Monte Carlo Simulation for Ground State Energies of Atoms

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Abstract

Quantum Monte Carlo (QMC) technique is a legitimate and influential tool for searching accurate approximate solutions of many body Schrödinger equations for atoms. The purpose of this study is to explore the application of this technique to find the ground state energies for He, Li, B and C (*n=2-6*). A modified *n*-parameters trial wave function is proposed which leads to good result in comparison with other trial functions presented before. To estimate the ground state energies, quantum variational principle with trial wave functions and random number is used to generate a large number sample of electron locations. In addition, equilibrium states of Energies as well as standard deviations are plotted. The experimental data are presented for comparison.

1. Introduction

To study the complex quantum systems, Quantum Monte Carlo comprehends a large family of computational methods whose common aim is to find the estimated results by using mathematical simulation. Furthermore, Variational Monte Carlo (VMC) is a quantum Monte Carlo method that applies the variational method to approximate the ground state of a quantum system. In quantum Chemistry calculations, VMC method has become a dominant tool [1-3] to approximate ground state energy and other properties. Recent applications of the VMC method in computational dynamics shows that VMC has become a valuable method because of a wide variety of wave function forms for which analytical integration would be difficult. These method gives the opportunity to choose freely the trial wave function in analytical form which is one of the major advantage for using

this method and trial wave function can contains highly sophisticated term in such a way that electron correlation is explicitly taken into account [4-5]. Atoms are electron based system that means electron plays a crucial role and that is why this method is extremely useful to study physical cases. In case of simplest few-body systems or two-electron system, VMC method provides exact approximations of the ground and excited state energies and properties of atomic and molecular arrangements [6]. Generally the correlated wave function in VMC is constructed as the product of function and correlation factor, which includes the dynamic correlations between the electrons, typical wave function and the exact wave function such as the spin and the angular momentum of the atom [7]. However, the combination of direct calculation of the difference delta between a true wave function and a trial wave function with importance sampling is used to greatly reduce systematic and statistical error.

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Considering the wave function and the dissimilar correlation features, the atoms He to C (Helium to Carbon) has been widely studied [8–11]. The Hartree-Fock solution has been used as common option for the typical wave function. To work with greater number of electrons the Hartree-Fock solution shows some problems to estimate the ground state of energy. First of all in the consideration of relativistic effects and the other is that it takes more time to calculate these systems. As the number of electrons increases both effects are increases.

In recent years researchers have been trying to develop an approach for constructing trial wave functions in order to calculate the ground state energy of the atoms and achieve high level of accuracy. The inter-electronic distances in the wave function included by the correlation effect was introduced in the Hylleraas [12]. In 2006, the ground state energy of the atoms Li through Kr has been studied using Jastrow correlation factor times a model function with 17 variational parameters by VMC method [7]. The obtained results showed a great improvement over all the previous results. In 2003, calculations on the ground state of boron atom have been done using the single and 150 term wave functions constructed with Slater orbitals by M. B Ruiz [13]. Although there is no fast way to get accurate wave functions for the atoms and some five-electron atomic ions, most of these studies search for accurate results but nevertheless compact wave functions. From this point of view, [14-18] suggested a simple nearby trial function for the ground state of the atoms which provided a precise accurate energy in such a way that it could considered as the most accurate among existent few-parameter trial functions. In the present study, VMC method is going to use to study two to six-electron system (He to C), which may be studied by using Monte Carlo Simulation process with random number and different form of trial wave functions. Accordingly, a compact n parameters wave function is considered to obtain the ground state energy.

2. Mathematical Model

2.1. The Many Bodies Stationary Schrödinger Equation

Let us consider a system of quantum particles interacting via Coulomb potentials for the many bodies stationary Schrödinger equation. Since the masses of nuclei and electrons differ by three orders of magnitude or more and the Hamiltonian is given by [19]

$$\widehat{H} = -\frac{1}{2}\sum_i \nabla_i^2 - \sum_{i,I}\frac{Z_I}{|r_i - x_I|} + \sum_{j<i}\frac{1}{|r_i - r_j|} \tag{1}$$

Where, i and j represents the electrons and I runs over the

ions with charges Z_I. Throughout the calculation, atomic units $m_e = h = e = 4\pi\varepsilon_0 = 1$ has used for simplicity, where m_e the mass of electron e, is the charge of electron and ε_0 is the permittivity of a vacuum. The Schrödinger equation is

$$H\Psi = E_0\Psi$$

$$\Rightarrow -\frac{1}{2}\sum_i \nabla_i^2\Psi + V\Psi = E_0\Psi \tag{2}$$

Here, ∇_i^2 is the Laplacian operator, Ψ is any trial solution, and E_0 is the ground state energy of atoms. V represents the electrostatic potential in the molecule is given by

$$V = \sum_{i,I}\frac{-Z_I}{|r_i - x_I|} + \sum_{j<i}\frac{1}{|r_i - r_j|} \tag{3}$$

