Open Access

Baghdad Science Journal **Vol.12(3)2015**

Calculation of Radial Electron-Electron Distribution function and Expectation Values for Li-Atom in Excited States 1s 2p, 1s 3p and 1s 3d

Khalil H. AL-Bayati* ***Ali. A. Kareem*****

Naeemah CH. Madhkoor*

*Physics Department -College of Science for Women-University of Baghdad.

** Physics Department -College of Science- University of Baghdad.

***E-mail:** na_ch_ma@yahoo.com

Received 3, July, 2014

Accepted 15, September, 2014

Abstract:

The electron correlation for inter-shells *(1s 2p)*, *(1s 3p)* and *(1s 3d)* was described by the inter-particle radial distribution function $f(r_{12})$. It was evaluated for Li-atom in the different excited states $(1s^2\ 2p)$, $(1s^2\ 3p)$ and $(1s^2\ 3d)$ using Hartree-Fock approximation (HF). The inter particle expectation values $\langle r_{12}^n \rangle$ for these shells were also evaluated. The calculations were performed using Mathcad 14 program.

Key words: Radial electron-electron distribution function, Hartree Fock approximation; inter-shell, non-spherically symmetric system.

Introduction:

The distribution function $f(r_{12})$ of the interelectronic distance r_{12} provides an interesting indicator for electrons correlation in many-electron systems. The $f(r_{12})$ for two-electron atoms was first introduced by Coulson and Neilson [1], in their study of electron correlation in the ^{1}S He ground state. For atoms with more than two electrons, $f(r_{12})$ has a very convenient formulation [2] in terms of the (spin free) 2-matrix. The analytical procedure for obtaining $f(r_{12})$ from ^{1}s 2-electron wave functions containing no angular terms has been outlined in detail [1]. Extend the analysis to N-electron atomic systems described by wave functions which may be, but are not required to be, eigenfunctions of the total spin and angular momentum operators $\hat{S}^2$ and $\hat{L}^2$. In other words, attention for the general case of non-spherically symmetric system is not restricted to symmetry-adapted wave functions [3]. The distribution function $f(r_{12})$ for Li-atom has been examined in some detail for the ground states and first excited state which represent the simplest excited state by K. H. Al-Bayati [4] and for third excited state by A. A. Alzubadi [5].

In the present research, the analysis was extended to fourth excited state *3d* in addition to *2p* and *3p*. The uncorrelated description (HF) of each exited state was provided by the *2p*, *3p* and *3d* restricted HF or analytical self consistent field atomic wave functions of Weiss [6], by partitioning the second-order density into its pairwise components.

Theory

For any *N*-electron atomic system, the radial electron-electron distribution function is defined in terms of the spin-free second order density matrix as [7]

$$f_{ij}(r_{12}) = r_{12}\int \Gamma'_{ij}(\chi_1,\chi_2)\,\bar r_1\,\bar r_2\,d\bar r_1\,d\bar r_2\,\sin\theta_1\,d\theta_1\,d\phi_1\,d\omega$$

…(1)

where ω denotes the angle of rotation. For the spherically symmetric case (*s*-orbital) where the azimuthal (or orbital) angular momentum quantum number $\ell = 0$, *f(r₁₂)* can be evaluated from the following equation [1]

$$f(r_{12}) = 8\pi^2\, r_{12}\left\{\int_0^{r_{12}} \vec r_1 d\vec r_1 \int_{r_{12}-r_1}^{r_{12}+r_1} \Gamma'(\vec r_1,\vec r_2)\,\vec r_2 d\vec r_2 + \int_{r_{12}}^{\infty} \vec r_1 d\vec r_1 \int_{r_1-r_{12}}^{r_{12}+r_1} \Gamma'(\vec r_1,\vec r_2)\,\vec r_2 d\vec r_2\right\}$$

… (2)

