Abstract: In this paper, we have applied the complex rotation method to the calculations energies of the ground state \((1s^22s)^2S\) and the low-lying excited \((1s^2ns)^2S\) states with \(n = 3, 4\) and \(5\); of lithium and its isoelectronic series. For the ground state, the calculations were made up to \(Z = 20\) and for the low-lying excited states up to \(Z = 10\). These energies calculations were made using new special forms of Hylleraas-type wave functions designed by combining incomplete radial hydrogenic wave functions and Hylleraas-type wave functions. Using a numerical calculation program, the values of the resonance energies are calculated. Our results are compared with the results of ab-initio calculations using Hylleraas type wave functions and with semi-empirical results by Screening Constant by Unit Nuclear Charge (SCUNC) formalism. Analysis of the present results is achieved by calculating the ratio and the difference between our values and those of other authors. The results obtained are in good agreement with those of the theoretical methods available in the literature. This agreement shows the adequacy of our wave function with small bases to satisfactorily describe the ground state and the low-lying excited states of the three-electron atomic systems.

Keywords: Wave Function, Resonance Parameters, Correlation Factors, Resonant Width, Ground State, Low-lying Excited States, Li-like Ions

1. Introduction

Experimental and theoretical studies of the photoionization process are of fundamental importance as they have greatly increased understanding of the reactions of atoms or ions to electromagnetic radiation. Theoretical investigations on the autoionizing states of atoms and ions have developed thanks to the use of synchrotron radiation and lasers in experiments on photoabsorption and photoionization [1 - 4]. In addition, this development is also possible thanks to advanced techniques in the measurement of photoelectron spectroscopy [5].

These autoionizing states show the importance of the electron-electron correlation, which is necessary to understand the autoionization process. In recent years, experimental and theoretical studies of the properties of multi-electron systems have been of great interest in understanding electron-electron correlation effects.

On the experimental level, transitions between the doubly excited states, which have been observed in the Li atom [6]. Beam-foil spectroscopy [7] showed a strong excitation of...
these transitions. Based on these experimental observations since 1959, extensive theoretical researches on lithium isoelectronic series have been the objective of physicists. Among the calculations on the ground state of lithium and its isoelectronic series, we can cite the works of Eckart [8], Guillemin and Zener [9], Wilson [10], and James and Coolidge [11, 12]. Since then, the ground state energy of Li has been refined by Weiss [13], Larsson [14], Muszynska et al. [15], King et al. [16 - 18], McKenzie and Drake [19], Luchow and Kleindienst [20], and Yan et al. [21, 22]. All these studies, except that of Weiss [13], use Hylleraas-type wave functions, with several terms ranging in length from 100 terms [14] to 3502 terms [22].

In addition, one of the main problems faced by physicists in studying the properties of multiple electron systems via ab-initio techniques is related to the complexity of the calculations, which usually require a large base set. For the \((1s^2 \, ns) \, ^2S\) (with \(n = 3, 4 \) and 5) levels of the lithium isoelectronic sequence, Wang et al [23] applied the full-core-plus correlation with multiconfiguration-interaction wave functions to compute the total energies and the first ionization potential up to \(Z = 10\). These authors have also calculated, via the full-core-plus-correlation method, the energies and fine structure splitting of the \((1s^2 \, np) \, ^3P\) levels (with \(n = 3, 4 \) and 5) of \(Z = 3 – 10\) [24]. For both the \((1s^2 \, ns) \, ^2S\) and \((1s^2 \, ns) \, ^3P\) levels, Wang et al [23, 24] included all the corrections mentioned above. Hylleraas-type (HT), wave functions containing \(r_{ij}\) factors being widely used in atomic physics to study the correlation effects between electrons and/or between electrons and the nucleus for bound and scattering states [25]. It should be noted, however, that the problems faced by physicists were the construction of an adequate wave function and the stability of a correlation factor. Those, who pushed them to make approximations to study complex atomic systems.

Thus, we are interested in this work to design new Hylleraas-type wave functions containing fewer terms named special forms of Hylleraas-type wave functions, but which provide energies with good accuracy for both ground state \((1s^2 \, 2s) \, ^3S\) and the low-lying excited states \((1s^2 \, ns) \, ^3S\) \((n = 3, 4 \) and 5) of the lithium atom and its isoelectronic series. The method of the complex rotation which is particularized from the other methods because it makes it possible to obtain at the same time the energy and width resonance will be used in this work.

