

Compute Fermi hole and the Expectation values for Li-atom Using DZ, SZ, Mult-ZateData

حساب فجوة فيرمي والقيم المتوقعة لذرة الليثيوم باستخدام بيانات DZ,SZ, Mult-Zate

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Abstract

In this paper the partitioning method has been used for the atomic system consist of three-electrons (Li-atom), Hartree-Fock energy for Li-atom have been calculated using the Hartree-Fock wave functions of Clementi and Rotti by a single orbital "Single Zate" and "Double Zate", also it calculated using Hartree-Fock wave functions for Mult-Zate by Sarsa *et al*, these wave functions were found to give rather inaccurate values to DZ for Clementi and Rotti, but indicating some " exact" total Hartree-Fock energy as a functions of the Single-Zate and 7-term. The expectation values of $\langle r_1^k \rangle$, $\langle r_{12}^k \rangle$, Δr_1 , Δr_{12} , $D(r_1)$, $f(r_{12})$, $\langle V_{ee} \rangle$, $\langle V_{en} \rangle$, $\langle V \rangle$, $\langle E \rangle$ and Fermi hole considered by DZ, SZ, mult-Zate. The differences between intra-and inter-shell correlation estimation using the different wave functions is made.

الخلاصة

في هذه البحث استخدمت طريقة التجزئة للنظام الذري الذي يتألف من ثلاثة إلكترونات (ذرة الليثيوم). طاقة هارتري-فوك لذرة الليثيوم حسب استخدام الدوال الموجية لهارتري-فوك لروتتي وكلمنتي للأوربييتال المفرد "Single Zate" والأوربييتال الثنائي "Double-Zate" كذلك حسب استخدام الدوال الموجية لهارتري-فوك "Mult-Zate" لسارسا وآخرون وجد ان هذه الدوال تعطي في الواقع قيم غير مضبوطة للطاقة DZ, ولكن تضمنت الطاقة الكلية لهارتري-فوك بعض الدقة لدوال 7-حدود SZ. القيم المتوقعة لـ $\langle r_1^k \rangle$, $\langle r_{12}^k \rangle$, Δr_1 , Δr_{12} , $D(r_1)$, $f(r_{12})$, $\langle V_{ee} \rangle$, $\langle V_{en} \rangle$, $\langle V \rangle$, $\langle E \rangle$ وفجوة فيرمي درست باستخدام الدوال الموجية DZ, SZ, Mult-Zate. اختلاف الترابط بين القشرات الداخلية والوسطية ضمن بنجاح باستخدام الدوال المختلفة.

1.Introduction

The most important appliance of Hartree-Fock (HF) method was, in atomic and molecular physics, the study of Coulomb systems (atomic, ions and molecular) with a entirely Coulombic Hamiltonian of electrons interacting with static nuclei. In physics, the use of Hartree-Fock method to calculate the energy of ground state of atoms, ions and molecular, as well compute the atomic properties we refer, for example to papers[1,2,3,4]. Roothaan's open shell HF theory[5] is universally used to review the diverse of definite states of atoms, molecular and nuclei.

In this paper we used the partitioning technique has been used to analyze Li-atom for six-pairs electronic wave functions, two of these are for the intra-shells (K-and L-shells) and the rest for inter-shells by using Hartree-Fock wave functions published by Clementi and Rotti for single-and double Zate[6], and we used this method for study the Roothaan Hartree-Fock wave functions published by Sarsa, Gálvez and Buendía in paper them[7] for 7-term.

In this report we focus our work on the determination of the trial parameters for improved versions of ground state ($1S, 3S$) wave functions, for Li-atom. Mean energies, expectation value for distances for r_i , r_{ij} (electron-nucleus, electron-electron) respectively and Fermi hole are tabulated for tailored wave functions here posed. Atomic units are used unless otherwise stated.