In the present analysis the *2p*, *3p* and *3d* states are examples of non-spherically symmetric system. The expression for $f\left(r_{12}\right)$ can be obtained from [3]

$$f(r_{12}) = r_{12}\left\{\int_0^{r_{12}} \vec r_1 d\vec r_1 \int_{r_{12}-r_1}^{r_{12}+r_1} \Gamma'_{12}(\vec r_1,\vec r_2)\,\vec r_2 d\vec r_2 \times I + \int_{r_{12}}^{\infty} \vec r_1\, d\vec r_1 \int_{r-r_{12}}^{r_1+r_{12}} \Gamma'_{12}\left(\vec r_1,\vec r_2\right)\vec r_2 d\vec r_2 \times I\right.$$

… (3)

If (i , j) labels a pair of occupied φ_i and φ_j in the restricted HF description of the system, then the change, due to correlation in the (i , j) component of the second-order density $\Gamma_{ij}(\chi_m , \chi_n)$ which is derived from the HF wave-functions by using the partitioning technique [8] is given by:

$$\Gamma_{ij}\left(\chi_m,\chi_n\right) = \frac{1}{2}\begin{bmatrix}\varphi_i\left(\chi_m\right)\varphi_j\left(\chi_n\right) - \\ \varphi_j\left(\chi_m\right)\varphi_i\left(\chi_n\right)\end{bmatrix} \quad \ldots (4)$$

To study the physical properties for a three-electron systems, we must find the electron-pair density for each individual electronic shell, so

$$\Gamma(x_m, x_n) = \sum_{i<j}^{3} \Gamma_{ij}(x_m, x_n) \ldots \quad (5)$$

$\Gamma' =$ Γ spin less or $\Gamma' = \iint \Gamma_{ij}\left(\chi_m,\chi_n\right)d\sigma_m d\sigma_n$, the function φ is the spatial part of the spin orbital and it was constructed from a basis set of Slater-type orbital, where [6]

$$\varphi_{n,l} = \sum_i C_n^i \chi_{nl}^i \ \cdots \ (6)$$

and *n,l* = (*1s, 2p), (1s, 3p)* or (*1s, 3d).* The basis functions χ are standard normalized Slater-type orbitals (STO's) and are given by

$$\chi_{n,l,m_l}(\bar r,\theta,\phi,\xi) = R_n(\bar r,\xi)Y_{lm_l}(\theta,\phi)$$

… (7)

where the radial part *R* is given by:

$$R_n(\vec r,\xi) = \mathcal{N}\cdot r^{n-1}\cdot e^{(-\xi\cdot\vec r)} \ \ldots.\ (8)$$

and C_n represents the constant coefficient resulting from the self constant field (SCF) method, *n* is the principal quantum number, ξ is the orbital exponent, and $\mathcal{N}$ is a normalization constant given by

$$\mathcal{N} = \frac{(2\xi)^{n+1/2}}{[(2n)!]^{1/2}} \quad , \quad \ldots \ (9)$$

finally *I* represents the integrals of the most general type

$$I = \int Y_{\ell_1 m_1}(\theta_1,\phi_1)\,Y^*_{\ell_2 m_2}(\theta_1,\phi_1)\,Y_{\ell_3 m_3}(\theta_2,\phi_2)\,Y^*_{\ell_4 m_4}(\theta_2,\phi_2)\sin\theta_1 d\theta_1 d\phi_1 d\omega$$

…(10)

I can be written as [5]

$$I = \frac{1}{2}(-)^{m_2+m_4}\sum_{\ell=|\ell_1-\ell_2|}^{\ell_1+\ell_2}\ \sum_{\ell'=|\ell_3-\ell_4|}^{\ell_3+\ell_4}\left[\frac{L_1L_2L_3L_4}{LL'}\right]^{\frac{1}{2}}$$

