

Variational Monte Carlo Study of the Three-Body Atomic System

F. N. El-Gammal

Mathematics Department, Faculty of Science, Menofia University, Shebin El-Kom, Egypt.

E-mail: fatma_elzahraa4@yahoo.com

Abstract

Using variational Monte Carlo method we have calculated the ground state energies of the lithium atom and its ions up to $Z=10$. Our calculations are based on using a modified three parameters trial wave function which leads to good results comparing with the few parameters trial wave functions presented before. We have applied a new technique to optimize the three variational parameters. This technique depends on using the steepest descent method in order to obtain accurate values of the energies and to get good quality results. This technique was firstly investigated for the helium atom and leads to good results. Our calculations give good estimations for the ground state energy of the lithium atom and its ions comparing with the corresponding exact data.

Key Words: Variation method, Variational Monte Carlo method, Lithium atom.

PACS: 02.70-c, 31.15.-p, 31.15.B

1-Introduction

Variational Monte Carlo (VMC) method has become a powerful tool in Quantum Chemistry calculations [1-4]. In most of its current applications the VMC method has become a valuable method because of a wide variety of wave function forms for which analytical integration would be impossible. The major advantage of this method is the possibility to freely choose the analytical form of the trial wave function which may contain highly sophisticated term in such a way that electron correlation is explicitly taken into account [5,6]. This is an important feature valid for quantum Monte Carlo methods, which are therefore extremely useful to study physical cases where the electron correlation plays a crucial role. For two-electron system, which considered as the simplest few-body systems, VMC method provides accurate estimations of the ground and excited state energies and properties of atomic and molecular systems [7-10].

In recent years efforts have been done to develop an approach for constructing trial wave functions in order to calculate the ground state energy of the lithium atom and achieve high level of accuracy. In 2006, the VM Carlo method has been used to study the ground state energy of the atoms Li through Kr using explicitly correlated wave functions which consist of product of a Jastrow correlation factor times a model function with 17 variational parameters [11]. The obtained results were an improvement over all the previous results. In Ref [12], the ground state energies of Li and Be^+ are calculated using two types of wave functions, the first one is explicitly correlated Hylleraas type with very large number of terms (about 13944). The other type is the exponential-basis sets trial wave functions. In both cases, the obtained results were of good accurate values. Recently, A. M. Frolov [13] introduced a semi-exponential basis set of radial functions for variational computations of the ground-state of the lithium atom. The obtained variational energy was very close to the exact ground state energy.

Despite the fact that there is no shortage of extremely accurate wave functions for the Lithium atom and some three-electron atomic ions, most of these studies search for accurate results but nevertheless compact wave functions. From this point, Nicolais et. al. [14] proposed a simple compact seven-parameter trial function for the ground state of the lithium atom which provided a

very accurate energy in such a way that it could be considered as the most accurate among existing few-parameter trial functions.

In the present paper we shall use VMC method to study three-electron system (or lithium atom), which may be studied by using different methods and different forms of trial wave functions. Accordingly, we shall use a compact three-parameter wave function to obtain the ground state energies for lithium and its isoelectronic ions up to $Z = 10$. The calculations will be done in the frame of VMC method.

2- The Trial Wave Function

The calculations for the lithium atom in the $1s^2nl$ were obtained previously using trial wave functions which take the form [15]:

$$\Psi_1(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \exp(-\alpha_i(r_1 + r_2))R_{nl}(\alpha_0, r_3)Y_{1,m}(\hat{\mathbf{r}}_3), \quad (2.1)$$

where, the symbol $\hat{\mathbf{r}}_3$ denotes the angular variables of \mathbf{r}_3 and the function $R_{nl}(\alpha_0, r_3)Y_{1,m}(\hat{\mathbf{r}}_3)$ is the hydrogen-like wave function in the nl -state with effective charge α_0 .

