Numerical Evaluation for the Electron- Electron Distribution Function for the Four-Electron Systems for $1s^2\ 2s^2$-State by using Hartree- Fock Method

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Abstract

The electron- electron distribution function $f(r_{12})$ has been evaluated for $1s^2\ 2s^2$ -state by using Hartree-Fock type wave function for many electron systems (Li-, and Be-atom) where Z=3,4 respectively and the inter particle expectation values $< r_{12}^{n} >$ has been evaluated too. Expectation values are also evaluated with compression between two ion for each individual electronic shell .

حساب دالة توزيع الكثافة الالكترونية للأنظمة رباعية الالكترونات باستعمال طريقة هارتري- فوك

الخلاصة

تم حساب دالة التوزيع الالكترونية للأنظمة الذرية المغلقة باستعمال دالة هارتري–فوك لذرتي الليثيوم والبرليوم (العدد الذري= 3و4) حسب التسلسل وأيضا تم حساب القيم المتوقعة والمقارنة بين الذرتين لكل الأغلفة الالكترونية.

Introduction

In 1961 Coulson & Neilson derived analytic expression for $f(r_{12})$ for the ground state of helium atom using simple wave function. Dressel & King(1994) developed formulas for the calculation of $f(r_{12})$ for three- electron atoms which were based on more accurate wave function that are described by Hylleraas -type wave function.

1. Mathematical determination of electron-electron distribution function:

If $\Psi(x_1, x_2, \ldots\ldots, x_n)$ denotes an N- electron wave function , where x_a denotes a combined space and spin coordinate $x_i = (r_i, r_i)$ .the two particle density for N- electron system can be defined as Banyard & Al-Bayati (1986):

$$\Gamma(x_m, x_n) = \binom{N}{2} \int \psi^{*}(x_1, x_2, \text{----} x_n) \,.\, \psi(x_1, x_2, \text{---} x_p)\, dx_p, \text{---}\, dx_n \qquad \ldots..(1\text{-}1)$$

The factor $\binom{N}{2}$ ensures that the two- particle density , $\acute{\Gamma}(x_m, x_n)$ is normalized to the number of electron pairs with in the system:

$$\Gamma(x_m, x_n)\, dx\, dx = \binom{N}{2} \qquad \ldots.(1\text{-}2)$$

And dx_p ,---------- dx_n indicates integration-summation over combined space and spin coordinates of all N-electrons except m and n for four electron system. The density for individual electronic shells is obtained by partitioning (Γ) into its pair-wise components so that the two particle density can be written as:

$$\Gamma(x_m, x_n) = \sum_{i=1}^{N} \Gamma_{ij}(x_m, x_n) \qquad (1\text{-}3)$$

Where i and j labels occupied spin in restricted (HF) description of an N-electron system, then the radial electron -electron distribution function *f*(r_{12}).

The inter particle distribution function associated with the spin orbitals pairs(i,j)is given by Al-Bayati & Mashat(1987):

$$f_{ij}(r_{12})dr_{12} = \int \Gamma_{ij}(x_1,x_2)dx_1dx_2/dr_{12} \quad .(1\text{-}4)$$

Where $\Gamma_{ij}(x_m,x_n)$ is the spin free second order density x_1 and x_2 represent the space coordinates of electron 1 and electron 2, respectively .

Such that , for any pairs(i,j) label we have:

$$\int_0^\infty f(r_{12})\, dr_{12} = 1 \qquad .....(1\text{-}5)$$

Where for convenience we have set n , and m to be 1,2 respectively.

Since each distribution function for the inter-electronic separation r_{12} will be normalized to the same value , the condition of normalization(Banyard &Mashat,1977).

