiltonian for the molecule is

$$H = T_N + T_e + V_{Ne} + V_{ee} + V_{NN} \tag{2.6}$$
$$\equiv T_N + H^{el}$$

$$\text{where} \quad T_N = -\sum_{\alpha} (1/2) M_{\alpha} \nabla_{\alpha}^2, \tag{2.7}$$

$$T_e = -\sum_{\alpha} (1/2) \nabla_i^2 \tag{2.8}$$

$$V_{Ne} = -\sum_{\alpha,\, i} \frac{Z_{\alpha}}{|R_{\alpha} - r_i|} \tag{2.9}$$

$$V_{ee} = \sum_{i>j} \frac{1}{|r_i - r_j|} \tag{2.10}$$

$$V_{NN} = \sum_{\alpha>\beta} \frac{Z_{\alpha} Z_{\beta}}{|R_{\alpha} - R_{\beta}|} \tag{2.11}$$

Atomic units have been used, in which $\hbar = m_e = e = 1$

T_N and T_e are the summed kinetic energy operators of the nuclei α with mass M_{α} and the electrons i with mass m_e, respectively, and $V_{Ne}, V_{ee}, \text{and} \quad V_{NN}$ denote the summed Coulomb interaction energies between the nuclei and the electrons, between the electrons themselves, and between the nuclei themselves, respectively. Equation (2.5) is a (3n+3N) -dimensional second order partial deferential equation, which cannot be readily solved.

Because the masses of the nuclei are much larger than that of the electrons, the nuclei move slowly compared with the electrons. It is usually (but not always) a very good approximation to assume that the electronic energies (that is, the energies due to the motions of the electrons) can be determined accurately with the nuclei held fixed at each possible set of nuclear positions. In other words, it is assumed that the electrons adjust adiabatically to small or slow changes in the nuclear geometry. This approximation and its consequences were first examined by Born and Oppenheimer, and have carried their names ever since (Landau and Lifshitz, 1980).

In this approximation, the total wave function is separable

$$\Psi\left(\vec{x},\vec{R}\right)=\Psi^{el}\left(\vec{x};R\right)\Psi^{nuc}\left(\vec{R}\right) \tag{2.12}$$

into a nuclear part Ψ^{nuc} that depends only upon the nuclear coordinates $\vec{R}$ and an electronic part Ψ^{el} that depends on the electronic coordinates $\vec{x}$, but only parametrically on R. Ψ^{el} is the solution of the electronic eigenvalue equation

$$H^{el}\Psi^{el}\left(\vec{x};R\right)=E^{el}\left(R\right)\Psi^{el}\left(\vec{x};R\right) \tag{2.13}$$

Where $E^{el}(R)$ is the potential energy surface, or in the case of diatomic molecule, the potential energy curve of the molecule in a particular electronic state.

2.4 THE HATREE FOCK THEORY

The Hatree-Fock approximation which is also known as the self-consistent field approximation is proven to be an accurate description of many of the properties of multi-electron atoms and ions (Staemmler, 2006). In the Hartree-Fock formulations each electron is describe by a separate single-particle wavefunction that solves a Schrödinger-like equation.

The Hartree-Fock theory is based on restricting the trial wavefunction to be a Slater determinant:

$$\Psi(x_1, x_2, ..., x_N) = (N!)^{-1/2} \det \psi_\alpha(x_j) \quad (2.14)$$

Here, the $\psi_\alpha(x)$ are a set of N orthonormal single-particle wavefunction; they are functions of the coordinates of only a single electron and $x_j = \{r_j, \sigma_j\}$ represents the space and spin coordinates of an electron. The antisymmetry ensures that no two electrons can have the same set of quantum numbers and that the Pauli Exclusion Principle is satisfied. Since the trial wavefunction is are considered to be Slater determinants therefore in most cases the single-particle orbitals are assumed to be products of spatial and spin factors,

$$\psi_i(x_j) = \psi_i(r_j)\delta_{\sigma_i,\sigma_j} \quad \text{Where} \quad \delta_{\sigma_i,\sigma_j} = 1 \quad if \ \sigma_j = \sigma_i \quad \text{and zero}$$

otherwise.

The Hatree-Fock Hamiltonian operator is defined in terms of molecular orbitals through the operators of coulomb and exchange repulsion. The general procedure for solving the Hatree-Fock equations is to make the orbitals self-consistent with the potential field they generate. It is achieved through an iterative trial-and-error computational process, for which reason the entire procedure is called the self-consistent field method. In the case of open-shell systems one should distinguish between the spin-restricted Hatree-Fock (RHF) method and spin-unrestricted Hatree-Fock (UHF) method. In the former approach a single set of molecular is preset, some being doubly occupied and some being singly occupied with an electron of spin. In the UHF approach different spatial orbitals are assigned to electrons with $\alpha_1 \ and \ \beta_1$ spins and the orbitals ψ_i doubly occupied in the RHF method are replaced by two distinct orbitals $\psi_i(\alpha) and \ \psi_i(\beta)$.

2.4.1 LIMITATIONS OF HATREE-FOCK THEORY

Hatree-Fock is a simple theory which satisfies the commonly known features of fermionic wavefunctions. The theory generates the wavefunctions that are antisymmetric with respect to the exchange of electron positions and include exchange between like-spin electrons. The process of Hatree-Fock calculation formally scales with the cube of the number of basis functions, but depending on the implementation the scaling can be between linear and quadratic with system size. It is insufficiently accurate for quantitative predictions of properties of many compounds. By neglecting electron correlation, interaction energies are typically very poor. A Hatree-Fock wavefunctions a well-controlled approximation to the many-body wavefunction, and for this reason Hatree-Fock continue to be widely used: it is often predictably accurate or inaccurate, and therefore useful for determining qualitative information such as trend in a structural parameter with system size.

2.5 THE POST HATREE-FOCK THEORY

The drawbacks of the Hartree Fock theory could be simplified by going ahead of the basis of a single determinant wavefunction. The single-determinant Hartree-Fock theory includes the exchange effects arising from the antisymmetry of the many-electron wavefunction but failed to consider the electronic correlations caused by the electron-electron coulomb repulsion. Correlation can be included by using a linear combination of determinants in the post Hatree-Fock method. In the cause of simplifying the limitations of the Hartree-Fock theory, these two distinct divisions of approaches are adhered: those based on perturbation theory and those based on variational principles. Within the latter approach is the full configuration-interaction

in which all possible determinants is included in the calculation, but this yielded to expansion in excitation. However, the central problem with such expansions is that very large numbers of determinants are needed to describe many-electron wavefunctions accurately. The basis of configuration-interaction is the simple observation that an exact many-body wavefunction Ψ, may be written as a linear combination of Slater determinants. D_k

$$\Psi = \sum_{k=0}^{\infty} c_k D_k \tag{2.15}$$

Where D_k fully span the Hilbert space of wavefunction. The determinants can be any complete set of N-electron antisymmetric functions but are typically constructed from Hatree-Fock orbital such that D_0 is the ground-state Hatree-Fock determinant.

2.5.1 LIMITATIONS OF POST HATREE-FOCK THEORY

The fundamental problem is that there is an expansion in excitation (Mitas, 2006) there are two basic reasons for this poor convergence: Firstly, which applies equally in small and large systems is that many determinants are needed to describe the cusp like gradients discontinuities that occur whenever two electrons have the same position. Secondly, the required number of determinants increases very rapidly with system size.

2.6 THE DENSITY FUNCTIONAL THEORY

Density Functional Theory (DFT) is primarily a theory of electronic ground state structure, treated in terms of the electronic density distribution $n(r).$ since its discovery about three decades ago, it has become increasingly useful for understanding and calculation of ground state density, $n(r),$ and energy E, of molecules, clusters and solids- any system consisting of nuclei and electron- with or without applied static perturbations. It is an alternative, and complimentary, approach to traditional methods of quantum physics which are treated in terms of the many-electron wavefunction (Parr and Yang, 1989). Both Thomas-Fermi and Hatree-Fock ï Slater methods can be regarded as ancestors of modern DFT.

The density functional theory is based on the theory of Hohenberg and Kohn (Miltzer, 2008) who have shown that the ground state energy of a molecule is a unique functional of the of the electron density ρ. A break-through was the idea of Kohn and Sham to obtain the electronic density from an auxiliary system of non-interacting particles (Feynman and Hibbs, 1965). An advantage of DFT as compared to Hatree-Fock method is the inclusion of electron correlation. The accuracy of this approach depends on the choice of the appropriate exchange-correlation energy functional, the search for which is an active field of current research. In the Kohn-Sham formulation of the density functional theory (DFT), the electronic energy is separated in to two parts,

$$E = E^T + E^V + E^J + E^{XC}, \tag{2.16}$$

Here E^T *and* E^V are the kinetic and electron-nuclear interactions energies, E^j is the Coulomb self-interaction of the electron density ρ and E^{XC} is the remaining (exchange-correlation) part of the electron-electron repulsion energy, also treated as a

functional of the density ρ. The total energy expression in the density functional theory (DFT) can be mathematically represented as;

$$E_{TOT} = \int F[\rho(r)]dr \qquad (2.17)$$

Where the exact functional F is unknown, therefore various approximations are employed in that respect ranging from the local density approximation (LDA) and the generalised gradient approximation (GGA).

2.6.1 LIMITATIONS OF THE DENSITY FUNCTIONAL THEORY

In traditional methods such as the HF and PHF, an arbitrary level of accuracy can in principle be obtained for any system, given a sufficiently powerful computer. Density functional theory depends on the accurate knowledge of exchange correlation energy functional, and although more and more accurate forms are constantly being developed, there is no known systemic way to achieve an arbitrary high level of accuracy (Foulkes and Mitas, 2001), therefore this situation could be familiar that the systematical improvement is difficult because the fundamental proof is not constructive although the method could be efficient.

2.7 THE QUANTUM MONTE CARLO (QMC) METHODS

2.7.1 INTRODUCION

The term ñquantum Monte Carloò 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 couple with the fact that these 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 (D. Martins, (2007), Chen and Anderson, (1995), L. Mitas, (2006), W.M.C. Foulkes (2001) e.t.c. that larger extensions would be to implement a Path Integral Monte Carlo method and to 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 value.

Other QMC methods include the auxiliary-field QMC reviewed by Senatore and March, (1994), Diffusion Monte Carlo (DMC) reviewed by Ko Wing Ho (2004) in demonstrating quantum Monte Carlo methods through the study of hydrogen molecule, Greenôs Function Monte Carlo (GFMC) reviewed by Chen and Anderson (1995) in Improved Quantum Monte Carlo calculation of the ground state energy of the hydrogen molecule, Coupled Electronic Ionic Monte Carlo reviewed by M.D. Dewing (2001) in describing Monte Carlo methods as applied to hydrogen gas and hard spheres, Trotter Suzuki Monte Carlo reviewed by J. S. Wang (2001) in demonstrating quantum Monte Carlo methods etc.

2.7.2 MONTE CARLO METHODS

The fundamental illustration of Monte Carlo simulation methods is the evaluation of the multidimensional integral by sampling the integrand statistically and averaging the sampled values (Ceperley and Mitas, 1995). Numerical methods that are known as Monte Carlo methods can be comfortably described as statistical simulation methods, where statistical simulation is defined in quite general terms to be any method that utilizes sequence of random numbers to perform the simulation. Monte Carlo methods have been used for centuries, but only in the past several decades has the technique gained the status of fully fledged numerical method of capable of addressing the most complex application. Giving out the definition of Monte Carlo methods, it is now pertinent to describe briefly the major component of Monte Carlo method. These components comprise the foundation of most Monte Carlo applications. An understanding of these major components will provide a sound foundation for someone to construct his own Monte Carlo method. The primary components of a Monte Carlo simulation method include the following:

- Probability distribution functions (pdfôs) ï the physical (or mathematical) system must be described by a set of pdfôs.
- Sampling rule- a prescription for sampling from the specified pdfôs assuming the availability of random numbers on the unit interval, must be given.
- Random number generator- a source of random number uniformly distributed on the unit interval must be available.
- Scoring (or tallying) ï the outcomes must be accumulated in to overall tallies or scores for the quantities of interest.

- Error estimation ï an estimate of the statistical error (variance) as a function of the number of trials and other quantities must be determined.
- Variance reduction techniques ï methods for reducing the variance in the estimated solution to reduce the computational time for Monte Carlo simulation.
- Parallelization and vectorization ï algorithm to allow Monte Carlo methods to be implemented efficiently on advanced computer architectures.

2.7.3 MONTE CARLO INTEGRATION

In order to have a good perspective of Monte Carlo numerical integration methods, let us first discuss several classical methods of determining the numerical values of definite integrals. It could be observed that theses classical methods, although usually preferable in low dimensions, are impracticable for multi-dimensional integrals and that Monte Carlo methods are essential for the evaluation of the integral if the number of dimension is sufficiently high.

Consider the one-dimensional definite integral of the form

$$F = \int_a^b f(x)dx \tag{2.18}$$

For some choices of the integrand $f(x)$, the integration in (2.18) can be done analytically, found in table of integrals, or evaluated as a series. However, there are relatively few functions that can be evaluated analytically and most functions must be integrated numerically. The classical method of integration is based on the

geometrical interpretation of (2.17) as the area under the curve of the function $f(x)$ from x = a to x = b see figure below;

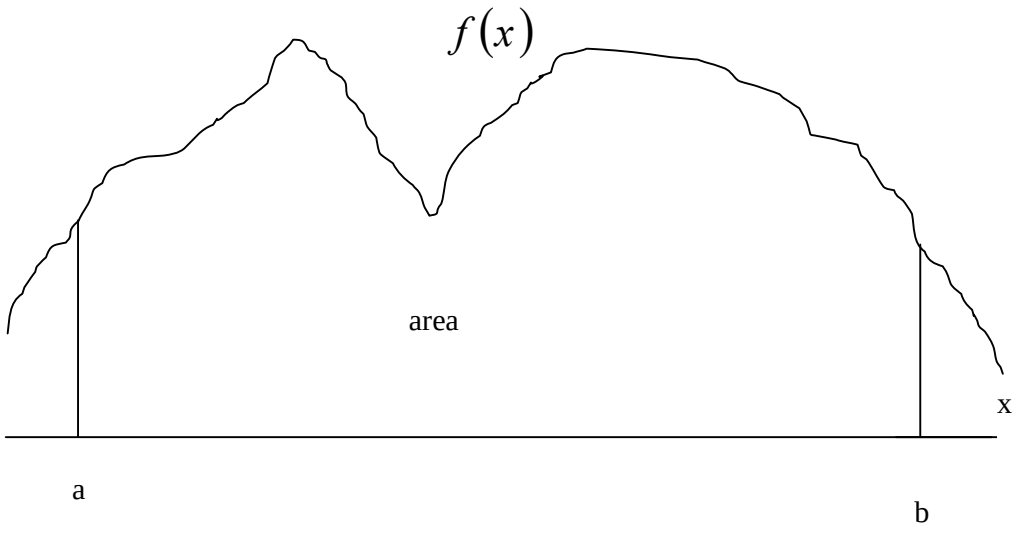


Figure 1: The integral F equals the area under the curve $f(x)$.

In trying to find the estimate of the integral (2.18) various approaches could be implemented ranging from the trapezoidal rule, rectangular approximation, and Simpsonôs rule e.t.c. We now explore a totally different method of estimating integrals. Let us introduce the method (Monte Carlo) of evaluating the integrals by starting with a common example, supposing a pond in the middle of a field of area A. One way to estimate the area of the pond is to throw the stones so that they land at random within the boundary of the field and count the number of splashes that occurs when a stone lands in the pond. The area of the pond is approximately the area of the field times the fraction of the stones that make a splash. This simple procedure is an example of Monte Carlo method.

Another Monte Carlo integration method is based on the mean-value theorem of calculus, which states that the definite integral (2.18) is determined by the average value of the integrand $f(x)$ in the range $a \le x \le b$, to determine this average, we choose the x_i at random instead at regular intervals and sample the value of $f(x)$. For the one-dimensional integral (2.18), the estimate F_n of the integral of the sample mean method is given by

$$F_n = (b-a)\langle f \rangle = (b-a)\frac{1}{n}\sum_{i=1}^{n} f(x_i). \qquad sample\,mean\,method$$

2.7.4 THE STRATEGY OF THE BASIC MONTE CARLO METHOD

Even though the real power of Monte Carlo methods is in evaluating multi-dimensional integrals, it is easiest to illustrate the basic ideas in a one dimensional situation, suppose that we are to evaluate the integral

$$I = \int_0^1 f(x)dx \qquad (2.19)$$

For some particular function f However, an alternative way of evaluating I is to think about it as the average of f over the interval [0,1]. In this light a plausible formula for the quadrature is

$$I = \frac{1}{N}\sum_{i=1}^{N} f(x_i). \qquad (2.20)$$

To estimate the uncertainty associated with (2.20) we can consider $f_i \equiv f(x_i)$ as a random variable and invoke the central limit theorem for large N. From the usual laws of statistics, we have

$$\alpha_I^2 \approx \frac{1}{N}\alpha_f^2 = \frac{1}{N}\left[\frac{1}{N}\sum_{i=j}^{N} f_i^2 - \left(\frac{1}{N}\sum_{i=j}^{N} f_i\right)^2\right]. \tag{2.21}$$

where α_f^2 is the variance in f i.e. a measure of the extent to which f deviates from its average value over the region of integration. Equation (2.21) reveals two important aspect of Monte Carlo quadrature. First the uncertainty in the estimate of the integral, α_I , decreases as $N^{-\frac{1}{2}}$. The second important aspect of the above equation is that the precision is greater if α_I is smaller; that is if f is as smooth as possible.

In this work two method of the quantum Monte Carlo [variational Monte Carlo and the Path Integral Monte Carlo] will be employed to evaluate the ground state energy and energy correlations.

2.7.5 TWO ELECTRON PROBLEM

For two electrons that donôt interact with each other, the ground state of their motion around a nucleus is the $1S^2$ configuration; i.e. both electrons are in same real, spherically symmetric spatial state, but have opposite spin projections. It is therefore natural to take a trial wave function for the interacting system that realizes this same configuration; the corresponding two single-particle wave functions,

$\psi_\alpha(x) = \chi_\alpha(r)|\rho_\alpha>$ are

$$\psi\ (x) = \frac{1}{(4\pi)^{\frac{1}{2}} r} R(r)\left|\pm \frac{1}{2}\ \right\rangle, \tag{2.22}$$

The many ï body wave function is

$$\Psi = \frac{1}{\sqrt{2}}\frac{1}{4\pi r_1 r_2} R(r_1)R(r_2)\left[1+\frac{1}{2}>\left|-\frac{1}{2}>-\right|\frac{1}{2}>\left|+\frac{1}{2}>\right.\right] \tag{2.23}$$

This trial wave function is antisymmetric under the interchange of electron spins but symmetric under the interchange of their space coordinates. It obeys the Pauli principle, since it is antisymmetric under the interchange of all variables describing the two electrons.

2.7.6 SINGLE-PARTICLE DESCRIPTION OF A MANY-PARTICLE SYSTEM

Many of the drawbacks of the Thomas-Fermi approach can be traced to the approximate treatment of the kinetic energy. The task of finding good approximations to the energy functional is greatly simplified by using a different separation introduced by Kohn and Sham.

$$E[n] = T_0[n] + \int d\vec{r}\; n(\vec{r})\left(V_{ext}(\vec{r}) + \frac{1}{2}\Phi(\vec{r}) \right) + E_{xc}[n] \qquad (2.24)$$

T_0 is the kinetic energy of a system with density n in the absence of electron-electron interactions, Φ is the classical Coulomb potential for electrons, and the remainder E_{xc} defines the exchange-correlation energy. T_0 differs from the true kinetic energy T, but it is of comparable magnitude and is treated exactly in this approach. This removes many of the deficiencies of the Thomas-Fermi approximation, such as the lack of a shell structure but the exchange-correlation energy E_{xc} can be evaluated exactly, so that the (unavoidable) approximations for E_{xc} play a central role in the following discussion.

The variational principle applied to Eq. (2.24) yields

$$\frac{\delta E[n]}{\delta n(\vec{r})} = \frac{\delta T_0}{\delta n(\vec{r})} + V_{ext}(\vec{r}) + \Phi(\vec{r}) + \frac{\delta E_{xc}[n]}{\delta n(\vec{r})} = \mu \qquad (2.25)$$

Where μ is the Lagrange multiplier associated with the requirement of constant particle number. If we compare this with the corresponding equation for a system with an effective potential $V(\vec{r})$ but without electron-electron interactions,

$$\frac{\delta E[n]}{\delta n(\vec{r})} = \frac{\delta T_0}{\delta n(\vec{r})} + V(\vec{r}) = \mu \tag{2.26}$$

we see that the mathematical problems are identical, provided that

$$V(\vec{r}) = V_{ext} + \Phi(\vec{r}) + \frac{\delta E_{xc}[n]}{\delta n(\vec{r})} \tag{2.27}$$

where the last term is referred to as the exchange-correlation potential V_{xc}. The solution of Eqs. (2.26), (2.27) can be found by solving the Schrodinger equation for non-interacting particles $\left(-\frac{1}{2}\nabla^2 + V(\vec{r})\right)\psi_i(\vec{r}) = \varepsilon_i \psi_i(\vec{r})$ (2.28)

yielding $n(\vec{r}) = \sum_{i=1}^{N} \left|\psi_i(\vec{r})\right|^2$ (Waalkens *et al,* 2003) (2.29)

The condition (2.27) can be satisfied in a self-consistent procedure.

The solution of this system of equations leads then to the energy and density of the lowest state, and all quantities derived from them. The formalism has also been generalized to the lowest state with a given set of quantum numbers. In this case E_{xc} depends on the values of the quantum numbers, and the density variations must remain within the space corresponding to the given quantum numbers. Instead of seeking these quantities by determining the wave function of the system of interacting electrons, the density functional method reduces the problem to the solution of a single-particle equation of Hartree form. In contrast to the HF potential,

$$V_{HF}\psi(\vec{r}) = \int d\vec{r}' V_{HF}(\vec{r}, \vec{r}')\psi(\vec{r}') \tag{2.30}$$

the effective potential, $V(\vec{r})$ is local, and the equations are no more complicated to solve than Hartree's. The kinetic energy, the electrostatic interaction between core and valence electrons and between valence electrons is treated exactly. Only the exchange energy, E_x and the even smaller correlation contribution require approximation. This is in marked contrast to the Thomas-Fermi and related methods, where the large kinetic energy term is approximated.