In Section II, we will describe the complex Hamiltonian and the matrix elements used by the complex rotation method, then present the special forms of Hylleraas-type wave functions that was used for calculating energies of the ground state \((1s^2 \, 2s) \, ^3S\) and the low-lying excited \((1s^2 \, ns) \, ^3S\) states (where \(n = 3, 4 \) and 5) of the lithium atom and its isoelectronic sequence. And finally, section III is devoted to the presentation of our results followed by a discussion. A comparison of our results with the available theoretical values is also made in this section.

2. Theory

2.1. Hamiltonian and Wave Function

The complex rotation method (CRM) or dilation method is widely used in atomic physics to determine the parameters of the autoionizing resonances of many electrons atomic systems governed by Coulomb interactions. It is based on the theorem of Balslev et al. [26]. The application of this theorem in the study of atomic resonances consists in the transformation of real Hamiltonian system \(\mathcal{H}(r)\) to a complex Hamiltonian \(\hat{\mathcal{H}}(r, \theta)\).

The non-relativistic Hamiltonian operator for three-electron systems is given by (in a.u.):

\[
\hat{H}(r) = \sum_{r_i} \left( -\frac{1}{2} \Delta_i - \frac{Z}{r_i} \right) + \sum_{i, j \neq i} \left( \frac{1}{r_{ij}} \right) = \hat{T} + \hat{V}
\]

The Hamiltonian complex \(\hat{H}(r, \theta)\) obtained after changing the radial variable \(r\) into a complex variable (with \(\theta\) a positive real designating the angle of rotation), comprises in addition to resonant states, a continuous spectrum formed of a series of lines in the complex plane beginning at the threshold of ionization of the residual ion of the studied atomic system, also bound discrete states which remain invariant in the rotation [27].

By this transformation, the complex Hamiltonian \(\hat{H}(r, \theta)\) is written in the case of the Coulomb interaction system in the form:

\[
\hat{H}(r, \theta) = \hat{T} e^{-2i\theta} + \hat{V} e^{-i\theta}
\]

In this relation (2), \(\hat{T} \) et \(\hat{V}\) respectively denote the operators of kinetic energy and Coulomb interaction energy.

In the case of atomic systems with three electrons, the relation (2) is written in the form (in atomic unit):

\[
\hat{H} (r, \theta) = -\frac{1}{2} \sum_{i=1}^{3} \Delta_i e^{-2i\theta} - Ze^{-i\theta} \sum_{i=1}^{3} \left( \frac{1}{r_i} \right) + \sum_{i, j \neq i} \left( \frac{1}{r_{ij}} \right) e^{-i\theta}
\]

(3)

Where:

\[
\hat{T} = -\frac{1}{2} (\Delta_1 + \Delta_2 + \Delta_3) e^{-2i\theta}
\]

(4)
is the kinetic energy operator of electrons;

\[ \Delta_i = \frac{1}{r_i^2} \frac{\partial}{\partial r_i} \left( r_i^2 \frac{\partial}{\partial r_i} \right) + \frac{1}{r_i \sin \theta_i} \frac{\partial}{\partial \theta_i} \left( \sin \theta_i \frac{\partial}{\partial \theta_i} \right) + \frac{1}{r_i^2 \sin^2 \theta_i} \frac{\partial^2}{\partial \phi_i^2} \]  

(5)

With \( i = 1, 2, 3 \).

The Laplacian is written as:

\[ \hat{\Delta} = -Z e^{-\theta} \left( \frac{1}{r_1} + \frac{1}{r_2} + \frac{1}{r_3} \right) \]

is the operator of the electron-nucleus interaction energy;

\[ \hat{W} = \left( \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}} \right) e^{-\theta} \]

is the operator of the interaction energy between electrons.

The resonance parameters are obtained by solving the complex eigenvalue equation below:

\[ \left[ \psi(r_1, r_2, r_3) | H_{\text{res}} | \psi(r_1, r_2, r_3) \right] = 0 \]  

(6)

The complex eigenvalue \( E_{\text{res}} \) is in the form:

\[ E_{\text{res}} = \frac{1}{2} \left( E_r - i \Gamma_r \right) \]  

(7)

Relation where, the real part \( E_r \) gives the resonance energy and the imaginary part \( \Gamma_r \) gives the resonance width.

The test wave function is of the Hylleraas type. This type of wave function called the Hylleraas type special wave function has been successfully applied by Biaye et al. [28-32], Dieng et al. [33, 34], Gning et al. [35, 36] for the calculation of the excited state resonance parameters of helium and its isoelectronic series. To broaden the field of research, we have made modifications to these wave functions originally designed for two-electron atomic systems in order to adapt them to the study of three-electron atomic systems.