From equation(1-2) the integration over the spin coordinates reduces to:

$$f(r_{12}) = \int \Gamma_{ij}(r_1,r_2)\, dr_1dr_2/dr_{12} \qquad ......(1\text{-}6)$$

Where the integration over all coordinates except r_{12} and the integration region in equation (1-6) is just used by Coulson & Neilson(1961) the f(r_{12}) con be defined by:

$$f(r_{12}) = 8\pi^2 r_{12}\left[\begin{array}{l} \displaystyle\int_{r_{12}}^{\infty} r_1 \int_{r_1-r_{12}}^{r_1+r_{12}} \Psi^2(r_1,r_2,r_{12})dr_2dr_1 + \\ \displaystyle\int_{0}^{r_{12}} r_1 \int_{r_{12}-r_1}^{r_{12}+r_1} \Psi^2(r_1,r_2,r_{12})dr_2dr_1 \end{array}\right] \qquad .....(1\text{-}7)$$

2.Theory and wave functions:

The wave function employed is given by (Enas Al-Robayi, 2001):

$$\phi_{nl} = \sum_{i=0}^{N} C_n^i X_{nl}^i \qquad .....(2\text{-}1)$$

where *Cn* are the variation ally determined expansion coefficient , and X_n is the spin function defined as :

$$X_{nlm}(r,\Theta,\Phi) = R_{nl}(r)\, Y_{lm}(\Theta,\Phi) \qquad .....(2\text{-}2)$$

$$\phi_{nl} = \sum_{i=1}^{N} C_n^i N_{nlm} r^{ni-1} e^{-(\xi i.r)} y_{lm} \qquad .....(2\text{-}3)$$

where ξ → the orbital exponent By using equation (1-8) to fined f(r_{12}) for K-shell for –electron system :

$$A = \int_0^{r12} r1dr1 \int_{|r12-r1|}^{r12+r1} 1S^2{}_{(1)}!S^2{}_{(2)} \qquad .....(2\text{-}4)$$

$$A = \int_0^{r12} 1S^2{}_{(1)}r1dr1 \int_{|r12-r1|}^{r12+r1} !S^2{}_{(2)} \qquad .....(2\text{-}5)$$

$$A = A_1 A_2$$

$$A_2 = \int_{|r12-r1|}^{r12+r1} \sum_i^4 \sum_j^4 C_iC_j N_i N_j (r_2)^{ni-1}$$

$$(r_2)^{nj-1} e^{-\xi i-r2}\ e^{-\xi j-r2}\ r_2 d\, r_2 \quad ...(2\text{-}6)$$

$$N_{n\ell m_\ell} = \frac{(2\xi)^{n+0.5}}{[(2n)!]^{0.5}} \quad \text{.....(2-7)}$$

$$A_2 = \sum_i^4 \sum_j^4 A_2^{ij} = A_2^{11} + A_2^{22} + A_2^{33} + A_2^{44} + 2A_2^{12} + 2A_2^{13} + 2A_2^{14} + 2A_2^{24} + 2A_2^{34} \quad \text{.....(2-8)}$$

$$A_2 = \int_{|r12-r1|}^{r12+r1} C_i C_j N_i N_j (r_2)^{2ni-1} e^{-2\xi i-r2}\, d r_2 \quad \text{.....(2-9)}$$

and so for all the terms in equation(2-8) take the form of equation(2-9)then:

$$A = \int_0^{r12} \{A_2^{11} + A_2^{22} + A_2^{33} + A_2^{44} \\ 2A_2^{12} + 2A_2^{13} + 2A_2^{14} + 2A_2^{23} + 2A_2^{24} + 2A_2^{34}\}. \\ \{A_1^{11} + A_1^{22} + A_1^{33} + A_1^{44} + \\ 2A_1^{12} + 2A_1^{13} + 2A_1^{14} + 2A_1^{23} + 2A_1^{24} + 2A_1^{34}\} dr_{12} \quad \text{.....(2-10)}$$

$$A_1^{11} = C_1 C_2 N_1 N_1 r_1^{2nl-1} e^{-2\xi . r1} dr1 \quad \text{.....(2-11)}$$

$$A = \sum_i^4 \sum_j^4 \sum_k^4 \sum_l^4 \int_0^{r12} A_2^{ij} A_1^{kl} \quad \text{.....(2-12)}$$

