

Simple Trial Wave Functions for The Ground State of the Lithium Atom using Variational Monte Carlo Method

S. B. Doma¹⁾, H. S. El-Gendy²⁾, M. A. Abdel-Khalek³⁾ and M. M. Hejazi⁴⁾

¹⁾Faculty of Science, Alexandria University, Alexandria, Egypt, sbdoma@alexu.edu.eg

²⁾Faculty of Science and Art, Shaqra University, Shaqra, KSA, hselgendy1@yahoo.com

³⁾Faculty of Science, Alexandria University, Alexandria, Egypt, monaelgamal@yahoo.com

⁴⁾Faculty of Science, Alexandria University, Egypt mohamedhejazi3@gmail.com

Abstract

In this paper, the variational quantum Monte Carlo method is applied to investigate the ground-state of the lithium atom. The calculations are carried out by using trial wave functions in the form of the Slater determinant wave function multiplied by correlation function due to the interaction between the electrons. Two types of the correlation functions are used with one and two variational parameters, and one of which satisfy the well-known cusp conditions. Interesting results for the ground state energy of lithium are obtained in comparison with results obtained by using other trial wave functions.

Keywords: Lithium atom; variational Monte Carlo method; trial wave functions.

PACS: 23.40.-s, 21.10.Tg, 21.10.ky

1. Introduction

The Variational Monte Carlo (VMC) method [1,2] is an extremely powerful tool based on a combination of two ideas namely the variational principal and Monte Carlo evaluation of integrals using importance sampling based on the Metropolis algorithm [3]. This method estimates the energy and all the desired properties of a given atom, molecule and nucleus by a suitably chosen trial wave function. In quantum mechanics, the Monte Carlo method has been extensively employed to evaluate the multi-dimensional integrals which arise in the different formulae of the many-body problem. These calculations contain the evaluation of integrals, whose dimensionality are three times the number of particles, typically hundreds. Consequently, they pose no restrictions on the functional form of the trial wave functions. They require only the evaluation of the wave function, its gradient and its Laplacian at any point of the integration space, and these can be easily computed. Moreover, the Monte Carlo technique is well adapted to computers since it consists of a simple, highly repetitive algorithm that takes advantage of the fast arithmetic capabilities of the machines.

Using the VMC algorithm, essentially a stochastic numerical integration scheme, the expectation value of the energy for any trial wave function form can be estimated by averaging the local energy $H\psi/\psi$ during a random walk in the configuration space using a Metropolis algorithm for example.

It was acknowledged since Chemical Physics have appeared that the energy E_{HF} of the Slater determinant (SlDet), $|\psi_{HF}\rangle$, acquired by the single-particle Hartree-Fock (HF) equation, does not synchronize with the lower energy of the functional $\langle\psi|H|\psi\rangle$ where $|\psi\rangle$ is a SlDet and H is the many-particle Hamiltonian. Nevertheless, in most textbooks, there is no mention of this fact. In Ref [4], Thanos et al. started from a Slater determinant $|\psi\rangle$ with its spin orbitals calculated by the standard HF equation, they looked for the maximum of the functional $|\langle\psi'|H|\psi\rangle|$, where $|\psi'\rangle$ is a SlDet and H is

the exact Hamiltonian of an atom. The element $|\langle\psi_1|H|\psi\rangle|$ with $|\psi_1\rangle$ the maximizing $|\psi'\rangle$ gives a value larger than $\langle\psi|H|\psi\rangle$. As a next step they calculated the corresponding maximum superposition $\langle\psi_2|H|\psi_1\rangle$ and thereafter $|\langle\psi_{n+1}|H|\psi_n\rangle|$ until $|\langle\psi_{m+1}|H|\psi_m\rangle - \langle\psi_{m-1}|H|\psi_m\rangle| \leq \varepsilon$, where ε determines the desired numerical precision. Consequently, they showed that the sequence $a_n = |\langle\psi_{n+1}|H|\psi_n\rangle|$ is ascending and showing a convergent. They applied this proceeding for identifying the eigenstate energies of a number of configurations of H3, the Lithium atom, LiH and Be. After comparing their results with those of the configuration interaction (CI) they concluded that their deviations are in the range 10^{-5} to 10^{-8} and the ground state energy is significantly lower than the standard HF calculations.

Eventually, the new single determinant approximation, SDA, according to three new theorems, gives a precision of the eigenstate energies, comparing to those of the CI, quite surprising for a single SIDet approximation. In all cases, the deviation from the CI calculations ranged from 10^{-8} to 10^{-5} . In order to emphasize that their calculations did not include any programming or numerical errors, they verified their minimum energy values obtained from the HF equation with those of other authors and noticed that they are practically the same. Consequently, for the $S = \frac{1}{2}$ state of Li they found that $E = -7.43269$ Hartrees, while the value acquired by Toshikatsu et al. [5] was -7.43272 Hartrees. A characteristic of their single-particle approximation with respect to the CI is that in the calculations of the matrix elements one has to do computations between two pairs of determinants while in the CI several determinants are included. Consequently, in most calculations, many functionals are used until one gets results which are well comparable with the experimental ones or with those of more precise methods. Therefore, the method had certain features with respect to DFT. Especially, the SIDet obtained from DFT are not a good approximation to the exact eigenstates, while these of the present method are.

