

## Radial atomic properties of excited states for Li-atom using Hartree –Fock approximation

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### Abstract:

Some radial atomic properties have been obtained using two electron density function  $I(r_1, r_2)$  in order to solve Hartree-Fock equations using Slater type orbitals for Li-atom in different excited states ( $1s^2 2P$ ,  $1s^2 3S$  and  $1S^2 3P$ ) using partitioning technique within the individual electronic shells of different configuration of Li-atom in position states. Radial expectations values for one electron  $\langle r_1^n \rangle$  and two electrons  $\langle r_1^n . r_2^n \rangle$ , correlation coefficients  $\tau_r$  and  $\tau_{1/r}$  and electron density at the nucleus  $\rho(o)$  have been calculated for these states of the same atom.

**Keywords:** Hartree-Fock-Roothaan, Slater type orbitals, two electron density function, radial expectation values, electron density at the nucleus, correlation coefficients.-

الخواص الذرية القطرية للحالات المثيجة لذرة الليثيوم باستخدام تقريب هارترى فوك

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الخلاصة :

تم حساب بعض الخواص الذرية باستعمال دالة كثافة الزوج لغرض حل معادلات هارترى فوك للاوربتالات نوع سليتر لذرة الليثيوم في حالات مثيجة مختلفة ( $1s^2 2P$ ,  $1s^2 3S$ ,  $1S^2 3P$ ) باستخدام تقنية التجزئة للقشرات الالكترونية لتراكيب مختلفة لذرة الليثيوم في فضاء الموقع. كما يتم حساب القيم المتوقعة للكترون واحد  $\langle r_1^n \rangle$  ولإلكترونين  $\langle r_1^n . r_2^n \rangle$  المعاملات الترابطية  $\tau_r$  و  $\tau_{1/r}$  وكذلك القيم المتوقعة عند النواة  $\rho(o)$  للحالات المثيجة لنفس الذرة.

الكلمات المفتاحية: هارترى فوك روثان، اوربتالات نوع سليتر، دالة كثافة الزوج، القيم المتوقعة القطرية، الكثافة عند النواة، المعاملات الترابطية.

**1- Introduction**

The Hartree–Fock method (HF) is widely employed for calculations of various properties of multi electron systems because of its internal logical rigidity and relative simplicity. It is noteworthy that the HF method enables calculation not only of the ground state but also excited states of atoms and ions, the symmetry of which differs from that of the ground state. Thus, many excited configurations giving excited states can be examined for any system. The potential of the HF method for this has not been fully studied although it is high for describing excited states generated by excited configurations. The HF equations are a system of nonlinear integral differential equations in partial derivatives for one-electron functions,  $\phi_i$  orbitals. [1]. The Hartree–Fock–Roothaan (HFR) or basis set expansion method is a convenient and powerful tool for the study of electronic structure of atoms and molecules. It is well known that the choice of the basis functions is very important when the algebraic approximation is employed, because it determines both the computational efficiency and accuracy of the results obtained within a given approach. The most frequently used basis functions for atomic calculations are Slater type orbitals (STO) or Gaussian-type functions (GTFs) [2]. It is well-known that the use of Slater-type orbitals (STOs) as basis functions in electronic structure calculations would be highly desirable since they are capable of producing much better approximations than the nonphysical Gaussian functions. Because of the potential advantages, the STOs basis defined by

$$\chi_{nlm_l}(\xi, r) = (2\xi)^{n+\frac{1}{2}} [(2n)!]^{-\frac{1}{2}} r^{n-1} \exp(-\xi r) Y_{lm_l}(\theta, \phi) \dots (1)$$

Here,  $\xi_i > 0$  is the orbital exponent. The quantity  $n$  occurring in eq. (1) is a positive principal quantum number of (STO). The

determination of nonlinear parameters  $n$  and  $\xi$  is very important for describing the atomic orbitals [3]. In the present paper we used the Hartree-Fock method to compute the excited state for Li atom in the  $1s^2 2P$ ,  $1s^2 3S$  and  $1S^2 3P$  states to study some radial atomic properties for these systems and compare with the results obtained in the literature [4]. Many studies are addressed this subject for example papers [5-7].

**2-Theory**

Most of the physically interesting properties of a quantum mechanical system can be calculated from the two-particle reduced density matrix for the system  $\Gamma(x_m, x_n)$ , without reference to the full wavefunction. If we can determine it, the wavefunction can be eliminated from the quantum mechanics and the  $\Gamma(x_m, x_n)$  take over its role [8,9]. The two electron reduced density matrix contains all of the information necessary to calculate the energy and many properties of the atom. It is obtained by integrating the spin and spatial coordinates of all electrons except two electrons ( $m, n$ ) from the  $N$ -particle density matrix [10], so the two-electron reduced density matrix  $\Gamma(x_1, x_2)$  given by [11,12],

$$\Gamma(x_1, x_2) = \frac{N(N-1)}{2} \int \dots \int |\psi(x_1, x_2, \dots, x_N)|^2 dx_3 \dots dx_N \dots (2)$$

Where  $x_i = (r_i, s_i)$  combined space and spin variable with  $s = \alpha(\text{spin up})$  or  $\beta(\text{spin down})$  [13].