The same way we solve the second part of integral for k- shell for (r_{12}).From equation (1-8) and finally we yet:

$$F(r_{12}) = 8\Pi^2 r_{12} \sum_i \sum_j \sum_k \sum_l \{\int_0^{r12} A_2^{ij} A_1^{kl} + \int_{r12}^{\infty} B_2^{ij} B_1^{kl}\} \quad \text{.....(2-13)}$$

where $\int$ B_2^{ij} B_1^{kl} represent the second part of integral for K-shell for f(r_{12}) from equation(1-7)and take the value as in equation(2-6),(2-8),(2-9),(1-13) respective except the limit of integration . for the Harare-Fock(HF)two particles density, the partitioning into-pair-wise components(i,j)is both exact and straightforward ,yielding:

$$\Gamma_{HF}(x_m,x_n) = \frac{1}{2}\sum_i^N [\phi_i(x_m)\,\phi_j(x_n) - \phi_j(x_m)\,\phi_i(x_n)]^2 \quad \text{....(2-14)}$$

where, ϕ_i is the occupied normalized HF spin ,orbital .

3.Two-particle density for four electron atom or ion:

The two particle density is:

$$\Gamma_{HF}(1,2) = \Gamma_{ij}(1,2) = \frac{1}{2}\sum [\phi_i(x_m)\,\phi_j(x_n) - \phi_j(x_m)\,\phi_i(x_n)]^2 \quad \text{......(3-1)}$$

where

ϕ_1(i)= 1s(i) α (i)

ϕ_2(i)= 1s(i) β(i)

ϕ_3(i)= 2s(i) α (i)

$\phi_4(i) = 2s(i)\,\beta(i)$ where i=1 or 2

$\Gamma = \Gamma_{12}+\Gamma_{13}+\Gamma_{14}+\Gamma_{23}+\Gamma_{24}+\Gamma_{34}$ ….(3-2)

$= \tfrac{1}{2}\,[1s_{(1)}\alpha_{(1)}\,1s_{(2)}\beta_{(2)} - 1S_{(1)}\beta_{(1)}1S_{(2)}\alpha_{(2)}]^2$

$+ \tfrac{1}{2}\,[1s_{(1)}\alpha_{(1)}\,2s_{(2)}\,\alpha_{(2)} - 2S_{(1)}\alpha_{(1)}\,2S_{(2)}\alpha_{(2)}{}^2$

$+ \tfrac{1}{2}\,[1s_{(1)}\alpha_{(1)}\,2s_{(2)}\,\beta_{(2)} - 1S_{(1)}\beta_{(1)}\,1S_{(2)}\alpha_{(2)}]^2$

$+ \tfrac{1}{2}\,[1s_{(1)}\beta_{(1)}\,2s_{(2)}\,\alpha_{(2)} - 2S_{(1)}\alpha_{(1)}\,1S_{(2)}\beta_{(2)}]^2$

$+ \tfrac{1}{2}\,[1s_{(1)}\beta_{(1)}\,2s_{(2)}\,\beta_{(2)} - 2S_{(1)}\,\beta_{(1)}\,1S_{(2)}\beta_{(2)}]^2$

$+ \tfrac{1}{2}\,[2s_{(1)}\alpha_{(1)}\,2s_{(2)}\,\beta_{(2)} - 2S_{(1)}\beta_{(1)}\,1S_{(2)}\alpha_{(2)}]^2$

…..(3-3)

