Potential Energy Expectation Value for Lithium Excited State (1s2s3s)

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Abstract:

The purpose of the present work is to calculate the expectation value of potential energy $\langle V \rangle$ for different spin states **(ααα ≡ βββ, αβα ≡ βαβ)** and compared it with spin states (**αββ , ααβ**) for lithium excited state **(1s2s3s)** and Li- like ions **(Be^+, B^{+2})** using Hartree-Fock wave function by partitioning techanique .The result of inter particle expectation value shows linear behaviour with atomic number and for each atom and ion the $\langle V \rangle$ shows the trend **ααα < ααβ < αββ < αβα .**
Key words: Lithium excited state , potential energy , 1s2s3s

Introduction:

The system considered in this article consists of three electrons [**Li**– atom and **Li** - like ions **(Be^+, B^{+2})**] , one in **K**- shell ,the second in **L** – shell and the third in **M** – shell with different spin states (**ααα , βββ, αβα, βαβ , ααβ , αββ**) this is the general distribution of electrons in orbitals for excited state **($1s^1 2s^1 3s^1$)** of present system . For partitioning technique , we deal with single electron in each shell (**K**- shell ,**L** –shell , **M** – shell). The inter shells represented by $K_\alpha L_\alpha$ and $K_\beta L_\alpha$ shells and the same way for (KM-shell , LM-shell) and our state **($1s^1 2s^1 3s^1$)** represented by ($K_\alpha L_\alpha M_\alpha$, $K_\beta L_\beta M_\beta$, $K_\alpha L_\beta M_\alpha$, $K_\beta L_\alpha M_\beta$, $K_\alpha L_\alpha M_\beta$, $K_\alpha L_\beta M_\beta$) shells, as shown in the diagram:
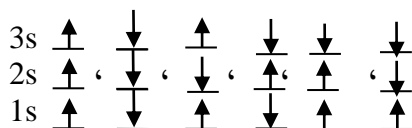
In each state we have two electrons with parallel and anti – parallel spin directions . such as the state ($K_\alpha L_\alpha M_\alpha$) that have two electrons [($K_\alpha L_\alpha$), ($K_\alpha M_\alpha$) , ($L_\alpha M_\alpha$)] each of the electrons interacts with the nucleus by coulomb interaction(attractive interaction$\langle r_1^n \rangle$, expressed here by HF-approximation takes into account this interaction . the problem is the calculation of the interaction between the two-electrons (repulsive interaction $< r_{12}^n >$) . Because *HF* - wave function leaves much of the correlation out when the two electrons with opposite direction, this will causes an accumulation of electrons and this yield incorrect energy.

Theory:

The potential energy expectation value $\langle V \rangle$ has been evaluated for different spin for **Li** excited state (**1s2s3s**) and Li- like ions (**Be^+, B^{+2}**) . One – particle radial density distribution **D(r1)** which gives the distribution of electronic charge can be defined by [1] :

$$D(r_1) = \int_0^\pi \int_0^{2\pi} r_1^2 \, \rho(r_1) \, d\Omega = 4\pi \, r_1^2 \rho(r_1) \ldots (1)$$

Where:

$$d\Omega = \sin\theta \, d\theta \, d\phi$$

and $\rho(r_1)$ is equal to

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$$\rho(r_1) = N \int \psi^*(X_1, X_2 .... X_N) \psi(X_1, X_2 ... X_N)$$
$$d\delta_1 \, dX_2 \, dX_3 ... dx_N$$

…(2)