In Ref [6], S. B. Doma et al. applied the VMC method to study the ground state and some excited ones of the lithium atom and its ions up to $Z = 10$ undergoing an external magnetic field regime with $\gamma = 0-100$ arb. units. They studied the effect of increasing field strength on the ground state energy and accurate values for the crossover field strengths were obtained. Their calculations were based on using accurate forms of trial wave functions, which were put forward in calculating energies in the absence of a magnetic field. The obtained results were in good agreement with the most recent values and with the exact ones, too. Moreover, they calculated the value of γ at which the ground-state energy of the lithium atom approaches to zero. They concluded that the VMC method is flexible enough to yield accurate results for arbitrary field strengths. For a weak field, their calculations were based on using few-parameter trial wave functions, which can be considered as the most precise ones among several existing few-parameter trial wave functions for the lithium atom and its ions. Their results were considered the first published ones in this respect.

Also, by using the VMC method, S. B. Doma et al. [7] calculated the ground-state energies of the lithium atom and its ions up to $Z = 10$. Their calculations were based on using a modified trial wave function of three parameters [8] which led to good results comparable with the few parameters trial wave functions presented before. They applied a new mechanism to minimize the three variational parameters. That mechanism depended on using the steepest descent (SD) method in order to acquire precise values of the energies. This method was first applied to the helium atom and led to good results. In comparison with the corresponding exact data, their calculations gave good approximations for the ground state energy of the lithium atom and its ions.

The trial wave function which they used were previously presented to calculate the ground state energy for the lithium atom only and without taking the electron-electron correlation into consideration. First, they calculated the lithium isoelectronic series up to $Z = 10$. Then, they modified the form of the wave function by multiplying it by the factor $f(r_{ij})$. That factor, which represents the interactions between the electrons, improved the results and led to more precise results. Also, they outlined the steps of optimizing the trial wave function using a new mechanism introduced firstly and applied to calculate the ground-state energy of the helium atom [9]. This mechanism was based on plotting the energy as a function of two variational parameters whereas the third parameter was fixed. They considered the values of the two parameters at which the energy took its minimum value as initial values for using in the SD method. The SD method provided precise values for the variational parameters. To calculate the energy, they used the final values of the three variational parameters with a very large number of Monte Carlo points to get a standard deviation as small as possible. The obtained results were of good precision comparing with the exact values.

In Ref [10], A. Nagy and V. Savona developed a variational method to simulate the nonequilibrium steady state of Markovian open quantum systems based on VMC methods and on a neural network representation of the density matrix. The application of the variational principle is, by virtue of the stochastic reconfiguration scheme, put into the actual integration of the quantum master equation. They tested the efficiency of the method by modeling the two-dimensional dissipative XYZ spin model on a lattice.

In Ref [11], Nicolais et. al. proposed a simple seven-parameter trial function to describe the ground state of the Lithium atom. It included both spin functions. Inter-electronic distances appeared in exponential form and in a pre-exponential factor. The necessary energy matrix elements were evaluated by numerical integration in the space of the relative coordinates. Encouraging precise values of the energy and the cusp parameters, and for some expectation values were obtained. Simple and compact few-parameter trial functions were suggested for the ground state of the lithium atom. Those already provided a very precise ground state energy. Those functions ψ_{1-6} are the most precise amongst existent few-parameter trial functions. Nevertheless, the suggested analysis did not seem final because one could explore the more extended pre-factor.

The VMC method was also used in Ref [12] to evaluate the ground-state energy of a confined hydrogen molecule H₂. In [12], the authors considered the case of H₂ molecule confined by a hard prolate spheroidal cavity when the nuclear positions are clamped at the foci. They used an accurate trial wave function depending on many variational parameters for this purpose. They also calculated the energies for both confined H₂ molecule and its free case. In all cases, their results exhibited a good accuracy compared to previous values obtained using different methods and different forms of trial wave functions. As a conclusion, they concluded that the applications of the VMC method can be extended to cover the case of compressed molecules.

Finally, in Ref [13], S. B. Doma et al. employed the VMC method to study the total energies of several excited states of the helium atom. They investigated also the effect of the strong magnetic field on the energy. Consequently, they concluded that the VMC method was succeeded to study the two-electron system under the effect of a strong magnetic field.

In the present paper, we used two trial wave functions having the same orbital and spin shapes but differ in the shape of the correlation part, due to the interaction between the electrons, to calculate the ground-state energy of the lithium atom.