2. Theory:

The orbital effective potential method which using in this paper have been obtained by[7] is a variational approximation to the many-electron problem which uses single-particle wave functions as variational ansatz as in Hartree-Fock mehod. The single particle orbitals satisfy a single-particle Schrödinger equationwith a certain local potential that is taken to be central[8],

$$\left(-\frac{1}{2}\nabla^2 + V(r) \right) \phi_{\lambda\sigma}(\vec{r}) = \varepsilon_{\lambda}\phi_{\lambda\sigma}(\vec{r}), \quad (1)$$

Where $\lambda = (n, l, m_l)$ stands for the spatial quantum numbers of atomic orbital and $\sigma = \pm 1/2$ is the third component of the electron spin, ∇_i^2 the Laplace operator, ε_{λ} is energy and given by

$$\varepsilon_{\lambda} = I_{\lambda} + \sum_{\mu} (J_{\lambda\mu} - K_{\lambda\mu}), \quad (2)$$

I, J and K are usuall single-particle, direct and exchange integrals calculated starting from the single-particle orbitals. The wave function $\psi_{HF}(r_1, r_2, \dots, r_N)$ is a Slater determinant constructed from the orbital ϕ_i [9],

$$\psi_{HF}(r_1, r_2, \dots, r_N) = A(\phi_1, \dots, \phi_N) \quad (3)$$

Where A is the antisymmetrizer and N is the total number of electrons. The orbitals are expanded in terms of a set of basis functions[10],

$$\phi_i(r) = \sum_j C_{ij} x_{ij}(r) \quad (4)$$

Where the basis functions $x_{ij}(r)$ are Slater type orbitals with integer quantum numbers. The expanded coefficients C_{ij} and orbital exponents(denoted ξ_j) for each Slater-type orbital are provided in tables by Clementi and Roetti. The basis functions $x_{ij}(r)$ are slater-type orbitals with integer quantum number, namely[11]

$$x_{ij}(r) = R(r) Y(\theta, \phi) \quad (5)$$

where $Y(\theta, \phi)$ are normalized spherical harmonics $R(r)$ is the radial part[12],

$$R(r) = [(2n)!]^{-1/2} (2\xi)^{n+1/2} r^{n-1} e^{-\xi r} \quad (6)$$

The exponent ξ , and principle quantum numbers, n , of the wave functions of Clementi and Roetti based on Slater-type function(STF_s) and showed that the optimum choice of n improves notably the double-zeta(DZ) approximation of atoms. A double-Zeta function is an approximate Roothaan-Hartree-Fock function in which a given electron orbitals is described by two Slater functions. While single-zeta function is described by one Slater functions. And milt-zeta function is described by mulit Slater functions[6]. We calculated the one-particle expectation value by equation[13]

$$\langle r_1^n \rangle = \int_0^{\infty} D(r_1) r_1^n dr_1 \quad (7)$$

Where $D(r_1)$ is the one particle density distribution function. The two-particle expectation values calculated from equation[14],

$$\langle r_{ij}^n \rangle = \int_0^\infty f(r_{ij}) r_{ij}^n dr_{ij} \quad (8)$$

$f(r_{ij})$, interparticle radial density distribution function, we determined, fermi hole Fermi hole $\Delta f_F(r_{12})$ is defined as a difference between the electron-electron distribution function $f(r_{12})$ for triplet state and these for singlet state[15],

$$\Delta f_F(r_{12}) = f_{\alpha\alpha}(r_{12}) - f_{\alpha\beta}(r_{12}) \quad (9)$$

3. Results and discussion

Tables 1, 2 summarize the RHF one expectation values, two-expectation values respectively, for Li atom obtained from SZ and DZ wave functions published by Clementi and Rotti and multi-Zeta wave function published by Sarsa *et al*(2004).

From Table 1 and Table 2, we showed that the results of the one-particle expectation values, two-particle expectation values and standard deviations $\Delta r_1, \Delta r_{12}$ by Single-exponent ζ , and single principle quantum number agree with multi-exponent ζ and with Ref[7] with smallest different, comparison with Double-exponent ζ .

Table 1: Comparison of the one-particle expectation values for Li atom obtained from wave functions Single- Double-Zeta(RHF) by Clementi and Rotti with wave functions (RHF) obtained from 7-term by Sarsa *et al*.