This wave function was used to calculate the energy of lithium in the states $1s^2nl$ with quite accurate results. In the present paper we introduce some modifications to this trial wave function in order to get more accurate results and extend the calculations to include lithium ions up to $Z=10$. Firstly, we will consider the correlation between each two electrons. In order to include the electron-electron correlation we have to modify the form of this trial wave function by multiplying by the following factor:

$$f(r_{ij}) = \exp\left[\frac{r_{ij}}{\alpha(1+\beta r_{ij})}\right], \quad (2.2)$$

which expresses the correlation between the two electrons i and j due to their Coulomb repulsion. That is, we expect f to be small when r_{ij} is small and to approach a large constant value as the electrons become well separated. The second goal is to use this trial wave function to calculate the energies of lithium isoelectronic ions up to $Z = 10$, then we set the variational parameter α_i in Eq. (2.1) to be the nucleus charge Z .

Then, for the ground-state of the lithium ($1s^22s$) and its isoelectronic series $Z = 3, \dots, 10$ Eq. (2.1) reduces to the following form:

$$\Psi_1(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \exp(-Z(r_1 + r_2))R_{nl}(\alpha_0, r_3) \prod_{i<j} f(r_{ij}), \quad (2.3)$$

where the indices i, j run over the number of the electrons. The variational parameters α_0 and β will be determined for each value of Z by minimizing the energy. The function $Y_{1,m}(\hat{\mathbf{r}})$ of Eq. (2.1) is constant for the ground-state of lithium.

3. Method of Calculations

In this paper we shall use the well known VMC method which 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 [16]. It is used to compute quantum expectation values of an operator,

$$\langle A \rangle = \frac{\sum_i [\Psi(\mathbf{x}_i) A \Psi(\mathbf{x}_i) / w(\mathbf{x}_i)]}{\sum_i [\Psi(\mathbf{x}_i)^2 / w(\mathbf{x}_i)]}, \quad (3.1)$$

and its standard deviation (i.e., statistical error)

$$\sigma^2 = \sum_i \left\{ \frac{[A\Psi(x_i) - \langle A \rangle \Psi(x_i)]^2 \Psi(x_i)^2}{w(x_i)^2} \right\} / \left\{ \sum_i \left[\frac{\Psi(x_i)^2}{w(x_i)} \right] \right\}^2, \quad (3.2)$$

where $\Psi(x_i)$, is the value of the trial wave function at the Monte Carlo integration point x_i and the weight function $w(x_i)$ is the relative probability of choosing this point.

In particular, if the operator is the Hamiltonian, its expectation value will be the variational energy E_{VMC} . According to the Variational principal, a trial wave function for a given state must produce an energy which is above the exact value of that state, that is $E_{VMC} \geq E_{exact}$.

The non-relativistic Hamiltonian for three-electron atom (in atomic units (a. u)) takes the form [17]

$$H = -\frac{1}{2} \sum_{l=1}^3 \nabla_l^2 + \sum_{i=1}^3 \frac{-Z}{r_i} + \sum_{i<j} \frac{1}{r_{ij}}. \quad (3.3)$$

In our calculations we use the form of H in Hylleraas Coordinates [18]

$$H = -\frac{1}{2} \left(\sum_{i=1}^3 \frac{\partial^2}{\partial r_i^2} + \sum_{i=1}^3 \frac{2}{r_i} \frac{\partial}{\partial r_i} + \sum_{i<j}^3 2 \frac{\partial^2}{\partial r_{ij}^2} + \sum_{i<j}^3 \frac{4}{r_{ij}} \frac{\partial}{\partial r_{ij}} + \sum_{i \neq j}^3 \frac{r_i + r_{ij} - r_j}{r_i r_{ij}} \frac{\partial^2}{\partial r_i \partial r_{ij}} + \sum_{i \neq j}^3 \sum_{k>j}^3 \frac{r_{ij} + r_{ik} + r_{jk}}{r_{ij} r_{ik}} \frac{\partial^2}{\partial r_{ij} \partial r_{ik}} \right) + \sum_{i=1}^3 \frac{-Z}{r_i} + \sum_{i<j}^3 \frac{1}{r_{ij}}, \quad (3.4)$$

where, $r_i = |\mathbf{r}_i|$ and \mathbf{r}_i denotes the relative radius vector of the three electrons with respect to the nucleus and r_{ij} is the distance between each two electrons, i.e. $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$.

Now, we will explain the method of calculations, which we have used to calculate the ground-state of the lithium atom and its ions.

1- Firstly, we shall use the cusp conditions [19] which leads easily to the precise value of the variational parameter α as $\alpha = 2$.