2. The Metropolis Algorithm

The Metropolis algorithm N. Metropolis and collaborators [14] is a powerful technique continues to be a versatile tool in a great many numerical simulations in several different branches of science [15,16]. The Markov chain Monte Carlo (MCMC) method is a technique for obtaining a sequence of random samples from a probability distribution for which direct sampling is difficult. The Metropolis algorithm is the most widely used algorithm for generating a sequence of phase space points that sample a given probability distribution. In Quantum Monte Carlo (QMC), each phase space point is a vector $\mathbf{R} = (r_1, r_2, \dots, r_N)$ in the $3N$ dimensional space of the position coordinates of all the N electrons, and the sequence of phase space points provides a statistical representation of the ground state of the system. If we are to build up a statistical picture of the overall system of electrons and nuclei, it is necessary to move the electrons around to cover all possible positions and hence all possible states of the system. As we move the electrons around, we can keep track of physical quantities such as the total energy, polarization, etc., associated with the instantaneous state of the electron configuration. The sequence of individual samples of these quantities can be combined to arrive at average values which describe the quantum mechanical state of system. This is the fundamental idea behind the Monte Carlo method, and the Metropolis algorithm is used to generate the sequence of different states to sample physical quantities such as the total energy efficiently. In Metropolis algorithm, a random walk is performed through the configuration space of interest. The walk is designed so that the points on the walk are distributed according to the required probability distribution. At each point on the walk a random trial move from the current position in configuration space is selected. This trial move is then either accepted or rejected according to a simple probabilistic rule. If the move is accepted then the walker moves to the new position in configuration space; otherwise the walker remains where it is, (By a walker we mean a point in the $3N$ -dimensional configuration space of the problem). Another trial step is then chosen, either from the new accepted position or from the old position if the first move was rejected, and the process is repeated. In this way it should be possible for the walker to explore the whole configuration space of the problem. The Metropolis algorithm provides a prescription for choosing which moves in configuration space to accept or reject. If the average over many steps of the random walk follows the specified probability distribution, then the walk is said to have reached equilibrium. In this case, the average number densities of points on the walk at \mathbf{R} and $\hat{\mathbf{R}}$, $N(\mathbf{R})$ and $N(\hat{\mathbf{R}})$, should be constant. That means that the probability of making a transition from \mathbf{R} to $\hat{\mathbf{R}}$ must be equal to the probability of making a transition in the opposite direction, from $\hat{\mathbf{R}}$ to \mathbf{R} . The transition probability of a trial move being made from \mathbf{R} to $\hat{\mathbf{R}}$ is denoted by $P_{\text{trial}}(\mathbf{R} \rightarrow \hat{\mathbf{R}})$ and the transition probability of a trial move being made from $\hat{\mathbf{R}}$ to \mathbf{R} by $P_{\text{trial}}(\hat{\mathbf{R}} \rightarrow \mathbf{R})$. The trial moves are chosen from a fixed probability distribution around the current position and since there is nothing special about the points \mathbf{R} or $\hat{\mathbf{R}}$, we will have

$$P_{\text{trial}}(\mathbf{R} \rightarrow \hat{\mathbf{R}}) = P_{\text{trial}}(\hat{\mathbf{R}} \rightarrow \mathbf{R}). \quad (2.1)$$

The probability of a trial move from \mathbf{R} to $\hat{\mathbf{R}}$ being accepted is $P_{\text{accept}}(\mathbf{R} \rightarrow \hat{\mathbf{R}})$ and the probability of accepting the reverse move is $P_{\text{accept}}(\hat{\mathbf{R}} \rightarrow \mathbf{R})$. Total probabilities for moves occurring in either direction are then

$$\begin{aligned} P(\mathbf{R} \rightarrow \hat{\mathbf{R}}) &= P_{\text{trial}}(\mathbf{R} \rightarrow \hat{\mathbf{R}})P_{\text{accept}}(\mathbf{R} \rightarrow \hat{\mathbf{R}}), \\ P(\hat{\mathbf{R}} \rightarrow \mathbf{R}) &= P_{\text{trial}}(\hat{\mathbf{R}} \rightarrow \mathbf{R})P_{\text{accept}}(\hat{\mathbf{R}} \rightarrow \mathbf{R}), \end{aligned}$$

and the equilibrium condition implies that:

$$N(\mathbf{R})P(\mathbf{R} \rightarrow \dot{\mathbf{R}}) = N(\dot{\mathbf{R}})P(\dot{\mathbf{R}} \rightarrow \mathbf{R}), \quad (2.2)$$

or

$$\frac{N(\mathbf{R})}{N(\dot{\mathbf{R}})} = \frac{P(\dot{\mathbf{R}} \rightarrow \mathbf{R})}{P(\mathbf{R} \rightarrow \dot{\mathbf{R}})}$$

The equilibrium walker density $N(\mathbf{R})$ is therefore proportional to $P(\mathbf{R} \rightarrow \dot{\mathbf{R}})$ and the probability of finding any given walker in $d\mathbf{R}$ is $P(\mathbf{R} \rightarrow \dot{\mathbf{R}})d\mathbf{R}$ as required.

In the Metropolis algorithm the probability of accepting the random move, $P_{\text{accept}}(\mathbf{R} \rightarrow \dot{\mathbf{R}})$, is chosen to be

$$P_{\text{accept}}(\mathbf{R} \rightarrow \dot{\mathbf{R}}) = \min \left\{ 1, \frac{N(\dot{\mathbf{R}})}{N(\mathbf{R})} \right\}. \quad (2.3)$$

This satisfies the equilibrium conditions for the distribution. The mechanism for accepting a move with probability $\frac{N(\dot{\mathbf{R}})}{N(\mathbf{R})}$, within the QMC code, is to generate a random number in the range $[0,1]$. If this random number is less than $\frac{N(\dot{\mathbf{R}})}{N(\mathbf{R})}$ then the move is accepted. If this random number is greater than $\frac{N(\dot{\mathbf{R}})}{N(\mathbf{R})}$ then the move is rejected.