Shell	$\langle r_1^{-2} \rangle$	$\langle r_1^{-1} \rangle$	$\langle r_1^1 \rangle$	$\langle r_1^2 \rangle$	Δr_1
$k_\alpha k_\beta$ SZ	14.40451	2.68048	0.55988	0.42219	0.32974
$k_\alpha k_\beta$ DZ	15.45881	2.69024	0.54265	0.41380	2.11295
multi-term $k_\alpha k_\beta$	14.88317	2.68386	0.57361	0.44830	0.34534
Ref [16]	14.8883	2.6850	0.5731	0.4468
$K_\alpha L_\alpha(1s)$ SZ	4.52714	1.53041	2.28267	9.67073	2.11191
$K_\alpha L_\alpha(1s)$ DZ	6.24240	1.04327	0.50560	0.85385	0.77345
$K_\alpha L_\alpha(1s)$ multi-term	7.67179	1.51575	2.22188	9.05982	2.03053
Ref [17]	2.2231	9.0874	...
$K_\beta L_\alpha(3s)$ SZ	7.59728	1.54000	2.27913	9.65896	2.11295
$K_\beta L_\alpha(3s)$ DZ	7.59728	1.53996	2.27912	9.65896	2.11295
$K_\beta L_\alpha(3s)$ multi-term	7.67179	1.51575	2.221188	9.05982	2.11295
Ref[18]	7.662	1.515	2.223	9.088	...

*Note energies are expressed in Atomic units.

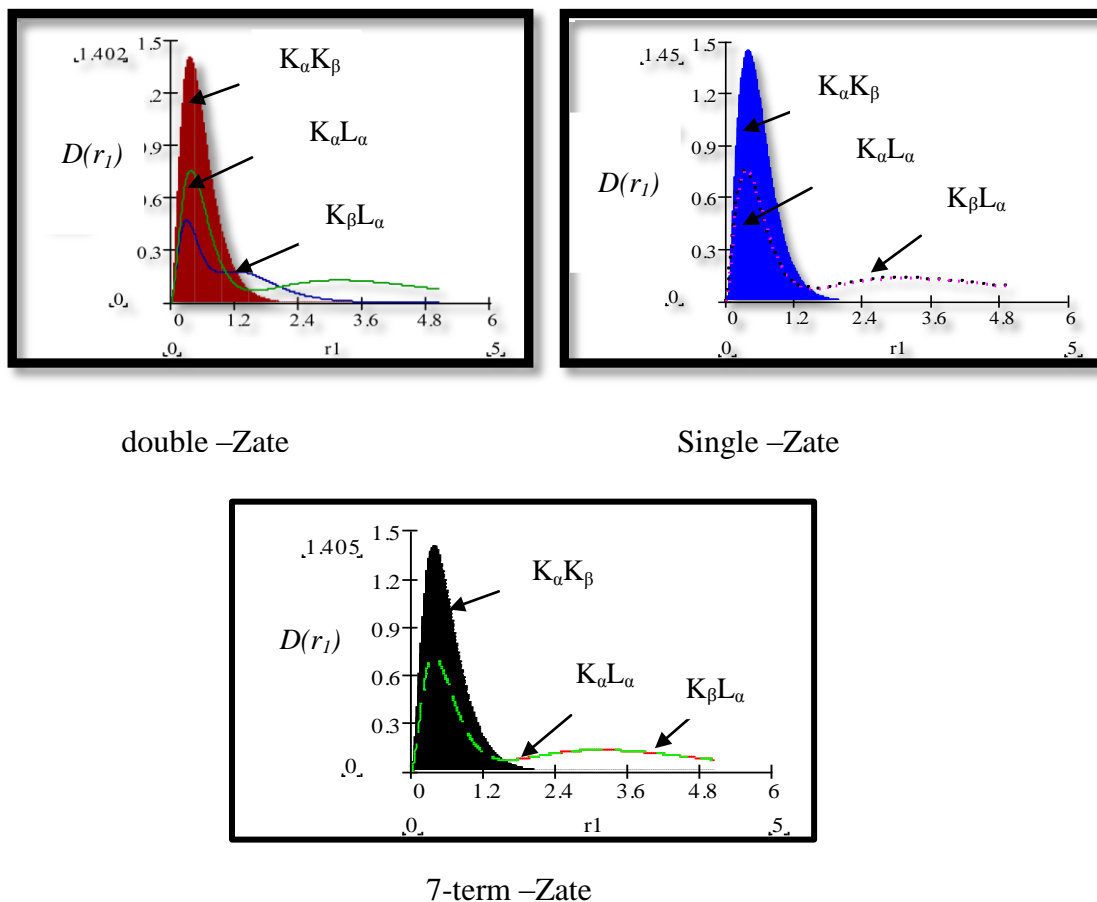
Table 2: Comparison of the two-particle expectation values for Li atom obtained from wave functions Single- Double-Zeta(RHF) by Clementi and Rotti with wave functions (RHF) obtained from 7-term by Sarsa *et al.*