Here, the first summation works over all electrons and nuclei, where Z_I and x_I are the nuclear charges and locations respectively. The second summation works over all pairs of electrons. To evaluate the lowest eigenvalue, the variational principle shows us [20] that from (2),

$$\frac{\int[\Psi_i H\Psi_i]dR}{\int \Psi_i^2 dR} \geq E_0 \tag{4}$$

The limit of equality holds not only for the accurate solution of Ψ, but also for estimated solutions, called variational estimates of the ground-state energy. The left-hand side of equation (4) is usually quite close to E_0. The main problem is how to evaluate the high dimensional integrals; this is impossible to do analytically and not feasible even numerically. But, Monte Carlo is the process that can easily simulate high dimensional integrals.

Let us preliminary illustrate the local Energy by,

$$E_L = \frac{H\Psi}{\Psi} = -\frac{1}{2}\frac{\sum_i \nabla_i^2\Psi}{\Psi} + V \tag{5}$$

Rewritten the left side of (4) as

$$\frac{\int E_L\Psi_i^2 dR}{\int \Psi_i^2 dR} \tag{6}$$

It is the best way to get an estimation of E_0 by averaging the 10000 values of E_L. Unluckily, this estimate will be very imprecise since random model of configurations tolerates at this point, there are no relationship to Ψ^2 of equation (6). Observing the progressive sample averages of E_L, no systematic change happened but after reaching a so-called equilibration found only random variations. After reaching in equilibrium state, reduce the statistical error of the final estimate by changing the configuration for as many steps (called iterations) as feasible. This is not much difficult to calculate, to do so, combining all the individual sample averages into one. But there is one more little snag; the result has an error proportional to the step size. The step size should

be accustomed to yield a reasonable amount of rejections, say between 10% and 30%.

2.2. Variational Monte Carlo for the Atom

Variational Monte Carlo (VMC) is based on a straight application of Monte Carlo integration to explicitly correlated many-body wave functions. The variational principle of quantum mechanics states that a trial wave function's energy will be greater than or equal to the energy of the exact wave function. Optimized forms of many-body wave functions enable to determine the accurate of expectation values. Variational Monte Carlo is a method of computing the total energy and its variance,

$$\langle H \rangle = \frac{\sum_i [\Psi_i H \Psi_i]}{\sum_i [\Psi_i^2]} \qquad (7)$$

$$\sigma^2 = \frac{\sum_i (H\Psi_i - E_0 \Psi_i)^2 \Psi_i^2}{\left(\sum_i [\Psi_i^2]\right)^2} \qquad (8)$$

Here, H is the Hamiltonian, Ψ_i is the value of the trial wave

function at the Monte Carlo integration point x_i. The constant E_0 is fixed at a value close to the desired state in order to start the optimization in the proper region. The exact wave function is able to give both the lowest value of H and a zero variance. It is possible when minimization of variance favours those wave functions which have a constant local energy. Previous studies have shown that the rate of convergence of a variational calculation can be tremendously accelerated by using basis functions which satisfy the two-electron cusp condition and which have the correct asymptotic behaviour [17]. Unfortunately, the integrals of such functions can hardly be evaluated rationally. Because in this method uses Monte Carlo integration and can easily build into the trial wave function many features which will accelerate convergence.

2.3. The Trial Wave Function

The calculations for the particle atom obtained previously using trial wave functions which takes the form [18]:

$$\Psi_1(r_1, r_2) = \text{Exp}(-\alpha(r_1))R_{nl}(\alpha_0, r_2)Y_{l,m}(\hat{r}_2)$$

$$\Psi_2(r_1, r_2, r_3) = \text{Exp}(-\alpha(r_1 + r_2))R_{nl}(\alpha_0, r_3)Y_{l,m}(\hat{r}_3)$$

$$\Psi_3(r_1, r_2, r_3, r_4) = \text{Exp}(-\alpha(r_1 + r_2 + r_3))R_{nl}(\alpha_0, r_4)Y_{l,m}(\hat{r}_4)$$

$$\Psi_4(r_1, r_2, r_3, r_4, r_5) = \text{Exp}(-\alpha(r_1 + r_2 + r_3 + r_4))R_{nl}(\alpha_0, r_5)Y_{l,m}(\hat{r}_5)$$

$$\Psi_5(r_1, r_2, r_3, r_4, r_5, r_6) = \text{Exp}(-\alpha(r_1 + r_2 + r_3 + r_4 + r_5))R_{nl}(\alpha_0, r_6)Y_{l,m}(\hat{r}_6) \qquad (9)$$

Where, the symbol $\hat{r}_i$; $i = 1,2,3,4,5,6$ denotes the angular variables of r_i and the function $R_{nl}(\alpha_0, r_i)Y_{1,m}(\hat{r}_i)$ is the hydrogen-like wave function in the *nl*-state with effective charge α_0.

