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Calculation of the Standard deviation and Nuclear Magnetic Shielding Constant for Lithium atom

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Abstract:

The division Technique has been used for the analysis of atomic open- shell of Lithium atom in the($1S^22S$) state by using Hartree-Fock(HF) wavefunction published by W.Weiss. The HF method is widely used and its based on the variational theory [1]. The aim of this work to study the Standard deviation and nuclear magnetic shielding constant for each shell where there are three shells for Li- atom (K-shell, KL(singlet),KL(triplet)

الخلاصة :

أستخدمت طريقة التجزئه للأنظمة الذرية ذات الاغلفة المفتوحة لذرة الليثيوم للحالة($1S^22S$) بأستخدام دالة هارتري – فوك التي وضعها . W.Weiss . طريقة هارتري فوك واسعة الاستخدام وتعتمد على نظرية التغاير [1]. لهدف من هذا البحث دراسة الانحراف المعياري وثابت التدريع المغناطيسي النووي لكل غلاف حيث ان هناك ثلاثة أغلفة هي(الغلاف K , الغلاف KL(الحالة المنفردة) , الغلاف KL((الحالة الثلاثية))

Theory:

1- Standard deviation

The standard deviation of the distance of the test electron from the nucleus r_1, is defined as [2]:

$$\langle r_1^n \rangle = \int D_{ij}(r_1)\, r_1^n \, dr_1 \qquad ......(2)$$

Where

$$\Delta r_1 = \sqrt{\left\langle r_1^2 \right\rangle - \left\langle r_1 \right\rangle^2} \qquad ......(1)$$

and the notation $\langle\ \rangle$ Represented the expectation value**.**

The radial density distribution function $D_{ij}(r_1)$ is a measure of the probability of finding an electron in each shell and it is defined as [3]:

$$D_{ij}(r_1) = \int_0^\infty D_{ij}(r_1, r_2)\, dr_2 \qquad ......(3)$$

In each individual electronic shell, the two-particle radial density distribution function $D(r_1\ r_2)$ is defined by [4] .

$$D(r_1, r_2) = \iint \Gamma(r_1, r_2)\, r_1^2\, r_2^2\, d\Omega_1\, d\Omega_2 \qquad ......(4)$$

where $d\Omega_i$ denotes integration over all angular coordinates of the position vector r_i, and it is defined as:

$$d\Omega_i = \sin\theta_i \, d\theta_i \, d\phi_i \qquad \text{......(5)}$$

The normalize condition for the two-particle radial density distribution function $D(r_1,r_2)$ is defined as:

$$\iint D(r_1, r_2)\, dr_1\, dr_2 = 1 \qquad \text{......(6)}$$

For an N-electrons system, the two-particle density can be written as [4]:

$$\Gamma(x_m, x_n) = \begin{pmatrix} N \\ 2 \end{pmatrix} \int \Psi^*(x_1, x_2 \cdots, x_N)\Psi(x_1, x_2 \cdots x_N)\, dx_p \cdots dx_N \quad \text{..... (7)}$$

Where $dx_p.....dx_N$ indicate integrations of all N-electrons except m and n (m,n refer to electron labels).

The factor $\begin{pmatrix} N \\ 2 \end{pmatrix}$ ensures that the second-order density matrix $\Gamma(x_m, x_n)$ is normalized to the number of electron pairs within the system. We also have:

$$\int \Gamma(x_m, x_n)\, dx_m dx_n = \begin{pmatrix} N \\ 2 \end{pmatrix} \qquad \text{.......(8)}$$

and $\begin{pmatrix} N \\ 2 \end{pmatrix}$ can be written as:

$$\begin{pmatrix} N \\ 2 \end{pmatrix} = \left[\frac{N!}{2!(N-2)!} \right] \qquad \text{......(9)}$$

$$\begin{pmatrix} N \\ 2 \end{pmatrix} = 3 \qquad \text{(for Li – atom)} \qquad \text{......(10)}$$

2- Standard Deviation Δr_{12}

The standard deviation of the inter electronic distance of the two electrons, is defined as [5]:

$$\Delta r_{12} = \sqrt{\langle r_{12}^2 \rangle - \langle r_{12} \rangle^2} \qquad \text{......(11)}$$

The inter-particle expectation values can be calculated from [6]:

$$\langle r_{12}^{n} \rangle = \int f_{ij}(r_{12}) r_{12}^{n} \, dr_{12} \quad \text{.. …(12)}$$

The inter-particle distribution function associated with the spin-orbital pair (i, j) is given by [6]:

$$f(r_{12}) = 8\pi^2 r_{12} \left\{ J_1 + J_2 \right\} \quad \text{......(13)}$$

Where i , j represented the spin-orbital labels [7] .