It could be noted that the problem of the "self-interaction correction" (SIC) where the Coulomb energy of interaction of an electron with itself must be cancelled by a contribution to E_{xc} , the importance of SIC is obvious immediately if we consider a single-electron system such as the hydrogen atom. We also note the scaling condition on the exchange energy.

$$E_x[\lambda^3\ n(\lambda\vec{r})] = \lambda E_x\ [n(\vec{r})] \tag{2.31}$$

this has proved to be useful in constructing functional approximations.

2.7.7 IMPORTANCE SAMPLING

Monte Carlo calculations can be carried out using sets of random points picked from an arbitrary probability distribution. The choice of the distribution obviously makes a difference to the efficiency of the method. In most cases Monte Carlo calculations carried out using uniform distribution give poor estimates of high-dimensional integrals and are not a useful method of approximation. In 1953, however, Metropolis *et. al* introduce a new algorithm for sampling points from a given probability function, this algorithm enabled the incorporation of "importance sampling" in to Monte Carlo integration. Instead of choosing points from a uniform distribution, they

are now chosen from a distribution which concentrates the points where the function being integrated is large. Consider the one dimensional integral

$$I = \int_a^b \frac{f(x)}{g(x)} g(x) dx \,. \qquad (2.32)$$

Where the function $g(x)$ is chosen to be a reasonable approximation to $f(x)$, the integral can be calculated by choosing the random points from the probability distribution $g(x)$ and evaluating $f(x_i)/g(x_i)$ at these points. To enable $g(x)$ o be act as a distribution function it must be of one sign everywhere, and the best possible choice is $g(x) = |f(x)|$, the average of these evaluation gives an estimate of *I*. another way of looking at these new integral is to define $dy = g(x)dx$, in which case

$$I = \int_A^B \frac{f(x(y))}{g(x(y))} dy \qquad (2.33)$$

where the limits of the integration are changed to correspond to the change of variable.

2.7.8 THE ALGORITHM OF METROPOLIS *et al*

One of the most effective and prominent way of producing random variables with a given probability distribution of arbitrary form is known as the algorithm of metropolis *et al* (1953).

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 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:

a) Start the walker at random position **R.**

b) Make a trial move to a new position R' chosen from some probability density function $T(R' \leftarrow R)$. after the trial move the probability that the walker initially at **R** is now in the volume element dR' *is* $dR' X\ T(R' \leftarrow R)$.

c) Accept the trial move to R' with probability

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

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 $\rho(R)$ 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.

2.8 THE VARIATIONAL QUANTUM MONTE CARLO

2.8.1 INTRODUCTION

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 where ever the potential is finite, and the integrals ψ_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:

$$E_V = \frac{\int \psi_T^*(R)\hat{H}\psi_T(R)dR}{\int \psi_T^*(R)\psi_T(R)dR} \geq E_0 \qquad (2.34)$$

In a VQMC simulation this bound is calculated using the metropolis Monte Carlo method. Equation (2.8.1.1) is rearranged as follows;

$$E_V = \frac{\int |\psi_T(R)|^2 \left[\psi_T(R)^{-1}\hat{H}\psi_T(R)\right] dR}{\int |\psi_T(R)|^2 dR}, \qquad (2.35)$$

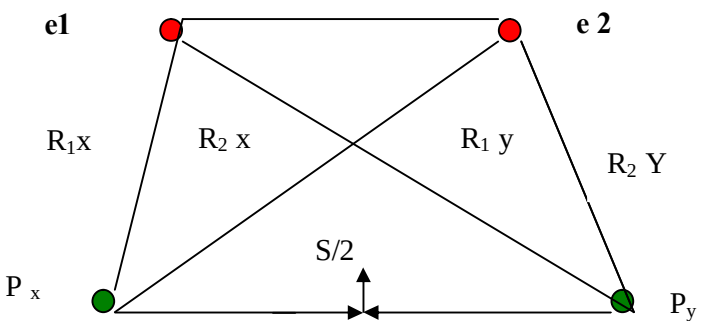
And the metropolis is used to sample a set of points $\{\mathbf{R_m}: m = 1, M\}$ from the configuration-space probability density

$$\rho(R) = \frac{\int |\psi_T(R)|^2}{\int |\psi_T(R)|^2 dR}. \qquad (2.36)$$

At each of these points the ñlocal energyò is evaluated and the average energy accumulated is given by

$$E_V \approx \frac{1}{M}\sum_{m=1}^{M} E_L(R_m). \qquad (2.37)$$

2.8.2 OPTIMIZATION OF TRIAL WAVEFUNCTION



e= electron, p = proton

Figure: 2 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:

$$\hat{H} = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) + \left(\frac{1}{S} + \frac{1}{r_{12}} - \frac{1}{r_{1X}} - \frac{1}{r_{1Y}} - \frac{1}{r_{2X}} - \frac{1}{r_{2Y}}\right) \tag{2.38}$$

Where ∇_1^2 and ∇_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 (2.8.2.1), therefore the trial wavefunction used in the non fixed nuclei restriction is the product of the four terms:

$$\psi_0 = \psi_1\psi_2\psi_3\psi_4 \tag{2.39}$$

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

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

$$\psi_1 = \exp(-ar_{1X}) + \exp(-ar_{1Y}) \tag{2.40}$$

$$\psi_2 = \exp(ar_{2X}) + \exp(-ar_{2Y}) \tag{2.41}$$

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 $\alpha = X \text{ or } Y$ it has the form

$$\psi_3 = \exp\left[\sum_{ij} \frac{a_{ij}^{(0)} r_{ij}}{1 + b_{ij}^{(0)}} + \sum_{ij} \frac{a_{ijkl}^{(1)} r_{ij} r_{kl}}{1 + b_{ijkl}^{(1)} r_{ij} r_{kl}}\right], \tag{2.42}$$

Where i j and k l include the interaction, 12, 1X. 1Y, 2X, and 2Y the wavefunction in (14) can be reduced to

$$\psi_3 = \exp\left(\frac{br_{12}}{1 + br_{12}}\right) \tag{2.43}$$

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

$$\psi_4 = \exp\left[-d(r_{XY} - c)^2\right] \tag{2.44}$$

The parameters *a, b, c,* and *d* made use of the following atomic unit respectively: 1.1750, 0.500, 1.401 and 10.0 (Chen and Anderson, 1995)

Equations (2.42, 2.43 and 2.44) 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_1 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 ñcuspò at $r_{iX} \to 0$ (Huang *et al*, 1990). This implies that the molecular orbital should satisfy;

$$\lim_{r_{1X}\to 0}\left[\frac{-\hbar^2}{2m}\frac{1}{\psi(r_{1X})}\nabla_1^2\psi(r_{1X})-\frac{e^2}{r_{1X}}\right]=finite\ terms \tag{2.45}$$

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

$$f(r)=\exp\left(\frac{r}{\alpha(1+\beta r)}\right) \tag{2.46}$$

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

$\alpha=\frac{1}{1+e^{-S/a}}$, and that $\alpha = 2a_0$ *where* $a_0=\frac{\hbar^2}{me^2}$ is the Bohr radius. Thus β 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:

$$\Phi(r_1,r_2)=\psi_1\psi_2 f(r_{12}) \tag{2.47}$$

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 orbital centred about each proton,

$$\psi(r_i)=e^{-r_{i\,X}/\alpha}+e^{-r_{iY}/\alpha}, \tag{2.48}$$

Putting (2.8.2.11) and (2.8.2.9) in (2.8.2.10) a collection of a justifiable trial wavefunction is attained:

$$\psi(r_1, r_2) = \left(e^{-r_{i1\,X}/\alpha} + e^{-r_{1Y}/\alpha}\right)\left(e^{-r_{i2\,X}/\alpha} + e^{-r_{2Y}/\alpha}\right)\exp\left(\frac{r_{12}}{2(1+\beta r_{12})}\right) \tag{2.49}$$

(2.49) 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:

$$\alpha = \frac{1}{1+e^{-S/a}}. \tag{2.50}$$

2.8.3 THE COULOMB CUSP CONDITION

When two coulomb particles get closer to themselves, the potential of the coulomb particles exhibit singularity $\left[\frac{1}{r}\right]$ at short distances which introduces some constraints on the trial wavefunction, therefore the trial wavefunction must have the correct form to cancel this singularity.

First of all let us consider an electron and a nucleus, the important portion of the Schrödinger equation is

$$\left[-\frac{1}{2M}\nabla_n^2 - \frac{1}{2}\nabla_e^2 - \frac{Ze^2}{r}\right]\psi = E\psi \tag{2.51}$$

Where M and Z represent the mass and charge of the nucleus respectively, if we assume that $M << m_e$ therefore the first term in (2.48) can be ignored then the second term can be represented in spherical coordinates as

$$-\frac{1}{2}\psi'' - \frac{1}{r}\left(Ze^2\psi + \psi'\right) = E\psi \tag{2.52}$$

In order for the singularity to cancel at small r, the term multiplying $\frac{1}{r}$ must vanish,

so that we have $\frac{1}{\psi}\psi' = -Ze^2$ (2.53)

If $\psi = e^{-cr}$ we must have $c = Ze^2$.

For the case of two electrons the Schrödinger equation takes the form

$$\left[-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + \frac{e^2}{r_{12}}\right]\psi = E\psi \quad (2.54)$$

Where r_{12} is the separation between the two electrons. Switching to relative coordinates $r_{12} = r_1 - r_2$ gives us

$$\left[-\nabla_{12}^2 + \frac{e^2}{r_{12}}\right]\psi = E\psi \quad (2.55)$$

Electrons that do not require antisymmetry have no additional factor of $\frac{1}{2}$ in the cusp condition compared with the electron-nucleus case. Hence we can have $c = -\frac{e^2}{2}$.

In the antisymmetric case, the electrons will be in a relative p state, reducing the cusp condition by1/2, so $c = e/4$.having the correct cusp for like spin electrons gains very little in the energy or the variance, because the antisymmetry requirements controls the repulsive forces between the electrons.

2.8.4 FIXED SAMPLE REWEIGHING

Fixed sampling reweighing with minimization of variance was made well known by (Umrigar and Fillipi, 2000) and has been extensively since then. The core of the method is the single sided reweighing method in which a number of configurations

are sampled from a distribution with variational parameters β . The energy at an arbitrary value of the variational parameter β, is computed by

$$E(\beta)=\sum_i w(R_i;\beta)E_L(R_i;\beta)/\sum_i w(R_i;\beta) \tag{2.56}$$

where $w(R_i;\beta)=\psi^2(R_i;\beta)/\psi^2(R_i;\beta_0)$. Alternatively, one could compute the variance by

$$A(\beta)=\sum_i w(R_i;\beta)(E_L(R_i;\beta)-E_T)^2/\sum_i w(R_i;\beta) \tag{2.57}$$

where E_T can either be the weighted average energy (2.51) or it could be a guess at the desired energy.

The weights in this expression can get very large when the variational parameters move far from the sampled value β_0 , and especially when the parameters that affect the nodes are adjusted.

2.9 THE PATH INTEGRAL MONTE CARLO METHOD (PIMC)

2.9.1 INTRODUCTION

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 (Johnson and Broughton, 1997) 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 (Feynman and Hibbs, 1965).

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 the 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 Planckôs constant $\hbar$:

$$K(x_b, t_b : x_a, t_a) \propto \sum_{all\ paths\ x_t} e^{iS[x(t)]/\hbar} \qquad (2.58)$$

$$with \quad x(t_a) = x_a, x(t_b) = x_b$$

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

$$K(x_b, t_b : x_a, t_a) \equiv \left\langle x_b \left| \exp\left(-\frac{1}{\hbar} H(t_b - t_a)\right) x_a \right\rangle = \left\langle x_b \left| \left(\exp\left(-\frac{1}{\hbar} H \Delta t\right)\right)^N \right| x_a \right\rangle \qquad (2.59)$$

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

$$K(x_b, t_b : x_a, t_a) = \int_{-\infty}^{\infty} dx_1 - \int_{-\infty}^{\infty} dx_{N-1} \prod_{k=1}^{N} \left\langle x_k \left| \exp(-iH\Delta t/\hbar) \right| x_{k-1} \right\rangle \qquad (2.60)$$

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

PIMC is mathematically similar to diffusion Monte Carlo [DMC] and shares many of the same advantages (Johnson and Broughton, 1997). 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 hopeless but, Feynmanôs imaginary time path integral (Koonin and Meredith, 1990) 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.

2.9.2 SIMULATING THE HYDROGEN MOLECULE AND THE HELIUM ATOM

A. 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 protonsô 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:

$$U(S) = \frac{e^2}{S} + E_0(S) \qquad (2.61)$$

Where e is the columbic 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:

$$H(S)\psi_0(r_1,r_2;S) \equiv [K+V(S)]\psi_0 = E_0(S\psi_0)(r_1,r_2;S) \tag{2.62}$$

$$\begin{aligned} &= -\frac{\hbar^2}{2m}\sum_{i=1}^{2}\nabla_i^2\psi(r_1,r_2;S) + V(r_1,r_2;S)\psi(r_1,r_2;S) \\ &= E_0(S\psi_0)(r_1,r_2;S) \end{aligned} \tag{2.63}$$

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

$$\text{V(}\mathbf{R}\text{)} = V(r_1,r_2;S)\psi = e^2\left[\frac{1}{r_{12}} - \frac{1}{r_{1L}} - \frac{1}{r_{1R}} - \frac{1}{r_{2L}} - \frac{1}{r_{2R}}\right] \tag{2.64}$$

Where r_{ij} are distances between particles as labelled in fig 1 and **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 (2.49) 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, $a, \alpha, and\ \beta$ are variational parameters. Because the wavefunction is required to meet the Coulomb ócuspô conditions, it is found that $\alpha = 2a_0$ (where a_0 is the Bohr radius), and α satisfies the transcendental equation (2.50): 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:

$$E_L(R) = -\frac{1}{2}\sum_{i=1}^{2}\left[\frac{2}{r_{12}\alpha(1+\beta r_{12})^3} + \frac{1}{a^2} + \frac{1}{\alpha^2(1+\beta r_{12})^4} + \frac{2\left(e^{-r_{iL}/\alpha/r_{iL}} + e^{-r_{iR}/\alpha/r_{iR}}\right)}{\alpha\left(e^{-r_{iL}/\alpha} + e^{-r_{iR}/\alpha}\right)} + \frac{(-1)^i.2\left(e^{-r_{iL}/\alpha}\vec{r_{iL}}.\vec{r_{12}} + e^{-r_{iR}/\alpha}\vec{r_{iR}}.\vec{r_{12}}\right)}{a\alpha(1+\beta r_{12})^2\left(e^{-r_{iL}/\alpha} + e^{-r_{iR}/\alpha}\right)}\right]$$

(2.65)

B. The Helium Atom

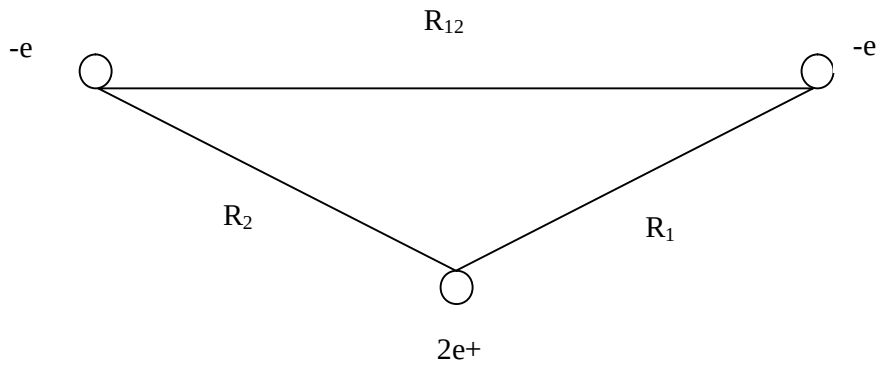


Figure 3: Coordinates used in describing the helium atom

The diagram above represents two electrons with charge ï e and a nucleus with charge +2e.

At this point it can be considered that we had already treated the hydrogen ï like atoms i.e. the hydrogen molecule to some certain extent, we now proceed to discuss the next simplest system: the helium atom. In this situation we have two electrons with coordinates r_1 and r_2 revolving round a nucleus with charge Z = 2 located at point S. In dealing with the hydrogen molecule we were able to ignore the motion of the nucleus by transforming the center of mass. We then obtain a Schrödinger equation for a single effective particle with a reduced mass that was very close to the electron mass orbiting the origin. It turns out to be fairly difficult to transform the center of mass when considering the three particle systems, as in the case of helium. However, because the nucleus is much more massive than either of the two electrons (M_{Nuc} ≈ 700 M_{elec})(Bhattacharyya *et'al,* 1996). It is a very good approximation to assume that the nucleus sits at the center of mass of the atom in this approximate set of center of mass coordinates, then S = 0 and the electron coordinates r_1 and r_2 measure the distance between each electron and the nucleus. Therefore considering the figure representing the coordinates (fig 1) that describe

the hydrogen molecule, it is therefore simply a case where the interproton separation S = 0 i.e. (fig 2) the protons are on top of each other. Since we are considering the Born-Oppenheimer approximation therefore holding the protons fixed and taking into account the coulomb interaction, hence there is no need to concern ourselves with the neutrons.

The helium atom can also be represented and simulated by equation (2.65), since the value of the interproton [S] for helium is known it provides a convenient system for which the value of β can be determined, whilst at the same time evaluating the complete ground state energy of a system, whose energy is known from an experiment.

The ground state of helium and helium ï like atoms are calculated by using wavefunctions constructed from the conventional orbital product, times a correlation function depending on the inter electronic distance r_{12}. These wavefunctions involve in general, a number of adjustable parameters which are constrained to satisfy some kind of variational principles to give an improved value for the ground state energy. The equation governing the hydrogen molecule described earlier solves almost all the available adjustable parameters living us with the variational parameter β to be varied numerically. It is then found that integration of the functions of r_{12} is quite difficult so that knowledge of electron correlation can only be perceived by using numerical routines only.

2.10 STRONG NUCLEAR FORCE IN THE HELIUM ATOM

The helium atom contains two electrons and two protons, but its mass is four times as great as that of a hydrogen atom. The extra mass comes from particles called neutrons, which are about as heavy as protons but carry no electrical charge.

Although atoms are small, atomic nuclei are much smaller still: about 100,000 times smaller in diameter, or roughly 10^{-15} meters in diameter. Within this tiny space are the positively charged protons that pulled on the electrons electrostatically. But the protons also repel each other, and this repulsion is extremely strong because they are so closed together. Despite the electromagnetic repulsion taking place in between the two protons in the helium atom a special kind of force exist at short range that keeps same coulomb particles together, these are the strong nuclear force and the weak nuclear force.

The strong nuclear force is the kind of forces that holds protons and neutrons together in the nucleus of an atom. According to (Barrow and Tipler, 1986) these forces are 10^{40} times more powerful than the force of gravity. This force binds electrically charged particles of the same polarity (e.g. +ve/+ve or -ve/-ve) by continuously alternating the polarity (helication direction) of the emitted photons of the medium between them and thus continually attract and repel the particles.

The weak nuclear force which is currently defined as the force responsible for radioactivity or the half-life of an isotope does not in fact exist.

CHAPTER THREE

COMPUTATION

3.1 THE PROGRAM PACKAGE

The programme employed in this work is written in FORTRAN language (Koonin and Meredith, 1990). There are four categories of files included in the package: the source code, common utility codes, data codes, and include codes.

3.1.1 THE SOURCE CODE

The source code (Appendix I) is organized in subroutines, each performing limited and well defined tasks. The subroutines that perform the calculation are at the beginning of the code with a header that describes the purpose of the subroutine and the variable it uses. There are five types; input and output variables (which are passed to the subroutines in the call statement), LOCAL variables (which are used only within that subroutine), FUNCTION (which are define FORTRAN functions) and GLOBAL variables (which are passed in common blocks). These are subroutines INIT, PARAM, PRMOUT, TXTOUT, GRFOUT and ARCHON. There purpose is to keep calls to subroutines as uncluttered, but as informative, as possible variables that are constant for one run are passed in common blocks.

3.1.2 THE COMMON UTILITY, DATA AND INCLUDE CODES

This code contains three main files: UTIL.FOR, SETUP.FOR and GRAPHIT.BLK. These files are called by and therefore must link with the source code. UTIL.FOR contains the routines for menuing, I/O, file opening/closing e.t.c. SETUP.FOR contains all variables and routines that are hardware and compiler dependent e.g. screen length and terminal unit number. (This file can be edited to get the most

efficient and attractive output). GRAPHIT.BLK contains and empty subroutines for non-existence package. This file is included so that there are no unsatisfied calls at link time. There are three data codes (files) all have .DAT extension and contain data to be read into the source code at run time. The last category of the file in the package is the include file which contains common blocks and variables type declarations that must be included in the FORTRAN source code to compile them.

3.2 COMPUTATIONAL PROCEDURE

In order to run this code the programmers work bench (PWB) editor was used, where the options menu was selected and a program list was further selected, this sub menu has two functions:

1. If you name a program list that already exist. The PWB saves the status of the current project (if any) and switches to the project you named.

2. If you name a program list that does not exist PWB prompts you to create it.

In this research the second option was performed, i.e. creating a new program list. This program list is having .MAK extension and is containing the following files: source code.for, setup.for, util.for and graphit.for, these are contained in the subdirectory of the source directory (i.e. default directory). PWB takes a few seconds to write the program list. At this instance the program is ready to be built. To build the program you go to make menu and choose either Rebuild All or Build of the compilation or link is unsuccessful, the compile results appears with a list of operations and errors.

