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Energy Calculation for Excited Lithium Atom in Position Space

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Abstract:

The energy expectation values $\langle E \rangle$ for Li and Li-like ions (Li, Be^{+} and B^{2+}) have been calculated and examined within the ground state $(1s2s\alpha)^{2}S$ and the excited state $(1s3s\alpha)^{2}S$ in position space. The partitioning technique of Hartree-Fock (H-F) has been used for existing wave functions.

Key words: Energy expectation value, Atomic systems, Ground and excited states, Hartree- Fock approximation.

Introduction:

Roothaan et al. (1960) presented the Analytical Self-Consistent Field Functions for the Atomic Configurations $1s^{2}, 1s^{2}2s$ and $1s^{2}2s^{2}$ for atoms and ions up to Z=10[1]. Banyard (1968) analysed and compared five wavefunctions for H^{-}. He discussed the two-particle density $\rho(r_1, r_2)$ and the radial density $D(r)$ [2]. Al-Bayati (1984) has examined the electron correlation in position and momentum spaces for a series of Li-like ions (Z=3 to 8) in their ground state $(1s2s\alpha)^{2}S$ and excited state $(1s2p\alpha)\ ^{2}P$ [3]. Banyard (1990) examined the coulomb correlation in a doubly occupied K- shell in position and momentum spaces [4]. Koga et al. (1999) studied the electron-pair densities of two group of atoms in their ^{1}P and ^{3}P states [5]. Chen and Wang (2005) studied the oscillator strengths for $2s^{2}-2p^{2}P$ transitions for lithium isoelectronic sequence from *NaIX* to *CaXVIII* [6]. Huang and Zhao (2010) systematically studied the ground-state ionization potentials for Boron and carbon isoelectronic sequence with Z=6-42 [7]. Bubin and Prezhdo (2013) studied the excited states of positronic Lithium and Beryllium using a variational method with an explicitly correlated Gaussian basis [8].

In this research, the energy expectation values of the ground state $(1s2s\alpha)^{2}S$ and the excited state $(1s3s\alpha)^{2}S$ for Li- like ions in position space have been studied.

Methodology

1 Hartree-Fock Aproximation

The Hartree-Fock (HF) atomic wave function is an independent particle-model approximation to non-relativistic Schrödinger equation. For the ground state $(1s2s\alpha)^2S$ and excited state $(1s3s\alpha)^2S$ of the Li-like ions in position space, it can be written as a single determinate of one-electron functions namely [9]:

$$\psi_{HF_{(1s2s\alpha)^2S}}(123) = (3!)^{-\frac{1}{2}}\left|\varphi_{1s}\alpha(1)\varphi_{1s}\beta(2)\varphi_{2s}\alpha(3)\right| \quad \text{……….. (1)}$$

$$\psi_{HF_{(1s3s\alpha)^2S}}(123) = (3!)^{-\frac{1}{2}}\left|\varphi_{1s}\alpha(1)\varphi_{1s}\beta(2)\varphi_{3s}\alpha(3)\right| \quad \text{……….. (2)}$$

The function $\varphi_{nlm}(r\theta\phi;\zeta)$ is the spatial part of the spin-orbital and was constructed from a basis set of s-type orbitals for the ground state $(1s2s\alpha)^2S$ and excited state $(1s3s\alpha)^2S$ and it can be written as:

$$\varphi_{nl} = \sum_{i=1}^{n} c_n^i x_{nl}^i \quad \text{………..…(3)}$$

For a given HF wave function, N. V. Novikov [10] minimized the total energy for all parameters including the exponent ζ for Li-like ions in ground state $(1s2s\alpha)^2S$ and excited state $(1s3s\alpha)^2S$. The basis functions χ are standard normalized Slater-type orbitals (STO's) and are given as following [1]:

$$\chi_{n\ell m}(r,\theta,\phi) = R_{n\ell}(r)Y_{\ell m}(\theta,\phi) \quad \text{….(4)}$$

$$R_{n\ell} = \frac{(2\zeta)^{n+\frac{1}{2}}}{\left[(2n)!\right]^{\frac{1}{2}}} \cdot r^{n-1} e^{-(\zeta r)} \quad \text{….(5)}$$

$Y_{lm}(\theta,\phi)$ represents the angular part of the wave function and its given by [11]:

$$Y_{lm}(\theta,\phi) = N_{lm}P_l^m(\cos\theta)e^{im\phi} \quad \text{…….(6)}$$

where $|N_{lm}|$ is the normalization factor and it is determined by :

$$|N_{lm}| = \left[\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}\right]^{\frac{1}{2}} \quad \text{….(7)}$$

and $P_\ell^m(\cos\theta)$ is associated Legendre function.