2- The variational parameter α_i in Eq. (2.3) will be fixed to be $\alpha_i = Z$ in order to calculate the lithium ions up to $Z = 10$. In this case, we will have two variational parameters α_0 and β .

3-To obtain a preliminary appropriate values for the remaining two parameters α_0 and β , we plot the ground state energy as a function of the two variational parameters α_0 and β . In fact, The plots does not give precise optimal parameters, but by merely looking at them, and where the energy has its minimum, we should be able to find very good initial values for the Steepest Descent (SD) method. Now, we have adequate values for the three parameters α_i , α_0 and β , which will considered as initial values for the next step.

4-In order to get accurate values for the three variational parameters we will use the SD method [20], which is considered as one of the most popular methods to optimize the wave function for Monte Carlo methods. The main merit of this method is the simplicity which can turn it into an efficient method at least for simple atoms. Using the initial values for α_i , α_0 and β , obtained in step one, and then iteratively update the values of the parameters according to the following relation:

$$\mathbf{c}^{k+1} = \mathbf{c}^k - a \mathbf{g}^k, \quad (3.5)$$

where the vector $\mathbf{c} = (c_1, c_1, \dots \dots \dots c_m)$ denotes the parameters in the wave function, k is the iteration step and a denotes the constant of the SD method.

In Eq. (3.5) \mathbf{g}^k is defined as the gradient vector of energy respect to the parameters and it is given by:

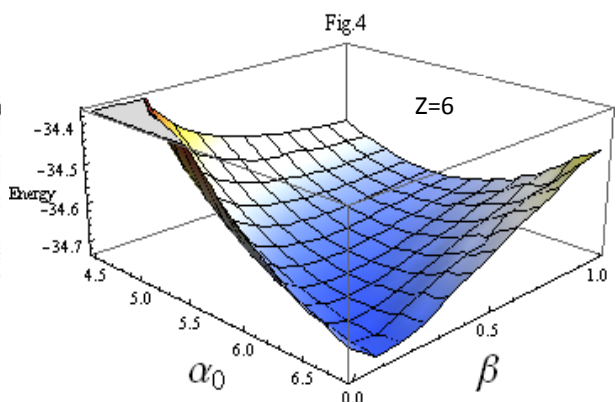
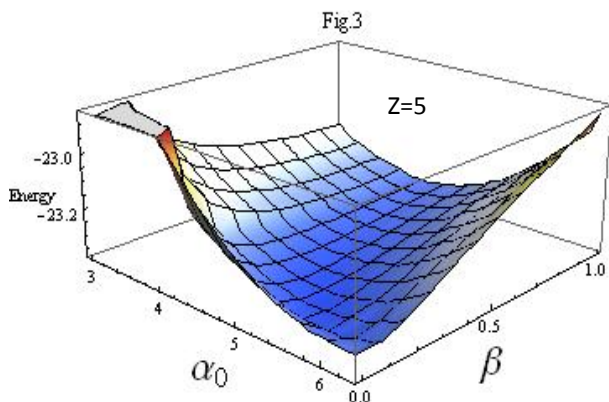
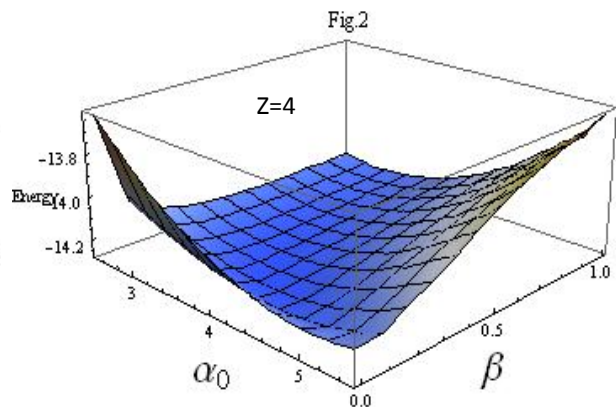
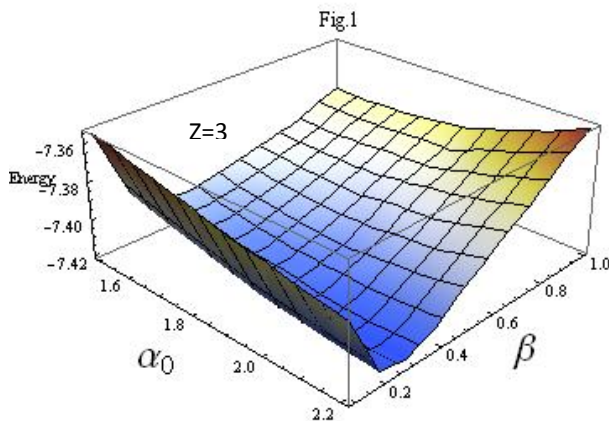
$$\mathbf{g} = \left(\frac{\partial E}{\partial c_1}, \frac{\partial E}{\partial c_1}, \dots \dots \dots, \frac{\partial E}{\partial c_m} \right). \tag{3.6}$$