3.3 COMPILATION

Before the compilation procedure takes effect, there is need for editing in some of the files. In the first place the FORTRAN compiler has to support the ñINCLUDEò statement, if it doesnôt support it, then the source code and the utility codes have to be edited to include the common block files, in this case the FORTRAN compiler supports the include statements and the ñ!ò comment delimiter, the next step is to edit the subroutine SETUP in the file SETUP.FOR. Instructions are given in that file regarding the constant values for variables that controls the input/output to be edited, for example one would need to know how many lines there are on the terminal (usually 24), unit numbers for I/O to the screen (these are 5 and 6 on VAX), unit numbers for output files and personal preference for default output (e.g. will you usually want graphics sent to terminal?).

With these changes completed, the main program (as in appendix 1), UTIL.FOR, SETUP.FOR, and GRAPHIT.FOR are compiled, linked and saved together in a mak. file which has a .MAK extension.

3.4 EXECUTION

If there were no errors detected during the compilation then the execution of the program began. This is beginning with choosing the option RUN in the file menu of the PWB then executes the program. At this stage a dialogue box will appear giving further options then among the options run program was selected.

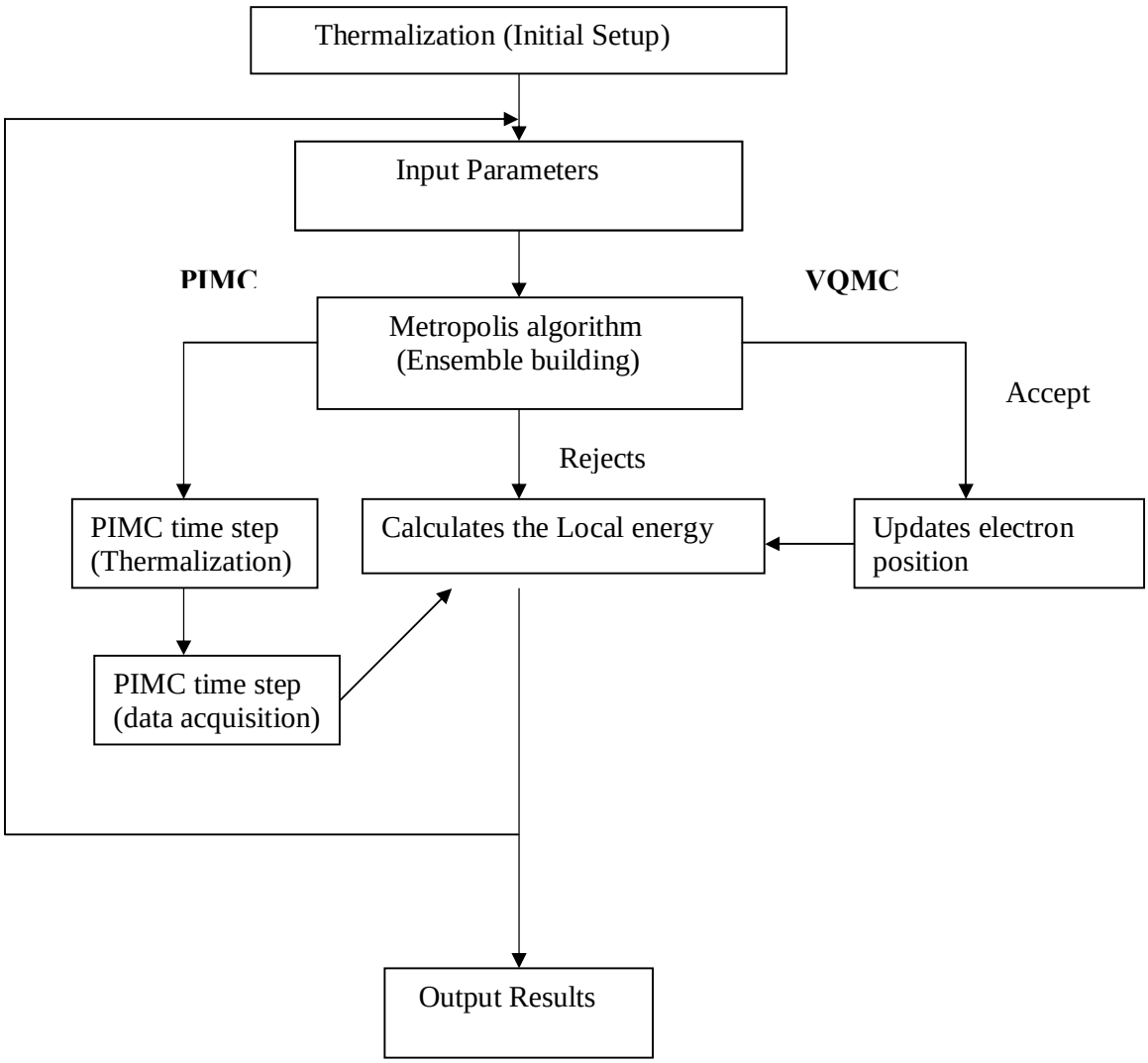
The program was designed to run interactively therefore it begins with a title page describing the physical problem to be investigated and the output that will be produced, and then the main menu is displayed giving choices of entering parameters value, examining parameters value running the program or terminating the program.

All parameters have default values. The enter key can be pressed for effecting the default value and if there is need to input any value the correct format is used and the change is effected automatically.

3.5 THE ALGORITHM OF THE PROGRAM

The program solves the two-center, two-electron of the H_2 molecule using the two techniques (Variational and Path Integral Mote Carlo) applied in this work. It calculates either the ground state energy (Eigenvalue) of the electron or the correlation in the energy. Before calculation begin equation (2.50) is solved for α (subroutine PARAM) and the initial configuration (for the variational, subroutine INTCFG) or ensembles (for PIMC, subroutine INTENS) are generated. The main calculations are done in subroutine ARCHON, thermalization in loop 10 and data taking in loop 20. The metropolis steps for the variational calculations are taken in the subroutine METROP, while time step for the PIMC calculations are taken in the subroutine TSTEP. Both methods uses functions ELOCAL (to find the ground state energy of a given configuration) and PHI (to calculate the wavefunction for a given configuration; each of these in turn calls subroutine RADII to calculate relative distance. In addition, TSTEP also calls subroutine DRIFT to calculate the drift vector and uses the function GUASS to generate a random number from a Gaussian distribution with zero mean and unit variance. The electronic ground state energy is found from either method, using observation taken every NFREQôth step, and divided in to groups to estimate the step-to-step correlations in the energy. The flowchart of the codes algorithm can be illustrated as in overleaf;

FLOWCHART OF THE CODE



3.6 INPUT

The physical parameters are the inter-proton separation [0.] (So that a neutral Helium atom is being described) and the variational parameter β [.25] (All lengths are in angstroms, all energies are in eV). The numerical parameters include the method of calculation [variational] (rather than PIMC), ensemble size (PIMC only) [20], time step (PIMC only) [.01], sampling step in configuration space [.4], number of thermalization sweeps [20], quantity to calculate [Energy] (rather than correlations), sampling frequency (energy only) [10].maximum correlation length (correlation only) [40], number of groups [10], and random number seed [34767]. Note that the sampling step for PIMC is set equal to $1.5a$ in subroutine PARAM. For correlations, the frequency and group size are set equal to one. The maximum ensemble size is fixed by MAXENS = 100, and the maximum number of groups allowed for correlations is fixed by MAXCRR= 500. It should be noted that for correlations the number of groups must be significantly larger than the maximum correlation length (so that the averages in Eqn 2.5.2 are statistically significant), But must also be smaller than MAXCRR. These checks are performed in subroutine PARAM. The text output parameter allows one to choose the short version of the output for which the samples sum are not displayed [long version enabled].

3.7 OUTPUT

Every NFREQ'th step the text output displays the group index, sample index, group size, and energy (unless the short version of the output is requested). For the electronic eigenvalue calculation when each group is finished (every NFREQ*NSMPL'th step), the text displays the group index, number of groups, average group energy, and group uncertainty as well as the total (including all group calculated so far) average energy, the two estimates for uncertainty in the energy, the total energy of the H_2 system, and the acceptance ratio (variational method only). For the correlation calculations, when all groups are complete, the program displays correlation Vs correlation length; the results could be plotted if graphics are requested or else are written as text.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1 RESULTS

The lowest eigenvalue of the hydrogen H_2 molecule ($\boldsymbol{E_0}$) for different interproton separations were computed using the variational quantum Monte Carlo [VQMC] and the Path Integral Monte Carlo methods with respect to Born-Oppenhiemer approximations. The results were presented graphically in Figure 3 and Figure 4 respectively and in a tabular form in tables 4.1,(comparative analysis with other researchers in the field) 4.3 and 4.5 (sample results in the group size been selected by the user. These two results were further accumulated in Figure 5 and compared with the exact values obtained by (Kolos and Wolniewcz, 1968) 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 (2.8.1.12). The numerical calculations from the PIMC method show a significant improvement towards approaching 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 with the following units; the interproton separation measured in Angstroms (Å) 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 Bohr radius = 0.529177249À

1 Hatree = 27.2eV

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

Results from the case of helium atom indicates also that the ground state energy can be numerically obtained precisely by the path integral method of calculation as results from the PIMC shows much consistencies with the experimental findings. Samples of the results obtained for the case of this physical system of Helium atom were presented in tabular form in s 4.2 (comparative analysis with other workers in the field) 4.5, and 4.6 (represents samples in the group size been requested by the user) in this report as portion of the results being generated by the Monte Carlo procedures.

4.2 DISCUSSIONS

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 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 the work of Traynor, Anderson and Boghosian (1991) where they compare results obtained from Greenôs 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 of the hydrogen molecule was obtained at an interproton separation of about 0.75Å 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. The graph also indicates the relationship between the ground state energy and the interproton separation as parabolic, therefore the ground state energy is a function of interproton separation and the coefficient of the square of the interproton separation is positive (+ve) that is why in all cases the parabola opens upward, and this further relates the graph to be a quadratic function.

In the case of helium atom the results obtained from this work can be compared with the exact results calculated by Kinoshita, T (1957) and result obtained by Doma and El-Gamal (2010) where a variational approach was used to determine the ground state energy of the helium atom, it can also be compared with the result gotten by Koki, F. S. (2009) and Martin D. (2007) where the ground state energy of Helium atom was calculated using Heyllaras algorithm and the Green Functions Quantum Monte Carlo respectively.

The results obtained in this work were further represented graphically, Fig 4 is representing at each point on the energy axis a grand average of the energy at a specified inter nuclear distance in which the variational quantum Monte Carlo is applied to the system of Hydrogen molecule and thereby presents a parabola indicating that the relationship between the ground state energy and the interproton separation is quadratic, therefore the ground state energy is a function of internuclear distance and it can also be observed from the graph that the lowest possible ground state energy in the Hydrogen molecule occurs at an interproton separation of 0.75Å which is in agreement with other workers in the field. The parabolic shape of the graph is pointing upwards; this indicates that the coefficient of the square of the parameters in the interproton separation axis is positive. The lowest energy value of the ground state energy obtained by the variational

quantum Monte Carlo method for the 10 group size x 13 requested by the user was found to be -31.73eV. Each point on the graph is an average value of the ground state energy of 10 sample size as per the corresponding interproton separation. Fig 5 is a graph interpreting the result obtained when the Path Integral Monte Carlo is applied to the physical system of Hydrogen molecule at some specified interproton separation. The graph is a parabolic curve pointing upwards as in the case of Fig 4 where the VQMC is applied but in this case the apex of the graph points more downward than it is observed in Fig 4, this indicates that the value of the ground state energy observed in the PIMC is much lower than the one obtained by the VQMC therefore this shows that PIMC is more precise in determining the GSE of the Hydrogen molecule. The result obtained by the path Integral method is -31.92eV,this value is much closer to the standard and commonly refered value byb authors in this field. The standard theoretical value obtained by Kolos and Wolniewcz is -31.94eV. this precision could be connected to the application of stochastic gradient approximationby the PIMC which generates quantum distribution directly from the Hamiltonian. The ground state energy of the Hydrogen molecule obtained by the PIMC method was also found to occur at an interproton separation of 0.75Å which is in order of accuracy when compared with other researchers in the field.

Fig 6 this is a comparative description of the analysis implemented by the two quantum monte Carlo methods employed to determine the ground state energy of the Hydrogen molecule at some values of some interproton separation. Clearly from the graph it can be observed that at any point of intersection between the ground state energy and the interproton separation, the PIMC shows a more order of accuracy than the VQMC. It can also be observed that an interproton separation

of 0.75Å they all converge to their lowest value of the energy though the result obtained from PIMC is much lower. The two graphs have the same function i.e they are all quadratic function and parabolic pointing upwards.

Fig 7. This is a graphic representation of the value of ground state energy obtained for samples of ensembles in a group by the PIMC method at an interproton separation of 0.9Å. The points on the graph appears to be randomly distributed, this could be attributed to the Monte Carlo procedures involved. All the points fall within the range of -30.8eV to -31.7eV. Although the standard value of the GSE is -31.94eV. This indicates that the interproton separation is dependent on the value of ground state energy.

Fig 8 This graph can be similarly explained as in Fig 6 only that the PIMC method was applied at a different interproton separation i.e 0.75Å and the ground state energy range obtained for this class of ensembles is from -31.3eV - -32.0eV. the points in the graphs are also randomly distributed, that can be attributed to the application of Monte Carlo procedures coupled with the path integral formulations.

Fig 9 this graph is another set of samples of ensembles plotted against the ground state energy of the Hydrogen molecule obtained by the PIMC method at an interproton separation of 0.5Å while the ground state energy range obtained is between ï 29.6eV ï 30.1eV. This value deviated very far from the standard value which testifies the impact of internuclear separation.

Fig 10-12 These are set of graphs that presents sets of samples of ensembles in some requested groups by the variational quantum Monte Carlo methods at different interproton separation ranging as the case of path integral Monte Carlo i.e 0.9Å, 0.75Å and 0.5Å. The ground state energies obtained in these graphs are

not very close to the standard values. This could be attributed to the intelligent guess of the trial wave function being involved in the variational principles thereby creating some kind of optimization parameters. All the graphs were randomly distributed within some specified range of ground state energy.

Fig 13 The time step requested by the user during the implementation of the path integral Monte Carlo on the physical system of Hydrogen molecule and the ground state energy was plotted and a straight line intersecting both axis when extrapolated was found to be a straight line with a positive gradient. This indicates that the relationship between this two parameters of the graph is linear and shows that the greater the value of the ground state energy the least value of time step required.

Fig 14.The standard errors observed in both methods that were applied to the physical system of Hydrogen molecule in determining the ground state energy is represented graphically in this figure. The precision is obtained by subtracting from the theoretical standard values obtained by (Kolos and Wolniewcz, 1968) commonly referred values by authorôs i.e -31.94eV. From the graph it indicates a higher precision at intermediate interproton separation and diverting from the standard value at lower interproton separation

Fig 15 this is a graph that describes the relationship of ground state energies been calculated when the VQMC method is applied at different variational parameters. However this energy curve is parabolic as the case of Hydrogen molecule but the values of the corresponding energy is lower than that of Hydrogen molecule obtained by VQMC.

Fig 16. Similarly this graph represents the relationship between the ground state energies observed when the path integral Monte Carlo method was applied to the

system of Helium atom at different variational parameters. The graph is also parabolic pointing upward indicating the quadratic nature of the graph. The interproton separation in this case is set equals to zero (0). The average value of the ground state energy is found to be the lowest point on the graph which indicates a higher order of accuracy as compared with other theoretical values that are essentially exact.

Fig 17. This graph is the graphical representation of the comparative analysis of the two methods been implemented on the Helium atom in order to determine its precise ground state energy. From the graph it confirms that the PIMC method is more precise than the VQMC.

Fig 18 ï 20 these are graphs presenting the results of the ground state energies of sample of ensembles been requested by the user as the VQMC method is applied to the system of Helium atom. The ground state energies in each of the graph was calculated at a given value of variational of parameter and hence represents randomly distributed points on the graph within some values of the ground state energies.

Fig 21 ï 23 These graphs presents the results of the ground state energies of sample of ensembles been requested by the user as the PIMC method is applied to the system of Helium atom. The ground state energies in each of the graph was calculated at a given value of variational of parameter and hence represents randomly distributed points on the graph within some values of the ground state energies.

Fig 24. This is the graphical representation of the comparative analysis between the two methods implemented (PIMC and VQMC) on the Helium atom at some specified values of variational parameters. The graph also indicates that the

ground state energy value obtained by the path integral method of calculations is more precise and approaches the required order of accuracy when compared with standard theoretical value. In all cases the ground state energy is obtained at 0.2ч which also corresponds to the standard value.

Table of comparative analysis of ground state energies of hydrogen molecule as well as the helium atom calculated by other researchers at some specified interproton separations and variational parameters are shown overleaf.

A. HYDROGEN MOLECULE

Table 4.1: Comparison of GSE results of Hydrogen molecule

S/N	AUTHOR	DATE	METHOD	GSE (a.u)
1	Koloz & Wolniewicz	1968	Exact (theory) BO Variational;	-1.1744
2	Traynor, Anderson & Boghosian	1991	DQMC/GFQMC (Non Restricted)	-1.163
3	Chen & Anderson	1995	GFQMC (Non restricted)	-1.1728
4	Ko, Wing Ho	2004	VMC/DMC (BO)	-1.1750
5	This work	2011	PIMC (BO)	-1.1736

B. HELIUM ATOM

Table 4.2: Comparison of GSE results of Helium atom

S/N	AUTHOR	DATE	METHOD	GSE (a.u)
1	Kinoshita, T	1957	Variational (Exact)	2.9037
2	Martin, D	2007	GFQMC	-2.9021
3	Koki, F. S	2009	Hyllerass Algorithm	-2.9042
4	Doma and El-Gamal	2010	Variational	-2.8981
5	This work	2011	PIMC (BO)	-2.9023

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

4.3 **SAMPLE RESULTS**

Output from: Numerical Calculation of ground State Energy of Hydrogen molecule using QMC methods
Interproton separation (Angstroms) **0 .5**
Variational parameter Beta (Angstroms Å **-1) = .2500

Variational Monte Carlo method
Metropolis step in coordinate space (Angstroms Å) = .4000
Number of thermalization sweeps = 10
Group size = 10

Table 4.3

Variational Quantum Monte Carlo Method (Hydrogen molecule)

Group properties	Energy (eV)
Group 1, sample 1 of 10	= -29.4113
Group 1, sample 2 of 10	= -29.6323
Group 1, sample 3 of 10	= -29.5243
Group 1, sample 4 of 10	= -29.4714
Group 1, sample 5 of 10	= -29.7082
Group 1, sample 6 of 10	= -29.7351
Group 1, sample 7 of 10	= -29.6810
Group 1, sample 8 of 10	= -29.7334
Group 1, sample 9 of 10	= -29.6287
Group 1, sample 10 of 10	= -29.4087
Group 1 of 10 Eigenvalue =	-29.601eV
Grand average E = -29.601eV	

This is a sample result of one group out of the 10 groups being requested by the user during run time.

Output from: Numerical Calculation of ground State Energy of Hydrogen molecule using QMC methods
Interproton separation (Angstroms Å) = **0 .5**

Path Integral Monte Carlo method
Time step = 0.01
Number of thermalization sweeps = 10
Group size = 10

Table 4.4

Path Integral Monte Carlo Method (Hydrogen molecule)

Group properties	Energy (eV)
Group 1, sample 1 of 10	= -29.8902
Group 1, sample 2 of 10	= -29.9186
Group 1, sample 3 of 10	= -29.8713
Group 1, sample 4 of 10	= -29.9289
Group 1, sample 5 of 10	= -30.0352
Group 1, sample 6 of 10	= -29.8911
Group 1, sample 7 of 10	= -29.9071
Group 1, sample 8 of 10	= -30.0083
Group 1, sample 9 of 10	= -30.0141
Group 1, sample 10 of 10	= -29.9601
Group 1 of 10	Eigenvalue = -29.9411eV
Grand average E = - 29.9411eV	

This is a sample result of one group out of the 10 groups being requested by the user during run time.

Output from: Numerical Calculation of ground State Energy of Helium atom using QMC methods

Interproton separation (Angstroms) **0 .0**

Variational parameter Beta (Angstroms Å **-1) = **0.05**

Variational Monte Carlo method

Metropolis step in coordinate space (Angstroms Å) = .4000

Number of thermalization sweeps = 10

Group size = 10

Table 4. 5

Variational Quantum Monte Carlo Method (Helium atom)

Group properties	Energy (eV)
Group 1, sample 1 of 10	= -78.734
Group 1, sample 2 of 10	= -78.503
Group 1, sample 3 of 10	= -78.638
Group 1, sample 4 of 10	= -78.623
Group 1, sample 5 of 10	= -78.669
Group 1, sample 6 of 10	= -78.628
Group 1, sample 7 of 10	= -78.564
Group 1, sample 8 of 10	= -78.582
Group 1, sample 9 of 10	= -78.599
Group 1, sample 10 of 10	= -78.621
Group 1 of 10	Eigenvalue = -78.614eV
Grand average E = -78.614eV	

This is a sample result of one group out of the 10 groups being requested by the user during run time.