These wave functions were used to calculate the energy of atoms ground state with quite accurate results. In the present paper some modifications has introduced to these trial wave functions in order to get more perfect results. Firstly, considering the correlation between each two electrons and in order to include the electron-electro correlation multiplying

the form of this trial wave function by the following factor:

$$f(r_{ij}) = Exp\left[\frac{r_{ij}}{\alpha(1 + \beta r_{ij})}\right] \qquad (10)$$

which expresses the correlation between the two electrons i and j due to their Coulomb repulsion. That is, f to be small when r_{ij} is small and to approach a large constant value as the electrons become well separated which is expected. Then, for the ground-state of the atoms (He to C), Eq. (9) reduces to the following form:

$$\Psi_1(r_1, r_2) = \text{Exp}(-\alpha(r_1))R_{nl}(\alpha_0, r_2)Y_{l,m}(\hat{r}_2) \prod_{i<j} f(r_{ij})$$

$$\Psi_2(r_1, r_2, r_3) = \text{Exp}(-\alpha(r_1 + r_2))R_{nl}(\alpha_0, r_3)Y_{l,m}(\hat{r}_3) \prod_{i<j} f(r_{ij})$$

$$\Psi_3(r_1, r_2, r_3, r_4) = \text{Exp}(-\alpha(r_1 + r_2 + r_3))R_{nl}(\alpha_0, r_4)Y_{l,m}(\hat{r}_4) \prod_{i<j} f(r_{ij})$$

$$\Psi_4(r_1, r_2, r_3, r_4, r_5) = \text{Exp}(-\alpha(r_1 + r_2 + r_3 + r_4))R_{nl}(\alpha_0, r_5)Y_{l,m}(\hat{r}_5) \prod_{i<j} f(r_{ij})$$

$$\Psi_5(r_1, r_2, r_3, r_4, r_5, r_6) = \text{Exp}(-\alpha(r_1 + r_2 + r_3 + r_4 + r_5))R_{nl}(\alpha_0, r_6)Y_{l,m}(\hat{r}_6) \prod_{i<j} f(r_{ij}) \qquad (11)$$

where *i, j* indices the run over the electrons number. The variational parameters α_0 and β will determined for each value of Z by minimizing the energy. The function $Y_{l,m}(\hat{r}_n)$ of equation (11) is constant for the ground-state of atoms

3. Result and Discussion

For finding an accurate approximation of E_0, repeating the simulation process with significantly more iterations and then calculating the average of the E_L values. In this research paper, this close to -14.552 atomic units for Beryllium, -24.5540 atomic units for Boron with an average acceptance rate of about 85%-90%. The best way isto implement the same program independently 5 to 10 times to find the corresponding statistical error and combine the individual results. This procedure improves the estimate to -14.552 atomic units with the standard error of ±0.06979 for the case of Beryllium. Figure 1 shows the number of iteration required (100 times) to estimate the ground-state energy for atoms (He to C).