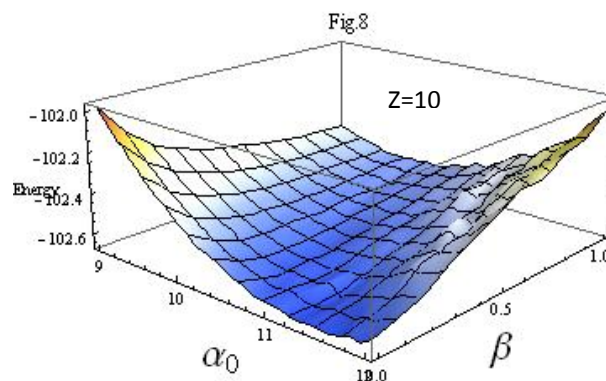
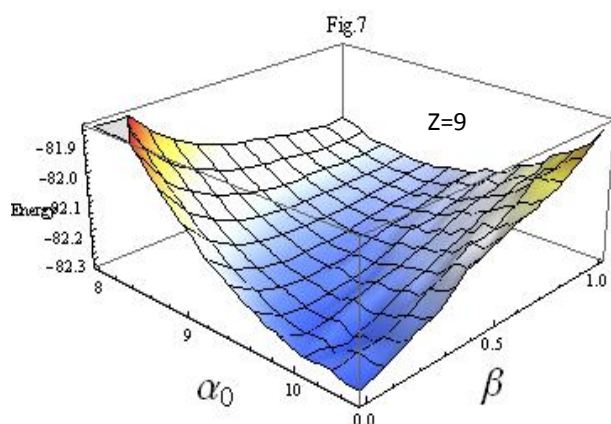
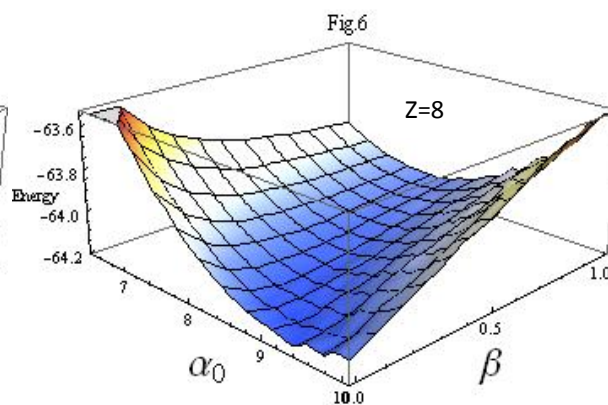
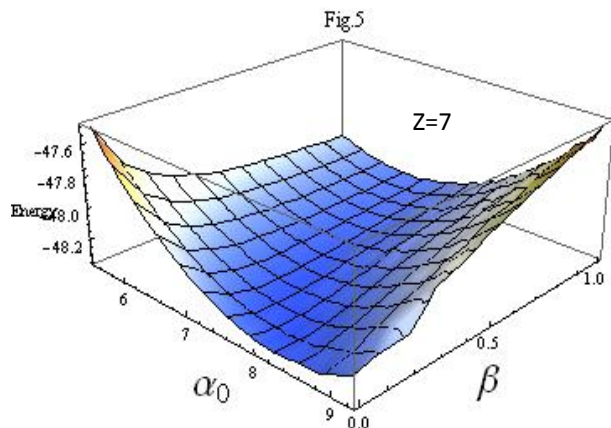
The energy gradient vector is computed according to the following relation [21]

$$\frac{\partial E}{\partial c_m} = \lim_{N \rightarrow \infty} \frac{2}{N} \sum_{s=1}^N \left\{ \left(E_L \times \frac{\partial \Psi}{\partial c_m} \right)_s - E \times \left(\frac{\partial \Psi}{\partial c_m} \right)_s \right\}. \tag{3.7}$$

Then, we proceed with some iterations of Eq. (3.5) until we obtain the optimum values of the parameters.