The above description was for a configuration space in which any one point could be reached from any other point in one move. If the configuration space is very large, then if small moves are made it is not possible to reach any other point in one move. If any one point can be reached from any other point the random walk is said to be ergodic and the Metropolis algorithm is still valid. A straightforward extension of the above argument can be made to justify the use of the Metropolis algorithm in this situation. To ensure that points are sampled correctly from the probability distribution, the random walk must be allowed to proceed from some arbitrary initial starting point until the average over an ensemble of moves represents the distribution to be sampled. At this point equilibrium has been reached. It is only at this point that the importance sampling Monte Carlo calculation can be carried out. It should be noted that one does not need to compute the normalization of Ψ_T , $\int |\Psi_T|^2 d\mathbf{R}$, which can be extremely difficult to calculate for a wave function with a complex functional form since we are only computing ratios. Indeed, in the Metropolis algorithm Ψ_T appears only in terms that are independent of its overall normalization factor. Moreover, as the trial wave function approaches an eigenstate of the Hamiltonian, the VMC estimate of the energy converges more rapidly with the number N of steps in the random walk, and therefore the algorithm is more efficient in computing energy expectation values. If Ψ_T coincides with an eigenstate, the variance of the local energy will go to zero since the local energy will be a constant and therefore the statistical error will vanish. This property is the zero-variance principle and suggests that it is very important to deal with a well optimized trial wave function. Although only the operator which commute with the Hamiltonian benefit from this principle, Assaraf and Caffarel [17] have demonstrated that a significant variance reduction can be obtained also by other appropriate estimators, constructed to satisfy the zero-variance principle. The algorithm which exploits the decomposition of the transition probability into the acceptance and the trial probability is the generalized Metropolis algorithm.

3. The Variational Monte Carlo Method

The VMC method [3] is based on a combination of two ideas namely the variational principle and the Monte Carlo evaluation of integrals using importance sampling based on the Metropolis algorithm. It is used to compute quantum expectation values of

operators. If the operator is the Hamiltonian, its expectation value is the variational energy

$$E_{VMC} = \frac{\int \Psi_T^*(\mathbf{R}) \hat{H} \Psi_T(\mathbf{R}) d\mathbf{R}}{\int \Psi_T^*(\mathbf{R}) \Psi_T(\mathbf{R}) d\mathbf{R}} \quad (3.1)$$

where Ψ_T is a trial wave function and " \mathbf{R} " is the $3N$ - dimensional vector of the electron coordinates. The trial wave function Ψ_T is supposed to be as close as possible to the true ground state of the system, or to an exact eigen-state of the Hamiltonian.

According to the variational principal, the expectation value of the Hamiltonian is an upper bound to the exact ground state energy E_0 that is, $E_{VMC} \geq E_0$. To evaluate the integral in Eq. (3.1) we construct first a trial wave function $\Psi_T(\mathbf{R})$ depending on α -variational parameters $\alpha = (\alpha_1, \alpha_2, \dots, \alpha_N)$ and then optimize the parameters to obtain minimum energy. VMC calculations determine E_{VMC} by writing it as

$$E_{VMC} = \int P(\mathbf{R}) E_L(\mathbf{R}) d(\mathbf{R}) \quad (3.2)$$

where

$$P(\mathbf{R}) = \frac{|\Psi_T(\mathbf{R})|^2}{\int |\Psi_T(\mathbf{R})|^2 d\mathbf{R}} \quad (3.3)$$

is positive everywhere and interpreted as a probability distribution and $E_L = \frac{\hat{H} \Psi_T}{\Psi_T}$ is the local energy function. The value of E_L is evaluated using a series of points \mathbf{R}_{ij} proportional to $P(\mathbf{R})$. These series of points are chosen according to the Metropolis algorithm. At each of these points the weighted average

$$\langle E_L \rangle = \frac{\int \hat{H} \Psi_T^2(\mathbf{R})}{\int \Psi_T^2(\mathbf{R})}, \quad (3.4)$$

is evaluated. After a enough evaluations, the VMC estimate of E_{VMC} will be

$$E_{VMC} = \langle E_L \rangle = \lim_{N \rightarrow \infty} \lim_{M \rightarrow \infty} \frac{1}{N} \frac{1}{M} \sum_{j=1}^N \sum_{i=1}^M E_L(\mathbf{R}_{ij}), \quad (3.5)$$

where M is the ensemble size of random numbers $\{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_M\}$ and N is the number of ensembles. These ensembles so generated must reflect the distribution function itself.