Output from: Numerical Calculation of ground State Energy of Helium atom using QMC methods
Interproton separation (Angstroms Å) = **0 .0**
Variational parameter Beta (Angstroms Å **-1) = **0.05**

Path Integral Monte Carlo method
Time step = 0.0025
Number of thermalization sweeps = 10
Group size = 10

Table 4. 6

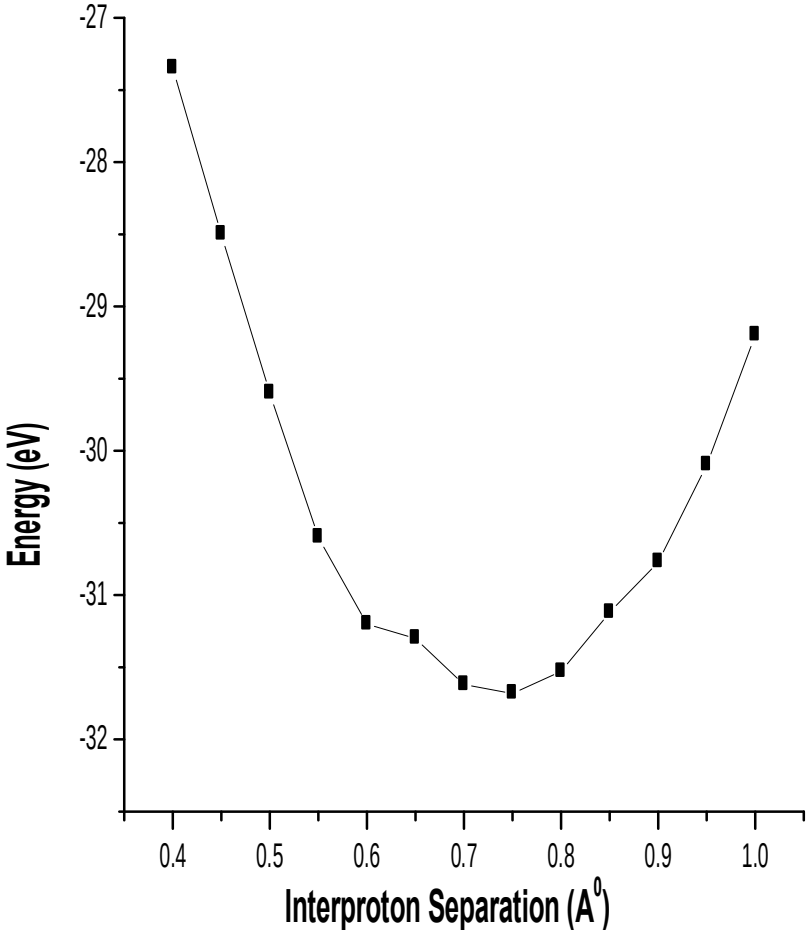
Path Integral Monte Carlo Method (Helium atom)

Group properties	Energy (eV)
Group 1, sample 1 of 10	= -78.792
Group 1, sample 2 of 10	= -78.774
Group 1, sample 3 of 10	= -78.708
Group 1, sample 4 of 10	= -78.797
Group 1, sample 5 of 10	= -78.703
Group 1, sample 6 of 10	= -78.773
Group 1, sample 7 of 10	= -78.749
Group 1, sample 8 of 10	= -78.782
Group 1, sample 9 of 10	= -78.737
Group 1, sample 10 of 10	= -78.765
Group 1 of 10	Eigenvalue = -78.748eV
Grand average E = - 78.748 eV	

This is a sample result of one group out of the 10 groups being requested by the user during run time.

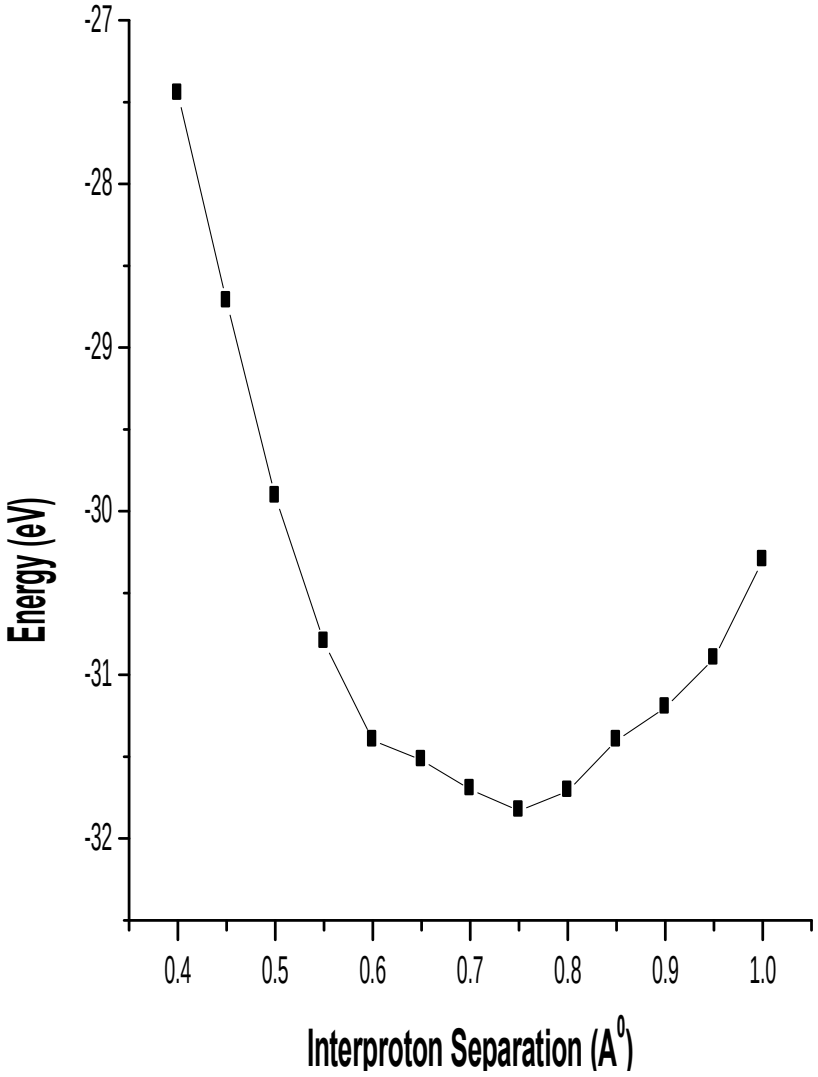
4.4 GRAPHS

Case 1: **HYDROGEN (H_2) MOLECULE**



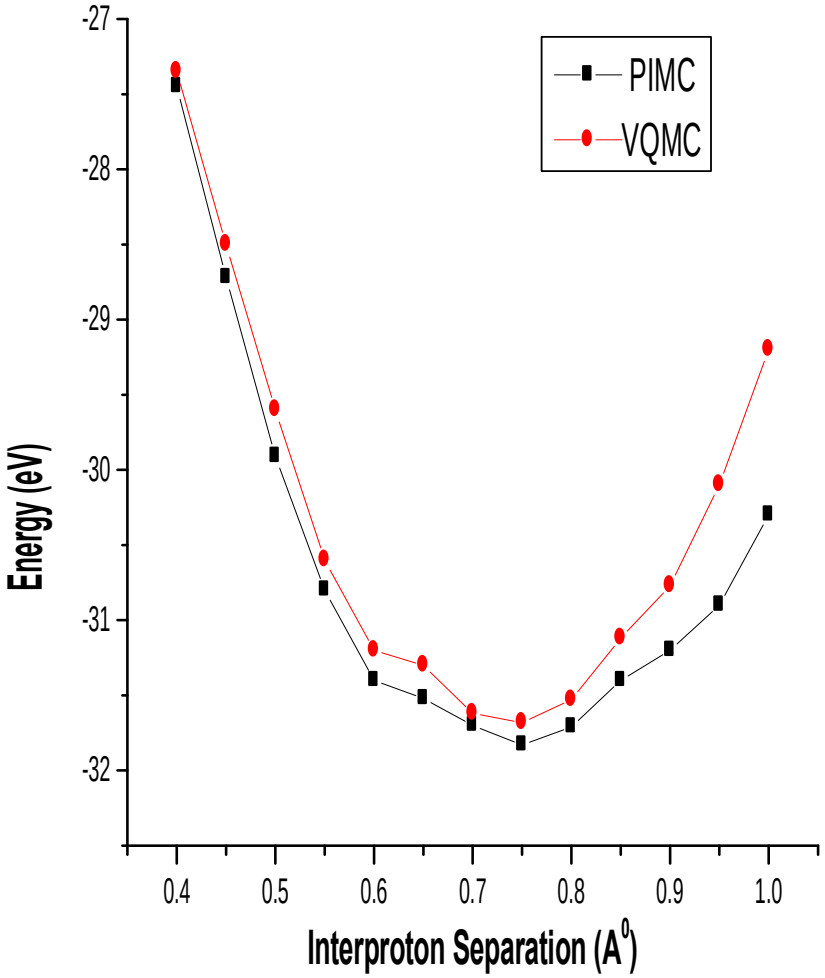
Standard value for the ground state energy of Hydrogen molecule by VQMC (Kolos and Wolniewcz) is -31.94eV

Figure 4 Graph of Ground State Energy Vs Interproton Separation (VQMC) for H_2 Molecule



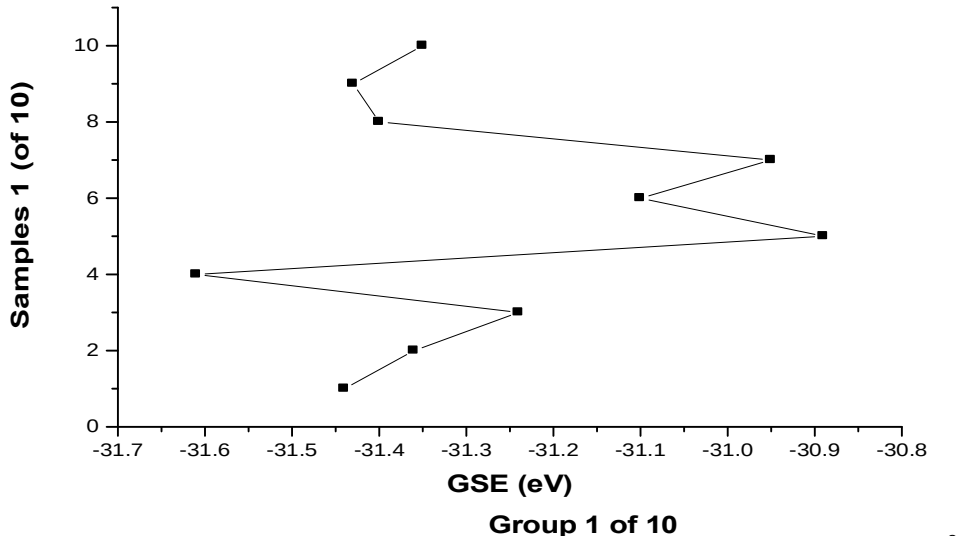
Standard value for the ground state energy of Hydrogen molecule by VQMC (Kolos and Wolniewcz) is -31.94eV

Figure 5 Graph of Ground State Energy Vs Interproton Separation (PIMC) for H_2 Molecule



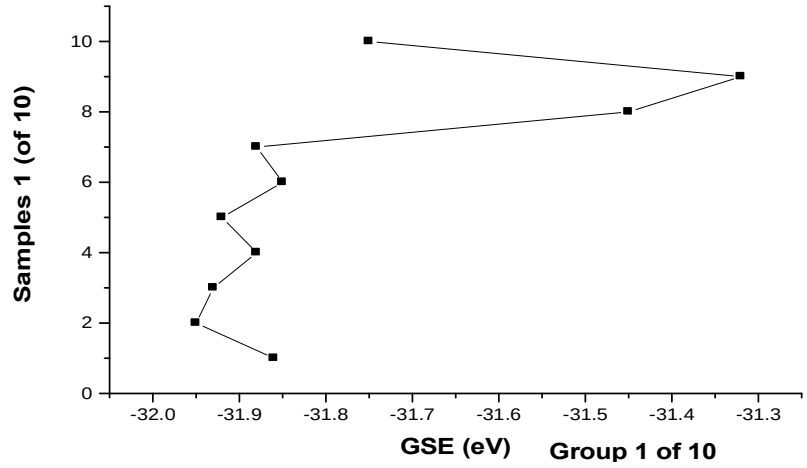
Standard value for the ground state energy of Hydrogen molecule by VQMC (Kolos and Wolniewcz) is -31.94eV

Figure 6 Graph of Ground State Energy Vs Interproton Separation for VQMC and PIMC (H_2 Molecule)



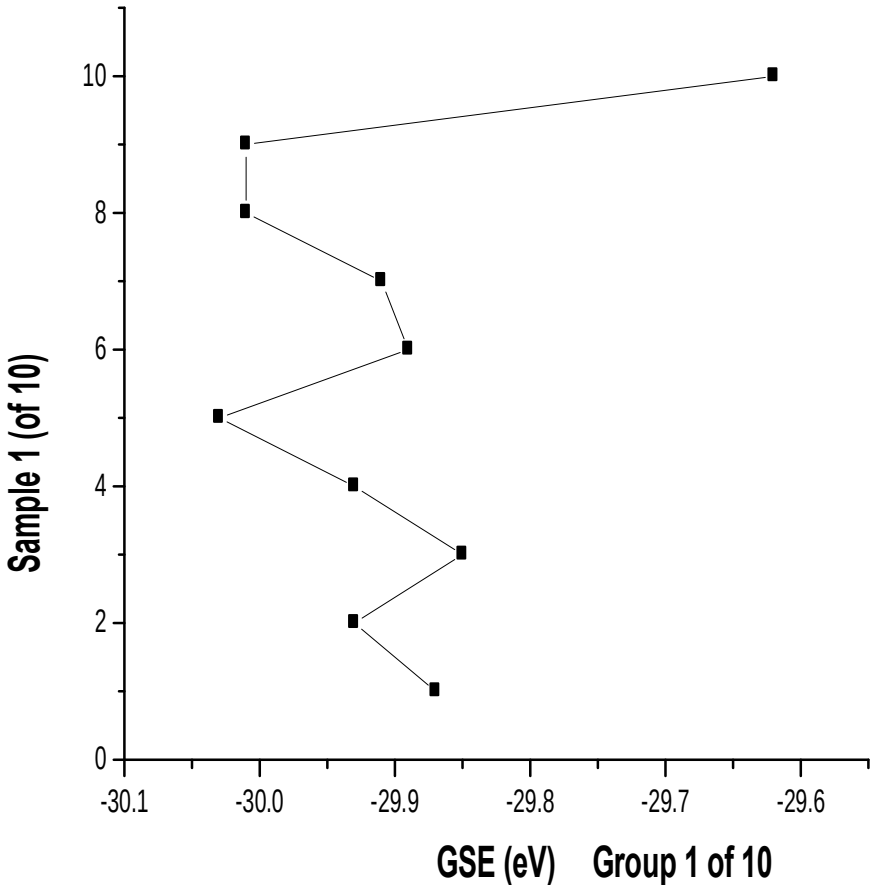
Standard value for the ground state energy of Hydrogen molecule by VQMC (Kolos and Wolniewcz) is -31.94eV

Fig 7 Graph of Samples of Ensembles Vs GSE (Group 1 PIMC, S = $0.9A^0$)



Standard value for the ground state energy of Hydrogen molecule by VQMC (Kolos and Wolniewcz) is -31.94eV

Figure 8 Graph of Samples of Ensembles Vs GSE (Group 1 PIMC, S = $0.75A^0$)



Standard value for the ground state energy of Hydrogen molecule by VQMC (Kolos and Wolniewcz) is -31.94eV

Figure 9 Graph of Samples of Ensembles Vs GSE for Hydrogen molecule (Group 1 PIMC, $S = 0.5A^0$)

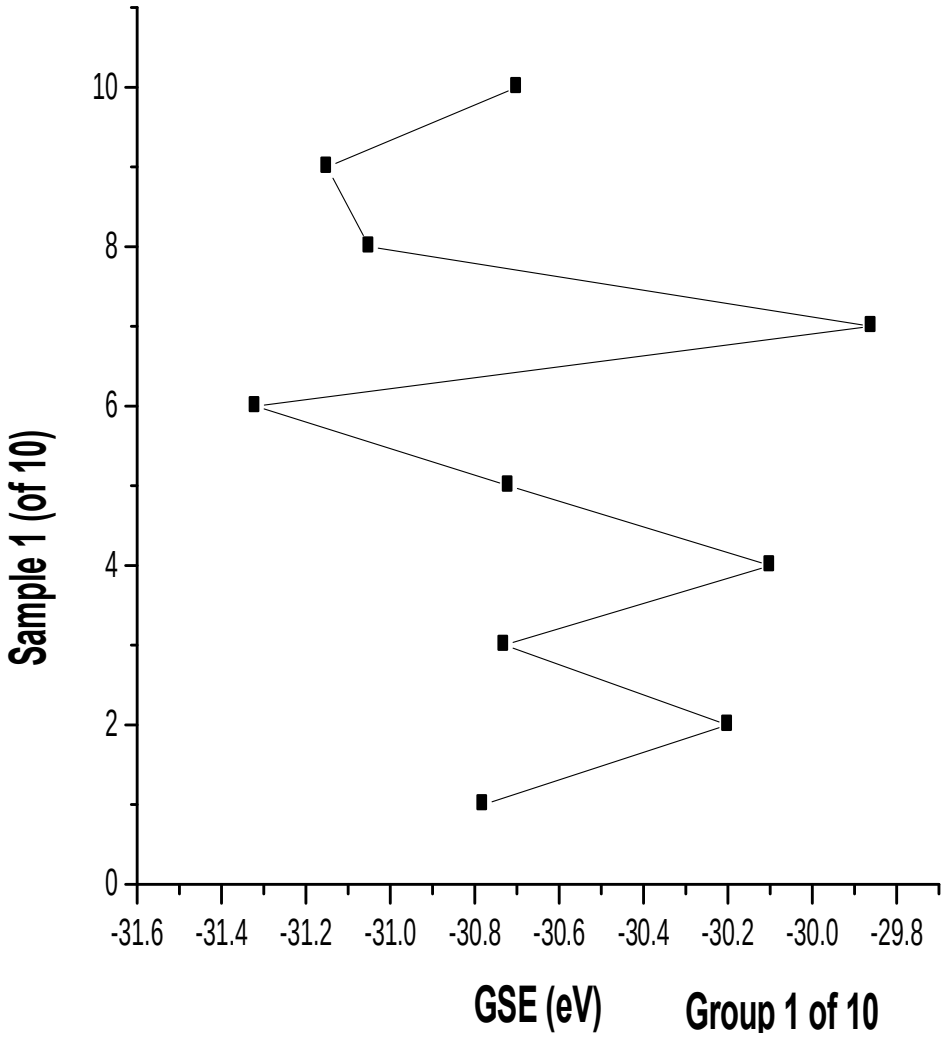
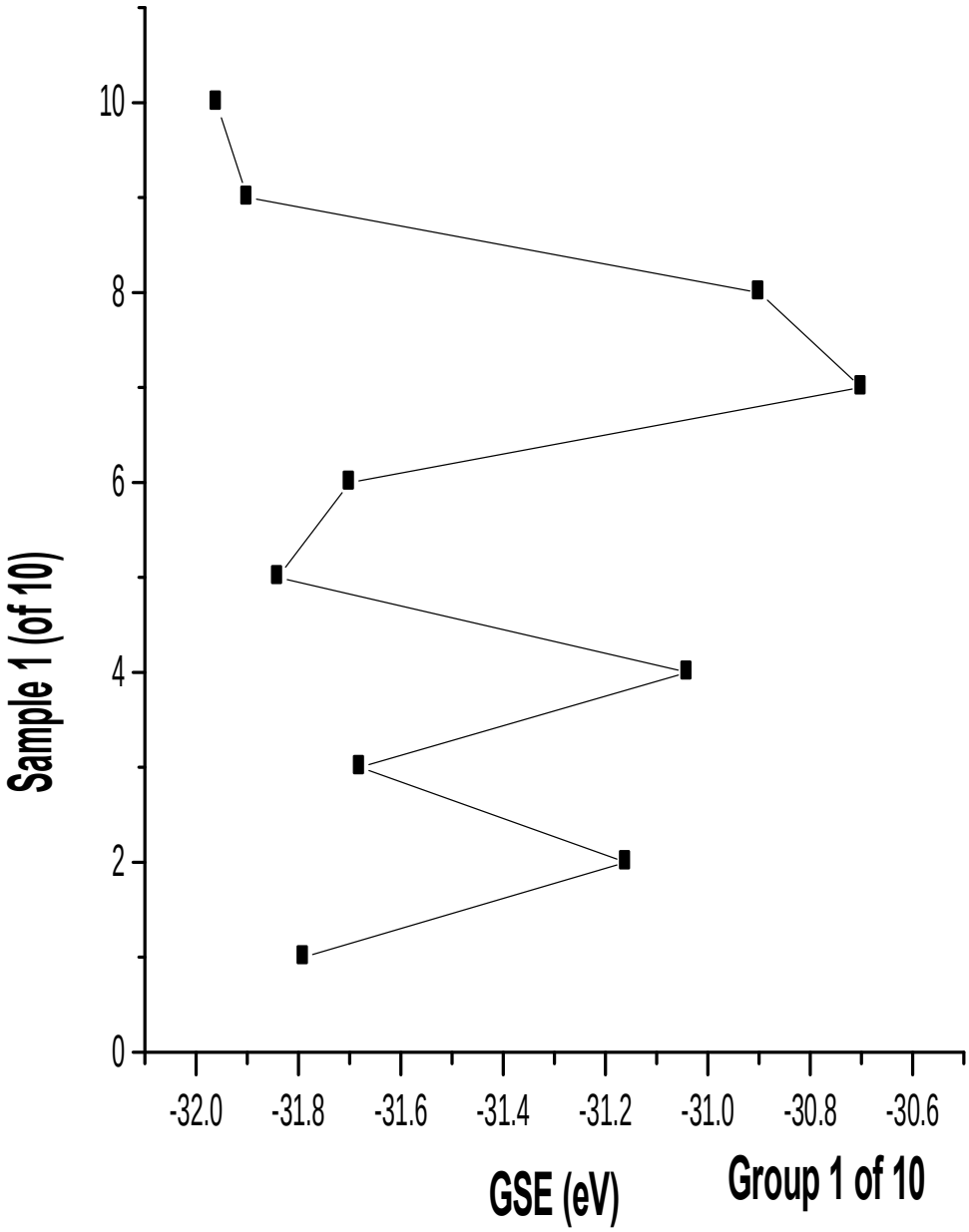
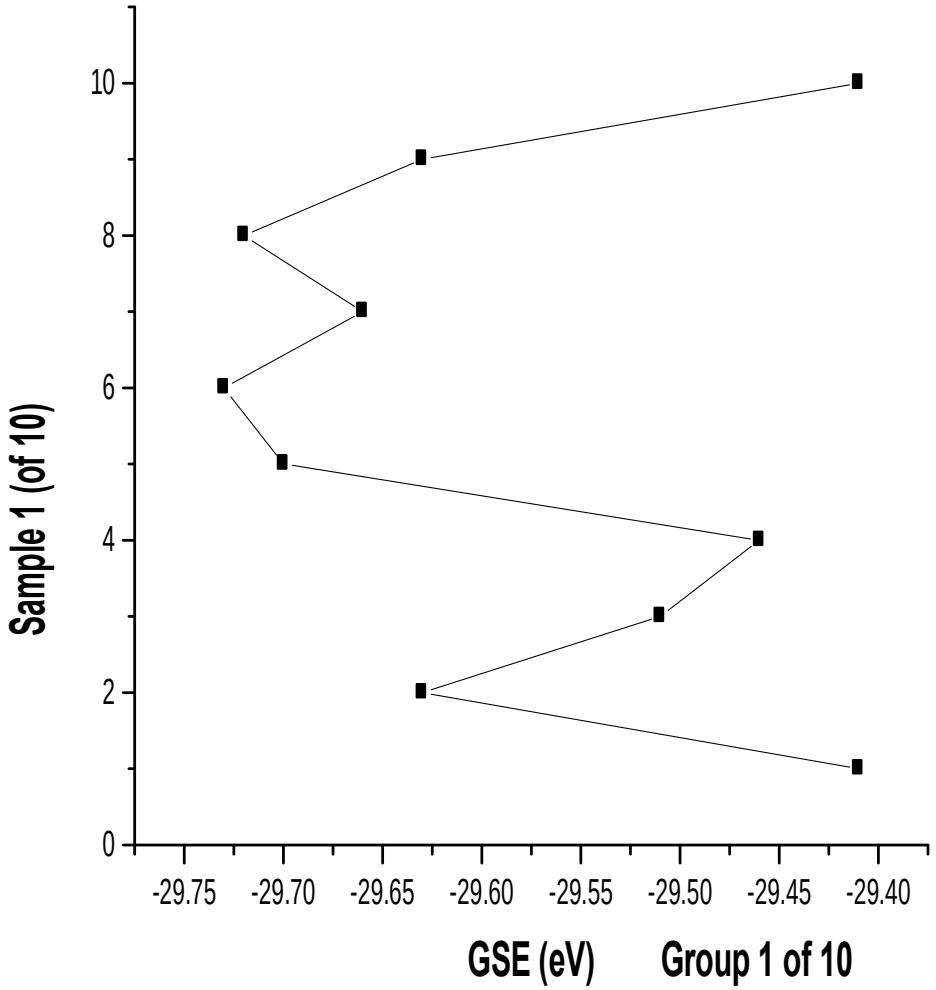