Shell	$\langle r_{12}^{-2} \rangle$	$\langle r_{12}^{-1} \rangle$	$\langle r_{12}^1 \rangle$	$\langle r_{12}^2 \rangle$	Δr_{12}
$k_{\alpha}k_{\beta}$ SZ	4.79282	1.67353	0.81718	0.84439	0.42024
$k_{\alpha}k_{\beta}$ DZ	0.24171	0.33328	4.03955	19.31792	1.73203
mult-term $k_{\alpha}k_{\beta}$	4.71247	1.64896	0.84032	0.89659	0.43640
Ref [18]	4.7172	1.6498	0.8393	0.8936	0.4346
$K_{\alpha}L_{\alpha}$ (1s)SZ	0.12288	0.30951	4.05158	19.34146	1.71060
$K_{\alpha}L_{\alpha}$ (1s)DZ	0.33266	0.35686	0.82803	17.0771	1.01098
$K_{\alpha}L_{\alpha}$ (1s) mult-term	0.12013	0.30841	3.92457	18.11964	1.64845
Ref [19,17]	0.1901	0.3227	3.9221	18.1848
$K_{\beta}L_{\alpha}$ (3s)SZ	0.24171	0.33328	4.03955	19.31792	1.73202
$K_{\beta}L_{\alpha}$ (3s)DZ	0.24171	0.33328	4.03955	19.31792	1.73202
$K_{\beta}L_{\alpha}$ (3s) mult-term	0.19020	0.32341	3.91892	18.11964	1.66184
Ref [19,17]	0.1199	0.3084	3.9274	18.1848

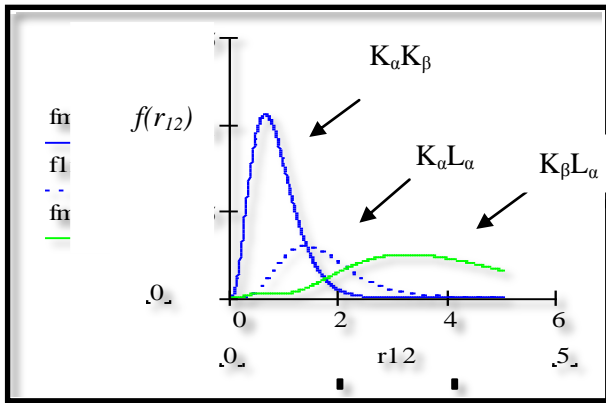
Table 3: Expectation values of the potential energy $\langle V \rangle$ and total energy $\langle E \rangle$ of the HF wave function for Li-atom for data(1974) [6], and data for Li-atom(2004) [7].

Shell	$-V_{en} = -Z^* \langle r^{-1} \rangle$	V_{ee}	$-\langle V \rangle$	$\langle -E \rangle$
$k_{\alpha}k_{\beta}$ SZ	8.04144	1.67353	6.36791	3.18396
$K_{\alpha}L_{\alpha}$ (1s)SZ	4.59123	0.30951	4.28172	2.14086
$K_{\beta}L_{\alpha}$ (3s)SZ	3.03069	0.33328	4.25700	2.12850
Total energy(SZ)	14.90663	7.45332
$k_{\alpha}k_{\beta}$ DZ	8.07072	0.33328	7.73744	3.86872
$K_{\alpha}L_{\alpha}$ (1s)DZ	3.12981	0.35686	2.77295	1.38647
$K_{\beta}L_{\alpha}$ (3s)DZ	4.61988	0.33328	4.28660	2.14330
Total energy(DZ)	14.79699	7.39850
$k_{\alpha}k_{\beta}$ mult-term	8.05158	2.68386	6.40262	3.20131
$K_{\alpha}L_{\alpha}$ (1s) mult-term	4.54725	0.30841	4.23884	2.11942
$K_{\beta}L_{\alpha}$ (3s) mult-term	4.54725	0.30841	4.23884	2.11942
Total energy _{mult-term}	14.86530	7.43265
Experimental[20]	7.47807