This method uses an acceptance and rejection process of random numbers that have a frequency probability distribution like Ψ^2 . The acceptance-and-rejection method is performed by obtaining a random number from the probability distribution, $P(\mathbf{R})$, then testing its value to determine if it will be acceptable for use in approximation of the local energy. After an ensemble of random numbers is generated, the acceptance criterion is such that the probability of moving from an initial random number of the ensemble, \mathbf{R}_i , to a new random number, \mathbf{R}_k , is defined according to the ratio

$$A = \frac{\Psi^2(\mathbf{R}_k)}{\Psi^2(\mathbf{R}_i)}. \quad (3.6)$$

If A is larger than one, this trial step is accepted (i.e. we put $\mathbf{R}_{i+1} = \mathbf{R}_k$) and the new \mathbf{R}_k is a member of the next ensemble. While if A is less than one, the step is accepted with probability A . This latter is conveniently accomplished by comparing A with random number η uniformly distributed in the interval $[0,1]$ and accepting the step if $\eta < A$. If the trial step is not accepted, then it is rejected, and we put $\mathbf{R}_{i+1} = \mathbf{R}_i$.

This process is repeated for each member of an ensemble and is done in order to broaden subsequent ensembles for a wider sampling range. Any arbitrary point \mathbf{R}_0 can

be used as the starting point for the random walk. Finally, it is important to calculate the standard deviation of the energy,

$$\sigma = \sqrt{\frac{\langle E_L^2 \rangle - \langle E_L \rangle^2}{M(N-1)}}. \quad (3.7)$$

4. Ground State Trial Wave Functions for the Lithium Atom

One of our goals in this paper is to solve the Schrödinger wave equation for the ground state of the lithium atom in order to calculate the ground-state energy eigenvalues. We first construct the Hamiltonian operator for the three-particle system in a state with total spin $S = \frac{1}{2}$ and z -projection $M_S = \frac{1}{2}$. For this purpose, we make use of the Born-Oppenheimer approximation of zero order, that is, with the Li nucleus assumed to be of infinite mass. The non-relativistic Hamiltonian for the Lithium atom (in Hartree-atomic units) is given by

$$\hat{H} = -\sum_{i=1}^3 \left(\frac{1}{2} \nabla_i^2 + \frac{Z}{r_i} \right) + \sum_{i=1}^3 \sum_{j>i}^3 \frac{1}{r_{ij}} \quad (4.1)$$

where ∇_i is the 3-vector of the momentum of the i th electron, Z is the nuclear charge (here, $Z = 3$), r_i is the distance between the i th electron and the Li nucleus, and r_{ij} are the interelectron distances.

The ground-state trial wave function for Li may be symbolically written in the form

$$\psi(\text{Li}) = \psi_0 f(r_{12}, r_{13}, r_{23}) \quad (4.2)$$

where f is the correlation function due to the interactions between the electrons. If we neglect the interaction between the electrons, then the ground-state trial wave function of Lithium may be symbolically denoted by

$$\psi_0 = \frac{1}{\sqrt{3!}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\alpha(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 2s(3)\alpha(3) \end{vmatrix} \quad (4.3)$$

which is a linear combination of terms constructed from the single-particle hydrogenic wave functions constructed in such a way that the total spin of the system is $S = \frac{1}{2}$ and its z -component is $M_S = \frac{1}{2}$. By some simple algebra and substituting for the hydrogen wave functions $1s(i)$ and $2s(i)$ in atomic units we get

$$\begin{aligned} \psi_0 = & \frac{2}{\sqrt{3}} \left(\frac{1}{\sqrt{4\pi}} \right)^3 \times (Z)^{\frac{9}{2}} \\ & \left\{ \alpha(1)\beta(2)\alpha(3) \left[e^{-\frac{(2r_1+2r_2+r_3)Z}{2}} \left(1 - \frac{r_3Z}{2} \right) - \left(1 - \frac{r_1Z}{2} \right) e^{-\frac{(r_1+2r_2+2r_3)Z}{2}} \right] \right. \\ & + \alpha(1)\alpha(2)\beta(3) \left[\left(1 - \frac{r_1Z}{2} \right) e^{-\frac{(r_1+2r_2+2r_3)Z}{2}} - \left(1 - \frac{r_2Z}{2} \right) e^{-\frac{(2r_1+r_2+2r_3)Z}{2}} \right] \\ & \left. + \beta(1)\alpha(2)\alpha(3) \left[\left(1 - \frac{r_2Z}{2} \right) e^{-\frac{(2r_1+r_2+2r_3)Z}{2}} - \left(1 - \frac{r_3Z}{2} \right) e^{-\frac{(2r_1+2r_2+r_3)Z}{2}} \right] \right\} \quad (4.4) \end{aligned}$$

For the correlation function f we considered two different types of correlations. The first one is given by

$$f(r_{12}, r_{13}, r_{23}) = e^{-d(r_{12}+r_{13}+r_{23})} \quad (4.5)$$

So that we have two variational parameters in the first trial wave function, namely z and d and the first trial wave function is given by

$$\psi_1 = \psi_0 e^{-d(r_{12}+r_{13}+r_{23})} \quad (4.6)$$

The second correlation function is the Jastrow correlation function which is product of functions of the form [18]

$$f(r_{ij}) = \exp\left[\frac{r_{ij}}{l(1+kr_{ij})}\right], \quad i < j \quad (4.7)$$