5- The values of the variational parameters which obtained in step 4 will be now used again with a very large number of Monte Carlo points = 2×10^8 to find the energy in a fine tune and make the statistical error as low as possible.





Figs. (1-8) The energy as a function of α_0 and β where α_i is fixed to be $\alpha_i = Z$ for $Z = 3, \dots, 10$ respectively.

Results

In this paper we have calculated the ground state energies of the lithium atom and its ions using a modified wave function which was introduced previously to calculate the ground state energy of the lithium atom, but without taking into account the electron-electron correlation which plays a critical role in improving the accuracy of the results. Moreover, we have succeeded to use this trial wave function to obtain the energies of the lithium ions up to $Z = 10$. All energies are obtained in atomic units i.e. ($\hbar = e = m_e = 1$).

Figures (1-8) present the energy as a function of α_0 and β using a set of 10^7 Monte Carlo points. From these figures we could obtain the values of α_0 and β at which the energy takes its

minimum. It is clear from the figures that the values of the energies approached to the corresponding exact values but it is not accurate enough to be considered as the final results. To this reason, we used the obtained values of the parameters as initial values for using in SD method. The values of the parameters will be updated according to the relation given by Eq. (3.5) until the energy approximately approaches the exact ground state energy. After about 5 – 6 iterations, variational parameters should have reached to the vicinity of their ultimate values. We put their latest values in the code and re run it. The process of updating the values of the variational parameters α_i , α_0 and β was done using 3×10^5 Monte Carlo points. In our calculations, the SD constant a was taken to be 0.0001.

Table-1 shows the optimum values of α_i , α_0 and β and the corresponding final results of the energies using a very large of MC points together with the standard deviation given by Eq. (3.2). The exact values are also introduced for comparison [22]. It is clear from Table-1 that, in most cases, the obtained results are of good agreement with the exact values. Also, the associated standard deviations have very small values, which vary between 10^{-5} and 10^{-4} , this is due to the large number of MC points. The electron-electron correlation factor $f(r_{ij})$, which has been included in the trial wave function, played a crucial role in improving the results. In fact, the ground state energy of the lithium atom which was obtained previously [15] using the same trial wave function, but without introducing the factor $f(r_{ij})$, was -7.48049. It is clear from Table-1 that our result for the lithium atom ($Z=3$) is -7.479342, which is more accurate. This means that VMC method introduced a very well description for the lithium ions using a trial wave function expressed in hydrogen-like orbitals with a rather simple factor, describing the correlations between the electrons.

Table-1 the variational parameters α_i , α_0 and β , the energies for lithium isoelectronic sequence up to $Z=10$ together with the standard deviation σ .

| Z | α_i | α_0 | β | Energy | Standard deviation σ |
|----|------------|------------|------------|---|-----------------------------|
| 3 | 2.997463 | 2.296722 | 0.3029 | -7.479342 ^a -7.47810 ^b | 7×10^{-5} |
| 4 | 3.993215 | 3.992936 | 0.206942 | -14.26267 ^a -14.3248 ^b | 8×10^{-5} |
| 5 | 4.993554 | 5.293983 | 0.2028472 | -23.36611 -23.4246 ^b | 1×10^{-4} |
| 6 | 5.997396 | 6.397672 | 0.2003033 | -34.72284 ^a -34.7755 ^b | 2×10^{-4} |
| 7 | 6.990715 | 7.79241 | 0.1988 | -48.34916 ^a -48.3769 ^b | 3×10^{-4} |
| 8 | 7.996480 | 8.897046 | 0.09949416 | -64.22855 ^a -64.2285 ^b | 3×10^{-4} |
| 9 | 8.991982 | 9.6934750 | 0.1972059 | -82.30032 ^a -82.3303 ^b | 2×10^{-4} |
| 10 | 9.998321 | 11.19313 | 0.1963 | -102.62150 ^a -102.6822 ^b | 5×10^{-4} |

a Our results

b Exact values [22]