$$\times C(\ell_1\,\ell_2\,\ell;m_1-m_2\,m)\,C(\ell_3\,\ell_4\,\ell';m_3-m_4\,m')$$
$$C(\ell_1\,\ell_2\,\ell;\,000)\,C(\ell_3\,\ell_4\,\ell';\,000)\times(-)^{m'}P_{\ell'}^{m'}(\cos\theta_{12})\,\delta_{\ell\ell'},\delta_{m-m'}\quad\ldots(11)$$

where

$C(\ell_1\,\ell_2\,\ell;m_1-m_2\,m)$ is the Clebsch-Gorden coefficient defined by [9], and is sometimes expressed in traditional notation $\langle\,\ell_1\,\ell_2\,m_1\,m_2|\,\ell_1\,\ell_2\,\ell\,m\rangle$, $L_i=2l_i+1$, $m=m_1-m_2$, $m'=m_3-m_4$, δ_{xy} is the Kronecker delta function and $P_l^{|m_l|}(cos\,\theta)$ is the associated Legendre function.

Equ.(11) can be written in term of Wigner *3j* symbols by using the following relation

$$\langle\,\ell_1\,\ell_2\,m_1\,m_2\left|\begin{matrix}\ell_1\,\ell_2\,\ell\,m\rangle=\\(-1)^{-\ell_1+\ell_2-m}\sqrt{2\ell+1}\end{matrix}\right.\begin{pmatrix}\ell_1&\ell_2&\ell\\m_1&m_2&-m\end{pmatrix}\quad\ldots(12)$$

The important properties and the values of Wigner 3j symbols were given and tabulated in Refs. [10, 11] . The inter-particle expectation values $\langle\,r_{12}^n\rangle$ can be determined from the formula [4]

$$\langle\,r_{ij}^n\,\rangle=\int_0^\infty f(\,r_{ij}\,)r_{ij}^n\,dr_{ij}\quad\ldots\ (13)$$

where *n* was taken as $-2\le n\le 2$. The value of $\left\langle r_{12}^{-1}\right\rangle$ is of additional importance since it gives directly the electron-electron repulsion energy. Besides the lower bound for the electronic density at the nucleus can be obtained in term of the moment $\langle\,r_{12}^{-2}\,\rangle$. Finally the standard deviation $\Delta\,r$ is a square root of the variance; which it is especially useful for representing the diffuseness of each radial density distribution, because it has the unit of $\vec{r}$. It is defined by [5]

$$\Delta\,r=\sqrt{\langle\,r^{\,2}\,\rangle-\langle\,r\rangle^{\,2}}\quad\ldots\ (14)$$

Results and Discussion

The results for the radial electron-electron distribution function *f(r₁₂)* between electrons unlike and like spin in *KL* and *KM* shells for Li-atom in the different excited states are shown in the Fig. (1). A and B, and the difference between them can be seen in Fig. (2). At very small r_{12} which represents the K-shell, $f(r_{12})$ distribution function is influenced mainly by the electron pair behavior so we see a flat region and in the farther region of r_{12} which represents the L-shell, the principal maxima in each curve in *(1s² 3p)* refer to the probability behaviour, one for L-shell and the other for M-shell, when the outer electron has penetrated the *2p*, but in states *(1s² 2p)* and *(1s² 3d)* the difference in symmetry between *1s* and *2p* or *3d* remains a flat region . For comparison between the states we find the maximum of $f(r_{12})$ occurs at $r_{12}\approx 3.86$ for *1s 2p*, $r_{12}\approx 9.029$ for *1s 3d* and $r_{12}\approx 11.73$ for *1s 3p*.