Figure 10 Graph of Samples of Ensembles Vs GSE for Hydrogen molecule (Group 1 VQMC, S = $0.9A^0$)



Standard value for the ground state energy of Hydrogen molecule by VQMC (Kolos and Wolniewcz) is -31.94eV

Figure 11 Graph of Samples of Ensembles Vs GSE for Hydrogen molecule (Group 1 VQMC, S = $0.75A^0$)



Standard value for the ground state energy of Hydrogen molecule by VQMC (Kolos and Wolniewcz) is -31.94eV

Figure 12 Graph of Samples of Ensembles Vs GSE for Hydrogen molecule (Group 1 VQMC, S = $0.5A^0$)

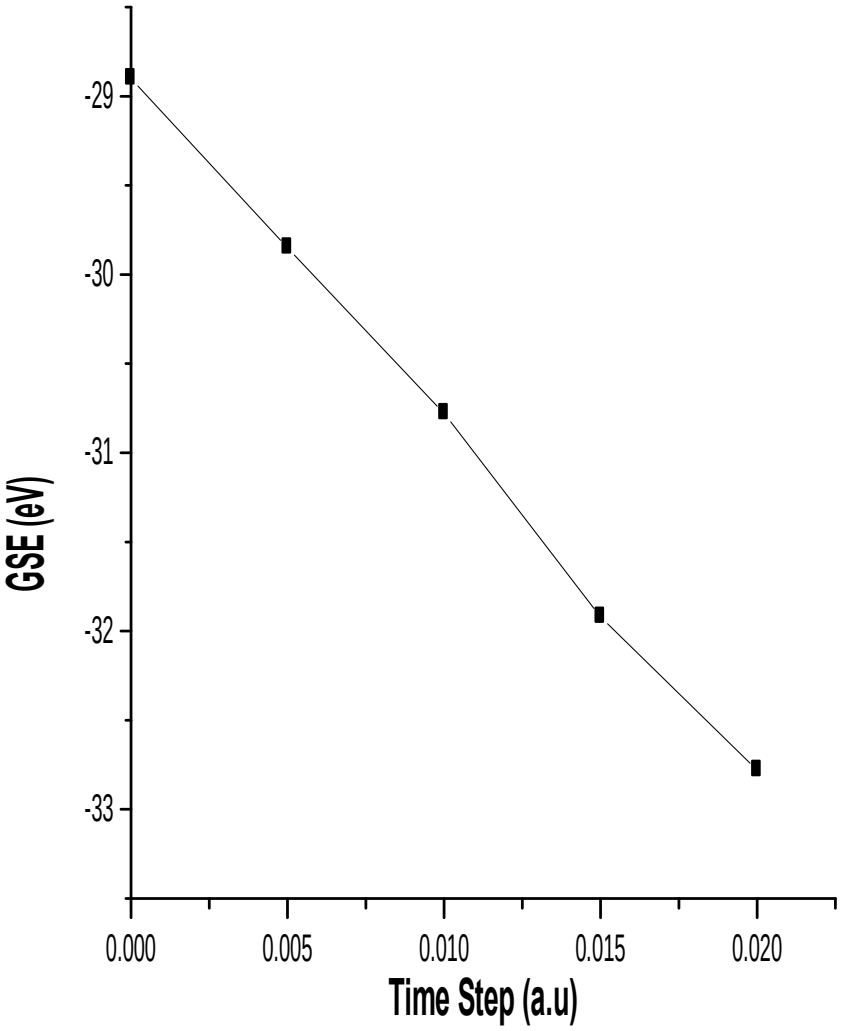


Figure 13 Graph of GSE Vs Time Step (PIMC) Extrapolated to Zero Time Step

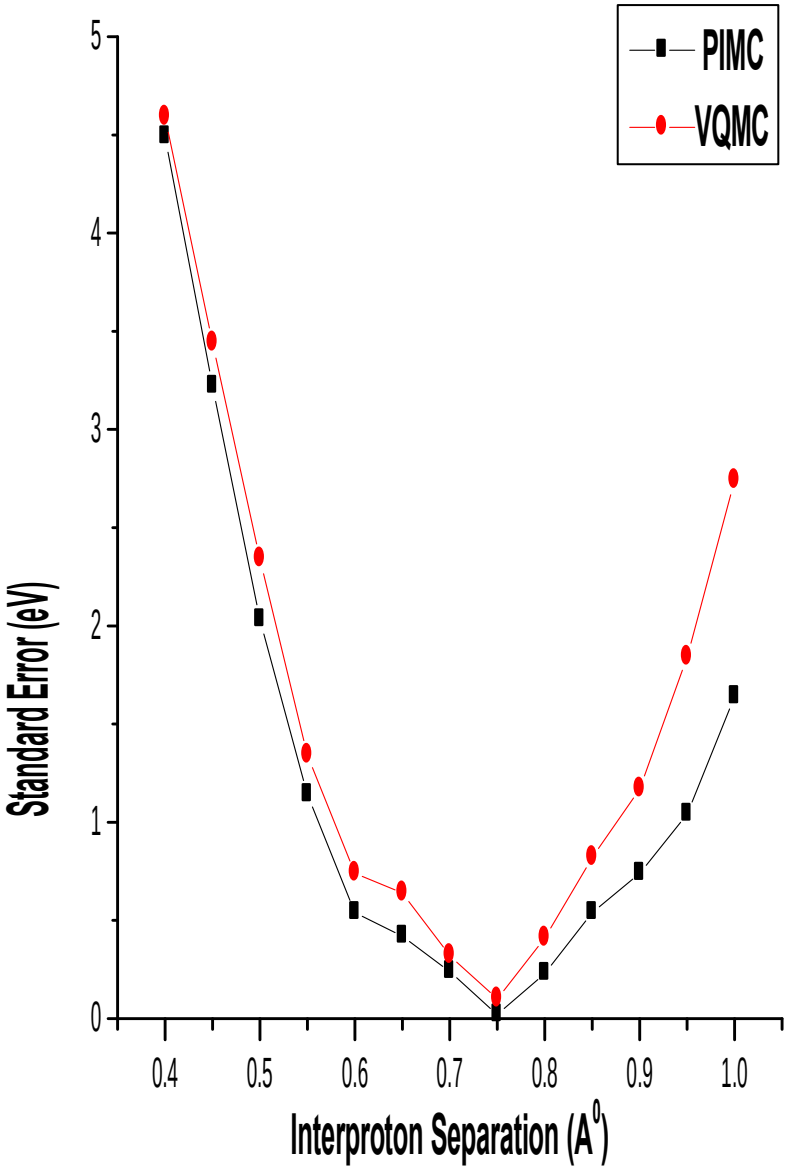
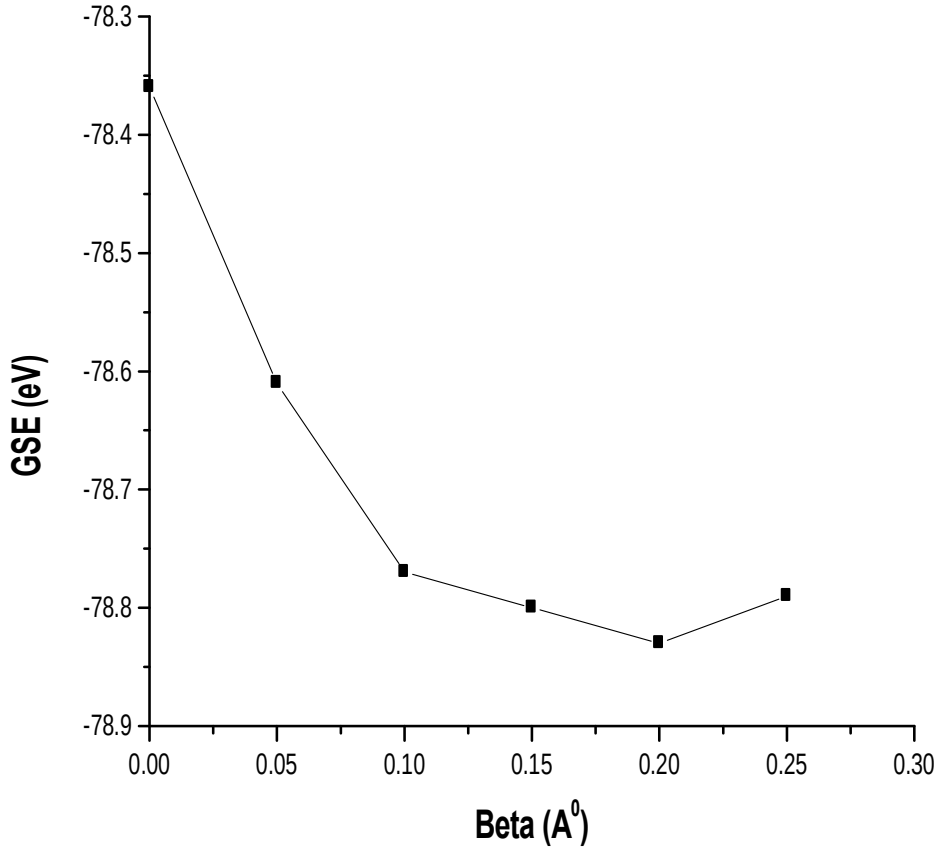


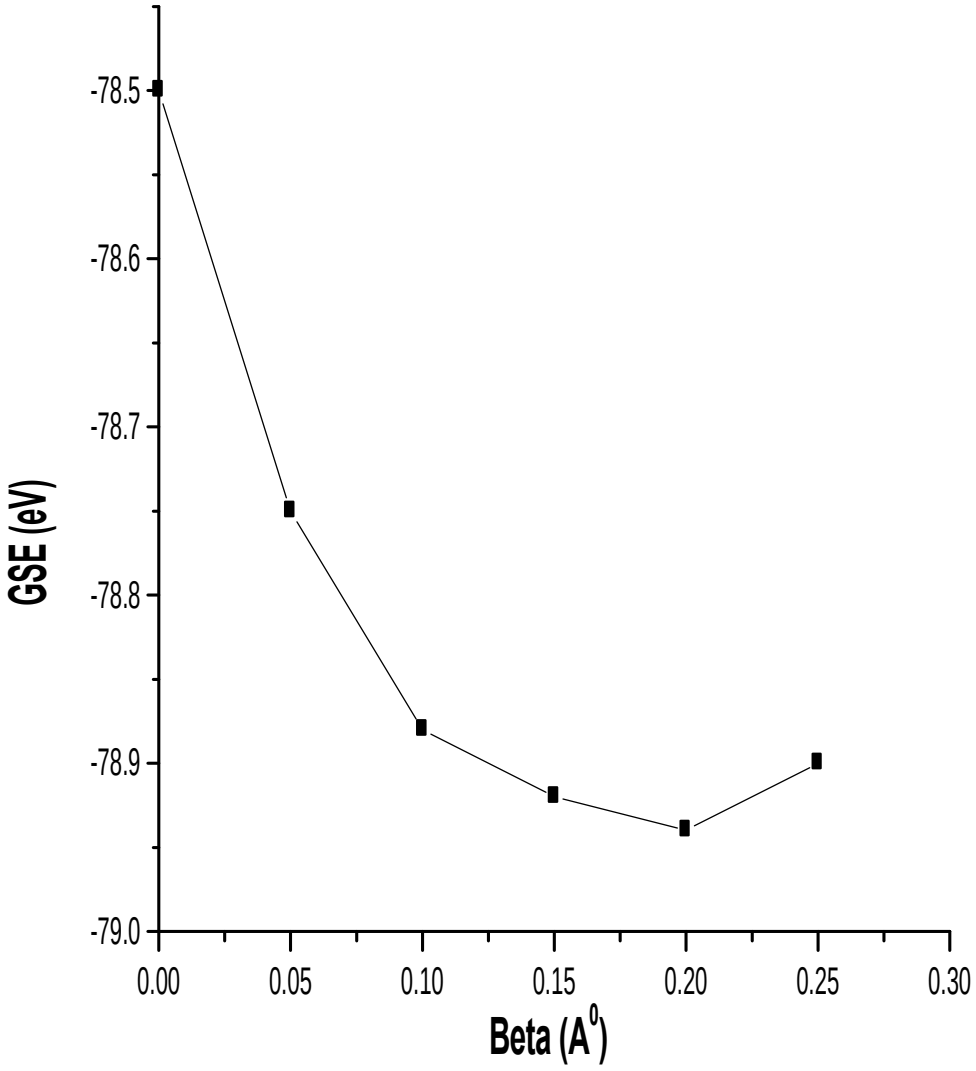
Figure14 Graph of Standard Error Vs Interproton Separation for PIMC and VQMC (H_2) Molecule

Case 2: **HELIUM ATOM**



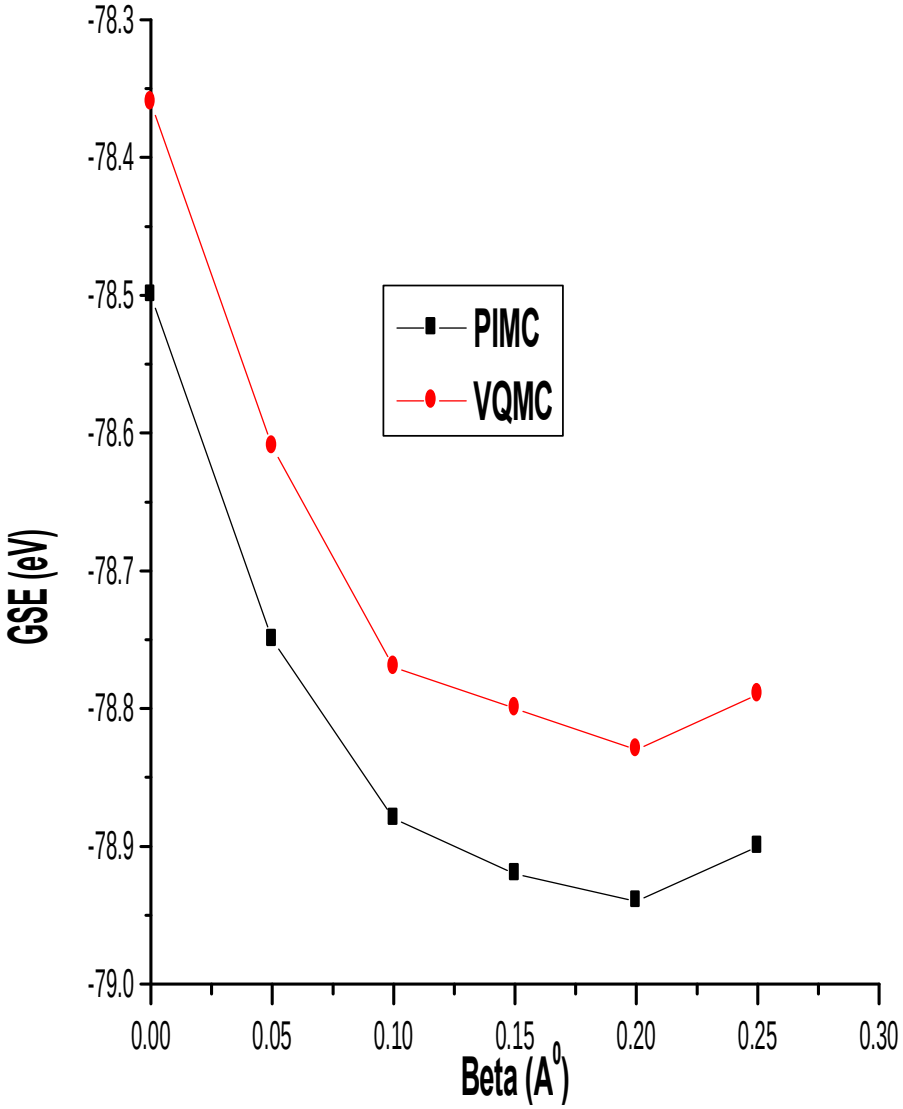
Standard value for the ground state energy of Helium atom by Variational principles (Kinoshita is -78.96eV)

Figure 15 Graph of GSE Vs Variational Parameter Beta for Helium Atom VQMC method



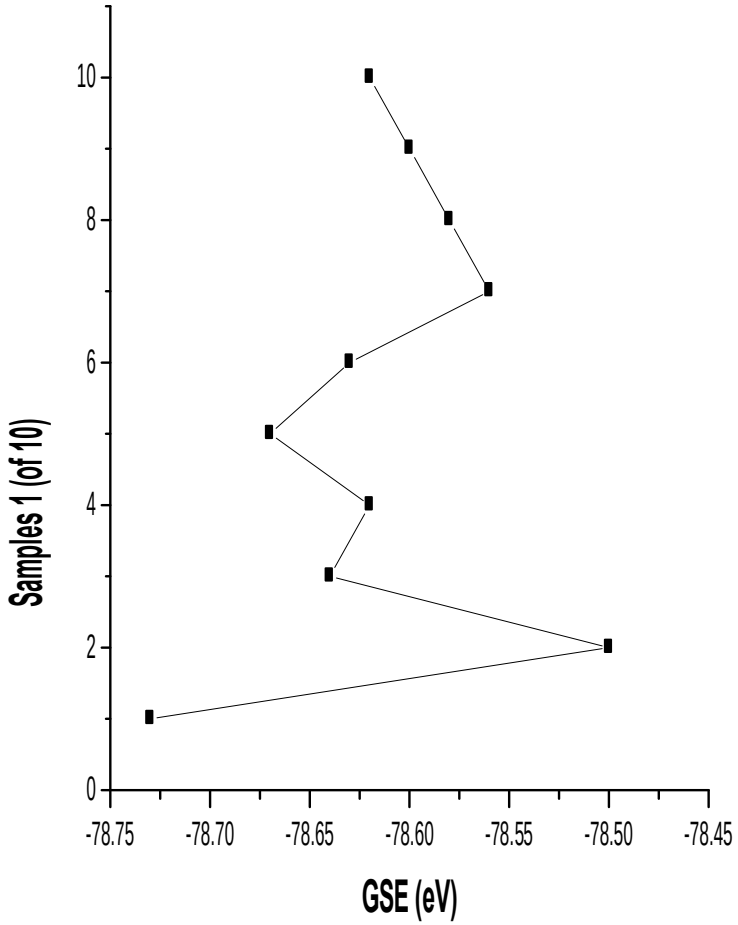
Standard value for the ground state energy of Helium atom by Variational principles (Kinoshita is -78.96eV)