2 Calculation Method

To calculate the energy expectation value $\langle E \rangle$, the one-particle expectation value $\langle r_1^{-1} \rangle$ and the inter-particle expectation value $\langle r_{12}^{-1} \rangle$ have been calculated.

The one particle radial electronic distribution function $D(r_1)$ in position space is a measure of a probability of finding an electron on a shell of radius r1 and it is defined as [12]:

$$D(r_1) = \int D(r_1, r_2)\, dr_2 \quad \text{……..(8)}$$

The inter-particle distribution function $f(r_{12})$ in position space is a measure of a probability of finding an electron on the distance between the two positions of the electrons in the same shell or in different shells and it is defined as [13]:

$$f(r_{12}) = 8\pi^2 r_{12} \iint \psi^2(1,2) r_1 r_2 dr_1 dr_2 \quad \text{...(9)}$$

The one-particle expectation values in position space $\langle r_1^n \rangle$ can be calculated from [14]:

$$\langle r_1^n \rangle = \int D(r_1)\, r_1^n\, dr_1 \quad \text{……(10)}$$

In the case $(n=0)$ one gets the normalization condition

The inter-particle expectation values in position space $\langle r_{12}^n \rangle$ can be calculated from [14]:

$$\langle r_{12}^n \rangle = \int f(r_{12})\, r_{12}^n\, dr_{12} \quad \text{…..(11)}$$

The energy expectation value $\langle E \rangle$ related to the potential energy is written as [14]:

$$\langle E \rangle = 1/2 \langle V \rangle \quad \text{…….. (12)}$$

The potential energy is simply the sum of the electron-nucleus attraction energy and the interelectronic repulsion energy, which are proportional to the expectation values of $1/r_1$ and $1/r_{12}$ respectively. Therefore it can be written in position space as [14]:

$$\langle V \rangle = -Z\langle r_1^{-1} \rangle + \langle r_{12}^{-1} \rangle \quad \text{…… (13)}$$

Results and Discussion:

The results for one-particle expectation value $\langle r_1^{-1} \rangle$ and the two-particle expectation value $\langle r_{12}^{-1} \rangle$ of the ground state $(1s2s)\ ^2S$ and the excited state $(1s3s)\ ^2S$ for Li-like ions in position space are tabulated in tables(1 and 2) respectively.

The energy expectation values $\langle E \rangle$ results of the ground state $(1s2s)\ ^2S$ and the excited state $(1s3s)\ ^2S$ in position space for Li-like ions are tabulated in tables (3 and 4) respectively.

Table (5) shows the difference of the energy expectation values between $(1s2s)\ ^2S$ and $(1s3s)\ ^2S$ states in position space for Li-like ions.

By inspecting tables (1 and 2)**,** the one-particle expectation values $\langle r_1^{-1} \rangle$ of $(1s2s)\ ^2S$ and $(1s3s)\ ^2S$ states in the position space increase when the atomic number (Z) increases for the all shells, and the two-particle expectation values $\langle r_{12}^{-1} \rangle$ show similar behavior for Li-like ions.

Comparison between $(1s2s)\ ^2S$ and $(1s3s)\ ^2S$ states in position space, shows that the one-particle expectation values $\langle r_1^{-1} \rangle$ of $(1s2s)\ ^2S$ state are larger than that of $(1s3s)\ ^2S$ state for the all shells except the K-shell. The two-particle expectation values $\langle r_{12}^{-1} \rangle$ shows the same behavior for Li-like ions.

By inspecting tables (3 and 4)**,** we see that the absolute values of the energy expectation values $\langle E \rangle$ of $(1s2s)\ ^2S$ state in the position space are larger than that of $(1s3s)\ ^2S$ state except the K-shell for Li-like ions. The energy expectation values $\langle E \rangle$ decrease with increasing atomic number (Z) for both of $(1s2s)\ ^2S$ state and $(1s3s)\ ^2S$ state .The table (5) shows this behavior very clear.

This result is due to the attraction force of the nucleus to the charge which leads to increase the probability of finding the electron near the nucleus.

A comparison between the values of this work with the previous works [3, 9 and 15] are also shown in tables (1-4).

Table (1): The one- and two- particle expectation values of the ground state $(1s2s)\ ^2S$ in position space for Li-like ions.