X_i : is the combined position –spin coordinate of the electron i

The benefit of calculation one – particle density distribution to evaluate the expectation value for one – particle $\langle r_1^n \rangle$ where $-2 \leq n \leq +2$ [2,3]:

$$<r_1^n> = \int_0^\infty D(r_1) \, r_1^n \, dr_1 \qquad ....(3)$$

Following Coulsion and Neilson the electron – electron distribution function $f(r12)$ has been evaluated for Lithium atom and Li- like ions (Be^+, B^{+2}) [4] :

$$f(r_{12})_{K,L,M} = 8\pi^2 r_{12} \begin{bmatrix} \int_{r_{12}}^\infty r_1 \int_{r_1-r_{12}}^{r_1+r_{12}} \phi_{K,L,M}^2(1)\phi_{K,L,M}^2(2) \, r_2 dr_2 dr_1 + \\ \int_0^{r_{12}} r_1 \int_{r_{12}-r_1}^{r_{12}+r_1} \phi_{K,L,M}^2(1)\phi_{K,L,M}^2(2) \, r_2 dr_2 dr_1 \end{bmatrix}$$

….(4)

$$\phi_{K,L,M}^2(i) = R_{K,L,M}^*(r_i) Y_{K,L,M}^*(\Omega_i)$$
$$R_{K,L,M}(r_i) Y_{K,L,M}(\Omega_i)$$

$i = 1$ and 2

And for orbital (s) for spherical harmonic function $Y_{\ell,m}(\theta,\phi)$ is equal :

$$Y^*(\Omega)Y(\Omega) = \frac{1}{\sqrt{4\pi}} \cdot \frac{1}{\sqrt{4\pi}} = \frac{1}{4\pi}$$

Substituting it in eq. 4 ,we obtain:

$$f(r_{12})_{K,L,M} = 0.5 r_{12}$$

$$\begin{bmatrix} \int_{r_{12}}^\infty r_1 \int_{r_1-r_{12}}^{r_1+r_{12}} R_{K,L,M}^2(r_1) R_{K,L,M}^2(r_2) r_2 dr_2 dr_1 + \\ \int_0^{r_{12}} r_1 \int_{r_{12}-r_1}^{r_{12}+r_1} R_{K,L,M}^2(r_1) R_{K,L,M}^2(r_2) r_2 dr_2 dr_1 \end{bmatrix}$$

….(5)

is used this equation to calculate the inter – particle distance that is defined by the equation [5]:

$$\langle r_{12}^n \rangle = \int_0^\infty f(r_{12}) \, r_{12}^n \, dr_{12}$$

….(6)

where $\langle r_{12}^n \rangle$ represent the repulsion energy between two electrons.

Potential energy :
The potential energy is defined as the sum of the electron – nuclear attraction energy and the inter-electronic expectation energy. This sum is proportional to the expectation value of $<r_1^{-1}>$ and $<r_{12}^{-1}>$, the expectation value of the potential energy can be written as follows [6] ,