Conclusion

In frame of the variational Monte Carlo method we calculated the ground state of the lithium atom and its ions up to $Z=10$. The trial wave function we used was presented previously to calculate the ground state energy for lithium atom only and without taking the electron-electron correlation into consideration. We firstly, generalized it to calculate the lithium isoelectronic series up to $Z=10$. Then, we have modified the form of the wave function by multiplying by the factor $f(r_{ij})$. This factor, improved the results and lead to more accurate results. Also, we have outlined the steps of optimizing the trial wave function using a new technique which introduced firstly and applied to calculate the ground state energy of the helium atom [4]. This technique is based on plotting the energy as function of two variational parameters while the third parameter was fixed. The values of the two parameters at which the energy takes its minimum value will be considered as initial values for using in the Steepest Descent method. The SD method will provide accurate values for the variational parameters. The final values of the three variational parameters are used again to calculate the energy using a very large number of Monte Carlo points to make the standard deviation as small as possible. The obtained results are of good accuracy comparing with the exact values.

Reference

- [1] B. L. Hammond, W. A. Lester Jr., P. J. Reynolds, **Monte Carlo Methods in ab-Initio Quantum Chemistry**, World Scientific, Singapore (1994).
- [2] S. Pottorf, A. Puzer, M. Y. Chou, *Eur. J. Phys.* **20**: 205 (1999).
- [3] E. Buendía, F. J. Gálvez, A. Sarsa, *Chem. Phys. Lett.* **465**: 190 (2008).
- [4] H. Sandsdalen, M. Sc. Thesis, Oslo University, (2010).
- [5] S. A. Alexander, R. L. Coldwell, *Int. J. Quantum Chem.* **63**: 1001 (1997).
- [6] K. E. Riley, J. B. Anderson, *Chem. Phys. Lett.*, **366**: 153 (2002).
- [7] K. Kobayashi, H. Yokoyama, *J. Phys. Chem. Sol.* **66**: 1384 (2005).
- [8] S. A. Alexander, R. L. Coldwell, *Int. J. Quantum Chem.* **107**: 345 (2007).
- [9] S. Datta, S. A. Alexander, R. L. Coldwell, *Int. J. Quantum Chem.* **8** (2011).
- [10] S. B. Doma, F. N. El-Gammal, *Appl. Math. Inf. Sci.* **5**: 315S (2011).
- [11] E. Buendía, F. J. Gálvez, A. Sarsa, *Chem. Phys. Lett.*, **428**: 241 (2006).
- [12] M. Puchalski, D. Kędziera, K. Pachucki, *Phys. Rev. A* **80**: 032521 (2009).
- [13] A. M. Frolov, *Eur. Phys. J. D*, **61**: 571 (2011).
- [14] N. L. Guevara, F. E. Harris, A. Turbiner, *Int. J. Quantum Chem.*, **109**: 3036 (2009).
- [15] D. Ruenn Su, *Chin. J. Phys.*, **27**: 157 (1989).
- [16] N. Metropolis, A. W. Rosenbluth, N. M. Rosenbluth, A. M. Teller, E. Teller, *J. Chem. Phys.* **21**: 1087 (1953).
- [17] B. H. Bransden, C. J. Joachain, **Physics of Atoms and Molecules**, Longman Scientific and Technical, London (2003).
- [18] M. B. Ruiz, *Int. J. Quantum Chem.* **101**: 246 (2005).
- [19] T. A. Galek, N. C. Handy, A. J. Cohen and G. K. Chan, *Chem. Phys. Lett.* **404**: 156 (2005).
- [20] M. E. Foulaadvand, M. Zarenia, *Int. J. Mod. Phys. C*, **21**: 523 (2010).
- [21] X. Lin, H. Zhang, A. M. Rappe, *J. Chem. Phys.*, **112**: 2650 (2000).
- [22] <http://php.indiana.edu/~davidson/atom/tub.4>.