In order that the function f satisfies the cusp conditions we must have:

$$l = \begin{cases} 4 & \text{for like spins} \\ 2 & \text{for unlike spins} \end{cases} \quad (4.8)$$

Hence, the second trial wave function is as follows

$$\begin{aligned} \psi_2 = & \frac{2}{\sqrt{3}} \left(\frac{1}{\sqrt{4\pi}}\right)^3 (z)^2 \times \\ & \left\{ \alpha(1)\beta(2)\alpha(3) \left[\left(1 - \frac{r_3 z}{2}\right) e^{-\frac{(2r_1+2r_2+r_3)z}{2}} - \left(1 - \frac{r_1 z}{2}\right) e^{-\frac{(r_1+2r_2+2r_3)z}{2}} \right] \times \right. \\ & \left. \frac{r_{12}}{e^{2(1+kr_{12})}} \times \frac{r_{13}}{e^{4(1+kr_{13})}} \times \frac{r_{23}}{e^{2(1+kr_{23})}} \right. \\ & + \alpha(1)\alpha(2)\beta(3) \left[\left(1 - \frac{r_1 z}{2}\right) e^{-\frac{(r_1+2r_2+2r_3)z}{2}} - \left(1 - \frac{r_2 z}{2}\right) e^{-\frac{(2r_1+r_2+2r_3)z}{2}} \right] \times \\ & \left. \frac{r_{12}}{e^{4(1+kr_{12})}} \times \frac{r_{13}}{e^{2(1+kr_{13})}} \times \frac{r_{23}}{e^{2(1+kr_{23})}} \right. \\ & \left. + \beta(1)\alpha(2)\alpha(3) \left[\left(1 - \frac{r_2 z}{2}\right) e^{-\frac{(2r_1+r_2+2r_3)z}{2a_0}} - \left(1 - \frac{r_3 z}{2}\right) e^{-\frac{(2r_1+2r_2+r_3)z}{2}} \right] \times \right. \\ & \left. \frac{r_{12}}{e^{2(1+kr_{12})}} \times \frac{r_{13}}{e^{2(1+kr_{13})}} \times \frac{r_{23}}{e^{4(1+kr_{23})}} \right\} \quad (4.9) \end{aligned}$$

Accordingly, the function ψ_2 has two variational parameters, namely k and z .

5. Results and Discussions

The VMC method is applied with number of points up to 20×10^6 in order to achieve the best convergence for our results with the corresponding experimental values. In Figure-1 we present the variation of the ground state energy of the Lithium atom with the number of VMC points by using the first trial wave function ψ_1 . Similarly, in Figure-2 we present the variation of the standard deviation associated with the ground state energy of the Lithium atom with the number of VMC points by using the first trial wave function ψ_1 .

The results of varying the binding energy of Lithium with respect to the variational parameter d showed that no minimum points occurred for the first trial wave function ψ_1 except at the value $d = 2$. Accordingly, we present in Figure-3 the variation of the binding energy of Lithium with respect to the parameter z .

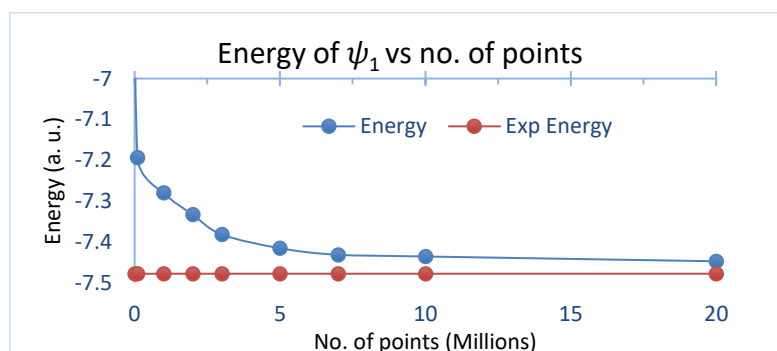


Figure-1 The variation of the ground state energy of Lithium by using the trial wave function ψ_1 with respect to the number of VMC points.

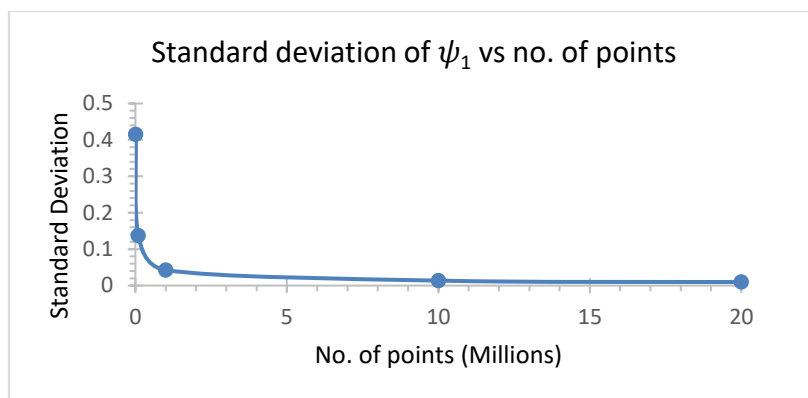


Figure-2 The variation of the standard deviation by using ψ_1 with respect to the number of VMC points.