Thus, the Hylleraas-type special wave function that we used to calculate the ground state energy (1s\(^2\) 2s)\(^2\)S and the excited states (1s\(^2\) ns)\(^2\)S with \( n = 3, 4 \) and 5 of lithium and Li-like ions of nuclear charge \( Z = 3 – 10 \) is defined as follows:

\[ \psi_{ijknpq} (r_1, r_2, r_3) \]  

(8)

Where \( \phi_{npq} (r_1, r_2, r_3) \) are basic spatial functions and \( \chi_{ijk} (r_1, r_2, r_3) \) are functions involving the spherical harmonics of the three electrons.

The basic spatial functions are conventionally of the form Hylleraas:

\[ \phi_{npq} (r_1, r_2, r_3) = \sum_{l=0}^{n} \left( \frac{2}{\pi r_0} \right)^{1/2} \frac{n!}{l!(n-l)!} \rho^{l} \exp \left( -\frac{r_1}{r_0} \right) \rho^{l} \exp \left( -\frac{r_2}{r_0} \right) \rho^{l} \exp \left( -\frac{r_3}{r_0} \right) \]  

(9)

The functions involving the spherical harmonics of the three electrons are of the form:

\[ \chi_{ijk} (r_1, r_2, r_3) = \sum_{l_1=0}^{n_1} \sum_{l_2=0}^{n_2} \sum_{l_3=0}^{n_3} \left( \frac{2}{\pi r_0^2} \right)^{3/2} \frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi^3} \rho^{l_1} \exp \left( -\frac{r_1}{r_0} \right) \rho^{l_2} \exp \left( -\frac{r_2}{r_0} \right) \rho^{l_3} \exp \left( -\frac{r_3}{r_0} \right) \]  

(10)

In relations (9) and (10), \( r_1, r_2, r_3 \) are the electron-nucleus distances; \( r_{12}, r_{13}, r_{23} \) are the inter-electronic distances and \( r_0 \) the Bohr radius.

The parameters \( \{i, j, k, n, p, q\} \) are non-zero positive integers. The set consisting of the six parameters \( \{i, j, n, p, q\} \) represents a state base (i.e. configuration) of the three-electron system and obeys the condition: \( i + j + k + n + p + q \leq \Omega \), where \( \Omega \) is a positive integer.

The exponents \( \alpha, \beta \) and \( \gamma \) are the nonlinear variational parameters, \( n_1, n_2 \) and \( n_3 \) are respectively the main quantum numbers of electrons 1, 2 and 3; \( l_1, l_2 \) and \( l_3 \) are respectively the orbital angular moments of the three electrons; \( L_{12} = l_1 + l_2 \) is the angular momentum coupling the electrons 1 and 2; \( S_{12} \) being total spin of electrons 1 and 2;
\[ Y_{00}^{(1)}, Y_{12,0}^{(2)}, \text{ and } Y_{00}^{(3)} \] are respectively the spherical harmonics of electron 1, 2 and 3. The correlation factor \( r_{ij}^{\text{ex}} \) (where \( i, j = 1, 2, 3 \) with \( i < j \)) model considers spherical harmonics and hypergeometrical functions. It is defined as follows [35, 36, 37]:

\[
r_{ij}^{\text{ex}} = 4\pi \sum_{l=0}^{\infty} \frac{1}{2l+1} \left( \frac{n}{2} \right) \left( \frac{1}{2} \right) \left( r_{ij}^{l} \right)^{2l+1} \left( \frac{(2l-n)(1+n)}{2(2l+3)} r_{ij}^{l} \right)
\]

where \( l \) is the angular momentum quantum number. 

\[ r_{ij}^{l} \]

The correlation factor \( r_{ij}^{\text{ex}} \) is calculated by optimizing the energy for the small-base \( \alpha \) adopted and the parameters \( \{ \alpha = \beta, \gamma \} \) for each state are determined by minimizing the energy relative to the rotation angle \( \theta = 0.30 \) and the exponential parameters \( p, q \) satisfying the conditions \( i, j, k, n, p, q > 0 \) and \( i + j + k + n + p + q = \Omega \) and then we vary the positive exponential parameters.