**3-2 The two particle expectation values**

Two particle expectation value  $\langle r_1^n r_2^n \rangle$  is defined as [14].

$$\langle r_1^n r_2^n \rangle = \int_0^\infty \int_0^\infty D(r_1, r_2) r_1^n r_2^n dr_1 dr_2 \dots (3)$$

where  $D(r_1, r_2)$  is the two-electrons radial density function which represents the probability density that one electron is located at a radius  $r_1$  and the other electron at a radius

$r_2$  simultaneously .The two-electron radial density  $D(r_1, r_2)$  can be written as [15].

$$D(r_1, r_2) = \iint \Gamma(x_1, x_2) r_1^2 r_2^2 ds_1 ds_2 d\Omega_1 d\Omega_2 \dots(4)$$

$$d\Omega_i = \sin \theta_i d\theta_i d\phi_i \dots(5)$$

Where  $\Omega_i$  is the solid angle

### 3.5: The One-Electron Expectation Value $\langle r_1^m \rangle$

The one-electron expectation value  $\langle r_1^m \rangle$  is determined by the expression as [16],

$$\langle r_1^n \rangle = \int_0^\infty D(r_1) r_1^n dr_1 \dots(6)$$

Where  $n$  integer number ( $2 \leq n \leq 2$ ), the one-electron radial density function  $D(r_1)$  represents the probability density function of finding an electron at a distance between  $r_1$  and  $r_1 + dr_1$  from the coordinate origin ( i.e nucleus) . Though  $D(r_1)$  is a one-dimensional condensation of the wave function  $\psi(x_1, x_2, \dots, x_N)$  , radial physical properties which depend solely on the radial variable  $r$  are completely determined by the knowledge of  $D(r_1)$ . the single-electron radial density  $D(r_1)$  is obtained from integration over two–electron radial density function  $D(r_1, r_2)$  and defined as[17,18],

$$D(r_1) = \int_0^\infty D(r_1, r_2) dr_2 \dots(7)$$

### 4-Electron density at the nucleus $\rho(0)$

The electron density at the nucleus can be evaluated using the following form[19].

$$\rho(0) = \left[ \frac{D_0(r)}{4\pi r^2} \right]_{r \rightarrow 0} \dots(8)$$

### 4-correlation coefficients $\tau_r$ and $\tau_{1/r}$

The correlation coefficients  $\tau_r$  and  $\tau_{1/r}$  are similar to those used in classical statistics .for two electron shell they are defined as [20].

$$\tau_r = \frac{\langle r_1^{-1} r_2^{-1} \rangle - \langle r_1^{-1} \rangle^2}{\langle r_1^{-2} \rangle - \langle r_1^{-1} \rangle^2} \dots\dots\dots(9)$$

$$\tau_{1/r} = \frac{\langle r_1^{-1} r_2^{-1} \rangle - \langle r_1^{-1} \rangle^2}{\langle r_1^{-2} \rangle - \langle r_1^{-1} \rangle^2} \dots\dots(10)$$

## 5.Results and discussion

Different excited configurations have been tested. In this work we have used the configuration  $1S^2 2P, 1S^2 3S$  and  $1S^2 3P$  states to describe the Li atom using Hartree-Fock wave function .This wave function provides better description of one and two body densities in position space in the term of two electron density function  $\Gamma(x_1, x_2)$  , we have examined the one electron expectation value  $\langle r_1^n \rangle$  , two electron expectation values  $\langle r_1^n r_2^n \rangle$ , electron density at the nucleus and radial correlation coefficient for Li atom in its excited state. Table (1) shows the one electron expectation values and standard deviation for studied systems. Table (2) represents expectation values for two electrons ,we could see from those tables the expectation values for one electron and two electron decrease when  $n$  goes from -2 to 2 for each individual electronic shell, also we could see for K-shell the  $\langle r_1^n \rangle$  and  $\langle r_1^n r_2^n \rangle$  values decrease when  $n$  goes from -2 to -1 and from 1 to 2 ,whereas for inter shell  $KL(^1S)$  ,  $KL(^3S)$  ,  $KM(^1S)$  and  $KM(^3S)$  the expectation values decrease when  $n$  goes from -2 to -1 and increase when  $n$  changes from 1 to 2 for all states of Li-atom under studied .standard deviation  $\Delta r_1$  which measure the radial diffuseness of the electron charge distribution also calculated in this work, it is clear from table (1) standard deviation decrease when we goes from  $1S^2 2P$  to  $1S^2 3S$  to  $1S^2 3P$  states .

Table (3) contain the values of correlation coefficients, it is observed from this table for inter shell ( $KL(^3S)$  ,  $KL(^1S)$ ,  $KM(^3S)$  and  $KM(^1S)$  ,the values of  $\tau_r < \tau_{1/r}$  for all studied system ,also we could see, these values equal zero for K-shell due to there is no correlation between the two electrons in the same shell which means the positions of two electrons are independent which agree with Pauli exclusion principle.