$$\langle V \rangle = -Z \langle r_1^{-1} \rangle + \langle r_{12}^{-1} \rangle \qquad ....(7)$$
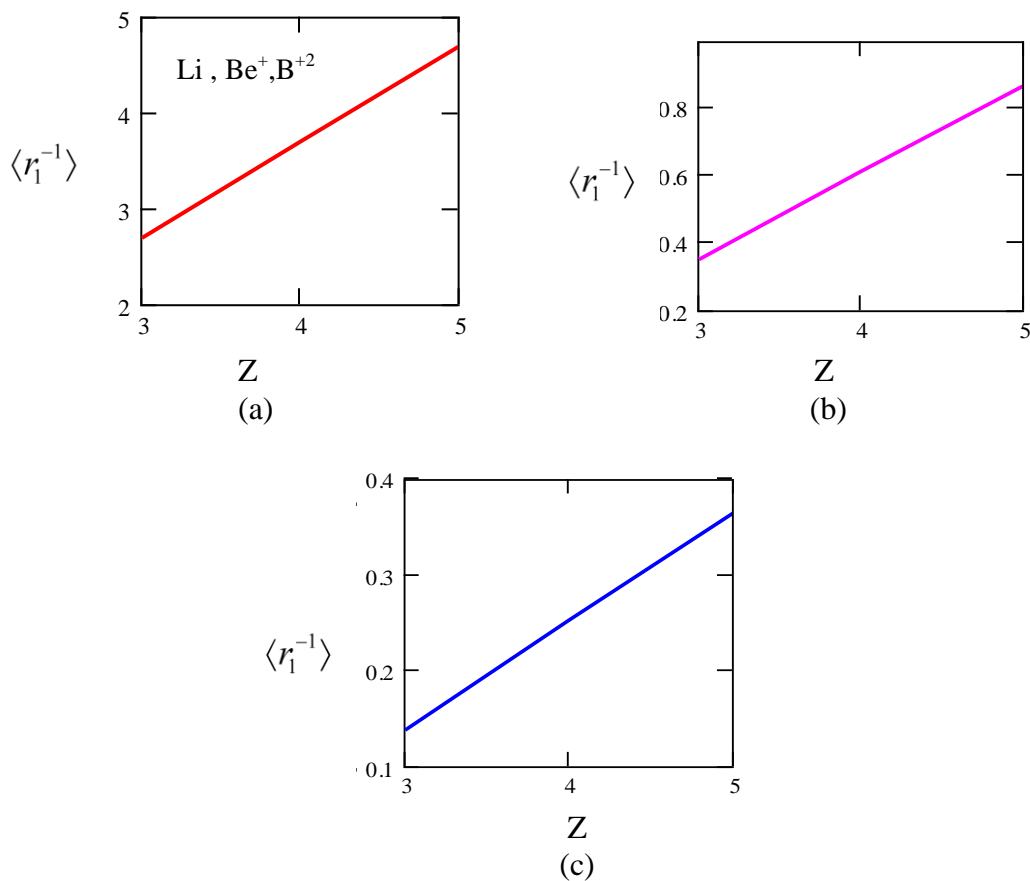
Where Z is the atomic number

Results:
The results for n=-1 are presented in table (1) for different spin states and the relation between the $\langle \frac{1}{r_1} \rangle$ with atomic number are plotted in figure (1).

Table (1) One-particle expectation value $\langle r_1^{-1} \rangle$ for (K, L , M) shells for Li excited state (1s2s3s) and Li- like ions (Be^+, B^{+2})

| Atom or ion (1s2s3s)	Z	shell	$\alpha\alpha\alpha \equiv \beta\beta\beta \equiv \alpha\beta\alpha$ $\equiv \beta\alpha\beta \equiv \alpha\alpha\beta \equiv$ $\alpha\beta\beta$ $\langle r_1^{-1} \rangle$
Li	3		2.685033
Be+	4	K	3.682449
B+2	5		4.680601
Li	3		0.345394
Be+	4	L	0.607477
B+2	5		0.863305
Li	3		0.136571
Be+	4	M	0.251487
B+2	5		0.364333

(a)

(b)

(c)

Fig(1) :The relation between $\langle r_1^{-1} \rangle$ with Z for **Li** excited state (1s2s3s) and Li- like ions (**Be⁺,B⁺²**) where :

**a** : for K- shell .   b : for L- shell .   c : for M- shell .

The results for n=-1 are presented in table (2)and the relation between $\langle \frac{1}{r_{12}} \rangle$ with atomic number are plotted in figures (2,3,4).

Table (2) Inter-particle expectation value $\langle r_{12}^{-1} \rangle$ for(KL, KM, LM) shells for Li excited state (1s2s3s) and Li- like ions (Be⁺,B⁺²)