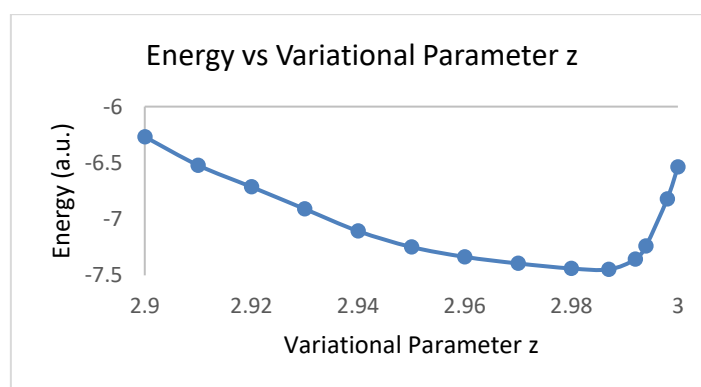


Figure-3 The variation of the ground state energy of Lithium by using the trial wave function ψ_1 with respect to the variational parameter z .

In Figure-4 we present the variation of the ground state energy of Lithium with respect to the number of VMC points by using the second trial wave function ψ_2 . In Figure-5 we present the variation of the standard deviation associated with the ground state energy of Lithium with respect to the number of VMC points by using the second trial wave function ψ_2 . Finally, in Figure-6 we present the variations of the ground state energy of Lithium calculated by using the trial wave function ψ_2 with respect to the parameters z and k .

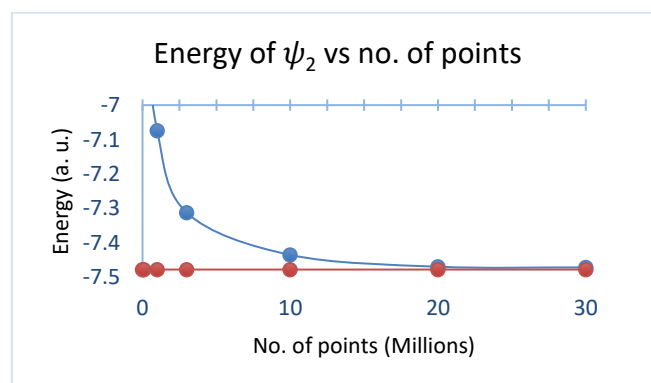


Figure-4 The variation of the ground state energy of Lithium with respect to the number of VMC points by using ψ_2 .

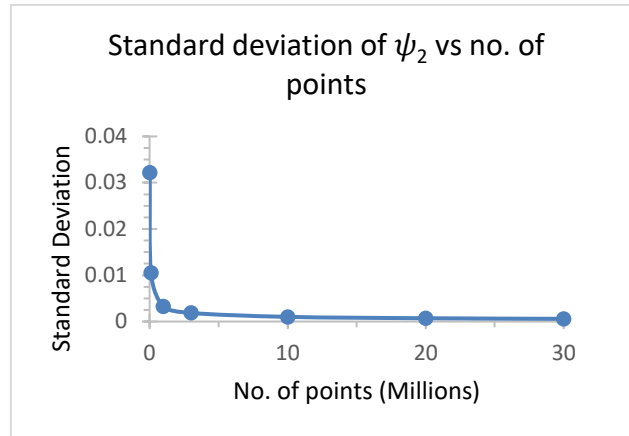


Figure-5 The variation of the standard deviation associated with the ground state energy of Lithium with respect to the number of VMC points by using ψ_2 .

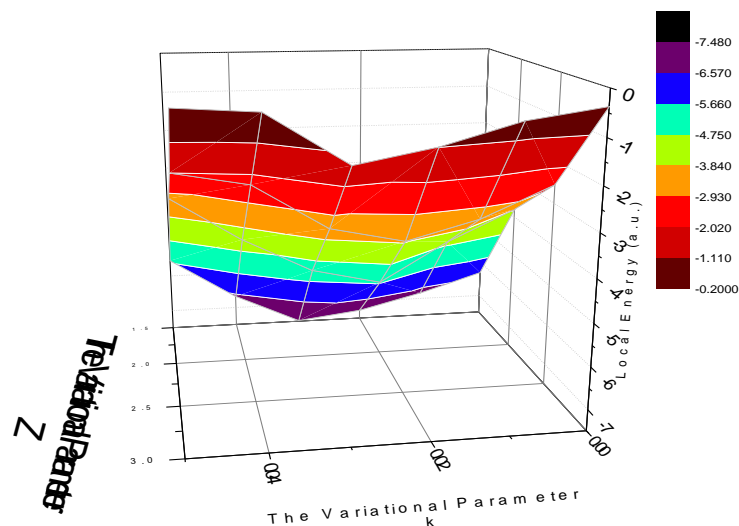


Figure-6 The variations of the ground state energy of Lithium, calculated by using the trial wave function ψ_2 with respect to the parameters z and k .

