Evaluation the Energy of the ($1s^2$ ns) state of the Li atom and Li-like ions

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Abstract:

The aim of this work is the evaluation of the energy, repulsion energy (vee),attraction energy (ven), the potential energy (V),total energy (E),one-electron expectation value $\langle r_1^k \rangle$ and inter –electron expectation value $\langle r_{12}^k \rangle$ (where k is an integer takes the value -2,-1,1,2)for the ground state and for the different excited states (1s2 ns) and(n=3,4,5) of Li atom and Li-like ions such as Be+1,B +2 and C+3by using Hartree –Fock approximation in position space. A systematic study of the differences in electronic distributions between the singlet and triplet states are carried out . Finally all the studied properties are calculated using atomic units and using software MATHCAD 2001i.

***Keywords** : Hartree- FockEnergy, position space .Li atom*

1- Introduction:

The Hartree –Fock (HF) approximation were first proposed by Fock in 1930 .Since then ,the HF method has taken a central role in studying the atomic and molecular electronic properties[1].theHartree –Fock(HF) method enables calculation not only of the ground state but also excited states of atoms and ions. Thus,it can be studied and *examinedmany configurations for different excited states for any system[2].The Hartree-Fock atomic wave function are independent-particle-model approximations to the nonrelativistic Schrodinger's equation for stationarystates . the use of Slater determinants ccountsfor the Pauli principle ,and for an N-electron system the HF equations yield NHartree –Fock spin orbitals. In conventional Hartree-Fock calculation, the spin orbitals are expressed as products of a radial function times spherical harmonic times a spin function, the radial functions are taken to depend only on the quantum numbers* ***n*** *and* ***ℓ****, and the total wave function is required to be an Eigen function of the total orbital and spin angular momentum ; the form of the spin orbitals guarantees that* ***Lz*** *,* ***Sz*** *, and parity are good quantum numbers.[3,4]*

2-Theory

For any N-electron system, the two-particle density $\Gamma(\chi_m,\chi_n)$ *can be written as [5-7]*

$$\Gamma(\chi_m,\chi_n) = \binom{N}{2}\int \psi^*(\chi_m,\chi_n,\dots,\chi_N)\psi(\chi_m,\chi_n,\dots,\chi_N)d\chi_m \dots d\chi_N \dots (1)$$

Where χ_m *stands for the spin and space coordinate of electrons and* $d\chi_m$ *indicates that the integration performed for all electrons within system except m and n, while the binomial factor* $\binom{N}{2}$ *is introduced to ensure that the second order density matrix* $\Gamma(\chi_m,\chi_n)$ *is normalized to the number of electron pairs in the system mathematically it is equal to*

$$\int \Gamma(\chi_m,\chi_n)d\chi_m \dots d\chi_n = \binom{N}{2} \dots\dots\dots\dots\dots\dots(2)$$

The binomial factor $\binom{N}{2}$ *can be written as[8,9]*

$$\binom{N}{2} = \left[\frac{N!}{2!\,(N-2)!}\right]$$

(2-1): Two-particle radial distribution function $D(r_1,r_2)$:

Two-particle density distribution function $D(r_1,r_2)$ is defined as [10,11]

$$D(r_1,r_2)=\int\int\Gamma(r_1,r_2)r_1^2r_2^2\,d\Omega_1 d\Omega_2 d\sigma_1 d\sigma_2 \qquad \text{..................(3)}$$

Where $d\Omega_i$ denotes that the integration is over all angular coordinates of the position vector and it is simply defined as:

$$\int d\Omega_i=\int_0^{2\pi}\int_0^{\pi}\sin\theta_i\ d\theta_i d\phi_i \qquad \text{...............................(4)}$$

Where i=1 or 2and $d\sigma$ denotes spin-part (α spin up, β spin down).

the normalization condition for two-particle radial density distribution function $D(r_1,r_2)$ can bedefine as

........................(5)

This means the two-particle density distribution $D(r_1,r_2)dr_1dr_2$ is a measure of probability of finding the two-electron simultaneously and their radial coordinates are in the range r_1 and r_1+dr_1 ,and r_2 to r_2+dr_2[11,12]

(2-2):One-particleRadial distribution function $D(r_1)$:

The radial density distribution function is of extreme importance in the studying atom and ions because it measure the probability of finding an electron in each shell, and it is defined as [13-15]

$$D(r_1) = \int_0^{\infty} D(r_1, r_2)\, dr_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

(2-3): One – particle expectation value :

The one particle expectation value can be calculated from [16].