Figure 16 Graph of Variational Parameter Beta for Helium Atom PIMC method



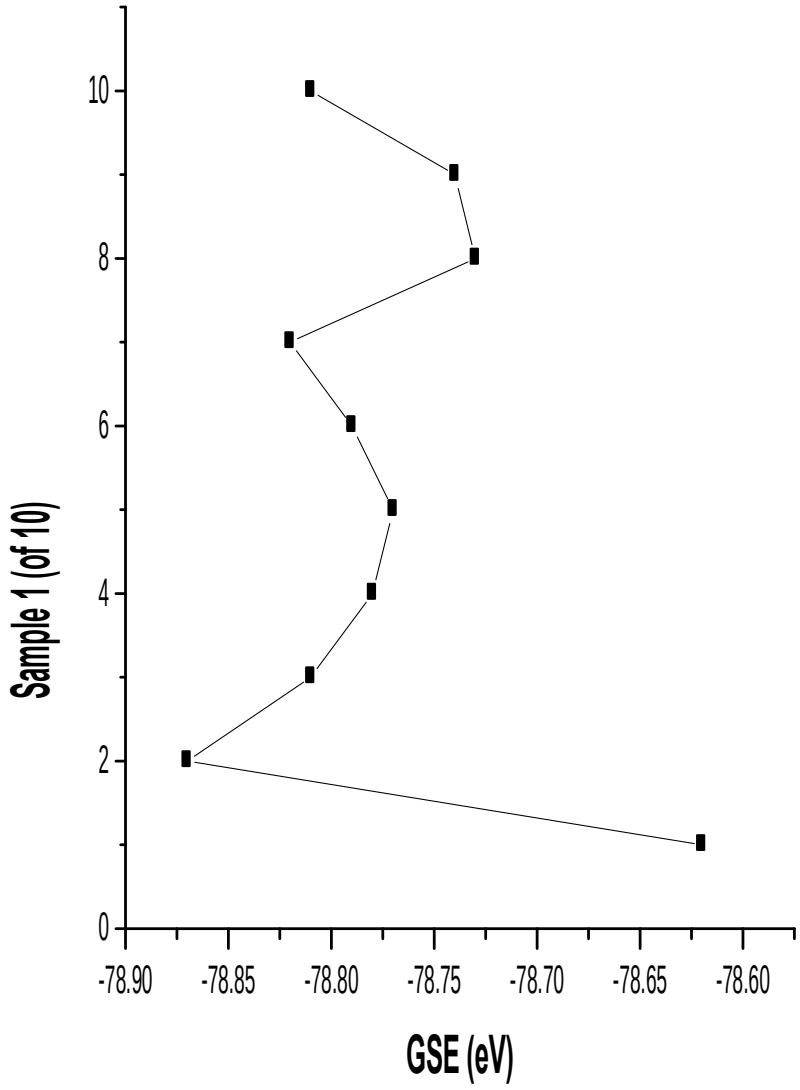
Standard value for the ground state energy of Helium atom by Variational principles (Kinoshita is -78.96eV)

Figure 17 Graph of GES Vs Variational Parameter Beta for Both PIMC and VQMC Methods (Helium Atom)



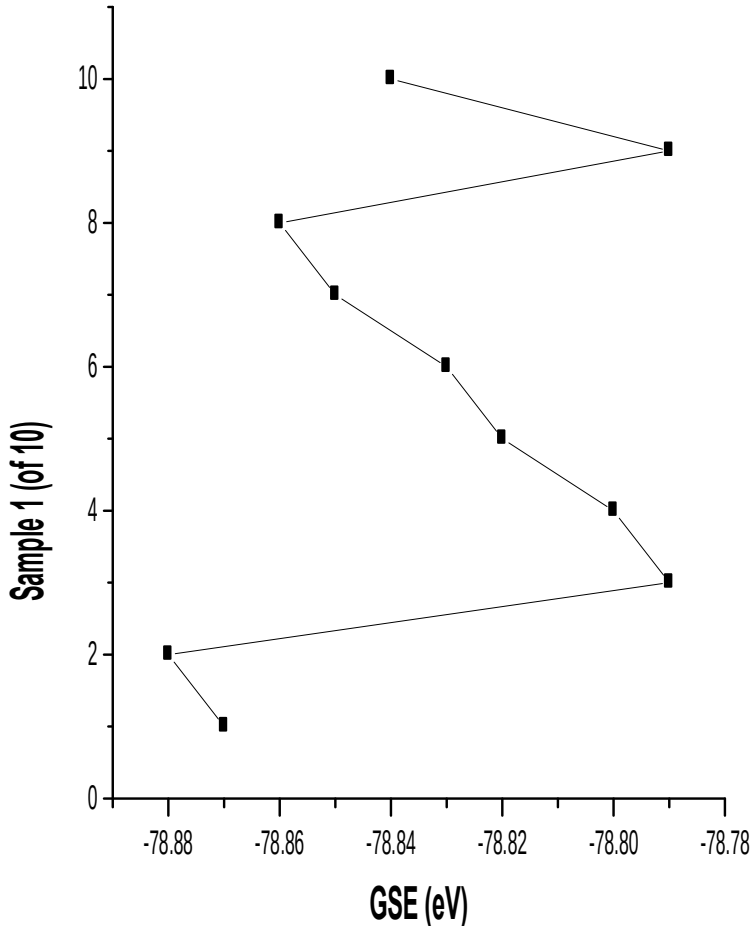
Standard value for the ground state energy of Helium atom by Variational principles (Kinoshita is -78.96eV)

Figure 18 Graph of Samples of Ensembles Vs GSE (Group 1 VQMC, β = 0.05A^0) Helium atom



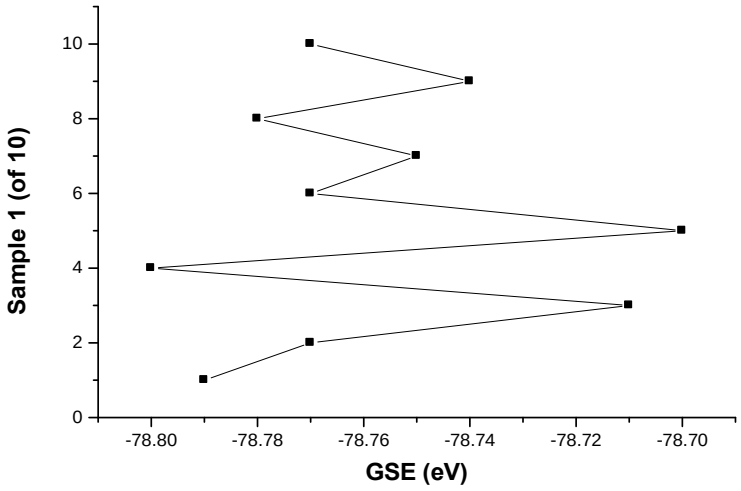
Standard value for the ground state energy of Helium atom by Variational principles (Kinoshita is -78.96eV)

Figure 19 Graph of Samples Vs GSE (Group 1VQMC, β =0.1A^0) Helium atom



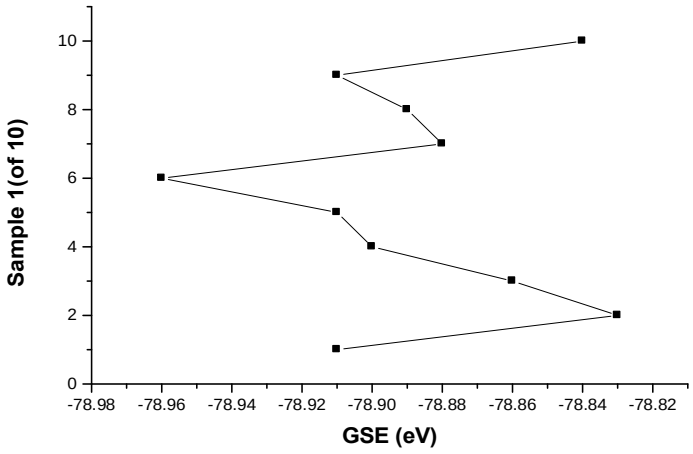
Standard value for the ground state energy of Helium atom by Variational principles (Kinoshita is -78.96eV)

Figure 20 Graph of Samples Vs GSE (Group 1VQMC, β =0.2A^0) Helium atom



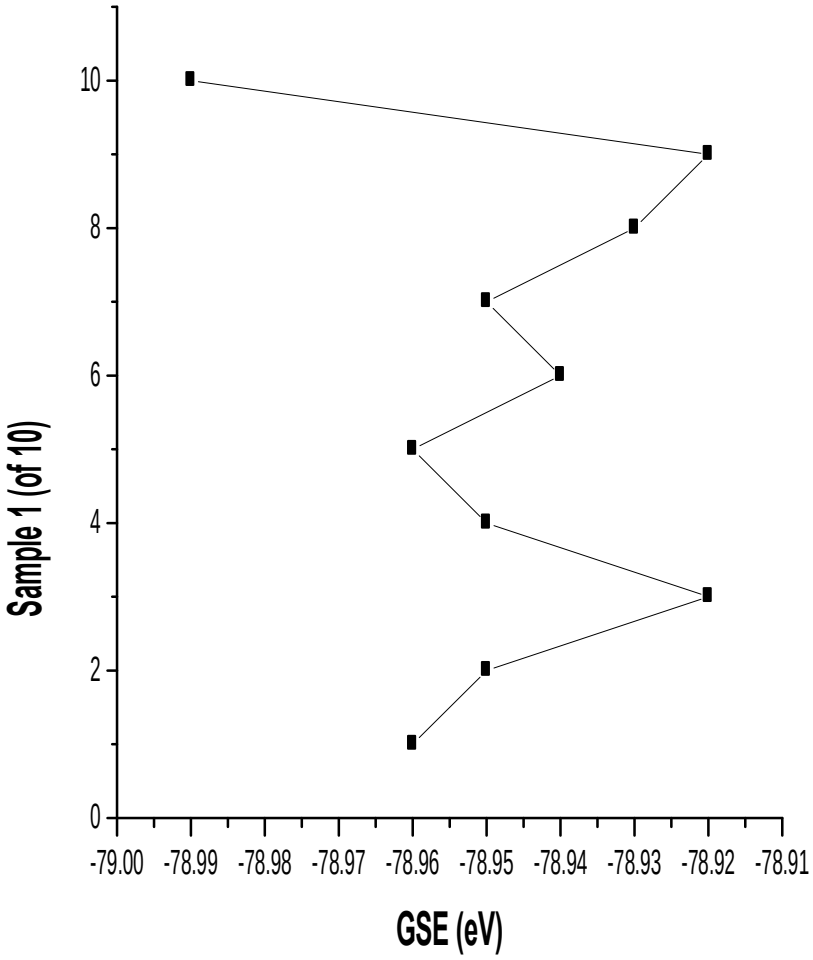
Standard value for the ground state energy of Helium atom by Variational principles (Kinoshita is -78.96eV)

Figure 21 Graph of Ensembles Vs GSE (Group 1 PIMC, β = 0.05A^0) Helium atom



Standard value for the ground state energy of Helium atom by Variational principles (Kinoshita is -78.96eV)

Figure 22 Graph of Ensembles Vs GSE (Group 1 PIMC, β = 0.05A^0) Helium atom



Standard value for the ground state energy of Helium atom by Variational principles (Kinoshita is -78.96eV)

Figure 23 Graph of Ensembles Vs GSE (Group 1 PIMC, β = 0.2A^0) Helium atom

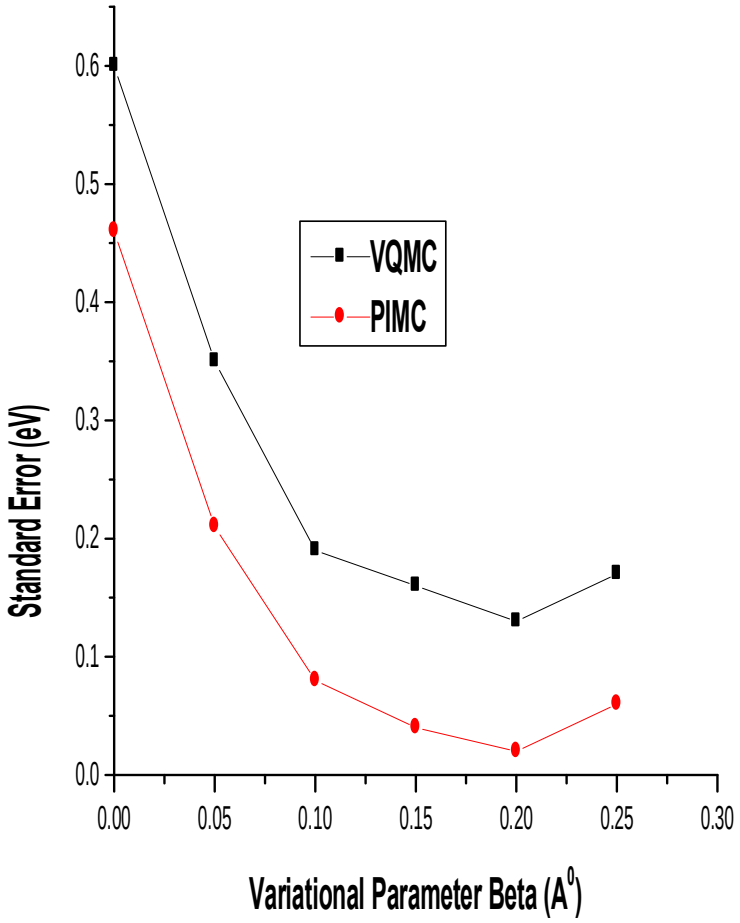


Figure 24 Graph of Standard Error Vs Variational Parameter (β) For both VQMC and PIMC Methods (Helium atom)

CHAPTER FIVE

SUMMARY, CONCLUSION AND RECOMMENDATIONS

5.1 SUMMARY AND CONCLUSION

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. Theoretical results from Koloz & Wolniewiz shows that the GSE of Hydrogen molecule is -1.1744 Hartree (commonly referred value by most authors) while using the analytical VQMC method. However, in this work which is a numerical approach, the GSE was found to be -1.1736 Hartree which indicates a difference of -0.0008 Hartree (about 99.93% accurate) by PIMC.

Grand Average of GSE of H_2 molecule by VQMC = -31.73eV

Grand Average of GSE of H_2 molecule by PIMC = - 31.92eV

The trial wavefunction as the case of VQMC has been optimized to suite the cusp condition of the electron-electron and electron-proton conditions for the fact that the greater the quality of the trial wavefunction the more precise is the result. Standard errors were computed in both cases and the PIMC method of calculation was found to generate minimal errors. This could be attributed to the non utilization of the wavefunction and dependence on the principles of superposition.

Similarly the complete ground state energy of helium was numerically determined using the two above mentioned methods i.e. the variational quantum Monte Carlo and the path integral Monte Carlo methods under the context of Born-Oppenheimer

approximation. This is a situation that has been considered as the case where the inter proton separation is set to be zero (0) i.e. when the protons in the hydrogen molecule are ñon top of each otherò therefore it describes a natural helium atom. All those aforementioned methods were extensively applied to the system of helium atom and the ground state energy of the helium atom was found to have the lowest value from the path integral Monte Carlo method of -78.94eV at 0.2 Å value of the variational parameter β which also falls within the range that has been established by reviewers in the field. This value which is about 99.97% accurate is in consistent with the exact value (-78.96eV) that has been obtained analytically by Kinoshita, T (1957) and many other reviewers that worked in this research field; hence it falls within the error bars of the empirical results. The standard errors as been computed in the case of hydrogen molecule were also evaluated for the helium atom and the deviations from the exact values were observed.

In conclusion, this work has demonstrated that the path integral Monte Carlo method is more precise in determining the ground state energy of a molecular system, this could be attributed to the stochastic gradient approximation been employed by the method that generates a quantum distribution directly from the Hamiltonian. The work further contributed to the development of knowledge by introducing the path integral method which had not been implemented by other reviewers in the field.

The preliminary findings in this work are that theoretical result from Kolos and Wolniewcz shows that the GSE of Hydrogen molecule is -1.1744Hartree (commonly referred value by most authors) while using analytical variational method. However in this work, which is a numerical approach, the GSE was found to be -1.1736Hartree which indicates a difference of -0.0008Hartree (0.02176eV) by the path integral method.

Similarly the theoretical result from Kinoshita being the pioneer reviewer found that the GSE of Helium atom is -2.9037Hartree while implementing the variational principles. Regarding this work in which a comparative numerical analysis was implemented between the path integral Monte Carlo and the variational quantum Monte Carlo. The lowest GSE was found to be -2.9023Hartree which indicates a difference of 0.0014Hatree (0.03808eV) by the numerical PIMC.

5.2 FURTHER RESEARCH

The precision obtained from the result in this research can be improved further by implementing more accurate quantum Monte Carlo methods i.e. the fixed-node approximation e.t.c. by modifying the path integral Monte Carlo techniques employed in this research.

Another fundamental view of continuation of this work would be to implement quantum Monte Carlo methods on few-electron systems that require attention of the sign problem.

The ground state energies of higher elements can be determined numerically by making some kind of modifications in the code which will be based on the theoretical inputs derived from the analysis.

Variational quantum Monte Carlo depends on parameter optimization, but however the presence of noise makes it difficult and inaccurate (Dewing, 2001). Therefore further research will include examining different kind of optimization approaches and comparing them accordingly.

5.3 RECOMMENDATIONS

Since Quantum Monte Carlo methods are among the most accurate procedures for computing the properties of quantum systems and coupled with the experience acquired from this research, it would be very relevant to induce the Government, private sectors, philanthropists and scientific research grants foundations units to come in and facilitate in either of the following ways;

1. The Government should provide high performing computing facilities in Nigerian Universities to enable sound theoretical research that will complement the experimental approach.
2. The private sector should participate and encourage research involving Quantum Monte Carlo techniques which could be a very powerful tool of obtaining higher precision in productions.
3. The Universities in Nigeria should establish linkages with other foreign Universities in the field of Quantum Monte Carlo methods i.e. a kind of affiliated research groups. This will boost the morale of research students.
4. The philanthropist should be encouraged to participate in either counter or whole funding in researches involving Quantum Monte Carlo methods as it is one of the fundamental areas of research interest in theoretical condensed matter physics.