$\acute{\Gamma} = \acute{\Gamma}_{12}+\acute{\Gamma}_{13}+\acute{\Gamma}_{14}+\acute{\Gamma}_{23}+\acute{\Gamma}_{24}+\acute{\Gamma}_{34}$ ….(3-4)

not $\acute{\Gamma}$ spineless function

$\acute{\Gamma}=[1S_{(1)}1S_{(2)}]^2$ for $K\alpha\,K\beta$

$\acute{\Gamma}=[1S_{(1)}1S_{(2)}]^2$ for $K\alpha\,K\beta$

$+[\,2S_{(1)}2S_{(2\,)}\,]^2{}_4$

$+2[1S_{(1)}2S_{(2\,)}]^2{}_{(13+14+23+24)}$

first term

$+2[2S_{(1)}1S_{(2)}\,]^2{}_{(13+14+23+24)}$

second term

$-2[1S_{\,(1)}2S_{(1)}][2S_{(2\,)}1S_{\,(2)}]^2{}_{(13+24)}$

cross term($\alpha\,\alpha$ and $\beta\,\beta$)

....(3-5)

$\Gamma_{HF}(1,2)=\Gamma_{K(1S)}+\Gamma_{L}(_{1S})+\Gamma_{KL(3S)}+\Gamma_{KL(3S)}$
$+\Gamma_{KL(3S)}+\Gamma_{KL(1S)}$ …..(3-6)

$\Gamma_{HF}\,(1,2)=\Gamma_{K(\alpha B-B\alpha)}+\Gamma_{L(\alpha B-B\alpha)}$
$+\Gamma_{kL(\alpha\,\alpha)}+\Gamma_{KL(BB)}$
$+\,\Gamma_{KL(\alpha B-B\alpha)}+\Gamma_{KL(\alpha B-B\alpha)}$ …..(3-7)

$\Gamma_{HF}(1,2)=\Gamma_{K(1S)}+\Gamma_{L(1S)}+3\Gamma_{KL(3S)}+\Gamma_{KL(1S)}$ …..(3-8)

4.Expectation values are defined as :

$$< r_{12}^{n} > = \int_0^\infty f(ij)\, r_{ij}\; dr_{ij} \qquad ….(4\text{-}1)$$

Given the formula for $f(r_{12})$ in equation (1-7) then :

$$< r_{ij}^{n} > = 8\pi^2 \int \sum_i\sum_j\sum_k\sum_l \{\int_0^{r12} A_2^{ij}A_1^{ij} + \int_{r12}^{\infty} B_2^{kl}B_1^{kl}\} r_1 dr_1 \qquad …..(4\text{-}2)$$

Results

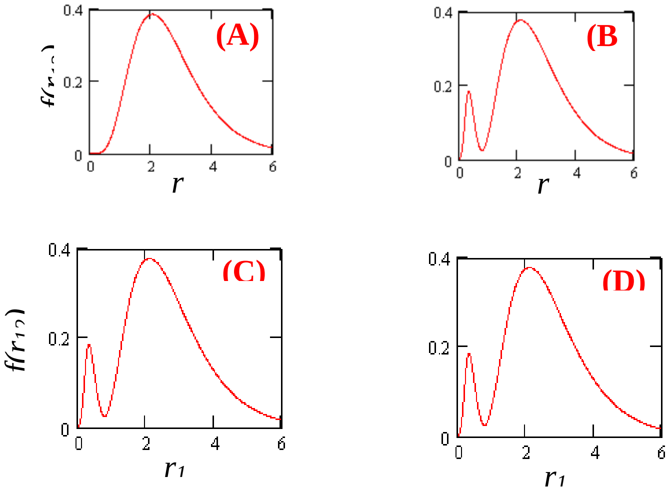
Table(I):The maximum and minimum values and their location which occur in the study of electron-electron destitution function $f(r_{12})$ in each individual electronic shell for Li-atom and Be-atom . Data for Li-atom was taken from Bushra(2002):

Table(II):The inter-particle expectation value for each individual electronic shell of Li-,and Be-atom and Δr_{12}. Data for published by Banyard & Mashat(1987):