Table (4) represents the electron density at the nucleus  $\rho(0)$  calculated from equation (8) . we could see the  $\rho(0)$  for  $K(^1S)$ -shell is larger than that for other shells because K-shell closer to the nucleus than other shells.

Table(1)one particle expectation value  $\langle r_1^n \rangle$  and standard deviation  $\Delta r_1$  for Li atom for each individual electronic shell in different excited states .

state	shell		$\langle r_1^{-2} \rangle$	$\langle r_1^{-1} \rangle$	$\langle r_1^1 \rangle$	$\langle r_1^2 \rangle$	$\Delta r_1$
1s <sup>2</sup> 2p	K( <sup>1</sup> S)		14.89018	2.68493	0.57331	0.44729	0.3444
	KL( <sup>1</sup> S)≡ KL( <sup>3</sup> S)		7.49375	1.47497	2.68434	14.13392	2.63215
	total		9.95923	1.87829	1.98066	9.57171	1.86956
1s23s	K( <sup>1</sup> S)	Present work	14.90562	2.68692	0.57252	0.44561	0.34327
		Ref	14.905527	2.686907	0.572518	0.445609	0.343268
	KM( <sup>1</sup> S) ≡ KM( <sup>3</sup> S)	Present work	7.50442	1.41175	5.38479	59.51712	5.5246
		Ref [4]	7.503674	1.411751	5.384773	59.516940	5.524596
	total		9.97148	1.83681	3.7807	39.82662	3.79749
1S <sup>2</sup> 3P	K( <sup>1</sup> S)	Present work	14.89601	2.68543	0.57246	0.44585	0.34372
		Ref [4]	14.901888	2.686471	0.572667	0.446011	0.343603
	KM( <sup>1</sup> S) ≡ KM( <sup>3</sup> S)	Present work	7.46739	1.40096	6.38079	86.02905	6.7316
		Ref [4]	7.465269	1.401202	6.382030	86.045952	6.731689
	total		9.94360	1.82912	4.44468	57.50132	4.60230

Table(2) two particles expectation values  $\langle r_1^n . r_2^n \rangle$  for Li atom for each individual electronic shell for different excited states .

state	shell		$\langle r_1^{-2} . r_2^{-2} \rangle$	$\langle r_1^{-1} . r_2^{-1} \rangle$	$\langle r_1^1 . r_2^1 \rangle$	$\langle r_1^2 . r_2^2 \rangle$
1s <sup>2</sup> 2p	K( <sup>1</sup> S)		221.71984	7.20893	0.32869	0.20007
	KL( <sup>1</sup> S)≡ KL(3S)		1.44748	0.71155	2.74927	12.44409
	total		74.8716	2.87734	1.94241	8.36275
1s <sup>2</sup> 3s	K( <sup>1</sup> S)	Present work	222.17607	7.21947	0.32778	0.19857
		Ref	222.176068	7.219470	0.327777	0.198567
	KM( <sup>3</sup> S)	Present work	0.46284	0.35004	5.83468	52.82606
		Ref [4]	0.462841	0.350042	5.837979	52.826063
	KM( <sup>1</sup> S)	Present work	1.51702	0.36702	5.83798	52.84404
		Ref [4]	1.517019	0.367019	5.837979	52.844045
total		74.36725	2.63985	3.99904	35.28356	
1S <sup>2</sup> 3P	K( <sup>1</sup> S)	Present work	221.97848	7.21439	0.32784	0.19886
		Ref [4]	222.066253	7.217124	0.327947	0.198925
	KM( <sup>1</sup> S) ≡ KM( <sup>3</sup> S)	Present work	0.42687	0.31139	6.98045	76.54417
		Ref [4]	0.426958	0.311448	6.981606	76.555868
	total		74.27741	2.61239	4.76291	51.09573

Table(3) the correlation coefficients  $\tau_r$  and  $\tau_{1/r}$  for Li atom in its excited states.

state	shell	$\tau_r$	$\tau_{1/r}$
$1s^2 2p$	$KL(^1S) \equiv KL(^3S)$	-0.64323	-0.27528
$1s^2 3s$	$KM(^3S)$	-0.75886	-0.29811
	$KM(^1S)$	-0.75875	-0.29503
$1s^2 3p$	$KM(^1S) \equiv KM(^3S)$	-0.74444	-0.29998

Table (4) the electron density at the nucleus  $\rho(0)$  for all shell in the excited states of Li- atom .

state	shell	$\rho(0)$
$1s^2 2p$	$K(^1S)$	6.82675
	$KL(^1S) \equiv KL(^3S)$	3.41425
$1s^2 3s$	$K(^1S)$	6.83432
	$KM(^1S) \equiv KM(^3S)$	3.45501
$1s^2 3p$	$K(^1S)$	6.82973
	$KM(^1S) \equiv KM(^3S)$	3.48249

### Conclusion:

It has been shown how the radial expectation values for one electron and two electrons act with different excited states for Li atom in the Hartree-Fock framework . Numerical results have been discussed . The Hartree-Fock method also allows one to study how the electron density at the nucleus  $\rho(0)$  behaves for all shells in different configurations . In the present work ,the correlation coefficients also calculated for studied states .

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