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

$$\left\langle r_{12}^k \right\rangle = \int_0^{\infty} f(r_{12}) r_{12}^k dr_{12} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

(2-4):Inter - particle expectation value :

Inter particle expectation value $\langle r_{12}^k \rangle$ is given by the relation [17].

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

Where(r_{12}) represents the distance between two-electrons . $f(r_{12})$ is inter electron-electron distribution function ,which describes the probability of locating two electrons *separated by distance (r_{12}) from each other, was first introduced by Coulson and Neilson in their study of electron correlation for*

He(1S)in the ground state. The electron-electron distribution function$f(r_{12})$ plays a central role inthe discussion of correlation holes in many electron systems [18,19].Pair distribution function can bewritten as [18].

$$f(r_{12}) = 8\pi^2 r_{12} \left[\begin{array}{l} \int_0^{r_{12}} r_1 dr_1 \int_{r_1 - r_{12}}^{r_1 + r_{12}} \Gamma(r_1, r_2)\, r_2 dr_2 + \\ \int_{r_{12}}^{\infty} r_1 dr_1 \int_{r_{12} - r_1}^{r_{12} + r_1} \Gamma(r_1, r_2) r_2 dr_2 \end{array} \right] ....(9)$$

(2-5):The expectation value of energy :

The potential energy is simply the sum of the attraction energy and the repulsion energy, which is proportional to the expectation values $\langle r_i^{-1} \rangle$ and $\langle r_{ij}^{-1} \rangle$respectively. Therefore can be written inatomic units (a.u.).[19,20]:

$$\langle V \rangle = -Z \sum_{i}^{N} \langle r_i^{-1} \rangle + \sum_{i<j}^{N} \langle r_{ij}^{-1} \rangle \text{.................}(10)$$

where Z is the atomic number .

The energy expectation value related to the potential energy by [20-22] :

$$\langle E \rangle = \frac{1}{2} \langle V \rangle \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(11)$$

<u>Results and discussions</u>

The results obtained in the one-particle expectation values for different powers (n=-2 to 2) for the total ground state and different excited states of Li- like ions up to Z=5 *are listed in tables (1,2,3,4).From this tables, we noted the effect of the increaseing in atomic number with fixed the number of electrons. It is observed when (k) takes negative values the expectation values of $\langle r_1^k \rangle$ increase with icreasing in the atomic number, the values of $\langle r_1^{-1} \rangle$ refer to attractive .energy between the nucleus and the electron, while when(k) takes positive values the expectation values of $\langle r_1^k \rangle$ are decreases because the distance between the electron and the nucleus become smallest as nuclear charge increases.normalization condition has been applied for all wavefunctions.*

Tables: (5,6,7,8) contain the results of inter-particle expectationvalue $\langle r_{12}^k \rangle$, we noted when(k) takes negative values the expectation values $\langle r_{12}^n \rangle$ increase as atomic number increasesforall different configurationsstateswhere $\langle r_{12}^{-1} \rangle$ value represents the repulsion energy between pair of electrons, while $\langle r_{12}^k \rangle$ decreases when(k) takes positive values.

Tables :(8,9,10,11) representthe expectation values ofall energies,attraction and ,repulsion,The potential energy and total energy of studied system from these results we observed all energies increase as atomic number increase,because increasing (Z) lead to decreasing in the distance between electrons and nucleus and the distance between two electrons , this lead to increasing in attraction energy and repulsion energy according to coulomb law .the attraction energy increases with atomic number for each of the studied systems, Also we noted that the lower value of the energy in the lithium atom attraction as that any electrically neutral atomic number equal to the number of electrons.this behavior can be understood from the fact that each shell contract toward nucleus as result of increasing the nuclear charges influence on the orbital electrons hence the separation distances are reduced thus reduction of attraction and repulsion forces according to Coulomb law.but the ions (Be^{+1},B^{+2},C^{+3})

have atomic number greater than the number of electrons because of the loss of electrons corn from the last shell resulting in increased energy attract electrons to nucleus.Also for all ions the expectation values of repulsion energy are increased as (Z) increases due to that the coulomb interaction became stronger as (Z)increased.