Z	Shell	$(1s2s)\ ^2S$			
		$\langle r_1^{-1} \rangle$ Present work	$\langle r_1^{-1} \rangle$ Ref.[3]	$\langle r_{12}^{-1} \rangle$ Present work	$\langle r_{12}^{-1} \rangle$ Ref.[3]
3	$K_\alpha K_\beta$	2.685034	2.6850	1.649886	1.6501
	$K_\alpha L_\alpha$	1.515212	1.5152	0.308370	0.3084
	$K_\beta L_\alpha$	1.515212	1.5152	0.322665	0.3227
	Total	1.905153	1.9051	0.760307	0.7604
4	$K_\alpha K_\beta$	3.682449	3.6824	2.273230	2.2748
	$K_\alpha L_\alpha$	2.144945	2.1449	0.512879	0.5127
	$K_\beta L_\alpha$	2.144945	2.1449	0.548457	0.5484
	Total	2.657447	2.6574	1.111522	1.1120
5	$K_\alpha K_\beta$	4.680601	4.6806	2.896984	2.9025
	$K_\alpha L_\alpha$	2.771962	2.7719	0.708023	0.7079
	$K_\beta L_\alpha$	2.771962	2.7719	0.765634	0.7658
	Total	3.408175	3.4081	1.456880	1.4587

Table (2): The one- and two- particle expectation values of the excited state $(1s3s)\ ^2S$ in position space for Li-like ions.

Z	Shell	$(1s3s)\ ^2S$			
		$\langle r_1^{-1} \rangle$ Present work	$\langle r_1^{-1} \rangle$ Ref.[15]	$\langle r_{12}^{-1} \rangle$ Present work	$\langle r_{12}^{-1} \rangle$ Ref.[15]
3	$K_\alpha K_\beta$	2.686913	2.68691	1.651311	1.65133
	$K_\alpha M_\alpha$	1.411742	1.41175	0.128126	0.12786
	$K_\beta M_\alpha$	1.411742	1.41175	0.131331	0.13122
	Total	1.836799	1.8368	0.636923	0.6368
4	$K_\alpha K_\beta$	3.686354	3.68636	2.276241	2.27625
	$K_\alpha M_\alpha$	1.968917	1.96896	0.228213	0.22865
	$K_\beta M_\alpha$	1.968917	1.96896	0.236718	0.23631
	Total	2.541396	2.54143	0.913724	0.91374
5	$K_\alpha K_\beta$	4.685933	4.68593	2.901119	2.90111
	$K_\alpha M_\alpha$	2.525132	2.52512	0.324813	0.32598
	$K_\beta M_\alpha$	2.525132	2.52512	0.338954	0.34068
	Total	3.245399	3.24539	1.188295	1.18926

Table (3): The energy expectation values of the ground state $(1s2s)\ ^2S$ in position space for Li-like ions.

Z	Shell	$(1s2s)\ ^2S$	
		$\langle E \rangle$ (a. u.)Present work	$\langle E \rangle$ (a. u.)Ref.[9]
3	$K_\alpha K_\beta$	-3.202608	--
	$K_\alpha L_\alpha$	-2.118633	--
	$K_\beta L_\alpha$	-2.111486	--
	Total	-7.432727	-7.432724
4	$K_\alpha K_\beta$	-6.228283	--
	$K_\alpha L_\alpha$	-4.033451	--
	$K_\beta L_\alpha$	-4.015662	--
	Total	-14.277396	-14.27739
5	$K_\alpha K_\beta$	-10.253009	--
	$K_\alpha L_\alpha$	-6.575893	--
	$K_\beta L_\alpha$	-6.547088	--
	Total	-23.375991	-23.37599

Table (4): The energy expectation values of the excited state $(1s3s)\ ^2S$ in position space for Li-like ions.

Z	Shell	$(1s3s)\ ^2S$	
		$\langle E \rangle$ (a. u.) Present work	$\langle E \rangle$ (a. u.) Ref.[9]
3	$K_\alpha K_\beta$	-3.204714	--
	$K_\alpha M_\alpha$	-2.053550	--
	$K_\beta M_\alpha$	-2.051948	--
	Total	-7.3102121	-7.310209
4	$K_\alpha K_\beta$	-6.234587	--
	$K_\alpha M_\alpha$	-3.823728	--
	$K_\beta M_\alpha$	-3.819476	--
	Total	-13.877791	-13.87777
5	$K_\alpha K_\beta$	-10.264272	--
	$K_\alpha M_\alpha$	-6.150424	--
	$K_\beta M_\alpha$	-6.143353	--
	Total	-22.558050	-22.55803

Table (5) The difference between the energy expectation values of $(1s2s)\ ^2S$ and $(1s3s)\ ^2S$ states in position space for Li-like ions.

atom or ion	(a. u.) $\langle E \rangle$ Position space		$-\Delta E$ (a. u.)
	$(1s2s)\ ^2S$	$(1s3s)\ ^2S$	
Li	-7.432727	-7.3102121	0.122515
Be^+	-14.277396	-13.877791	0.399605
B^{2+}	-23.375991	-22.558005	0.817941

Conclusions:

From the present work, we deduced the following:

(1)In the position space the one-and two-particle expectation values of $(1s2s)\ ^2S$ and $(1s3s)\ ^2S$ states increase when the atomic number (Z) increases for the all shells for Li-like ions.