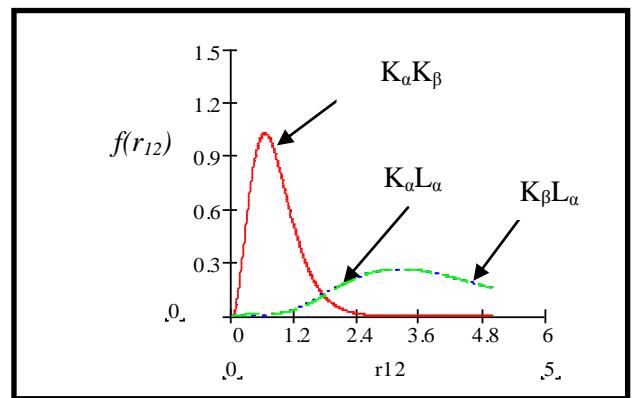
In table 3, evaluated the repulsion energy expectation values $\langle V_{ee} \rangle$, the attractive energy expectation values $\langle V_{en} \rangle$ and total energy expectation values $\langle E \rangle$ for Li-atom by using expectation values for $\langle r^{-1} \rangle$ and $\langle r_{12}^{-1} \rangle$ from tables 1,2. We can conclude the total energy expectation value obtained by two-Slater (DZ) determinant is in good agreement with multi-Slater (mult-term) determinant and with experimental value (-7.279913) but the total energy expectation value obtained by one-Slater (SZ) is inaccurate. This paper has been designed to investigate the physical properties reflected from the figures 1,2. The result which produced the main atomic properties are one-particle density $D(r_1)$ and inter particle distribution function $f(r_{12})$. One may find the following notes for double-Zeta orbital including those resulting errors in singlet and triple states where $KL(^1S) \neq KL(^3S)$, but given some accurate for both Single-, multi-zeta wave functions.



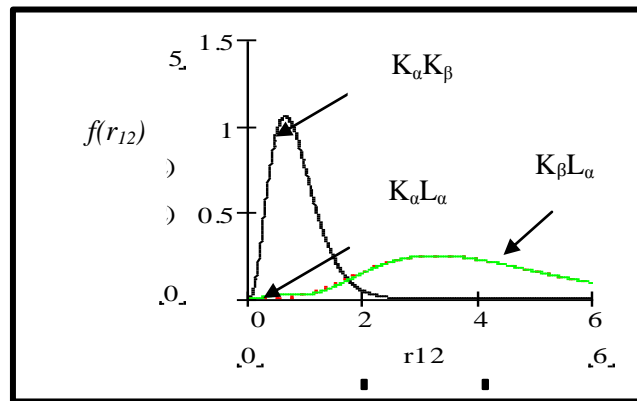
Figure(1): The one particle radial density function $D(r_1)$ for Li-atom