Thus, we first fixed the base \( \Omega \) to 9, the rotation angle at \( \theta = 0.30 \) and we minimize the energy with respect to the exponential parameters. A second test is done keeping the same exponential parameters but this time increasing the base \( \Omega \) to 12 and minimizing the energy relative to the rotation angle \( \theta \). The ground state \((1s^2 2s)\) \( ^2S \) energy of lithium \( E(\Omega) \) obtained in the two tests are listed in the following Table 1:

| \( \Omega \) | \( E(\Omega) \) | \( \theta \) | \( \alpha = \beta \) | \( \gamma \) |
|----------|---------------|---------|-----------------|-------|
| 9        | 7.478037459100333 | 0.300  | 6.850          | 0.282 |
| 12       | 7.47769660665282   | 0.683  |                 |       |

The energy obtained with the base \( \Omega = 9 \) is \( 6.5 \times 10^{-6} \) greater than \( -7.478031 \) a.u. from the 92-term Hylleraas-type wave function of Ho [25] and lower by \( 3.55 \times 10^{-5} \) than \( -7.4780730 \) a.u. from Bunge [38], whereas that obtained with the base \( \Omega = 12 \) is lower by \( 3.34 \times 10^{-4} \) than the 92-term Hylleraas-type wave function of Ho [25] and lower by \( 3.76 \times 10^{-4} \) than the value from Bunge [38]. Consequently, in our calculations of energies for the ground state and low-lying excited states \((1s^2 2n)\) \(^2S\) with \( n = 3, 4 \) and 5 of lithium and its isoelectronic series, we set the size of the wave functions \( \Omega \) to 9.

The rotation angle \( \theta \) is changed according to \( Z \) by increments of \(+0.1 \) up to \( Z = 15 \), then by increments of \(+0.05 \) from \( Z = 16 \) to 20 for the ground state \((1s^2 2s)\) \( ^2S \) and by increments of \(+0.05 \) for the low-lying excited states \((1s^2 2n)\) \( ^2S \) states for all \( Z \). The final set of the positive exponential parameters \( \alpha, \beta, \gamma \) used for all the series studied is collected in Table 2.

| \( Z \) | \( \alpha = \beta \) | \( \gamma \) | \( \alpha = \beta \) | \( \gamma \) | \( \alpha = \beta \) | \( \gamma \) | \( \alpha = \beta \) | \( \gamma \) |
|------|-----------------|-----|-----------------|-----|-----------------|-----|-----------------|-----|
| 3    | 6.850           | 0.282 | 10.475         | 0.145 | 11.938         | 0.197 | 11.150         | 0.263 |
| 4    | 8.558           | 0.266 | 12.491         | 0.157 | 15.020         | 0.208 | 14.868         | 0.266 |
| 5    | 9.981           | 0.307 | 14.430         | 0.169 | 17.983         | 0.210 | 18.055         | 0.270 |
| 6    | 11.125          | 0.300 | 16.240         | 0.179 | 19.495         | 0.226 | 20.973         | 0.280 |
| 7    | 12.380          | 0.329 | 17.983         | 0.190 | 22.250         | 0.241 | 23.765         | 0.302 |
| 8    | 13.633          | 0.350 | 19.800         | 0.211 | 24.516         | 0.250 | 26.467         | 0.312 |
| 10   | 14.930          | 0.365 | 21.395         | 0.217 | 26.790         | 0.265 | 28.526         | 0.320 |

Table 1. Convergence of non-relativistic energies for the ground state \((1s^2 2s)\) \( ^2S \) of lithium, in atomic units.

Table 2. Exponents parameters employed for the ground state \((1s^2 2s)\) \( ^2S \) and excited states \((1s^2 2n)\) \( ^2S \) (with \( n = 3, 4 \) and 5) wave functions for members of the Lithium and its isoelectronic series.
In Table 5, we compared our present results (\(-E^p\)) of the low-lying excited states (1s^2ns) ^2S with the theoretical results of Sakho [44] who applied the Screening Constant by Unit Nuclear Charge method (SCUNC-method), King [45] who applied the variational method on Hylleraas-type wave functions and Wang and al. [23, 24] who applied the Full-Core-Plus-Correlation (FCPC) with multiconfiguration-interaction wave functions. Here again, the agreement between the calculations is very good because the maximum energy differences in the (1s^2ns) ^2S and (1s^2ns) ^2S states are less than 0.0095 a.u, nevertheless, for Z ≥ 10 the energy differences never exceeded 0.0400 a.u. because the maximum energy differences with the values of Yan and al. [22], and Sakho and al. [40] are respectively 0.0228 and 0.0395. It should be mentioned that our data correspond more to ab-initio calculations using for the most part Hylleraas-type wave functions [22, 25, 39] than semi-empirical results of Sakho [40].
We have planned to do other works on Lithium energy with improved wave functions.

**References**

[1] R. P. Madden and K. Codling, Astrophys. J. 141, 364, (1965).

[2] P. Dhez and D. L. Ederer, J. Phys. B 6, L59 (1973).

[3] P. K. Carroll and E. T. Kennedy, Phys. Rev. Lett. 38, 1068, (1977).