Atom or ion (1s2s3s)	Z	shell	State	$\langle r_{12}^{-1} \rangle$
Li	3			0.308373
Be⁺	4		($\alpha\alpha\alpha \equiv \beta\beta\beta \equiv \alpha\alpha\beta$)	0.512915
B⁺²	5	KL		0.708005
Li	3			0.322668
Be⁺	4		($\alpha\beta\alpha \equiv \beta\alpha\beta \equiv \alpha\beta\beta$)	0.548494
B⁺²	5			0.765616
Li	3		$\alpha\alpha\alpha \equiv \beta\beta\beta \equiv \alpha\beta\alpha \equiv$	0.128126
Be⁺	4		($\beta\alpha\beta$)	0.228219
B⁺²	5	KM		0.324815
Li	3			0.131327
Be⁺	4		($\alpha\alpha\beta \equiv \alpha\beta\beta$)	0.236708
B⁺²	5			0.338929
Li	3			0.104392
Be⁺	4		($\alpha\alpha\alpha \equiv \beta\beta\beta \equiv \alpha\beta\beta$)	0.186632
B⁺²	5	LM		0.265819
Li	3			0.114231
Be⁺	4		($\alpha\alpha\beta \equiv \alpha\beta\alpha \equiv \beta\alpha\beta$)	0.204037
B⁺²	5			0.290676

(a)   (b)
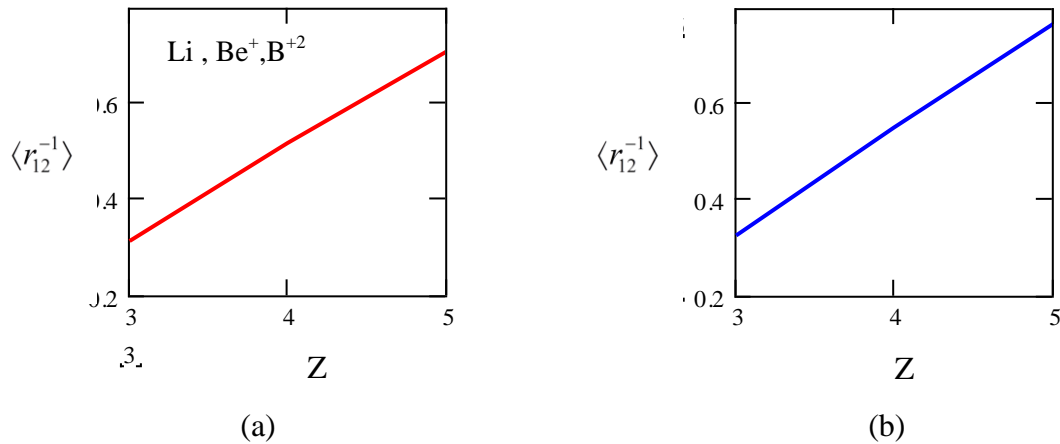
Fig(2) :The relation between $\langle r_{12}^{-1} \rangle$ **and   Z   for (KL- shell) (a) for states(ααα ≡βββ≡ααβ) and (b) for states (αβα ≡βαβ ≡αββ) for Li excited state (1s2s3s) and Li- like ions (Be⁺,B⁺²)**

(a)   (b)
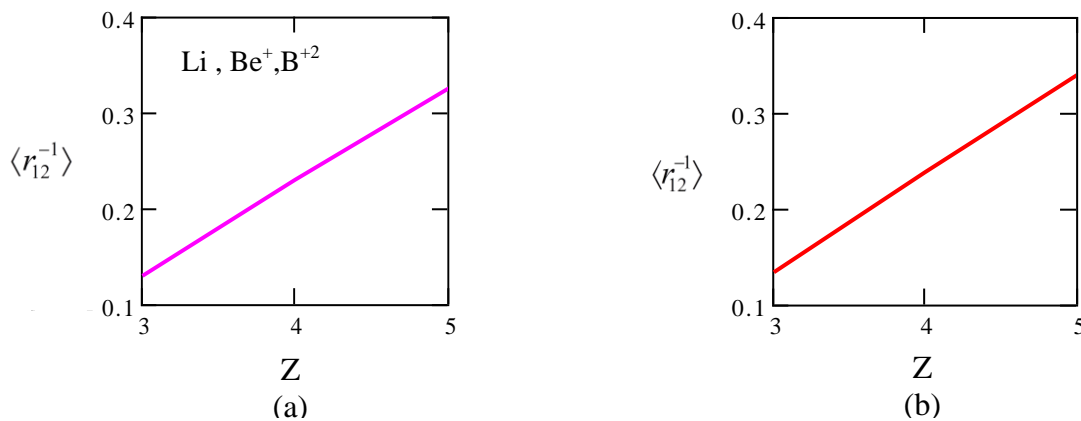
Fig(3) :The relation between $\langle r_{12}^{-1} \rangle$ **and   Z   for (KM- shell) (a) for states(ααα ≡βββ≡αβα≡βαβ) and (b) for states (ααβ≡αββ) for Li excited state (1s2s3s) and Li- like ions (Be⁺,B⁺²)**