Atom	Be(Z=4)		Li(Z=3)	
shell	r_{12}	$f(r_{12})$	r_{12}	$f(r_{12})$
K(^{1}s)	0.5	1.997	0.8	1.3650
L(^{1}s)	2.4	0.475	7	0.1183
KL(^{1}s)	0.35	0.182	0.6	0.0125
	0.52	0.591	3.14	0.1785
KL(^{3}s)	1.8	0.591	4	0.1785

Figure(I): Electron-electron distribution function $f(r_{12})$ for Li-atom for each individual electronic shells:

shell	Function	n=-1	n=0	n=1	Δr_{12}
K(^{1}s)	Present work	2.7951	0.9998	0.4997	0.2436
	Banyard & Mashat	2.7251	1	0.4925	0.2416
L(^{1}s)	Present work	0.5742	0.9999	2.5111	1.1546
	Banyard & Mashat	0.5441	1	2.5436	1.1470
KL(^{1}s)	Present work	0.7220	0.9998	1.8462	0.7998
	Banyard & Mashat	0.7110	1	1.2254	3.5241
KL(^{3}s)	Present work	0.6214	1	1.7441	0.8214
	Banyard & Mashat	0.6101	1	1.7991	0.8610



Discussion

From table (I) it is seen that the maximum probability of finding inter-particle distribution function *f(r₁₂)* when we go from Li^- to B^+ increases, and it is also observed that the location of these maximum decreases.

From comparison between the $f(r_{12})$ for the inner-shell $K_\alpha K_\beta$ and the outer shell $L_\alpha L\beta$ it can be seen that the density curve in L-shell is more diffuse than that for K-shell as a consequence of radius of is and 2S respectively ((as we seen in figure 1-A and B)), and the comparison between the $f(r_{12})$ for Be-atom is greater than that for Li-atom as expected.

The probability of finding the function $f(r_{12})$ for $KL(\alpha\beta-\beta\alpha)$

and $KL(\alpha\alpha,\beta\beta,\alpha\beta+\beta\alpha)$ for B-atom is shown in figure(I-C and D) respectively, we noticed that at small r_{12} the $f(r_{12})$ distribution function will be influenced mainly by the electron-pair behavior when the outer electron has penetrated the K-shell. For the triplet state curve, the existence of the Fermi effect produces a flat region at small r_{12}. on the other hand, by marked contrast, the singlet curve is seen to possess a small local maximum, clearly , when K- and L-shell electrons have different spin assignments but both described by orbital of S-type symmetry, a doubly occupancy can occur in the K-shell region with characteristics similar to that for L-shell. In table II the expectation values and the standard deviation Δr_{12} was reported. We found that the value of K-shell is greater than those for L-shell at n=-ve, whereas for n=+ve the result for L-shell is greater than those in K-shell because L-shell is the outer most shell (i.e. when we see the atom we begin from the outer shell to the inner shell), since the standard deviation Δr_{12} determine how the electron-electron distribution function $f(r_{12})$ for each shell diffused, as expected L-shell is more diffused than in K-shell. The values of $\langle r_{12}^n \rangle$ increase when n tends to increase. The total expectation values $\langle r_{12}^n \rangle$ when (n=1,-1) is in agreement with the result published by Banyard & Mashat(1987).

Conclusions

From this work , we deduce some notes from comparison ions:

1.Due to the Fermi effect , the inter-particle distribution function $f(r_{12})$ KL(^{3}S-triplet state)gives a flat region at small r_{12} ,where as the results for KL(^{1}S – singlet state) do not exhibit a flat region and further, we also not that for each system the values of $f(r_{12})$ KL(^{1}s) is larger than that for KL(^{3}S) where r_{12} is small .

2.The electron-electron distribution curves $f(r_{12})$calculated from HF wave function shrink in ward as the atomic number increases.

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