[4] H. D. Morgan and D. L. Ederer, Phys. Rev. A., 29, 1901, (1984).

[5] P. R. Woodruff and J. A. R. Samson, Phys. Rev. A., 25, 848, (1982).

[6] G. Herzberg and H. R. Moore, Can. J. Phys., 37, 1293, (1959).

[7] H. G. Berry, Phy. Scr., 12, 5–20, (1975).

[8] C. Eckart, Phys. Rev., 36, 878, (1930).

[9] V. Guillemin Jr., and C. Zener, Z. Phys., 61, 199, (1930).

[10] E. B. Wilson Jr., J. Chem. Phys., 1, 210, (1933).

[11] H. M. James, and A. S. Coolidge, Phys. Rev., 47, 700, (1935).

[12] H. M. James, and A. S. Coolidge, Phys. Rev., 49, 688, (1936).

[13] A. W. Weiss, Phys. Rev., 122, 1826, (1961).

[14] S. Larsson, Phys. Rev., 169, 49 (1968).
[15] J. Muszynska, D. Papierowska, and W. Woznicki, Chem. Phys. Lett., 76, 136, (1980).
[16] F. W. King, and V. Shoup, Phys. Rev. A., 33, 2940, (1986).
[17] F. W. King, Phys. Rev. A., 40, 1735, (1989).
[18] F. W. King, and M. P. Bergsbaken, J. Chem. Phys., 93, 2570, (1990).
[19] D. K. McKenzie, and G. W. F. Drake, Phys. Rev. A., 44, R6973, (1991).
[20] A. Luchow, and H. Kleindienst, Int. J. Quantum Chem., 51, 211, (1994).
[21] Z. C. Yan, and G. W. F. Drake, Phys. Rev. A., 52, 3711, (1995).
[22] Z. C. Yan, M. Tambasco, and G. W. F. Drake, Phys. Rev. A., 57, 1652, (1998).
[23] Z. W. Wang, X. W. Zhu, and K. T. Chung, Phys. Rev. A., 46, 6914 (1992).
[24] Z. W. Wang, X. W. Zhu, and K. T. Chung, Phys. Scr., 47, 65 (1993).
[25] Y. K. Ho, Intern. J. of Quant. Chem., 10, pp. 1077-1082, (1981).
[26] Y. K. Ho, Physics Reports 99, N°1, 1 – 68, (1983).
[27] Y. K. Ho, J. Phys. B, 12, p. 387 (1979).
[28] M. Biaye, M. Dieng, I. Sakho, and A. Wagué, Chin. J. Phys., 47, 166 (2009).
[29] M. Biaye, A. Konté, N. A. B. Faye, and A. Wagué, Eur. Phys. J. D, 13, 21 (2001).
[30] M. Biaye, A. Konté, A. S. Ndao, N. A. B. Faye, and A. Wague, Phys. Scr., 71, 39-42 (2005).
[31] M. Biaye, A. Konté, A. S. Ndao, and A. Wague, Phys. Scr., 72, 373 (2005).
[32] M. Biaye, Thèse de Doctorat d’Etat, Université Cheikh Anta Diop de Dakar (2005).
[33] M. Dieng, I. Sakho, M. Biaye, and A. Wague, Chin. J. Phys., 48, 1 (2010).
[34] M. Dieng, M. Biaye, Y. Gning, and A. Wague, Chin. J. Phys., 51, 4 (2013).
[35] Y. Gning, M. Sow, A. Traoré, M. Dieng, B. Diakhate, M. Biaye, and A. Wague, Rad. Phys. Chem., 106, 1, (2015).
[36] Y. Gning, Thèse de Doctorat, Université Cheikh Anta Diop de Dakar, (2016).
[37] D. A. Varshalovich al., (Copyright by Scientific Publishing cople ltd 1988).
[38] C. Bunge, Phys. Rev. A., 16, 249, (1977).
[39] A. J. Thakkar, T. Koga, T. Tanabe, and H. Teruya, Chem. Phys. Lett., 366, p. 95–99, (2002).
[40] I. Sakho, and A. Wague, Chin. J. Phys., 48, 5, (2010).
[41] K. T. Chung, Phys. Rev. A., 44, 9, (1991).
[42] K. T. Chung, Phys. Rev. A., 45, 11, (1992).
[43] K. T. Chung, and X. W. Zhu, Physica Scripta., 48, 292-296, (1993).
[44] I. Sakho, Chin. J. Phys., 52, 5, (2014).
[45] F. W. King, Phys. Rev. A., 43, 7, (1991).