(a)   (b)
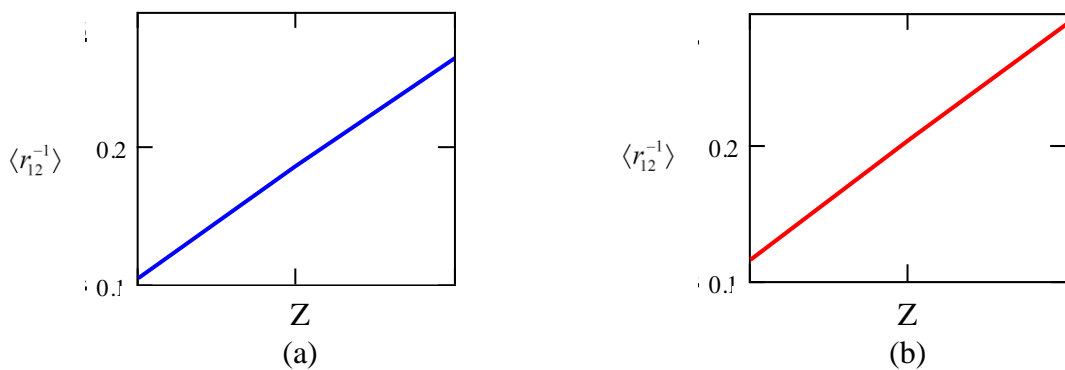
Fig(4) :The relation between $\langle r_{12}^{-1} \rangle$ **and   Z for (LM- shell) (a)   for states(ααα ≡βββ≡αββ) and (b) for states (ααβ≡αβα≡βαβ) for Li excited state (1s2s3s) and Li- like ions (Be⁺,B⁺²)**

The results for the potential energy are presented in table 3&4 .

Table (3) Total potential energy $\langle V \rangle$ for spin states($\alpha\alpha\alpha \equiv \beta\beta\beta, \alpha\beta\alpha \equiv \beta\alpha\beta$) for Li excited state (1s2s3s) and Li-like ions (Be$^+$,B^{+2})

Atom or ion	Z	STATE 1s2s3s)(	$\langle V \rangle$	$\Delta\langle V \rangle = Triplet state - Singlet state$
Li	**3**	$\alpha\alpha\alpha \equiv \beta\beta\beta$	-8.960105	-0.024134
		$\equiv \beta\alpha\beta$ $\alpha\beta\alpha$	-8.935971	
Be$^+$	**4**	$\alpha\alpha\alpha \equiv \beta\beta\beta$	-17.237887	-0.053084
		$\equiv \beta\alpha\beta$ $\alpha\beta\alpha$	-17.184803	
B^{+2}	**5**	$\alpha\alpha\alpha \equiv \beta\beta\beta$	-28.242553	-0.082467
		$\equiv \beta\alpha\beta$ $\alpha\beta\alpha$	-28.160086	

Table (4) Total potential energy for spin states ($\alpha\beta\beta$, $\alpha\alpha\beta$) for Li excited state (1s2s3s) and Li- like ions (Be$^+$,B^{+2})