The radial integration

$$J_1 = \int_0^{r_{12}} r_1 dr_1 \int_{r_{12}-r_1}^{r_{12}+r_1} \Gamma(r_1, r_2) r_2 dr_2 \qquad when \quad r_{12} > r_1 \quad \text{.......(14)}$$

and

$$J_2 = \int_{r_{12}}^{\infty} r_1 dr_1 \int_{r_{12}-r_1}^{r_{12}+r_1} \Gamma(r_1, r_2) r_2 dr_2 \qquad when \quad r_1 > r_{12} \quad \text{......(15)}$$

3- Nuclear Magnetic Shielding Constant σ_d

The Nuclear Magnetic Shielding Constant is determined from the formula [8]:

$$\sigma_d = \frac{1}{3}\alpha^2 \left\langle \Psi \left| \sum_{i=1}^{n} (r_i)^{-1} \right| \Psi \right\rangle \quad \text{.......(16)}$$

where α is the fine structure constant and it is equal to(7.297353*10^{-3} au(atomic unit))

and r_i represented the distance from the nucleus to the electron (i)

The results:

Table(1) : Values of one-particle expectation values for different values of (n) where n=(-1,0,1,2) ,Standard deviation and the Nuclear Magnetic Shielding Constant for individual electronic shells and the total values of Li- atom .

shell	n = -1	n = 0	n= 1	n = 2	Δr_1	$\sigma_d * 10^{-5}$
K- shell	2.6850	1.000	0.5731	0.4460	0.3440	4.7660
KL(S)	1.5155	1.000	2.2232	9.0876	2.0358	2.6906
KL(T)	1.5155	1.000	2.2232	9.0876	2.0358	2.6906
total	1.9053	1.000	1.6731	6.2070	1.4718	3.3824

The total values of $<r_1^n>$ are calculated from the equation :

$$<r_1^n>_{total} = 1/3\ [<r_1^n>_{K\text{-shell}} + <r_1^n>_{KL(S)} + <r_1^n>_{KL(T)}]$$

Table(2) : Values of 1nter-particle expectation values for different values of (n) where n=(,0,1,2) and Standard deviation for individual electronic shells and the total values of Li- atom .

shell	n = 0	n= 1	n = 2	Δr_{12}
K- shell	1.000	0.8395	0.8936	0.4345
KL(S)	1.000	3.9218	18.1753	1.6716
KL(T)	1.000	3.9272	18.1757	1.6589
total	1.000	2.8961	12.4148	1.2550

The total values of $<r_{12}^n>$ are calculated from the equation :

$$<r_{12}^n>_{total} = 1/3\ [<r_{12}^n>_{K\text{-shell}} + <r_{12}^n>_{KL(S)} + <r_{12}^n>_{KL(T)}]$$

Conclusions :

1- When n=0 , then $<r_1^n>= <r_{12}^n> =1$,this represent the normilzation condition .

2- For KL(S) and KL(T) , the Standard deviation Δr_1 and the Nuclear Magnetic Shielding Constant σ_d are prefect because the Hartree- Fock approximation neglected the electron correlation effect .

3-The values of Nuclear Magnetic Shielding Constant σ_d for K- shell larger than for KL(S) and KL(T) because K- shell is nearest for nucleus .

4-The values of Δr_{12} (K- shell) > Δr_{12} (KL(S)) > Δr_{12} (KL(T)) and these values increases as (n) increases because the nuclear charge effect increases .

References:

1- A. Krasheninnikov , Introduction to electronic structure simulations , lecture 3 (Hartree-Fock method) , 2006 .
2- R .Benesch , J .Phys. B : Atom . Mole . Phys . 4 ,1403 ,(1971) .
3- K. O.AL- Baiti Ph.D. Thesis, College of education (Ibn- Haithem) , (2004).
4- K. H. AL-bayati, Ph.D. Thesis, Leicester University, England, (1984).
5- G. K. Taylor and K. E Banyard, Physical Review A, 8,1157, (1973).
6- Russell J. Boyd, Can. J. Phys., 53,592, (1975) .
7- K. Schulten , Notes on Quantum Mechanics , Department of physics and Beckman Institute University of Illinois , 2000 .
8- F .W.King ,J. of molecular structure ,400 ,7 ,(1997) .