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# PATH INTEGRAL MONTE CARLO FORMULATIONS AND THE GROUND STATE ENERGY OF HELIUM ATOM

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**ABSTRACT**
Quantum Monte Carlo methods are among the most accurate for calculating the ground state properties of quantum mechanical systems. One of the most accurate QMC methods i.e. the path integral Monte Carlo (PIMC) was used in this report to determine the ground state energy of helium atom. The calculations were based on the principles of Born-Oppenheimer approximation and the principles of superposition; hence wave functions were not of great importance. The ground state energies were calculated at different values of variational parameters and presented graphically. The standard errors are found when compared with the standard theoretical values. The results obtained were presented for comparism as well.

**KEY WORDS:** Born-Oppenheimer approximation, principles of superposition and ground state energy

## INTRODUCTION

The ground state energies of molecular systems have been calculated using different methods ranging from the classical approaches to quantum approaches for quite a long time. These were based on solving the time-dependent and time-independent Schrödinger equations in which the Born-Oppenheimer approximations or the otherwise can be adopted.

In this work one of the quantum Monte Carlo methods i.e. the path integral Monte Carlo method is applied to evaluate the ground state energy of Helium atom. Though the ground state energy of helium had been determined using various quantum techniques such as the Green function Monte Carlo methods by D Martins (2007), and Hylerras algorithm by F S Koki (2009) and Variational Monte Carlo by Doma and El-Gamal (2009) that could be compared.

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 method (PIMC)**

The path integral Monte Carlo (PIMC) 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 Planck's constant $\eta$:

$$K(x_b,t_b:x_a,t_a) \propto \sum_{all\ paths\ x_t} e^{iS[x(t)]}/\eta \qquad 2.1$$

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

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

thus $$K(x_b,t_b:x_a,t_a) \equiv \left\langle x_b \left| \exp\left(-\frac{1}{\eta}H(t_b-t_a)\right) \right| x_a \right\rangle = \left\langle x_b \left| \left(\exp\left(-\frac{1}{\eta}H\Delta t\right)\right)^N \right| x_a \right\rangle \qquad 2.2$$

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

$$K(x_b,t_b:x_a,t_a) = \int_{-\infty}^{\infty} dx_1 - \int_{-\infty}^{\infty} dx_{N-1} \prod_{k=1}^{N} \left\langle x_k \left| \exp(-iH\Delta t/\eta) \right| x_{k-1} \right\rangle \qquad 2.3$$

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

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, Feynman's 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.

**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 electro statically. 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.

**Computing the ground state energy of Helium atom**

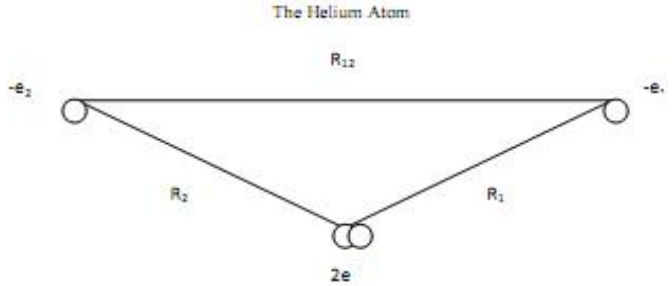


**FIGURE 1**: coordinates used in describing the helium atom

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

At this point it can be considered that we had already treated the hydrogen –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 ($M_{Nuc} \approx 700\ M_{elec}$)(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 inter proton separation S = 0 which indicates that one proton is on top of the other as shown in the figure above and the electron coordinates $r_1$ and $r_2$ measure the distance between each electron and the nucleus.

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

$$H = H_0 + H_1$$

Here 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.

4.1 **The algorithm of the code**

The program calculates the exact ground state energies of two-electron atoms $E_0$ at an inter proton separation S = 0 which describe a natural Helium atom indicating that one proton is on top of the other. The PIMC utilizes the time step for all its calculations which are taken in subroutine TSTEP and in turn uses the function ELOCAL for a given set of configurations. The ground state energy is found using observations taken in every step and can be divided into groups to estimate the step-to-step correlations in the energy. When the requested number of groups has been calculated, it will be prompted for the number of additional groups. This algorithm is illustrated in the flowchart overleaf; (figure 2)