Atom or ion	Z	STATE (1s2s3s)	$\langle V \rangle$	$\Delta\langle V \rangle$
Li	**3**	$\alpha\beta\beta$	-8.942608	0.00446
		$\alpha\alpha\beta$	-8.947065	
Be$^+$	**4**	$\alpha\beta\beta$	-17.193819	0.018174
		$\alpha\alpha\beta$	-17.211993	
B^{+2}	**5**	$\alpha\beta\beta$	-28.170829	0.032755
		$\alpha\alpha\beta$	-28.203584	

Discussion:

From the tables & figures, we conclude that:

1.The inter-distance function $\langle r_{12}^n \rangle$ increase at negative values of n with increasing atomic number Z, and decrease when Z increases for positive values of n due to the increasing influence of nuclear charge.

2. The total potential energy $\langle V \rangle$ increased by increasing atomic number (Z) ,this behaviour can be understood from the fact that each shell shrink toward the nucleus due to the increasing of attraction with the nucleus. The distance between the electron and the nucleus decreased. The potential energy of attraction and repulsion increased because the distance between each two electrons decreased (energy between the two charges directly proportional to the amount of charges and inversely with the distance between those two charges) [7].

3.From the results of energies in tables (3,4) for each atom and ion, one observed that the value of energy in singlet state **($\alpha\beta\alpha$, $\beta\alpha\beta$)** is greater than the value of energy in triplet states **($\alpha\alpha\alpha$,$\beta\beta\beta$)**,this reason belongs to the different electron spin,where in the states **($\alpha\beta\alpha$, $\beta\alpha\beta$)** in the **KL** shell the spin is **KL($\alpha\beta$)** and the spin in **LM** shell is **LM($\alpha\beta$)** while the spin in **KM** shell is **KM($\alpha\alpha$)** , this leads that the attraction energy between two electrons increased and the distance between them decreased and replusion energy decreased , while in triplet state **($\alpha\alpha\alpha$)** observed the similarity of spin in all shells **(KL($\alpha\alpha$) ,KM($\alpha\alpha$),LM($\alpha\alpha$))** , this leads to the increasing in repulsion energy between each two electrons then the attraction energy decreased.

4.For each atom and ion the results of $\langle V \rangle$ potential expectation values ($\alpha\alpha\alpha$) < ($\alpha\alpha\beta$) < ($\alpha\beta\beta$) < ($\alpha\beta\alpha$) because of the difference in electron spin leads to the increasing in attraction energy and the repulsion energy decreased .

5.For each atom or ion the result of $\langle V \rangle$ for triplet state is greater than singlet state due to the following reason:

i :The Fermi correlation effect keep the electron apart each other [8] .

ii :The attraction between 1s(α) and 2s(β) and 2s(β) and 3s(α) keep the

shells to be closer in singlet state than triplet state

6. For triplet and singlet states the value $\langle V \rangle$ increase as Z increases.

7. The difference between triplet and singlet states $\Delta\langle V \rangle$ increases as **Z** increases.

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القيمة المتوقعة لطاقة الجهد لحالة الليثيوم المتهيجة والايونات المشابهة لها (Be⁺,B⁺²)

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الخلاصة:

إن الغرض من العمل الحالي هو حساب القيمة المتوقعة لطاقة الجهد $\langle V \rangle$ لحالات البرم المختلفة (αββ , ααβ) ومقارنتها مع حالات البرم (ααα ≡ βββ,αβα ≡ βαβ) لحالة الليثيوم المتهيجة (1s2s3s) والايونات المشابهة لها (Be⁺,B⁺²) باستعمال الدالة الموجية هارتري-فوك بإستخدام تقنية التجزئة . ونتيجة القيمة المتوقعة للمسافة البينية يظهر السلوك الخطي مع العدد الذري ومع كل ذرة وأيون فأن $\langle V \rangle$ يظهر الاتجاه
(αβα > ββα > βαα > ααα) .

الكلمات المفتاحية: حالة الليثيوم المتهيج، طاقة الجهد ، 1S,2S,3S.

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