Table 1. Comparison of Approximate values of atoms ground state energies with experimental values.
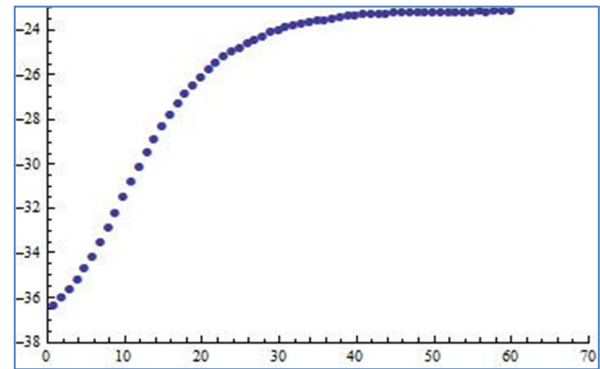
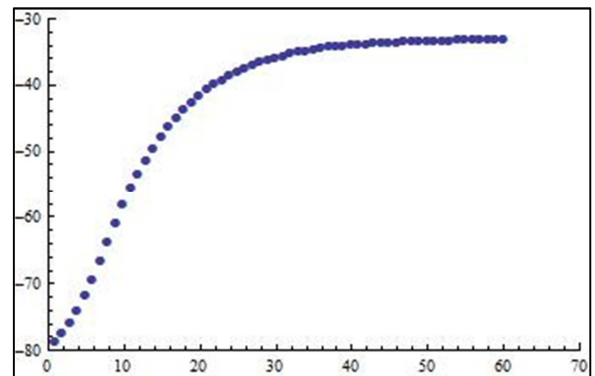| Atom	VMC Method	Exact Values (Experimental)
Helium	−2.939367	−2.9033864 [21]
Lithium	−7.365826	−7.47693 [22]
Beryllium	−14.55243	−14.64627 [23]
Boron	−24.55402	−24.541246 [7]
Carbon	−37.26656	−37.80828 [11]
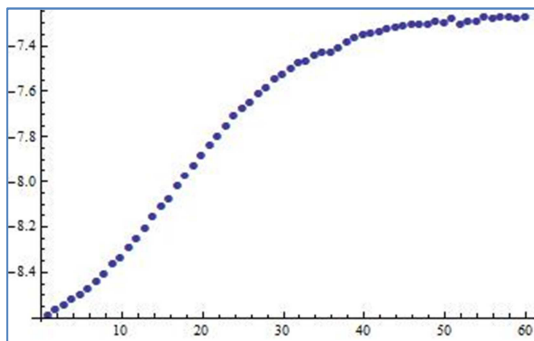
(a)
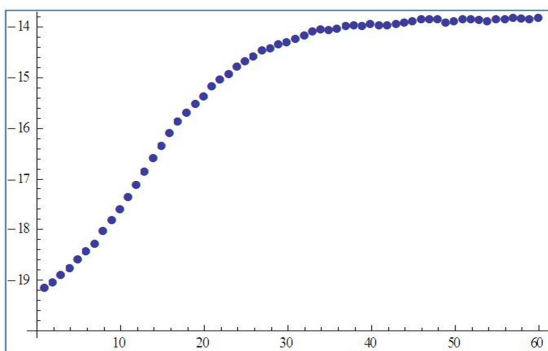
(b)

(c)

(d)

Figure 1. Approximate values for 10000 iterations of VMC to reach stable ground state of energy (a) Lithium (b) Beryllium (c) Boron (d) Carbon.

It is clear from figure 1, that after 3000 iteration, energy is started to stable. Despite the statistical error, there is clear difference between estimate value and the experiment or well established value. In accordance with the variational principle, the approximate values are not close to the experiment values, which are shown in table 1.

After each step, new estimates of E_0 is computed from corresponding weighted averages and combined with the usual grand mean. Yet, this procedure faces two different problems, but it can handle easily.

First one is, when an electron and nucleus come closer that means, electron moves close to nucleus then an unusual low value occur for mean deviation, making the corresponding weighted value rather large or sometimes larger than all the remaining weights combined. The best way is to solve this problem in a symmetrical manner by rounding the value to the nearest boundary of the interval.

Second one is, final estimate (grand-mean) of E_o may have a small biased value which proportional to the step size. For this type of problem can solve by repeating the simulation process, at several (say 4 to 5) dissimilar values of step size, and by performing a simple

polynomial regression getting an unbiased estimate of E_o. The final answer can get at the intercept of the resulting regression line.

By using a modified wave function in VMC method successfully found the ground state energies for the atoms He to C obtained in this work. The iteration averages of E_L will show that equilibration now takes many more steps (about 500, when step size 0.025) than in the case of variational simulation. Thus discard the first 1000 results and partition the remaining 6000 into six blocks of 1000. Then it is produces six such values with step size 0.050 and 0.075. It is now easy to find the resulting intercept. As for example, the following below table 3 shows the estimate for Beryllium.

Table 2. Monte Carlo Result for Boron.

|	Estimate	Standard Error	P-Value
1	−24.546707	0.034	2.4747×10^{-24}
x	99.5137	2.48945	3.1413×10^{-9}
x^2	−796.109	24.6392	7.3521×10^{-8}

The final estimated value of Beryllium is therefore -14.66702 ± 0.0012 for the corresponding regression line. This is in Reasonable agreement, in view of the nodal error, with the exact value of -14.66702 atomic units. This visualizes the regression fit is

Table 3. Monte Carlo Result for Beryllium.