(2)The one-and two-particle expectation values of $(1s2s)\ ^2S$ state are larger than that of $(1s3s)\ ^2S$ state for the all shells except the K-shell for Li-like ions.

(3)The absolute values energy expectation values $\langle E \rangle$ of $(1s2s)\ ^2S$ state are larger than that of $(1s3s)\ ^2S$ state except the K-shell for Li-like ions, and they are increase with increasing the atomic number (Z) for both states due to large binding.

References:

[1] Roothaan, C. C. J.; Sachs, L. M. and Weiss, A. W. 1960. Analytical Self- Consistent Field Functions for the Atomic Configuratio $1S^2$, $1S^2 1S^1$, and $1S^2 1S^2$. Rev. Modern Phys. 32, 2,186.

[2] Banyard, K. E. 1968. Correlation of Electrons within the Hydride Ion. J. Chem. Phys. 48, (5): 2121.

[3] Al-Bayati, K. H. 1984. Thesis: Electron Correlation in the ^2S and ^2P States of Li- Like Ions. Ph.D Thesis, University of Leicester, United Kingdom.

[4] Banyard, K. E.1990. Coulomb correlation in a doubly occupied K shell: the influence of outer electrons. J. Phys.-B: At. Mol. Opt. Phys., 23,: 777.

[5] Koga, T.; Matsuyama, H.; Molina J. M. and Dehesa, J. S. 1999. Electron-pair densities of group 2 atoms in their ^{1}P and ^{3}P terms Eur. Phys. J. D. 7(1) 17.

[6] Chen, C. and Wang, Z. 2005. Oscillator Strenghts for $2s^2 – 2p^2$ P Transition of Lithium isoelectronic sequence from NaIX to CaXVIII. Commun. Theor. Phys. (Beijing, China), 43(2): 305.

[7] Huang, J.; Zhao, Q. and Jiang, G. 2010. Systematical Study on Ground-State Ionization Potentials for Boron and Carbon Isoelectronic Sequences with Z = 6–42.Commun. Theor. Phys. (Beijing, China), 54(5):871.

[8] Bubin, S. and Prezhdo, O. V. 2013. Excited States of positronic Lithium and Beryllium ,Phys. Rev. Lett. 111, 193401.

[9] Weiss, A. W.1963. Wave Function and oscillator strengths for the Lithium isoelectronic sequence. Astrophysical Journal, 138, 1262.

[10] Mohammed, M. J. 2014. M.Sc. Thesis (College of Science for Women), Baghdad, Iraq. See reference 83

[11] March, N. H. 1975. Self-Consistent Field in Atoms, First Edition, Pergamon Press Ltd, U. K.

[12] Banyard, K. E. and Baker, C. C. r, 1969. Analysis of Electron Correlation in Tow –Electron Systems H^-, He and Li^+". J. Chem. Phys, 51(6): 2680.

[13] Coulson, C. A. and Neilson, A. H. 1961. Electron Correlation in the Ground State of Helium, .Proc. Phys. Soc.,(78):831.

[14] Boyd, R. J. 1975. Angular aspects of exchange correlation and the Fermi hole Can. J. Phys.,(53): 592.

[15] Al-Mukhtar, H. M. 1998. A Stady of electron density distribution in each individual electronic shell in $(1s^2 3s)$ state MSc Thesis, AL-Nahrain University (University of Saddam in past), Baghdad, Iraq.

حساب طاقة ذرة الليثيوم المتهيجة في فضاء الموضع

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الخـلاصــة:

تم حساب واختبار القيمة المتوقعة للطاقة $\langle E \rangle$ لانظمة ذرة الليثيوم وشبيهاتها من الايونات (Li ، Be^{+} ، B^{2+}) ضمن الحالة الارضيه $(1s2s\alpha)^2S$ والحالة المتهيجة $(1s3s\alpha)^2S$ في فضاء الموضع . تم استخدام تقنية التجزئة لهارتري- فوك(H-F) باستخدام الدوال الموجية المتوفره .

الكلمات المفتاحية: القيمة المتوقعة للطاقة ،الانظمة الذرية، الحالة الارضية والحالة المتهيجة،تقريب هارتري- فوك .