double -Zate

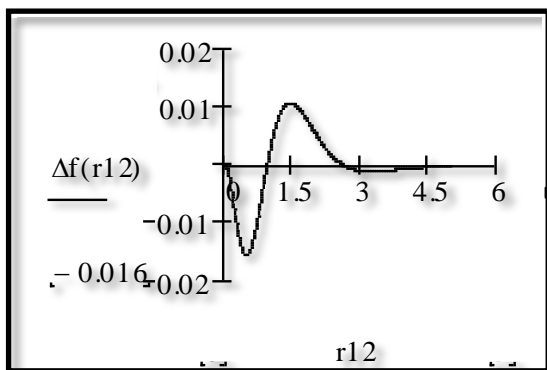


Single -Zate

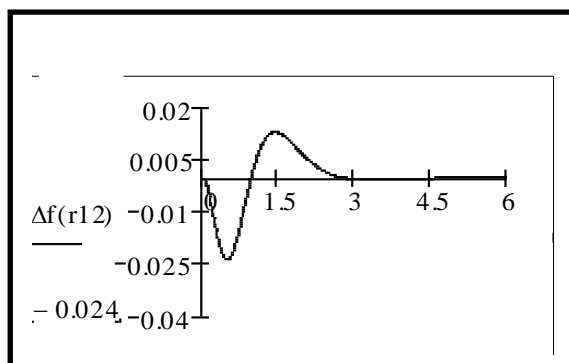


7-term -Zate

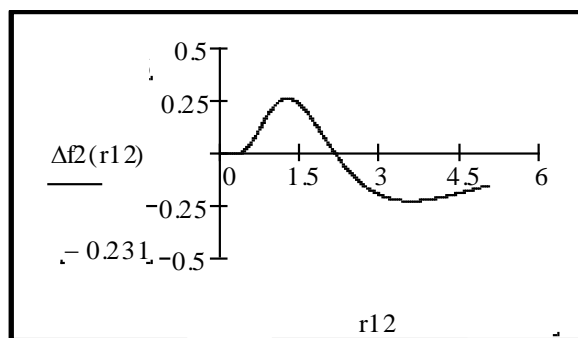
Figure(2) inter-particle distribution function $f(r_{12})$ for Li-atom.



7-term -Zate



Single -Zate



double -Zate

Figure3: Fermi hole is plotted as a difference between $f(r_{12})$ of $K\alpha$ $L\alpha$ -shell (triplet state) and $K\beta$ $L\alpha$ -shell (singlet state) for Li-atom

Fermi hole is plotted as a difference between $f(r_{12})$ of $K\alpha$ $L\alpha$ -shell (triplet state) and $K\beta$ $L\alpha$ -shell (singlet state) for Li, by using data(2004) for mult-term-Zeta, and both SZ,DZ for data (1974) by Clementi and Rotti presented in Figures3, From these figures it can be well-known in general that the radius of Fermi hole agreement in both SZ(0.013 when $r_{12} = 1.57$) and mult-term Zate(0.011 when $r_{12} = 1.56$), compared this result with Ref [21] we found agreement between them, while Double-Zate given error in result presented in figure 3.

Reference

- [1] S.M.Mekelleche , A.B.Ahmed., J.Theor ChemAcc ,V103(2000).
- [2] I.I.Guseinov, B.A.Mamedov,J.Mathamatical Chemistry,V43(2007).
- [3] T.Koga, H.Matsuyama ,J. Chemical physics latters,V392(2004).
- [4] P. Maldonado, A. Sarsa, E. Bendí a,F.J.Gálvez, J. Atomic Data andNuclearData tables(2010).
- [5] C.C.Roothaan,J.Rev.Mod .phys,V32(1960).
- [6] N.Clementi and C .Roetti,J. AtomicData and NuclearData tables(1974).
- [7] A.Sarsa, F.J.Gálvez, E. Bendí a, J.Atomic Data and Nuclear Data tables(2004).
- [8] A.Sarsa, F.J.Gálvez, E. Bendí a, J. Phy.B.V36(2003).
- [9]M.L.Rustg and P.Tiwar,J. chemical;physics ,V39(1963).
- [10]R.R.ZopeandB.I.Dunlap,j.chemical physics ,V124(2006).
- [11]I.Guseionv,J.Mod.Model.v10(2000)
- [12]S.M.Mekelleche and A.B.Ahemd , J.Theor.chem.Acc,V103(2000).
- [14]K.E.Banyard and G.J.Seddon,V.58 (1973).
- [15]A.B.KarramPh.D Thesis college of education (Ibn-AL-Haitham) Baghdad (2004).
- [16] C.Bunge, J.Barrientas andA.Bunge,J. Atomic Data and Nuclear Data Tables53(1993).
- [17] K.E.Banyard and K.H.AL-Bayati,J. Phys B; Atom Molec.phys.,19(1985).
- [18] M.N.Murshed,Ph.D. thesis college of education (Ibn-AL-Haitham) Baghdad(2001).
- [19] S.M.Ali,Ph.D,thesis college of science for women Baghdad university (2006).
- [20] N.H.Beebe and S.Lunell,J. Phys B; Atom Molec.phys.V8(1975),
- [21]E.M.AL-Robayai,Ph.D,thesis college of science for women Baghdad university (2006).