	Estimate	Standard Error	P-Value
1	−14.66702	0.0012	1.0773×10^{-28}
x	−1.1796	2.6141	0.6583
x^2	9.4364	5.8729	0.7204
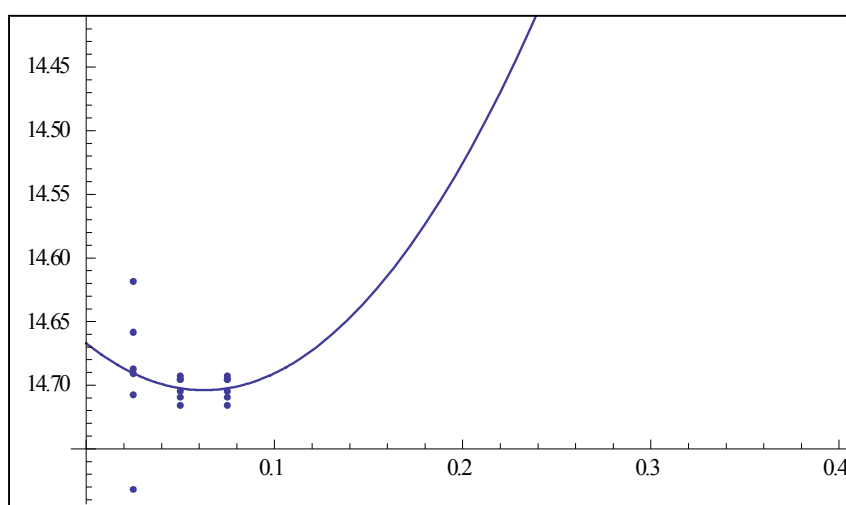
(a)
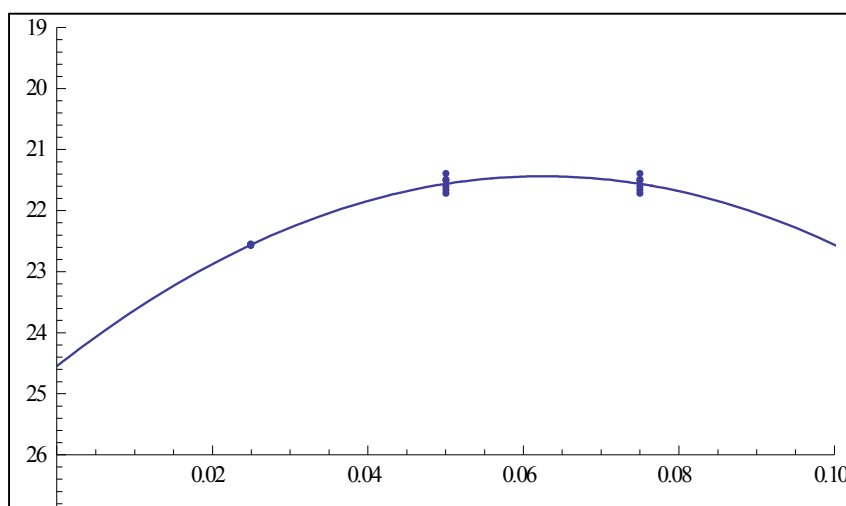
(b)

Figure 2. Presenting the energies level as a function of (a) Beryllium and (b) Boron by using a set of Monte Carlo points.

In similar way, Table 4 shows the final estimated ground state energies for the atoms (He to C). In all cases, estimated values are very close to exact value. Among them Estimated value for helium shows very good agreement with exact value.

Table 4. Estimated Ground state energies, standard errors and P-Values of Atoms.

	Estimate	Standard Error	P-Value
Helium	-2.90125	0.00032	1.6632×10^{-25}
Lithium	-7.47582	0.0092	1.9856×10^{-23}
Beryllium	-14.6670	0.0012	1.0773×10^{-28}
Boron	−24.5467	0.034	2.4747×10^{-24}
Carbon	-37.2333	0.0019	1.493×10^{-20}

By using a very large of MC trial function, Table 4 expresses the ultimate value of atom's energy together with standard error. Table 4 also shows that the obtained value is good agreement with the exact value. B. L. Hammond [1], found the ground state energy of Beryllium is -14.66737 using the same trail function but without introducing the factor $f(r_{ij})$. It is clear from Table-2 that obtained result is more accurate for the Beryllium atom (Z=4) is -14.66702.

4. Conclusion

Quantum Monte Carlo procedures provide a framework for calculating the ground state energy and properties of correlated quantum systems. In this study, the ground state energies of Helium to Carbon have been executed with standard error and P-value. The obtained values were found by using a correlation factor which mainly depends on vaiational parameters. To advance the results, the trial wave function with the electron-electron correlation factor was played a crucial role. Thus, It is important to remember that the trial wave functions for QMC calculations could be improved by developing new wave function forms and better optimisation methods.

Acknowledgements

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