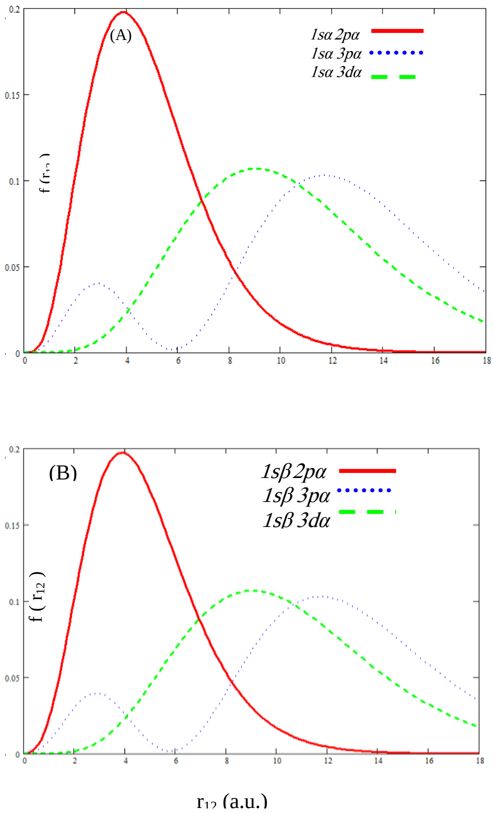

Fig. (1). The electron-electron distribution function f(r_{12}) for triplet states of (Li) atom in the different excited states (A) *1sα 2pα* , *1sα 3pα* and *1sα 3dα* (B) *1sβ2pα* , *1sβ3pα* and *1sβ3dα.*

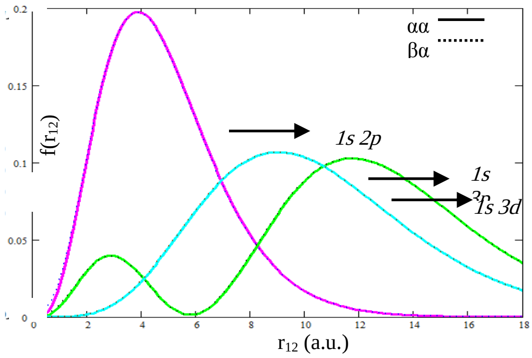

Fig. (2). The electron-electron distribution function f(r_{12}) for triplet αα and singlet βα states of (Li) atom in the different excited states 1s 2p, 1s 3p and 1s 3d

The spread or diffuseness of *f(r_{12})* about the mean value $\langle r_{12}^{n} \rangle$ is measured by the magnitude of Δr_{12}. Table (1) shows that in every individual shell, the $\langle r_{12}^{n} \rangle$ increases when *n* goes from 1 to 2 and decreases when $n \geq -1$. The distance between two electrons in unlike spin is smaller than in like spin and vise versa. The repulsion energy is represented by $\langle r_{12}^{-1} \rangle$. The $\langle r_{12}^{+1} \rangle$ increases in the order *1s 3p* > *1s 3d* > *1s 2p* but the repulsion energy between two electrons in *1s 2p* > *1s 3p* > *1s 3d.*

Table (1). The inter particle expectation values the standard deviation Δr_{12} for individual shells of (Li) atom in the different states. All values are in a. u.

State	*Shell*	$\langle r_{12}^{-2} \rangle$	$\langle r_{12}^{-1} \rangle$	$\langle r_{12}^{+1} \rangle$	$\langle r_{12}^{+2} \rangle$	Δr_{12}
$1s^2$ 2p	*1sα2pα*	0.092635	0.261185	4.840215	28.289438	2.204938
	1sα2pβ	0.101362	0.264139	4.834787	28.267757	2.208390
$1s^2$ 3p	*1sα3pα*	0.026999	0.114670	12.209042	172.070208	4.800777
	1sα3pβ	0.029900	0.115634	12.207368	172.063770	4.800106
$1s^2$ 3d	*1sα3dα*	0.014910	0.111134	10.516445	126.469347	3.984192
	1sα3dβ	0.014916	0.111135	10.516438	126.469344	3.984203

Conclusions:

From the present calculation, some important remarks can be deduced about the radial electron-electron distribution function $f(r_{12})$ for Li-atom excited states 1s 2p, 1s 3p and 1s 3d. When comparing the $f(r_{12})$ for Li-atom in the different excited state we see at small r_{12} a flat region in *(1s 2p)* and *(1s 3d)* but a small curved in *(1s 3p)* because the outer electron has penetrated the 2p. The maximum of $f(r_{12})$ for *1s 2p >1s 3d >1s 3p* and it's locations of these maxima decrease respectively. Also the max.$f(r_{12})$ for αα > βα in *(1s 2p)* and *(1s 3p)* states and vice in state *(1s 3d)* but these locations decreases when the max.$f(r_{12})$ increases but this difference is slight. We conclude that penetration into any orbital by other orbitals, occurs only between orbitals which are similar in spherical symmetry. Finally the distance between two electrons of parallel spin is greater as a result of the repulsion between them.

References:

[1] Coulson, C.A. and Neilson, A. H. 1961. Electron Correlation in the Ground State of Helium, Proc. Phys. Soc. 78(5):831-837.

[2] Benesch, R. and Smith, V. H. 1970. Radial Electron-Electron Distribution and the Coulomb Hole for Be. J. Chem. Phys. 55(2):482-488.

[3] Benesch, R. 1972. On the Determination of Radial Electron-Electron Distribution Function, Int. J. Quant. Chem. 6(1):181-192.

[4] AL-Bayati, K. H. 1984, Ph. D. Thesis "Electron Correlation in ($1s^2$ 2s) and ($1s^2$ 2p) states of the Lithium Isoelectronic Sequence in Position and Momentum Space, Leicester University.

[5] Alzubadi, A. A. 2005. Ph. D. Thesis Theoreticle Study on Atomic Shells of Lithium Atom and Ions in Excited States $1s^2$ 3p. University of Technology, Iraq.

[6] Weiss, A. W. 1963. Wave Function and Oscillator Strengths for the Lithium Isoelectronic Sequence, Astrophys. J. 138(6):1262-1276.

[7] Dressel, P. R. and King, F. W. 1994. Compact Expressions for the Electron–Electron Distribution Function for the ^2S States of Three‐Electron Systems, J. Chem. Phys. 100(10):7515-7527.

[8] Banyard, K. E. and Mashat, M. M. 1977. Coulomb Holes and Correlation Coeffeicient for Electronic Shell : The Be-Like Ions, J. Chem. Phys. 67(4):1405-1411.

[9] Rosse, M. E. 1967. Elementary Theory of Angular Momentum. John Wiley & Sons, New York PP 248.

[10] Cowan, R. D. 1981. The Theory of Atomic Structure Spectra. University of California Press, California PP 650.

[11] Edmonds, A. R. 1974. Angular Momentum in Quantum Mechanics. Princeton University Press, Princeton PP 146.

حساب دالة توزيع الكثافة القطرية والقيم المتوقعة بين الكترونين لذرة الليثيوم في الحالات المتهيجة 1s 2p , 1s 3p , 1s 3d

خليل هادي أحمد البياتي* **علي عبد اللطيف كريم**** **نعيمة جيجان مذكور***

* جامعة بغداد- كلية العلوم للبنات- قسم الفيزياء
** جامعة بغداد- كلية العلوم- قسم الفيزياء

الخلاصة:

العلاقة الإلكترونية للأغلفة البينية $(1s\ 2p)$ و $(1s\ 3p)$ و$(1s\ 3d)$ يمكن ان توصف من خلال تقييم دالة التوزيع القطري البيني $f(r_{12})$ لذرة الليثيوم في الحالات المتهيجة $(1s^2\ 2p)$ و $(1s^2\ 3p)$ و $(1s^2\ 3d)$ باستخدام دالة موجة هارتري-فوك (HF) . ولكل غلاف بيني تم حساب القيم المتوقعة للمسافة البينية $\langle r_{12}^{n} \rangle$.
جميع النتائج تم حسابها باستخدام برنامج Mathcad 14 .

الكلمات المفتاحية: دالة توزيع الكثافة القطرية للألكترون، تقريب هارتري-فوك، الأغلفة البينية، نظام عدم التماثل الكروي.