Table(1): one particle expectation value $\langle r_1^k \rangle$ *of(* $1s^2 2s^1$ *) configurationsof Li atomand Li– like ions.*

Atom or Ion	Z	$\langle r_1^{-2} \rangle$	$\langle r_1^{-1} \rangle$	$\langle r_1^{1} \rangle$	$\langle r_1^{2} \rangle$	$Z\langle r_1^{-1} \rangle$
Li	3	10.07064	1.90515	1.6733	6.21071	5.71545
Be^{+1}	4	18.99183	2.65745	1.03666	2.18472	10.6298
B^{+2}	5	30.74896	3.40817	0.76217	1.13746	17.0409
C^{+3}	6	45.34043	4.1585	0.60489	0.70152	24.951

Table(2): one particle expectation value $\langle r_1^k \rangle$ *of(* $1s^2 3s^1$ *)configurations of Li atomand Li– like ions.*

Atom or Ion	Z	$\langle r_1^{-2} \rangle$	$\langle r_1^{-1} \rangle$	$\langle r_1^{1} \rangle$	$\langle r_1^{2} \rangle$	$Z\langle r_1^{-1} \rangle$
Li	3	9.970842	1.83679	3.780184	39.80704	5.51037
Be^{+1}	4	18.66368	2.541396	2.158276	12.23963	10.16558
B^{+2}	5	30.07328	3.2454	1.531611	5.99125	16.227
C^{+3}	6	44.19918	3.94924	1.19161	3.56567	23.6954

Table(3): one particle expectation value $\langle r_1^k \rangle$ *of(* $1s^2 4s^1$ *)configurations of Li atomand Li– like ions.*

Atom or Ion	Z	$\langle r_1^{-2}\rangle$	$\langle r_1^{-1}\rangle$	$\langle r_1^{1}\rangle$	$\langle r_1^{2}\rangle$	$Z\langle r_1^{-1}\rangle$
Li	3	9.9515861	1.8157505	6.8861192	143.29597	5.447252
Be^{+1}	4	18.59477	2.50368	3.7802	41.61813	10.01472
B^{+2}	5	29.925559	3.191328	2.6346359	19.836496	15.95664
C^{+3}	6	43.943936	3.878897	2.0285251	11.624108	23.27338

Table(4): one particle expectation value $\langle r_1^{k}\rangle$ of($1s^2 5s^1$)configurations of Li atomand Li– like ions.

Atom or Ion	Z	$\langle r_1^{-2}\rangle$	$\langle r_1^{-1}\rangle$	$\langle r_1^{1}\rangle$	$\langle r_1^{2}\rangle$	$Z\langle r_1^{-1}\rangle$
Li	3	9.945689	1.806599	10.996437	379.30763	5.419797
Be^{+1}	4	18.57195	2.486845	5.902015	106.53485	9.94738
B^{+2}	5	29.87541	3.16693	4.070998	50.025002	15.83465
C^{+3}	6	43,854484	3.846972	3.115456	29.059875	23.08183

Table(5):inter –particles expectation values $\langle r_{12}^{k}\rangle$ of ($1s^2 2s^1$) configurations of Li atomand Li– like ions.

Atom or Ion	Z	$\langle r_{12}^{-2}\rangle$	$\langle r_{12}^{-1}\rangle$	$\langle r_{12}^{1}\rangle$	$\langle r_{12}^{2}\rangle$	$Z\langle r_1^{-1}\rangle$
Li	3	1.67743	0.76031	2.89636	12.42142	2.28093
Be^{+1}	4	3.27827	1.11152	1.75336	4.36945	4.44608
B^{+2}	5	5.4127	1.45688	1.2760	2.27492	7.2844
C^{+3}	6	8.08053	1.8003	1.00683	1.40304	10.8018

Table(6):inter –particles expectation values $\langle r_{12}^{k}\rangle$ of ($1s^2 3s^1$) configurations of Li atomand Li– like ions.