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APPENDIX 1

```
öCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCCC
      PROGRAM QMC [VQMC/PIMC] CODE
C
C  COMPUTATIONAL PHYSICS (FORTRAN VERSION)
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
      CALL INIT            !display header screen, setup
parameters
5      CONTINUE              !main loop/ execute once for
each set of param
        CALL PARAM        !get input from screen
        CALL ARCHON         !calculate the eigenvalue for
this value of S
      GOTO 5
      END
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
      SUBROUTINE ARCHON
C calculates the electronic eigenvalue or energy auto-
correlation
C for a given separation of the protons
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
C Global variables:
      INCLUDE 'PARAM.P8'
      INCLUDE 'IO.ALL'
C Local variables:
C     energy has two indices
C     first index is the level: sweep, group, or total
C      second index is the value: quantity, quant**2, or
sigma**2
      REAL ENERGY(3,3)           !energy
      REAL CONFIG(NCOORD)        !configuration
      REAL W                          !weight for single
variational config
      REAL WEIGHT(MAXENS)            !weight of ensemble
members
      REAL     ENSMBL(NCOORD,MAXENS)      !ensemble     of
configurations
      REAL ESAVE(MAXCRR)          !array of local energies
for corr
      REAL EPSILN                !local energy of CONFIG
      REAL ACCPT                 !acceptance ratio
      INTEGER ITHERM             !thermalization index
      INTEGER ISWP,ISMPL         !sweep and sample index
      INTEGER IQUANT             !quantity index
```

```
      INTEGER IGRP                !group index
      INTEGER NLINES              !number of lines printed
to terminal
      INTEGER MORE                !how many more groups
      INTEGER   SWEEP,GROUP,TOTAL      !which   level   of
calculation
      INTEGER VALUE,SQUARE,SIGSQ !which quantity
      INTEGER  CORR,EPS                   !what  is  being
calculated?
      INTEGER PIMC,VARY           !which method?
C Functions:
      REAL ELOCAL                 !local energy
      INTEGER GETINT                !get integer data from
screen
      DATA SWEEP,GROUP,TOTAL/1,2,3/
      DATA VALUE,SQUARE,SIGSQ/1,2,3/
      DATA EPS,CORR /1,2/
      DATA VARY,PIMC /1,2/
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
C     output summary of parameters
      IF (TTERM) CALL PRMOUT(OUNIT,NLINES)
      IF (TFILE) CALL PRMOUT(TUNIT,NLINES)
      IF (GFILE) CALL PRMOUT(GUNIT,NLINES)
C
C        generate  initial  configuration  or  ensemble  of
configurations
      IF (METHOD .EQ. VARY) THEN
         CALL INTCFG(CONFIG,W)
      ELSE IF (METHOD .EQ. PIMC) THEN
         CALL INTENS(ENSMBL,WEIGHT,CONFIG)
      END IF
C
C     take thermalization steps
      DO 10 ITHERM=1,NTHERM
        IF   (ITHERM   .EQ.   1)   WRITE   (OUNIT,*)   '
Thermalizing...'
        IF (ITHERM .EQ. NTHERM) WRITE (OUNIT,*) ' '
        IF (METHOD .EQ. VARY) THEN
           CALL METROP(CONFIG,W,ACCPT)
        ELSE IF (METHOD .EQ. PIMC) THEN
           CALL TSTEP(ENSMBL,WEIGHT,EPSILN)
        END IF
10    CONTINUE
C
      DO 11 IQUANT=1,3                          !zero total
sums
         ENERGY(TOTAL,IQUANT)=0.
11    CONTINUE
      ACCPT=0                                        !zero
acceptance
```

```
      MORE=NGROUP                          !initial number of
groups
C
15    CONTINUE                                !allow for more
groups
        DO 20 IGRP=NGROUP-MORE+1,NGROUP        !loop over
groups
C
           DO 21 IQUANT=1,3                    !zero group
sums
             ENERGY(GROUP,IQUANT)=0.
21         CONTINUE
C
           DO 30 ISWP=1,NFREQ*NSMPL             !loop over
sweeps
C
             IF (METHOD .EQ. VARY) THEN         !take a
Metrop step
                CALL METROP(CONFIG,W,ACCPT)
             ELSE IF (METHOD .EQ. PIMC) THEN !or a time
step
                CALL TSTEP(ENSMBL,WEIGHT,EPSILN)
             END IF
C
             IF (MOD(ISWP,NFREQ) .EQ. 0) THEN !sometimes
save the energy
                ISMPL=ISWP/NFREQ
                IF        (METHOD        .EQ.        VARY)
EPSILN=ELOCAL(CONFIG)

ENERGY(GROUP,VALUE)=ENERGY(GROUP,VALUE)+EPSILN

ENERGY(GROUP,SQUARE)=ENERGY(GROUP,SQUARE)+EPSILN**2
                IF (.NOT. TERSE) THEN
                  IF     (TTERM)     WRITE     (OUNIT,100)
IGRP,ISMPL,NSMPL,EPSILN
                  IF     (TFILE)     WRITE     (TUNIT,100)
IGRP,ISMPL,NSMPL,EPSILN
100                  FORMAT (5X,' Group ',I4, ',  sample
',I4,' of ',I4,5X,
     +                    'Energy =',F9.4)
                END IF
             END IF
C
30         CONTINUE                             !this group
is done
           IF (CALC .EQ. CORR) THEN                !save
energy for corr
              ESAVE(IGRP)=ENERGY(GROUP,VALUE)
           ELSE                                   !or calc
averages
```

```
            CALL AVERAG(ENERGY,ACCPT,IGRP)
          END IF
C
20      CONTINUE
        IF (CALC .EQ. CORR) CALL CRLTNS(ESAVE)    !calc
corr
C
C        allow for more groups, taking care not to exceed
array bounds
        MORE=GETINT(10,0,1000,'How many more groups?')
        IF ((CALC .EQ. CORR) .AND. (NGROUP+MORE .GT.
MAXCRR)) THEN
            WRITE (OUNIT,200) MAXCRR-NGROUP
200           FORMAT(' You will run out of storage space
for '
     +          'corr if you do more than ',I3,' more
groups')
            MORE=GETINT(MAXCRR-NGROUP,0,MAXCRR-NGROUP,
     +                  'How many more groups?')
        END IF
       IF (MORE .GT. 0) THEN
            NGROUP=NGROUP+MORE
            NLINES=0
            IF (TTERM) CALL CLEAR
            GOTO 15
       END IF
C
       RETURN
       END
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCCC
       SUBROUTINE TSTEP(ENSMBL,WEIGHT,EPSILN)
C take a time step using the Path Integral Monte Carlo
method
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCCC
C Global variables:
       INCLUDE 'PARAM.P8'
C Input/Output variables
       REAL  WEIGHT(MAXENS)            !weight  of  ensemble
members (I/O)
       REAL        ENSMBL(NCOORD,MAXENS)!ensemble        of
configurations (I/O)
       REAL EPSILN                  !local energy of CONFIG
(output)
C Local variables:
       REAL CONFIG(NCOORD)        !configuration
       REAL W                     !weight for single config
       REAL EBAR,WBAR               !ensemble average local
energy and weight
       INTEGER IENSEM             !ensemble index
```

```
      INTEGER ICOORD             !coordinate index
      REAL NORM                  !normalization of weights
      REAL SHIFT(NCOORD)           !array containing drift
vector
C Functions:
      REAL GAUSS                 !Gaussian random number
      REAL ELOCAL                    !local energy of the
configuration
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
      EBAR=0.                     !zero sums
      WBAR=0.
      DO 10 IENSEM=1,NENSEM                          !loop
over ensemble
         DO 20 ICOORD=1,NCOORD
            CONFIG(ICOORD)=ENSMBL(ICOORD,IENSEM)    !get a
configuration
20       CONTINUE
         CALL DRIFT(CONFIG,SHIFT)                    !calc
shifts
         DO 30 ICOORD=1,NCOORD
            CONFIG(ICOORD)=CONFIG(ICOORD)+          !shift
configuration
     +
GAUSS(DSEED)*SQHBDT+SHIFT(ICOORD)
30       CONTINUE
C
         EPSILN=ELOCAL(CONFIG)
!calculate energy
         WEIGHT(IENSEM)=WEIGHT(IENSEM)*EXP(-EPSILN*DT)
!calc weight
         EBAR=EBAR+WEIGHT(IENSEM)*EPSILN
!update sums
         WBAR=WBAR+WEIGHT(IENSEM)
C
         DO 40 ICOORD=1,NCOORD
            ENSMBL(ICOORD,IENSEM)=CONFIG(ICOORD)     !save
configuration
40       CONTINUE
10    CONTINUE
C
      EPSILN=EBAR/WBAR                           !weighted
average energy
      NORM=NENSEM/WBAR
      DO 50 IENSEM=1,NENSEM                   !renormalize
weights
         WEIGHT(IENSEM)=NORM*WEIGHT(IENSEM)
50    CONTINUE
C
      RETURN
      END
```

```
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
      SUBROUTINE METROP(CONFIG,W,ACCPT)
C take a Metropolis step
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
C Global variables:
      INCLUDE 'PARAM.P8'
C Input/Output variables:
      REAL CONFIG(NCOORD)          !configuration
      REAL W                             !weight for single
config
      REAL ACCPT                   !acceptance ratio
C Local variables:
      INTEGER ICOORD               !coordinate index
      REAL CSAVE(NCOORD)             !temp storage for last
config
      REAL WTRY                    !weight for trial config
C Function:
      REAL PHI                     !total wave function
      REAL RANNOS                  !uniform random number
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
      DO 10 ICOORD=1,NCOORD
       CSAVE(ICOORD)=CONFIG(ICOORD)          !save previous
values

CONFIG(ICOORD)=CONFIG(ICOORD)+DELTA*(RANNOS(DSEED)-
.5)!trial step
10    CONTINUE
      WTRY=PHI(CONFIG)**2                    !trial weight
C
      IF  (WTRY/W  .GT.  RANNOS(DSEED))  THEN    !sometimes
accept the step
         W=WTRY                                   !save new
weight
         ACCPT=ACCPT+1                          !update accpt
ratio
      ELSE
        DO 20 ICOORD=1,NCOORD
          CONFIG(ICOORD)=CSAVE(ICOORD)            !or  else
restore old config
20      CONTINUE
      END IF
      RETURN
      END
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
      REAL FUNCTION ELOCAL(CONFIG)
C calculate the local energy for CONFIG
```

```
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
C Global variable:
      INCLUDE 'PARAM.P8'
C Input variables:
      REAL CONFIG(NCOORD)        !configuration
C Local variables:
      REAL TPOP,VPOP               !kinetic and potential
contributions
      REAL EECORR                !elec-elec correlation
      REAL CROSS,CROSS1,CROSS2   !cross terms
      REAL ONEE1,ONEE2           !one electron terms
      REAL  X1,X2,Y1,Y2,Z1,Z2          !coordinates  of  2
electrons
      REAL R1L,R1R,R2L,R2R,R12   !relative distances
      REAL  CHI1,CHI2,F                !parts  of  the  wave
function
      REAL DOTR1L,DOTR2L,DOTR1R,DOTR2R !dot products with
R12
      REAL  R12DR1,SR12Z               !temp  vars  for  dot
products
      REAL CHI,FDCHI,SDCHI,LAPCHI !atomic orbitals
      REAL FEE,FDFEE,SDFEE,LAPFEE !elec-elec correlations
      REAL DIST                   !Euclidean distance
      REAL R,X,Y,Z                !dummy variables
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
C     define functions
      CHI(R)=EXP(-R/A)                                !atomic
orbital
      FDCHI(R)=-CHI(R)/A                          !its first
derivative,
      SDCHI(R)=CHI(R)/A/A                             !second
derivative,
      LAPCHI(R)=SDCHI(R)+2*FDCHI(R)/R                    !and
Laplacian
C
      FEE(R)=EXP(R/(ALPHA*(1+BETA*R)))          !elec-elec
correlation
      FDFEE(R)=FEE(R)/(ALPHA*(1.+BETA*R)**2)           !its
first,second deriv,
      SDFEE(R)=FDFEE(R)**2/FEE(R)-
2.*BETA*FEE(R)/ALPHA/(1+BETA*R)**3
      LAPFEE(R)=SDFEE(R)+2*FDFEE(R)/R                    !and
Laplacian
C
      DIST(X,Y,Z)=SQRT(X**2+Y**2+Z**2)          !Euclidean
distance
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
C     get coordinates and radii
```

```
      CALL
RADII(X1,X2,Y1,Y2,Z1,Z2,R1L,R2L,R1R,R2R,R12,CONFIG)
C
C     calculate dot products with R12
      R12DR1=X1*(X1-X2)+Y1*(Y1-Y2)+Z1*(Z1-Z2)  !convenient
starting place
      SR12Z=S*(Z1-Z2)/2                 !useful constant
      DOTR1L=R12DR1+SR12Z               !dot products with
R12
      DOTR1R=R12DR1-SR12Z
      DOTR2L=DOTR1L-R12**2
      DOTR2R=DOTR1R-R12**2
      DOTR1L=DOTR1L/R12/R1L               !dot products of
unit vectors
      DOTR2L=DOTR2L/R12/R2L
      DOTR1R=DOTR1R/R12/R1R
      DOTR2R=DOTR2R/R12/R2R
C
      CHI1=CHI(R1R)+CHI(R1L)                !pieces of the
total wave function
      CHI2=CHI(R2R)+CHI(R2L)
      F=FEE(R12)
C
      EECORR=2*LAPFEE(R12)/F                     !correlation
contribution
      ONEE1=(LAPCHI(R1L)+LAPCHI(R1R))/CHI1
!electron one
      ONEE2=(LAPCHI(R2L)+LAPCHI(R2R))/CHI2
!electron two
      CROSS1=(FDCHI(R1L)*DOTR1L+FDCHI(R1R)*DOTR1R)/CHI1
!cross terms
      CROSS2=(FDCHI(R2L)*DOTR2L+FDCHI(R2R)*DOTR2R)/CHI2
      CROSS=2*FDFEE(R12)*(CROSS1-CROSS2)/F
C
      TPOP=-HBM*(EECORR+ONEE1+ONEE2+CROSS)/2
!kinetic
      VPOP=-E2*(1./R1L  +  1./R1R  +  1./R2L  +  1./R2R  -
1./R12) !potential
      ELOCAL=TPOP+VPOP
!total
C
      RETURN
      END
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
      SUBROUTINE DRIFT(CONFIG,SHIFT)
C calculate the drift vector (SHIFT) for CONFIG
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
C Global variables:
      INCLUDE 'PARAM.P8'
```

```
C Input/Output variables:
      REAL CONFIG(NCOORD)         !configuration (input)
      REAL SHIFT(NCOORD)           !array containing drift
vector (output)
C Local variables:
      INTEGER ICOORD              !coordinate index
      REAL  X1,X2,Y1,Y2,Z1,Z2          !coordinates  of  2
electrons
      REAL R1L,R1R,R2L,R2R,R12    !relative distances
      REAL  CHI1,CHI2,F                 !parts  of  the  wave
function
      REAL CHI,FDCHI,SDCHI,LAPCHI !atomic orbital
      REAL FEE,FDFEE,SDFEE,LAPFEE !elec-elec correlations
      REAL R                      !dummy variables
      REAL FACTA,FACTB,FACTE      !useful factors
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
C     define functions
      CHI(R)=EXP(-R/A)                                 !atomic
orbital
      FDCHI(R)=-CHI(R)/A                            !its first
derivative,
      SDCHI(R)=CHI(R)/A/A                              !second
derivative,
      LAPCHI(R)=SDCHI(R)+2*FDCHI(R)/R                     !and
Laplacian
C
      FEE(R)=EXP(R/(ALPHA*(1+BETA*R)))          !elec-elec
correlation
      FDFEE(R)=FEE(R)/(ALPHA*(1.+BETA*R)**2)   !its first,
second deriv,
      SDFEE(R)=FDFEE(R)**2/FEE(R)-
2.*BETA*FEE(R)/ALPHA/(1+BETA*R)**3
      LAPFEE(R)=SDFEE(R)+2*FDFEE(R)/R                     !and
Laplacian
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
C     get coordinates and radii
      CALL
RADII(X1,X2,Y1,Y2,Z1,Z2,R1L,R2L,R1R,R2R,R12,CONFIG)
C
      CHI1=CHI(R1R)+CHI(R1L)                 !pieces  of  the
total wave function
      CHI2=CHI(R2R)+CHI(R2L)
      F=FEE(R12)
C
      FACTA=HBMDT*(FDCHI(R1L)/R1L+FDCHI(R1R)/R1R)/CHI1
!useful factors
      FACTB=HBMDT*(FDCHI(R1L)/R1L-FDCHI(R1R)/R1R)/CHI1
      FACTE=HBMDT*FDFEE(R12)/F/R12
C
```

```
      SHIFT(1)=FACTA*X1+FACTE*(X1-X2)        !shift    for
electron one
      SHIFT(2)=FACTA*Y1+FACTE*(Y1-Y2)
      SHIFT(3)=FACTA*Z1+FACTE*(Z1-Z2)+FACTB*S2
C
      FACTA=HBMDT*(FDCHI(R2L)/R2L+FDCHI(R2R)/R2R)/CHI2
      FACTB=HBMDT*(FDCHI(R2L)/R2L-FDCHI(R2R)/R2R)/CHI2
C
      SHIFT(4)=FACTA*X2-FACTE*(X1-X2)        !shift    for
electron two
      SHIFT(5)=FACTA*Y2-FACTE*(Y1-Y2)
      SHIFT(6)=FACTA*Z2-FACTE*(Z1-Z2)+FACTB*S2
C
      RETURN
      END
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
      REAL FUNCTION GAUSS(DSEED)
C returns a Gaussian random number with zero mean and
unit variance
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
      INTEGER IGAUSS                  !sum index
      DOUBLE PRECISION DSEED          !random number seed
      REAL RANNOS                          !uniform random
number
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
      GAUSS=0.                             !sum 12 uniform
random numbers
      DO 10 IGAUSS=1,12
         GAUSS=GAUSS+RANNOS(DSEED)
10    CONTINUE
      GAUSS=GAUSS-6.                      !subtract six so
that mean=0
      RETURN
      END
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
      REAL FUNCTION PHI(CONFIG)
C calculates the total variational wave function for
CONFIG
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
C Global variables:
      INCLUDE 'PARAM.P8'
C Input variables:
      REAL CONFIG(NCOORD)        !configuration
C Local variables:
      REAL  X1,X2,Y1,Y2,Z1,Z2          !coordinates  of  2
electrons
```

```
      REAL R1L,R1R,R2L,R2R,R12   !relative distances
      REAL CHI1R,CHI1L,CHI2R,CHI2L,F   !parts of the wave
function
      REAL CHI,FEE                    !terms in the wave
function
      REAL R                       !radius
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
      CHI(R)=EXP(-R/A)                    !atomic orbital
      FEE(R)=EXP(R/(ALPHA*(1+BETA*R)))          !electron-
electron correlation
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
C     calculate the radii
      CALL
RADII(X1,X2,Y1,Y2,Z1,Z2,R1L,R2L,R1R,R2R,R12,CONFIG)
C
      CHI1R=CHI(R1R)            !pieces of the total wave
function
      CHI1L=CHI(R1L)
      CHI2R=CHI(R2R)
      CHI2L=CHI(R2L)
      F=FEE(R12)
      PHI=(CHI1L  +CHI1R)*(CHI2L+CHI2R)*F      !the  whole
thing
C
      RETURN
      END
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
      SUBROUTINE INTENS(ENSMBL,WEIGHT,CONFIG)
C generate the ENSMBL at t=0 for PIMC
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
C Global variables:
      INCLUDE 'PARAM.P8'
C Output variables:
      REAL CONFIG(NCOORD)        !configuration
      REAL  WEIGHT(MAXENS)            !weight  of  ensemble
members
      REAL     ENSMBL(NCOORD,MAXENS)     !ensemble     of
configurations
C Local variables:
      INTEGER ISTEP              !step index
      INTEGER ICOORD             !coordinate index
      REAL W                           !weight for single
config
      REAL ACCPT                 !acceptance ratio
      INTEGER IENSEM             !ensemble index
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
```

```
      CALL  INTCFG(CONFIG,W)           !generate  a  single
intial configuration
C
      DO  10  ISTEP=1,20                              !do  20
thermalization steps
         CALL METROP(CONFIG,W,ACCPT)    !using Metropolis
algorithm
10    CONTINUE
C
      DO  30  ISTEP=1,10*NENSEM               !generate the
ensemble
         CALL  METROP(CONFIG,W,ACCPT)     !take  a  Metrop
step
         IF (MOD(ISTEP,10) .EQ. 0) THEN
             IENSEM=ISTEP/10              !save every 10th
config
             DO 20 ICOORD=1,NCOORD
                ENSMBL(ICOORD,IENSEM)=CONFIG(ICOORD)
20           CONTINUE
             WEIGHT(IENSEM)=1.         !set all weights=1
         END IF
30    CONTINUE
      RETURN
      END
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
      SUBROUTINE INTCFG(CONFIG,W)
C generate  a  configuration  (CONFIG)  and  calculate  its
weight (W)
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
C Global variable:
      INCLUDE 'PARAM.P8'
C Output variables:
      REAL CONFIG(NCOORD)        !configuration
      REAL W                           !weight  for  single
config
C Local variables:
      INTEGER ICOORD             !coordinate index
C Function:
      REAL PHI                   !total wave function
      REAL RANNOS                !uniform random number
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
      DO  10  ICOORD=1,NCOORD        !pick  configuration  at
random
         CONFIG(ICOORD)=A*(RANNOS(DSEED)-.5)
10    CONTINUE
      CONFIG(3)=CONFIG(3)+S2    !center elec 1. at right
      CONFIG(6)=CONFIG(6)-S2    !center elec 2. at left
      W=PHI(CONFIG)**2          !weight=phi**2
```

```
      RETURN
      END
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
      SUBROUTINE CRLTNS(ESAVE)
C calculate the energy auto-correlations
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
C Global variables:
      INCLUDE 'PARAM .P8'
      INCLUDE 'IO.ALL'
C Input variables:
      REAL  ESAVE(MAXCRR)                  !array  of  local
energies for corr.
C Local variables:
      REAL EI,EIK,ESQI,ESQIK,EIEK  !sums
      INTEGER I,K                  !index of ESAVE
      REAL  ECORR(0:MAXCRR)                !energy  auto-
correlations
      INTEGER NI                    !number of energies in
sum
      INTEGER SCREEN               !send to terminal
      INTEGER PAPER                !make a hardcopy
      INTEGER FILE                 !send to a file
      DATA SCREEN,PAPER,FILE/1,2,3/
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
      DO 10 K=0,NCORR               !loop over correlation
lengths
         EI=0.                     !zero sums
         EIK=0.
         ESQI=0.
         ESQIK=0.
         EIEK=0.
         NI=NGROUP-K
         DO 20 I=1,NI
            EI=EI+ESAVE(I)         !calculate sums
            EIK=EIK+ESAVE(I+K)
            ESQI=ESQI+ESAVE(I)**2
            ESQIK=ESQIK+ESAVE(I+K)**2
            EIEK=EIEK+ESAVE(I)*ESAVE(I+K)
20       CONTINUE
         EI=EI/NI                  !calculate averages
         EIK=EIK/NI
         ESQI=ESQI/NI
         ESQIK=ESQIK/NI
         EIEK=EIEK/NI
         ECORR(K)=(EIEK-EI*EIK)/(SQRT(ESQI-
EI**2))/(SQRT(ESQIK-EIK**2))
10    CONTINUE