In Table-1 we present the best values of the calculated ground state energy and standard deviation of the Lithium atom by using the two trial wave functions. The exact value of the binding energy of Li is taken from Ref. [19].

Table-1 Li ground-state energy (E) (in $a. u.$) and Standard Deviation (σ)

| | E | σ |
|----------|---------------|----------|
| ψ_1 | -7.447487 | 0.009679 |
| ψ_2 | -7.478057 | 0.00809 |
| Exact | -7.47806 [19] | --- |

The corresponding values of the variational parameters of the two trial wave functions, for which the best values of the ground state energy of Lithium is obtained, are given in Table-2.

Table-2 Best variational parameters for the two trial wave functions.

| | ψ_1 | ψ_2 |
|-----|----------|----------|
| z | 2.987 | 1.65 |
| d | 2 | - |
| k | - | 0.02371 |

It is of interest to notice that the resulting value of the ground state energy of Lithium by using the trial wave function ψ_2 is in better agreement with the exact value rather than the other case. This is, from our point of view, may be because the trial wave function ψ_2 is the function which takes the cusp conditions into consideration. On the other hand, the standard deviation significantly decreased faster when we used the first trial wave function. Also, from Figures 4, 5 and 6, we notice that when we applied the cusp conditions, the function ψ_2 , the energy converges to the exact value with smoother monotony.

6. Conclusions

In the present paper we applied the VMC method with trial wave functions of the form of the Slater determinant multiplied by two different correlation functions, due to the interaction between the electrons, to calculate the ground state energy of the Lithium atom. The first correlation function contains one variational parameter together with the effective charge z . The resulting wave function by using this correlation function does not provide us with value of the ground state energy of Lithium in good agreement with the exact value. The second correlation function which satisfies the cusp conditions, ψ_2 , provides us with a trial wave function which produce value of the ground state energy of Lithium in excellent agreement with the corresponding experimental value. The obtained result of the ground state energy of Lithium, by using the second trial wave function, is in good agreement with the corresponding experimental and previous results. This result leads us to the conclusion that the VMC method can successfully be applied for the evaluation of the ground state energies of atoms by a suitably chosen trial wave functions.

References

- [1] D. Ceperley, G.V. Chester, and M.H. Kalos, Phys. Rev. B **16**: 3081-3099 (1977).
- [2] W. A. Lester and B. L. Hammond, Ann. Rev. Phys. Chem. **41**: 283-311 (1990).
- [3] N. Metropolis, A.W. Rosenbluth, M.R. Rosenbluth, A.H. Teller, and E. Teller, J. Chem. Phys. **21**, 1087-1092 (1953).
- [4] S. Thanos, A. K. Theophilou, and M. Tassi, Single determinant approximation for ground and excited states with accuracy comparable to that of the configuration interaction, arXiv:1901.07811v1 [quant-ph] 23 Jan 2019.
- [5] T. Koga, S. Watanabe, K. Kanayama, R. Yasuda, and A. J. Thakkar, Journal of Chemical Physics **103**, 3000 (1995).
- [6] S. B. Doma, M. O. Shaker, A. M. Farag, F. N. El-Gammal, Variational Monte Carlo calculations of lithium atom in strong magnetic field, J. Exp. Theor. Phys. **124**: 1., (2017).

- [7] S. B. Doma and F. N. El-Gammal. Application of variational Monte Carlo method to the confined helium atom. *Journal of Theoretical and Applied Physics* **6**: 1 (2012).
- [8] D. Ruenn Su, *Chin. J. Phys.*, **27**: 157 (1989).
- [9] H. Sandsdalen, M. Sc. Thesis, Oslo University, (2010).
- [10] A. Nagy and V. Savona, Variational Quantum Monte Carlo Method with a Neural-Network Ansatz for Open Quantum Systems, *Physical Review Letters* **122**, 250501 (2019).
- [11] N. L. Guevara, F. E. Harris, A. Turbinger, An Accurate Few-Parameter Ground State Wave Function for the Lithium Atom, *Int. J. Quantum Chem.*, **109**: 3036 (2009).
- [12] S. B. Doma, F. N. El-Gammal & A. A. Amer, Ground-state calculations of confined hydrogen molecule H₂ using variational Monte Carlo method, *Molecular Physics*, **116**:14, 1827-1833 (2018).
- [13] S. B. Doma, M.O. Shaker, A. M. Farag, F. N. El-Gammal, Excited states of helium atom in a strong magnetic field using variational Monte Carlo technique. *Indian Journal of Physics*. 92. 10.1007/s12648-017-1105-0, (2017).
- [14] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller. *J. Chem. Phys.* 21: 1087 (1953).
- [15] G. Bhanott, *Rep. Prog. Phys.* 51: 429-457(1988).
- [16] P. Diaconis, J. W. Neuberger, *Experiment. Math.* 13(2): 207-213(2004).
- [17] R. Assaraf, M. Caffarel, *Phys. Rev. Lett.* 83(23): 4682-4685 (1999).
- [18] C. Filippi and C. J. Umrigar, *J. Chem. Phys.* **105**, 213 (1996).
- [19] Puchalski, M.; Pachucki, K. *Phys Rev A* 73: 022503 (2006).