Evaluation of the one electron expectation values for different wave functions

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Abstract

The aim of this work is to evaluate the one-electron expectation values $< r^n >$ from the radial electronic density function D(r) for different wave functions for the ^2S state of Li atom. The wave functions used were published in 1963,1974 and 1993 , respectavily. Using Hartree-Fock wave function as a Slater determinant has used the partitioning technique for the analysis open shell system of Li ($1s^2$ 2s) State.

WAVEFUNCTIONS

The properly antisymmetrized many electron wave function can be constructed from the spin orbital by forming a Slater determinant

$$\Phi(1,2,..,N) = (N!)^{-1/2} \, | \phi(1)\, \phi(2) \ldots \phi(N) | \qquad \ldots\ldots (1)$$

Where the one electron functions ϕ are called spin-orbital and depend on both spin function σ and spatial functionThe spatial function $\phi_{n\ell}$ is defined by.

$$\phi_{n\ell} = \sum_{i=1}^{J} c_n^i \, \chi_{nlm}^i \qquad \ldots\ldots (2)$$

j=6 for Clementi and Roetti [1] and j=6 for Weiss[2] and j=7 for Bunge et al [3].The basis function χ_{nlm} as standard normalized Slater-Type Orbitals (STO's) and is given by

$$\chi_{nlm}(r,\theta,\phi) = R_{nl}(r)\, Y_{lm}(\theta,\phi) \qquad \ldots\ldots (3)$$

where

$$R_{nl}(r) = N_{nlm}\, S_{nl}(r) \qquad \ldots\ldots (4)$$

$N_{n\ell m}$ is the normalization constant, and given as

$$N_{nlm} = (2\cdot\xi)^{(n+1/2)} / [(2\cdot n)!]^{1/2} \qquad \ldots\ldots (5)$$

Then

$$S_{nl}(r) = r^{n-1} \cdot e^{-(\xi \cdot r)} \qquad \ldots\ldots (6)$$

where $S_{n\ell}(r)$ is called the Slater-Type-Orbitals (STO's). c_n in Eq. (2) represents the coefficients of $\chi_{nlm}(r)$ *and* $Y_{lm}(\Omega)$, *and* ξ is the orbital exponent

THEORY

The radial electronic density function D(r) is evaluated from [4]

$$D(r) = \iint r^2 \rho(r)\, d \qquad \ldots\ldots (7)$$

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where

$$\rho(\mathbf{r}) = \int \Phi^*(1,2,..,N)\,\Phi(1,2,..,N)\,ds1$$

$$d(2,3....N) \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \;(8)$$

The following standard notation has been employed in Eqs.(7) and (8). $d\Omega = \sin\theta\, d\theta\, d\varphi$, 1,2,…N denote a combined spatial and spin coordinates for electrons ,$\Phi(1,2,..,N)$ is a normalized wave function. The one particle expectation values $< r1^n >$ can be calculated from The radial electronic density function D(r) :

$$< r1^n > = \int D(r1)\, r1^n\, dr1 \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\;(9)$$

Note that , when n=0 the value of $< r1^n >$ must be equal one.
By using the following integral :

$$\int x^n e^{-ax}\, dx = n! / a^{n+1} \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\;(10)$$

The $< r1^n >$ can be written as follows :

$$< r1^n > = \sum\sum \; C_i C_j N_i N_j \{(n_i + n_i + n)! / (\zeta_i + \zeta_j)^{n_i + n_j + n + 1} \} \;(11)$$

where C_i C_j are the variationally determined expansion coefficient for 1s or 2s orbitals, and N_i N_j are the normalization constant.

Results and Discussion

The examination of the one particle expectation value $\langle r1^n \rangle$ for kαkβ shell for different wave functions presented in Table 1 , and for kαLα (= kβLα) shell presented in Table 2 , and for total Li atom presented in Table 3. Figure 1 shows the expectation values $\langle r1^n \rangle$ for Kαkβ and kαLα (= kβLα) shell for different wave functions (published in 1963,1974,1993) plotted against n (where n takes values from –2,-1,0,+1,+2)

Table 1 Expectation values $\langle r1^n \rangle$ for kαkβ shell for different wave functions,Weiss (1963)[1], Clementi and Roetti (1974) [2] and Bunge et al (1993) [3].

$< r1^n >$ For Lithium Z=3			
n	1963[1]	1974[2]	1993[3]
- 2	14.88859	14.890732	14.888381
- 1	2.684978	2.685039	2.685000
+ 1	0.573123	0.573139	0.573125
+ 2	0.446807	0.446821	0.446803

Table 2 Expectation values $\langle r1^n \rangle$ for kαLα (= kβLα) shell for different wave functions,Weiss(1963)[1], Clementi and Roetti (1974) [2] and Bunge et al (1993) [3].