C
```

```
      IF (GTERM) THEN                    !display results
          CALL   PAUSE   ('to   see   the   energy   auto-
correlations...',1)
          CALL GRFOUT(SCREEN,ECORR)
      ELSE IF (TTERM) THEN
          CALL   PAUSE   ('to   see   the   energy   auto-
correlations...',1)
          CALL CRROUT(OUNIT,ECORR)
      END IF
      IF (TFILE) CALL CRROUT(TUNIT,ECORR)
      IF (GHRDCP) CALL GRFOUT(PAPER,ECORR)
      IF (GFILE) CALL GRFOUT(FILE,ECORR)
C
      RETURN
      END
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
      SUBROUTINE AVERAG(ENERGY,ACCPT,IGRP)
C calculate group averages, add to totals, print out
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
C Global variables:
      INCLUDE 'PARAM.P8'
      INCLUDE 'IO.ALL'
C Input variables:
C     energy has two indices
C     first index is the level: sweep, group, or total
C      second index is the value: quantity, quant**2, or
sigma**2
      REAL ENERGY(3,3)           !energy
      INTEGER IGRP               !group index
      REAL ACCPT                 !acceptance ratio
C Local variables:
      REAL EVALUE                !current average energy
      REAL SIG1,SIG2             !uncertainties in energy
      REAL U                      !total pot energy of the
system
      INTEGER NLINES              !number of lines printed
to terminal
      INTEGER   SWEEP,GROUP,TOTAL      !which   level   of
calculation
      INTEGER VALUE,SQUARE,SIGSQ !which quantity
      DATA SWEEP,GROUP,TOTAL/1,2,3/
      DATA VALUE,SQUARE,SIGSQ/1,2,3/
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
C     calculate group averages and uncertainties
      ENERGY(GROUP,VALUE)=ENERGY(GROUP,VALUE)/NSMPL
      ENERGY(GROUP,SQUARE)=ENERGY(GROUP,SQUARE)/NSMPL
      ENERGY(GROUP,SIGSQ)=
```

```
     +                                (ENERGY(GROUP,SQUARE)-
ENERGY(GROUP,VALUE)**2)/NSMPL
      IF        (ENERGY(GROUP,SIGSQ)        .LT.        0.)
ENERGY(GROUP,SIGSQ)=0.
C
C     add to totals

ENERGY(TOTAL,VALUE)=ENERGY(TOTAL,VALUE)+ENERGY(GROUP,VALU
E)

ENERGY(TOTAL,SQUARE)=ENERGY(TOTAL,SQUARE)+ENERGY(GROUP,SQ
UARE)

ENERGY(TOTAL,SIGSQ)=ENERGY(TOTAL,SIGSQ)+ENERGY(GROUP,SIGS
Q)
C
C     calculate current grand averages
      EVALUE=ENERGY(TOTAL,VALUE)/IGRP
      SIG1=(ENERGY(TOTAL,SQUARE)/IGRP-
EVALUE**2)/IGRP/NSMPL
      IF (SIG1 .LT. 0.) SIG1=0.
      SIG1=SQRT(SIG1)
      SIG2=SQRT(ENERGY(TOTAL,SIGSQ))/IGRP
C
C     calculate total energy of the system
      IF (S .GT. .01) THEN
          U=EVALUE+E2/S+E2/ABOHR
      ELSE
          U=0.
      END IF
C
      IF                    (TTERM)                    CALL
TXTOUT(IGRP,ENERGY,EVALUE,SIG1,SIG2,U,ACCPT,OUNIT)
      IF                    (TFILE)                    CALL
TXTOUT(IGRP,ENERGY,EVALUE,SIG1,SIG2,U,ACCPT,TUNIT)
C
      RETURN
      END
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
      SUBROUTINE
RADII(X1,X2,Y1,Y2,Z1,Z2,R1L,R2L,R1R,R2R,R12,CONFIG)
C calculates cartesian coordinates and radii given CONFIG
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
C Global variable:
      INCLUDE 'PARAM.P8'
C Input variables:
      REAL CONFIG(NCOORD)        !configuration
C Output variables:
```

```
      REAL  X1,X2,Y1,Y2,Z1,Z2          !coordinates  of  2
electrons
      REAL R1L,R1R,R2L,R2R,R12   !relative distances
      REAL DIST                  !Euclidean distance
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
      DIST(X1,Y1,Z1)=SQRT(X1**2+Y1**2+Z1**2)
!Euclidean distance
C
      X1=CONFIG(1)              !give the CONFIG elements
their real names
      X2=CONFIG(4)
      Y1=CONFIG(2)
      Y2=CONFIG(5)
      Z1=CONFIG(3)
      Z2=CONFIG(6)
C
      R1L=DIST(X1,Y1,Z1+S2)   !calculate separations
      R1R=DIST(X1,Y1,Z1-S2)
      R2L=DIST(X2,Y2,Z2+S2)
      R2R=DIST(X2,Y2,Z2-S2)
      R12=DIST(X1-X2,Y1-Y2,Z1-Z2)
C
      RETURN
      END
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
      SUBROUTINE INIT
C initializes constants, displays header screen,
C initializes menu arrays for input parameters
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
C Global variables:
      INCLUDE 'IO.ALL'
      INCLUDE 'MENU.ALL'
      INCLUDE 'PARAM.P8'
C Local parameters:
      CHARACTER*80 DESCRP          !program description
      DIMENSION DESCRP(20)
      INTEGER  NHEAD,NTEXT,NGRAPH    !number  of  lines  for
each description
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
C     get environment parameters
      CALL SETUP
C
C     display header screen
      DESCRP(1)= 'PROJECT 8'
      DESCRP(2)=   'Monte   Carlo   solution   of   the   H2
molecule'
      NHEAD=2
```

```
C
C     text output description
      DESCRP(3)=   'electronic   eigenvalue   and   its
uncertainty'
      DESCRP(4)= 'or energy auto-correlation'
      NTEXT=2
C
C     graphics output description
      DESCRP(5)= 'energy auto-correlation vs. correlation
length'
      NGRAPH=1
C
      CALL HEADER(DESCRP,NHEAD,NTEXT,NGRAPH)
C
C     calculate constants
      HBM=7.6359               !hbar*2/(mass)
      E2=14.409                !charge of the electron
      ABOHR=HBM/E2
C
C     setup menu arrays, beginning with constant part
      CALL MENU
C
      MTYPE(12)=TITLE
      MPRMPT(12)= 'PHYSICAL PARAMETERS'
      MLOLIM(12)=0.
      MHILIM(12)=1.
C
      MTYPE(13)=FLOAT
      MPRMPT(13)='Enter  the  interproton  separation  S
(Angstroms)'
      MTAG(13)='Inter proton separation (Angstroms)'
      MLOLIM(13)=0.
      MHILIM(13)=10.
      MREALS(13)=0.
C
      MTYPE(14)=FLOAT
      MPRMPT(14)=
     +  'Enter  value  for  variational  parameter  Beta
(Angstroms**-1)'
      MTAG(14)='variational  parameter  Beta  (Angstroms**-
1)'
      MLOLIM(14)=0.
      MHILIM(14)=10.
      MREALS(14)=.25
C
      MTYPE(15)=SKIP
      MREALS(15)=35.
C
      MTYPE(37)=TITLE
      MPRMPT(37)= 'NUMERICAL PARAMETERS'
      MLOLIM(37)=1.
```

```
      MHILIM(37)=1.
C
      MTYPE(38)=TITLE
      MPRMPT(38)='Methods of calculation:'
      MLOLIM(38)=0.
      MHILIM(38)=0.
C
      MTYPE(39)=MTITLE
      MPRMPT(39)='1) Variational'
      MLOLIM(39)=0.
      MHILIM(39)=0.
C
      MTYPE(40)=MTITLE
      MPRMPT(40)='2) Path Integral Monte Carlo'
      MLOLIM(40)=0.
      MHILIM(40)=1.
C
      MTYPE(41)=MCHOIC
      MPRMPT(41)='Make a menu choice and press return'
      MTAG(41)='44 42'
      MLOLIM(41)=1.
      MHILIM(41)=2.
      MINTS(41)=1
      MREALS(41)=1.
C
      MTYPE(42)=NUM
      MPRMPT(42)= 'Enter size of the ensemble'
      MTAG(42)= 'Ensemble size'
      MLOLIM(42)=1.
      MHILIM(42)=MAXENS
      MINTS(42)=20.
C
      MTYPE(43)=FLOAT
      MPRMPT(43)='Enter  time  step  (units  of  1E-16
sec/hbar)'
      MTAG(43)='Time step (units of 1E-16 sec/hbar)'
      MLOLIM(43)=0.
      MHILIM(43)=10.
      MREALS(43)=.01
C
      MTYPE(44)=FLOAT
      MPRMPT(44)=  'Enter  step  size  for  sampling  PHI
(Angstroms)'
      MTAG(44)= 'Sampling step size (Angstroms)'
      MLOLIM(44)=.01
      MHILIM(44)=10.
      MREALS(44)=.4
C
      MTYPE(45)=NUM
      MPRMPT(45)= 'Number of thermalization sweeps'
      MTAG(45)= 'Thermalization sweeps'
```

```
      MLOLIM(45)=0
      MHILIM(45)=1000
      MINTS(45)=20
C
      MTYPE(46)=TITLE
      MPRMPT(46)='Quantity to calculate:'
      MLOLIM(46)=1.
      MHILIM(46)=0.
C
      MTYPE(47)=MTITLE
      MPRMPT(47)='1) Energy'
      MLOLIM(47)=0.
      MHILIM(47)=0.
C
      MTYPE(48)=MTITLE
      MPRMPT(48)='2) Correlations'
      MLOLIM(48)=0.
      MHILIM(48)=1.
C
      MTYPE(49)=MCHOIC
      MPRMPT(49)='Make a menu choice and press return'
      MTAG(49)='50 53'
      MLOLIM(49)=1.
      MHILIM(49)=2.
      MINTS(49)=1
      MREALS(49)=1.
C
      MTYPE(50)=NUM
      MPRMPT(50)=   'Enter sampling frequency (to avoid
correlations)'
      MTAG(50)= 'Sampling frequency'
      MLOLIM(50)=1
      MHILIM(50)=100
      MINTS(50)=6
C
      MTYPE(51)=NUM
      MPRMPT(51)= 'Enter number of samples in a group'
      MTAG(51)= 'Group sample size'
      MLOLIM(51)=1
      MHILIM(51)=1000
      MINTS(51)=10
C
      MTYPE(52)=SKIP
      MREALS(52)=54.
C
      MTYPE(53)=NUM
      MPRMPT(53)= 'Enter maximum correlation length'
      MTAG(53)= 'Maximum correlation length'
      MLOLIM(53)=1
      MHILIM(53)=100.
      MINTS(53)=40
```

```
C
      MTYPE(54)=NUM
      MPRMPT(54)= 'Enter number of groups'
      MTAG(54)= 'Number of groups'
      MLOLIM(54)=1
      MHILIM(54)=1000
      MINTS(54)=10
C
      MTYPE(55)=NUM
      MPRMPT(55)= 'Integer random number seed for init
fluctuations'
      MTAG(55)= 'Random number seed'
      MLOLIM(55)=1000.
      MHILIM(55)=99999.
      MINTS(55)=34767
C
      MTYPE(56)=SKIP
      MREALS(56)=60.
C
      MSTRNG(MINTS(75))= 'proj8.txt'
C
      MTYPE(76)=BOOLEN
      MPRMPT(76)='Do you want the SHORT version of the
output?'
      MTAG(76)='Short version of output'
      MINTS(76)=0
C
      MTYPE(77)=SKIP
      MREALS(77)=80.
C
      MSTRNG(MINTS(86))= 'proj8.grf'
C
      MTYPE(87)=SKIP
      MREALS(87)=90.
C
      RETURN
      END
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
      SUBROUTINE PARAM
C gets parameters from screen
C ends program on request
C closes old files
C maps menu variables to program variables
C opens new files
C calculates all derivative parameters
C performs checks on parameters
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
C Global variables:
      INCLUDE 'MENU.ALL'
```

```
      INCLUDE 'IO.ALL'
      INCLUDE 'PARAM.P8'
C Local variables:
      REAL AOLD           !temp variable to search for A
      INTEGER CORR,EPS    !what is being calculated?
      INTEGER PIMC,VARY   !which method?
C gives the map between menu indices and parameters
      INTEGER
IS,IBETA,IMETHD,INENSM,IDT,IDELTA,ITHERM,ICALC,
     +        INFREQ,INSMPL,INCORR,IGROUP,IDSEED,ITERSE
      PARAMETER (IS     = 13)
      PARAMETER (IBETA  = 14)
      PARAMETER (IMETHD = 41)
      PARAMETER (INENSM = 42)
      PARAMETER (IDT    = 43)
      PARAMETER (IDELTA = 44)
      PARAMETER (ITHERM = 45)
      PARAMETER (ICALC  = 49)
      PARAMETER (INFREQ = 50)
      PARAMETER (INSMPL = 51)
      PARAMETER (INCORR = 53)
      PARAMETER (IGROUP = 54)
      PARAMETER (IDSEED = 55)
      PARAMETER (ITERSE = 76)
C Functions:
      LOGICAL LOGCVT       !converts 1 and 0 to true and
false
      INTEGER GETINT      !get integer from screen
      DATA VARY,PIMC /1,2/
      DATA EPS,CORR /1,2/
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
C     get input from terminal
      CALL CLEAR
      CALL ASK(1,ISTOP)
C
C     stop program if requested
      IF (MREALS(IMAIN) .EQ. STOP) CALL FINISH
C
C     close files if necessary
      IF (TNAME .NE. MSTRNG(MINTS(ITNAME)))
     +     CALL FLCLOS(TNAME,TUNIT)
      IF (GNAME .NE. MSTRNG(MINTS(IGNAME)))
     +     CALL FLCLOS(GNAME,GUNIT)
C
C     set new parameter values
C     physical and numerical
      S=MREALS(IS)
      BETA=MREALS(IBETA)
      METHOD=MINTS(IMETHD)
      NENSEM=MINTS(INENSM)
```

```
      DT=MREALS(IDT)
      DELTA=MREALS(IDELTA)
      NTHERM=MINTS(ITHERM)
      CALC=MINTS(ICALC)
      NFREQ=MINTS(INFREQ)
      NSMPL=MINTS(INSMPL)
      NCORR=MINTS(INCORR)
      NGROUP=MINTS(IGROUP)
      DSEED=DBLE(MINTS(IDSEED))
C
C     text output
      TTERM=LOGCVT(MINTS(ITTERM))
      TFILE=LOGCVT(MINTS(ITFILE))
      TNAME=MSTRNG(MINTS(ITNAME))
      TERSE=LOGCVT(MINTS(ITERSE))
C
C     graphics output
      GTERM=LOGCVT(MINTS(IGTERM))
      GHRDCP=LOGCVT(MINTS(IGHRD))
      GFILE=LOGCVT(MINTS(IGFILE))
      GNAME=MSTRNG(MINTS(IGNAME))
C
C     open files
      IF (TFILE) CALL FLOPEN(TNAME,TUNIT)
      IF (GFILE) CALL FLOPEN(GNAME,GUNIT)
      !files may have been renamed
      MSTRNG(MINTS(ITNAME))=TNAME
      MSTRNG(MINTS(IGNAME))=GNAME
C
C     check parameters for correlations, fix NFREQ, NSMPL
      IF (CALC .EQ. CORR) THEN
         NFREQ=1            !fixed for correlations
         NSMPL=1
         IF  ((NGROUP  .GT.  MAXCRR)  .OR.  ((NGROUP-NCORR)
.LE. 20)) THEN
           WRITE (OUNIT,*) ' '
           WRITE (OUNIT,20)
           WRITE (OUNIT,30) NGROUP,NCORR+20,MAXCRR
20            FORMAT (5X,' For reasonable values of the
correlations ')
30          FORMAT (5X,' NGROUP (',I4,') must be between
NCORR+20 (',
     +             I4,') and MAXCRR (',I4,')')
           WRITE (OUNIT,*) ' '
           NCORR=GETINT(NCORR,1,100,'Reenter NCORR')
           NGROUP=GETINT(NCORR+100,NCORR+20,MAXCRR,'Re-
enter NGROUP')
           MINTS(INCORR)=NCORR
           MINTS(IGROUP)=NGROUP
         END IF
      END IF
```

```
C
      CALL CLEAR
C
C     calculate derivative parameters
      A=ABOHR
      AOLD=0.
10    IF (ABS(A-AOLD) .GT. 1.E-6) THEN
         AOLD=A
         A=ABOHR/(1+EXP(-S/AOLD))
      GOTO 10
      END IF
      S2=S/2
      HBMDT=HBM*DT
      SQHBDT=SQRT(HBMDT)
      ALPHA=2*ABOHR
      IF (METHOD .EQ. PIMC) DELTA=1.5*A
C
      RETURN
      END
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
      SUBROUTINE PRMOUT(MUNIT,NLINES)
C write out parameter summary to MUNIT
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
C Global variables:
      INCLUDE 'IO.ALL'
      INCLUDE 'PARAM.P8'
C Input variables:
      INTEGER MUNIT                          !fortran unit
number
      INTEGER NLINES                       !number of lines
sent to terminal
C Local variables:
      INTEGER CORR,EPS                      !what is being
calculated?
      INTEGER PIMC,VARY               !which method?
      DATA EPS,CORR /1,2/
      DATA VARY,PIMC /1,2/
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
      IF (MUNIT .EQ. OUNIT) THEN
         CALL CLEAR
      ELSE
         WRITE (MUNIT,*) ' '
         WRITE (MUNIT,*) ' '
      END IF
C
      WRITE (MUNIT,5)
      WRITE (MUNIT,7) S
      WRITE (MUNIT,8) BETA
```

```
      WRITE (MUNIT,9) A
      WRITE (MUNIT,*) ' '
      IF (METHOD .EQ. PIMC) THEN
         WRITE (MUNIT,10) NENSEM, DT
      ELSE
         WRITE (MUNIT,11)
      END IF
      IF (CALC .EQ. CORR) WRITE (MUNIT,12) NCORR
      WRITE (MUNIT,13)DELTA
      WRITE (MUNIT,15) NTHERM
      WRITE (MUNIT,20) NFREQ,NSMPL
      WRITE (MUNIT,*) ' '
C
      NLINES=11
C
5     FORMAT (' Output from project 8:',
     +        ' Monte Carlo solution of the H2 molecule')
7     FORMAT (' Proton separation (Angstroms) = ',F7.4)
8      FORMAT (' Variational parameter Beta (Angstroms**-
1) = ',F7.4)
9      FORMAT (' Wave function parameter A (Angstroms) =
',F7.4)

10     FORMAT (' Path Integral Monte Carlo with ensemble
size = ',I4,
     +        ' and time step = ',1PE12.5)
11    FORMAT (' Variational Monte Carlo method')
12    FORMAT (' correlations will be calculated up to K =
', I4)
13      FORMAT (' Metropolis step in coordinate space
(Angstroms)=',F7.4)
15    FORMAT (' number of thermalization sweeps =',I4)
20      FORMAT (' sweep frequency = ',I4,' group size
=',I4)
C
      RETURN
      END
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
      SUBROUTINE
TXTOUT(IGRP,ENERGY,EVALUE,SIG1,SIG2,U,ACCPT,MUNIT)
C write out results to MUNIT
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
C Global variables:
      INCLUDE 'PARAM.P8'
      INCLUDE 'IO.ALL'
C Input variables:
C     energy has two indices
C     first index is the level: sweep, group, or total
```

```
C      second index is the value: quantity, quant**2, or
sigma**2
      REAL ENERGY(3,3)           !energy
      INTEGER IGRP               !group index
      REAL EVALUE                !current average energy
      REAL SIG1,SIG2             !uncertainties in energy
      REAL U                         !total energy of the
system at this S
      REAL ACCPT                 !acceptance ratio
      INTEGER MUNIT              !unit to write to
C Local variables:
      INTEGER   SWEEP,GROUP,TOTAL      !which   level   of
calculation
      INTEGER VALUE,SQUARE,SIGSQ !which quantity
      INTEGER PIMC,VARY          !which method?
      DATA SWEEP,GROUP,TOTAL/1,2,3/
      DATA VALUE,SQUARE,SIGSQ/1,2,3/
      DATA VARY,PIMC /1,2/
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
      WRITE (MUNIT,10) IGRP,NGROUP,
     +
ENERGY(GROUP,VALUE),SQRT(ENERGY(GROUP,SIGSQ))
      IF (METHOD .EQ. VARY) THEN
        WRITE                                        (MUNIT,20)
EVALUE,SIG1,SIG2,U,ACCPT/IGRP/NFREQ/NSMPL
      ELSE
        WRITE (MUNIT,30) EVALUE,SIG1,SIG2,U
      END IF
      IF (MUNIT .EQ. TUNIT) WRITE (MUNIT,*) ' '
C
      IF ((MUNIT .EQ. OUNIT) .AND. (.NOT. TERSE))
     +      CALL PAUSE('to continue...',1)

10    FORMAT (2X,'Group ', I4,' of ', I4,5X,'Eigenvalue =
',F9.4,
     +       ' +- ',F8.4)
20          FORMAT   (2X,'Grand   average   E   =',F9.4,'+-
',F8.4,'/',F8.4,
     +        '   U=',F9.4,'  acceptance=',F6.4)
30          FORMAT   (2X,'Grand   average   E   =',F9.4,'+-
',F8.4,'/',F8.4,
     +        '   U=',F9.4)
      RETURN
      END
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
      SUBROUTINE GRFOUT(DEVICE,ECORR)
C outputs energy auto-correlation vs. correlation length
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
```

```
C Global variables
      INCLUDE 'IO.ALL'
      INCLUDE 'PARAM.P8'
      INCLUDE 'GRFDAT.ALL'
C Input variables:
      REAL  ECORR(0:MAXCRR)                    !energy  auto-
correlations
      INTEGER DEVICE                   !which device is being
used?
C Local variables
      REAL K(0:MAXCRR)                 !correlation length
      INTEGER IK                          !correlation length
index
      CHARACTER*9 CB,CS,CG               !Beta, S, NGROUP as
character data
      INTEGER SCREEN                   !send to terminal
      INTEGER PAPER                    !make a hardcopy
      INTEGER FILE                     !send to a file
      INTEGER LB,LS,LG                        !true length of
character data
      DATA SCREEN,PAPER,FILE/1,2,3/
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
C     messages for the impatient
      IF (DEVICE .NE. SCREEN) WRITE (OUNIT,100)
C
C     calculate parameters for graphing
      IF (DEVICE .NE. FILE) THEN
          NPLOT=1                         !how many plots?
          IPLOT=1
C
          YMIN=-1.                        !limits on plot
          YMAX=1.
          XMIN=0.
          XMAX=NCORR
          X0VAL=0.
          Y0VAL=XMIN
C
          NPOINT=NCORR+1
C
          ILINE=1                           !line and symbol
styles
          ISYM=1
          IFREQ=1
          NXTICK=5
          NYTICK=5
C
          CALL CONVRT(BETA,CB,LB)                 !titles and
labels
          CALL CONVRT(S,CS,LS)
          CALL ICNVRT(NGROUP,CG,LG)
```

```
          INFO='NGROUP = '//CG(1:LG)
          TITLE   =   'H2   molecule,   S='//CS(1:LS)//',
Beta='//CB(1:LB)
          LABEL(1)= 'Correlation length'
          LABEL(2)= 'Energy auto-correlation'
C
          CALL GTDEV(DEVICE)                        !device
nomination
          IF (DEVICE .EQ. SCREEN) CALL GMODE  !change to
graphics mode
          CALL LNLNAX                            !draw axes
      END IF
C
      DO 10 IK=0,NCORR                           !fill array
of corr length
         K(IK)=REAL(IK)
10    CONTINUE
C
C     output results
      IF (DEVICE .EQ. FILE) THEN
          WRITE (GUNIT,*) ' '
          WRITE (GUNIT,25) NGROUP
          WRITE (GUNIT,70) (K(IK),ECORR(IK),IK=0,NCORR)
      ELSE
          CALL XYPLOT (K,ECORR)
      END IF
C
C     end graphing session
      IF  (DEVICE  .NE.  FILE)  CALL  GPAGE(DEVICE)!close
graphics package
      IF (DEVICE .EQ. SCREEN) CALL TMODE      !switch to
text mode
C
70    FORMAT (2(5X,E11.3))
25    FORMAT (6X,'corr length',5X,
     +    'energy auto-correlation for NGROUP=',I5)
100    FORMAT (/,' Patience, please; output going to a
file.')

      RETURN
      END
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
      SUBROUTINE CRROUT(MUNIT,ECORR)
C write out correlations to MUNIT
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
C Global variables:
      INCLUDE 'PARAM .P8'
      INCLUDE 'IO.ALL'
C Input variables:
```

```
      REAL  ECORR(0:MAXCRR)                   !energy  auto-
correlations
      INTEGER MUNIT                 !unit to write to
C Local variables:
      INTEGER K                     !correlation length
      INTEGER NLINES                      !number of lines
written to screen
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCC
      IF (MUNIT .EQ. OUNIT) THEN
         CALL CLEAR
      ELSE
         WRITE (MUNIT,*) ' '
      END IF
C
      NLINES=1
      WRITE (MUNIT,30) NGROUP
30    FORMAT(' Correlations with NGROUP = ',I5)
      DO 10 K=0,NCORR
         NLINES=NLINES+1
         WRITE (MUNIT,20) K,ECORR(K)
         IF ((MUNIT .EQ. OUNIT) .AND. (MOD(NLINES,TRMLIN-
3).EQ. 0)) THEN
            CALL PAUSE('to continue...',0)
            NLINES=0
         END IF
10    CONTINUE
      IF (MUNIT .NE. OUNIT) WRITE (MUNIT,*) ' '
20    FORMAT (5X,' Correlation length = ', I3, 5X,
     +        'Energy auto-correlation = ', F12.5)
      RETURN
      END
```