Atom or Ion	Z	$\langle r_{12}^{-2}\rangle$	$\langle r_{12}^{-1}\rangle$	$\langle r_{12}^{1}\rangle$	$\langle r_{12}^{2}\rangle$	$Z\langle r_{1}^{-1}\rangle$
Li	3	1.59985	0.63692	7.08986	79.6121	1.91076
Be^{+1}	4	3.05949	0.913724	3.978937	24.47918	3.654896
B^{+2}	5	4.99119	1.1883	2.79984	11.9825	5.9415
C^{+3}	6	7.39475	1.46209	2.16727	7.13133	8.77254

Table(7):inter –particles expectation values $\langle r_{12}^{k}\rangle$ of ($1s^2 4s^1$) configurations of Li atomand Li– like ions.

Atom or Ion	Z	$\langle r_{12}^{-2}\rangle$	$\langle r_{12}^{-1}\rangle$	$\langle r_{12}^{1}\rangle$	$\langle r_{12}^{2}\rangle$	$Z\langle r_{1}^{-1}\rangle$
Li	3	1.5847472	0.5973182	13.29147	86.4835923	1.791955
Be^{+1}	4	3.01239	0.845274	7.216664	82.229323	3.381096
B^{+2}	5	4.8962716	1.0921674	5.000855	39.672373	5.460837
C^{+3}	6	7.2363039	1.3386773	3.8367027	23.248074	8.032064

Table(8):inter –particles expectation values $\langle r_{12}^{k}\rangle$ of ($1s^2 5s^1$) configurations of Li atomand Li– like ions.

Atom or Ion	Z	$\langle r_{12}^{-2}\rangle$	$\langle r_{12}^{-1}\rangle$	$\langle r_{12}^{1}\rangle$	$\langle r_{12}^{2}\rangle$	$Z\langle r_{1}^{-1}\rangle$
Li	3	1.579936	0.57979	21.490015	757.708039	1.73937
Be^{+1}	4	2.996665	0.8138834	11.452276	212.936333	3.255534
B^{+2}	5	4.86391	1.047382	7.870087	100.02763	5.23691

Atom or Ion	Z	$-\langle V_{en}\rangle$	$\langle V_{ee}\rangle$	$-\langle V\rangle$	$-\langle E_{HF}\rangle$
Li	3	17.14637579	2.280921266	14.865454526	7.43272726
Be+1	4	31.88935853	3.334565995	28.554792538	14.2773963
B+2	5	51.12262312	4.370641359	46.751981762	23.3759909
C+3	6	74.85299699	5.400899534	69.452097456	34.7260487

C^{+3}	6	7.181603	1.280649	6.008245	58.114102	7.683894

Table(9) :The expectation values for all attraction ,repulsion, The potential energy and total energyof ($1s^2\ 2s^1$) configurations of Li atomand Li– like ions.

Table(10) :The expectation values for all attraction ,repulsion, The potential energy and total energy of ($1s^2 3s^1$) configurations of Li –atom and like ions.

Atom or Ion	Z	$-\langle V_{en}\rangle$	$\langle V_{ee}\rangle$	$-\langle V\rangle$	$-\langle E_{HF}\rangle$
Li	3	16.5311285	1.910767212	14.620425642	7.31021282
Be^{+1}	4	30.49675412	2.741172502	27.755581619	13.8777908
B^{+2}	5	48.68098557	3.56488646	45.116099105	22.5580496
C^{+3}	6	71.08631619	4.386259731	66.700056462	33.3500282

Table(11) :The expectation values for all attraction ,repulsion, The potential energy and total energy of ($1s^2 4s^1$) configurations of Li –atom and like ions

Atom or Ion	Z	$-\langle V_{en}\rangle$	$\langle V_{ee}\rangle$	$-\langle V\rangle$	$-\langle E_{HF}\rangle$
Li	3	16.3417546	1.791954718	14.549799887	7.27489994
Be^{+1}	4	30.0441608	2.53582307	27.508337686	13.7541688
B^{+2}	5	47.8699236	3.276502294	44.593421255	22.2967106
C^{+3}	6	69.8201558	4.016031938	65.80412385	32.9020619

Table(12) :The expectation values for all attraction ,repulsion, The potential energy and total energy of ($1s^2 5s^1$) configurations of Li –atom and like ions.