$< r1^n >$ For Lithium Z=3			
n	1963[1]	1974[2]	1993[3]
- 2	7.661916	7.663178	7.66193
- 1	1.515184	1.515223	1.515195
+ 1	2.223197	2.223328	2.22339
+ 2	9.08769	9.092319	9.092645

Table 3 Expectation values $\langle r1^n \rangle$ for total Li atom for different wave functions,Weiss(1963)[1], Clementi and Roetti (1974) [2] and Bunge et al (1993) [3] , where the normalized total $\langle r1^n \rangle$ value obtained here by taking $1/3 \sum < r1^n >$

$< r1^n >$ For Lithium Z=3			
n	1963[1]	1974[2]	1993[3]
- 2	10.070807	10.072363	10.070729
- 1	1.905115	1.905162	1.90513
+ 1	1.673171	1.673264	1.6733
+ 2	6.207419	6.210511	6.210721

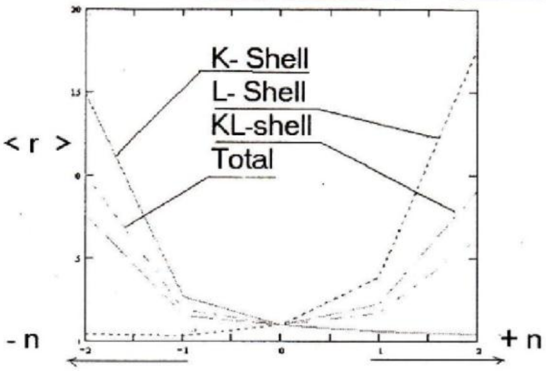

Figure 1 Variation of expectation values $\langle r1^{n} \rangle$ for Kαkβ and kαLα (= kβLα) shell for different wave functions (published in 1963,1974,1993) plotted against n (where n takes values from –2,-1,0,+1,+2)

From the above results we conclude the followings

1: A comparison of the HF values for $\langle r1^{n} \rangle$ for kαkβ shell shows that the relation

$(\langle r1^{-2} \rangle) \rangle (\langle r1^{-1} \rangle) \rangle (\langle r1^{+1} \rangle) \rangle (\langle r1^{+2} \rangle) \rangle$

will fit for all the types of the wave functions .

2: In the comparison of the one particle expectation values $\langle r1^{n} \rangle$ (when n=-2,-1,0,+1,+2 It is found that the results for n = -2 as

HF(1974) › HF(1963) › HF(1993) and for n = -1 as

HF(1974) › HF(1993) › HF(1963) and for n = +1 as

HF(1974) › HF(1993) › HF(1963) and for n = +2 as

HF(1974) › HF(1963) › HF(1993)

3: For the inter-shell (kαLα and kβLα) we get the $\langle r1^{n} \rangle$ for n>1 the relation HF(1974) › HF(1993) › HF(1963), whereas for n < 1 ,we get

HF(1993) › HF(1974) › HF(1963)

4: It was found that $\langle r1^{-n} \rangle$ value is greater than $\langle r1^{n} \rangle$ where n=+1and +2 for all types of the wavefunction in each individual electronic shell.

5: For total atom, it was found that $\langle r1^{-2} \rangle$ value is greater than $\langle r1^{-1} \rangle$ value and this is greater than $\langle r1 \rangle$ for all types of wave functions ,and also found that $\langle r1^{+2} \rangle$ value is greater than $\langle r1^{-1} \rangle$ and $\langle r1 \rangle$. $\langle r1^{-2} \rangle$ greater than $\langle r1^{2} \rangle$

Conclusion

All the wavefunctions give negligible deffernces for n = -1,1,2 ; whereas for n = - 2 the Clementi and Roetti wavefunction(1963) gives higher value than that derived from Bunge et al wavefunction (1993) . Weiss wavefunction(1974)gives lower results than that for Clementi and Rotti wavefunction

References

1. Weiss,A.W.1963 wavefunctions and oscillator strengths for the Lithium isoelectronic sequence, J.Chem.Phys.,39,1262
2. E.Clementi and C.Roetti, 1974 Atomic Data and Nuclear Data tables,Atom.Data Nucl.Data Tables, 14,177
3. C.F.Bunge,J.A. Barrientos And A.V. Bunge, 1993 Roothaan – Hartree – Fock ground – state atomic wave function,Atom. Data Nucl. Data Tables, 53,133
4. King, F.W. and P.R.Dressel 1989 Compact expressions for the radial electronic density functions for the ^{2}S states of three – electron system,J .Chem.Phys.90 6449

حساب القيمة المتوقعة للالكترون المفرد ولدوال موجية مختلفة

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الخلاصة

هدف البحث هو لحساب القيم المتوقعة للالكترون المنفرد $< r^n >$ بأستخدام دالة الكثافة الألكترونية القطرية $D(r)$ لدوال موجية مختلفة للحالة ^2S لذرة Li. الدوال الموجية المستخدمة منشورة للسنوات ١٩٦٣، ١٩٧٤، ١٩٩٣ على التوالي. أستخدمت دالة هارتوي فوك كمصفوفة سليتر وتقنية التجزئة لدراسة النظام المفتوح لذرة الليثيوم $(1s^2\,2s)$ Li.