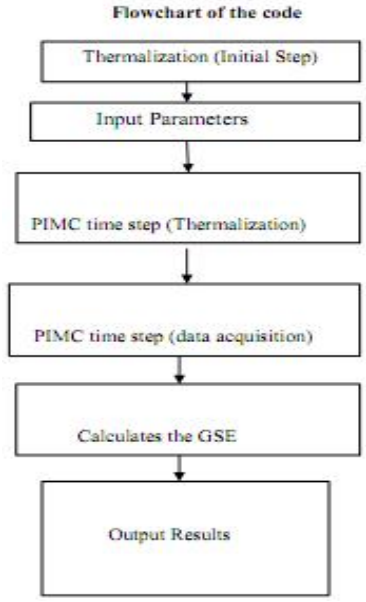


Fig 2

**RESULTS AND DISCUSSION**

**DISCUSSIONS**

The ground state energy of the Helium atom was calculated using the Path Integral method at different values of variational parameter (β) within the context of Born-Oppenhiemer approximations. The result is presented graphically in fig 3 while the standard errors at every point of variational parameter are presented in fig 4.

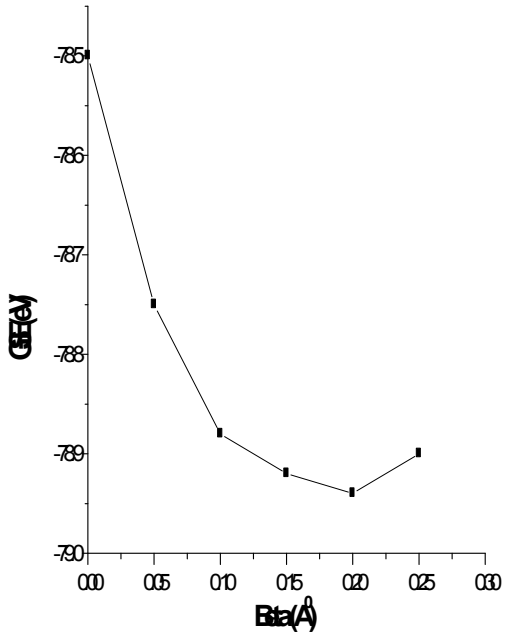


**FIGURE 3** Graph of Ground state energy Vs Variational Parameter Beta for Helium Atom by **PIMC** method

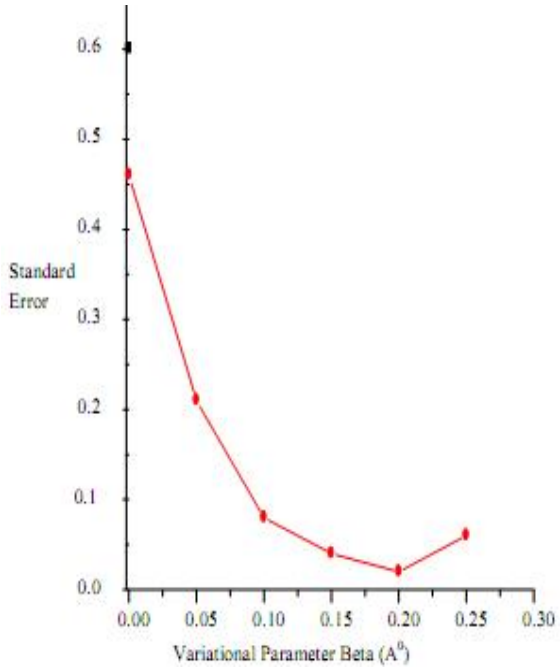


**FIGURE 4:** Graph of Standard errors Vs Variational Parameter (Beta) PIMC (Helium Atom)

Fig 3 presents the results of the ground state energies of the Helium atom at different values of variational parameters β as the path integral Monte Carlo

formulations are applied to the system. It can be observed that the lowest value of the ground state energy is found to be -78.94eV at 0.2 Å value of variational parameter which falls within the range that has been established by reviewers in the field. The graph represents an upward hyperbolic function showing that the coefficient of the square of parameters in the axis of variational parameter β is positive.

Fig 4 presents the deviations of the ground state energy obtained at different values of variational parameters in which the least deviation was recorded at 0.2 Å value of variational parameter.

Table of comparative analysis of ground state energies of the Helium atom obtained by other researchers in the field with this work is shown below.

**HELIUM ATOM**

**TABLE 1:** 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 |

**CONCLUSIONS**

The complete ground state energy of helium was numerically determined using 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 (koonin and Meredith, 1990) i.e. when the protons in the hydrogen molecule are "on top of each other" 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 as -78.94eV at 0.2 Å value of the variational parameter $\beta$ 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 have been evaluated for the helium atom and the deviations from the exact values were observed.

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