Atom or Ion	Z	$-\langle V_{en}\rangle$	$\langle V_{ee}\rangle$	$-\langle V\rangle$	$-\langle E_{HF}\rangle$
Li	3	16.2593919	1.73936895	14.52992303	7.26001152

			4	2	
Be^{+1}	4	29.8421474	2.44165031 3	27.40049711 8	13.7002486
B^{+2}	5	47.5039769	3.14213989 6	44.36183700 9	22.1809185
C^{+3}	6	69.2454964	3.84194797 2	65.40354838 6	32.7017742

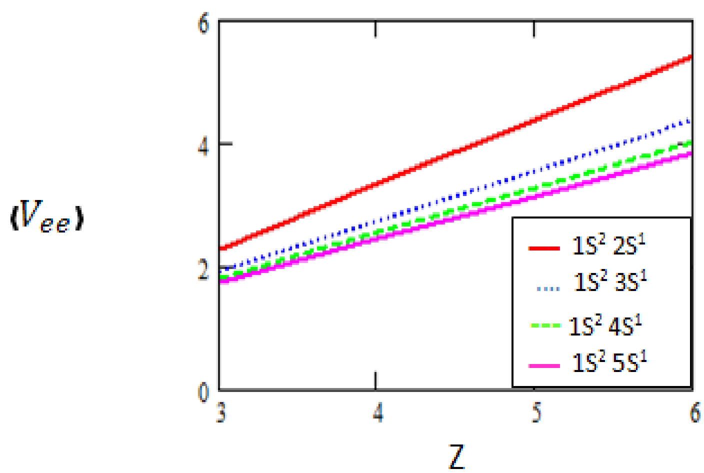

Figure (1) shows the relation between (V_{ee}) versus z of ($1s^2 2s^1$),($1s^2$ $3s^1$),($1s^2$ $4s^1$) and ($1s^2$ $5s^1$) configurations.

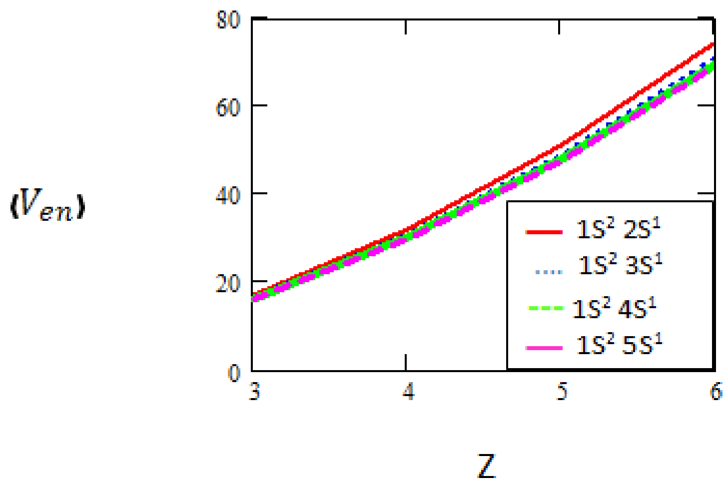

Figure (2) shows the relation between $\langle V_{en} \rangle$ versus z of ($1s^2 2s^1$),($1s^2$ $3s^1$),($1s^2$ $4s^1$) and ($1s^2$ $5s^1$) configurations.

Conclusions

From the results shown in tables (1−12) and Figures (1−2) the followingscan be concluded:

1. expectation values of $\langle r_1^k \rangle$ and $\langle r_{12}^k \rangle$ inrease when (n)takes negative values and the invers for positive values as atomic number increase while theexpectation values of all energies increase as nuclear charge increase.

2. As Z increases the $\langle V_{en} \rangle$ and $\langle V_{ee} \rangle$ increases

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