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Inequalities of the electron density at the nucleus and radial expectation values of the ground state for the lithium isoelectronic sequence*

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The electron density at the nucleus, $\rho(0)$, and the radial expectation values, $< r^n >$ $(-2 \leq n \leq 10)$, of the ground state for the lithium isoelectronic sequence are calculated with a full core plus correlation (FCPC) wavefunctions. By using these obtained expectation values, the accurate inequalities of the electron density at the nucleus and the radial expectation values derived by Gálvez and Porras for these systems are examined and verified. The final results show that FCPC wavefunctions used in this work can give satisfactory results in full configuration space.

Keywords: electron density, radial expectation values, full core plus correlation
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1. Introduction

During the past two decades the ground states of the lithium isoelectronic sequence have been a subject of extensive computational studies using Hartree–Fock, the configuration-interaction (CI) and Hylleraas wavefunctions. The efforts of all these calculations have been mainly focused on the non-relativistic ground state energy of these systems. Other properties, such as the radial electron density in position space, have also been obtained.[1] The radial electron density plays an important role in the description and understanding of the dynamics of atomic and molecular systems.[2−5] This important concept not only allows a more convenient and transparent interpretation of many physical and chemical phenomena, but also is the cornerstone of modern atomic density function theories.[6,7]

Gálvez and Porras[8] studied numerically the property of the function $f(r) = \rho(r) + \rho'(r)/2Z$, where $\rho(r)$ is the radial electron density of ground state of an atom, and showed that $f(r) \geq 0$ everywhere. Then they used the positivity property of $f(r)$ to obtain several inequalities related to the electron density at the nucleus and radial expectation values. They also examined them by using Clementi and Roetti's data[9] for atoms in their ground state from Z=2 to 54 in the Hartree–Fock framework, and obtained satisfactory results.

Previously, Chung[10] has developed an elegant and complete variation approach, namely, full core plus correlation (FCPC) method. This method has been successfully applied to three- and four-electron systems with the $1s^2$-core.[11−15] Elaborate and accurate calculations for the oscillator strengths,[16] the hyperfine structure[17] and the g_J -factors[18] of the lithium-like systems have also been carried out by using this method. In FCPC method a large CI $1s^2$-core wavefunction is predetermined. This core wavefunction is frozen as a single term in the total three-electron wavefunction of the lithium-like system. The effect of the valence electron is accounted for by multiplying the core wavefunction with a linear combination of single-particle Slater orbitals. The relaxation of the core and the effect of the core–valence interaction are taken care of in terms of another large CI wavefunction. Considering the fact that the accuracy of Gálvez and Porras' inequalities would be a probe to determine the quality of the wavefunction in full configuration space, in this work, we calculate the

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electron density at the nucleus, $\rho(0)$, and the radial expectation values, $< r^n >$ $(-2 \leq n \leq 10)$, of the ground state for the lithium-like systems from Z=3 to 10 with FCPC wavefunctions. We aim to further examine the behaviour of our FCPC wavefunctions over the whole configuration space for the ground states of these lithium-like systems.

2. Theory

The radial electronic density function $D_0(r)$ can be written as

$$D_0(r) = r^2\rho(r), \tag{1}$$

where

$$\rho(r) = N\int_0^{\pi}\int_0^{2\pi} \mathrm{d}\Omega_1 \int \Psi^*(x_1, x_2, x_N) \times \Psi(x_1, x_2, x_N)\mathrm{d}s_1\mathrm{d}x_2\mathrm{d}x_N. \tag{2}$$

In these expressions, $\mathrm{d}\Omega_1 = \sin\theta_1\mathrm{d}\theta_1\mathrm{d}\phi_1$ and $x_i = (r_i, s_i)$ is a combined spatial and spin coordinate for i-th electron. Ψ is a normalized wavefunction in the position-space representation. In this paper the number of electrons in the system is N=3. The FCPC wavefunction of the three-electron systems with a $1s^2$-core is given by

$$\Psi(1,2,3) = A\Big[\Phi_{1s1s}(1,2)\sum_i d_i r_3^i \times \exp(-\beta r_3)Y_{l(i)}(3)\chi(3) + \sum_i C_i\Phi_{n(i),l(i)}(1,2,3)\Big], \tag{3}$$

where A is an antisymmetrization operator. Φ_{1s1s} is a predetermined $1s^2$-core wavefunction which is represented by a CI basis set, i.e.,

$$\Phi_{1s1s}(1,2) = A\sum_{k,n,l} C_{knl} r_1^k r_2^n \times \exp(-\beta_l r_1 - \rho_l r_2)Y_l(1,2)\chi(1,2). \tag{4}$$

The angular part is

$$Y_l(1,2) = \sum_m \langle l, m, l, -m|0, 0\rangle \times Y_{lm}(\theta_1, \varphi_1)Y_{l-m}(\theta_2, \varphi_2). \tag{5}$$

$\chi(1,2)$is a two-electron singlet spin function. The linear and nonlinear parameters in Eq.(4) are determined by optimizing the energy of the He-like 1s1s system. The factor multiplied with Φ_{1s1s} is a linear combination of the Slater type orbitals for the valence electron. The second term on the right-hand side of Eq.(3) describes the core relaxation and the intrashell electron–electron correlation in the three-electron system. The basis function is chosen as

$$\Phi_{n(i),l(i)}(1,2,3) = \varphi_{n(i)}(R)Y_{l(i)}^{LM}(\hat{R})\chi_{SM_s}. \tag{6}$$

The radial and angular basis functions are

$$\varphi_{n(i)}(R) = \prod_{j=1}^{3} r_j^{n_j}\exp(-\alpha_j r_j) \tag{7}$$

and

$$Y_{l(i)}^{LM}(\hat{R}) = \sum_{m_j}\langle l_1 m_1 l_2 m_2|l_{12}m_{12}\rangle \times \langle l_{12}m_{12}l_3m_3|LM\rangle\prod_{j=1}^{3} Y_{l_j m_j}(\Omega_j), \tag{8}$$

respectively, where $l(i)$ represents the set of l_1, l_2, l_{12} and l_3. The angular component is simply denoted as

$$l_i = [(l_1, l_2)l_{12}, l_3], \tag{9}$$

where l_{12} and l_3 coupling into L is implicitly implied. Using a similar notation, the doublet spin function can be represented by

$$\chi_{SM_s} = [(s_1, s_2)s_{12}, s_3]. \tag{10}$$

It has two possible spin doublets

$$\chi_1 = [(s_1, s_2)0, s_3], \tag{11}$$

$$\chi_2 = [(s_1, s_2)1, s_3]. \tag{12}$$

In this paper, these FCPC wavefunctions for the ground state of the lithium isoelectronic sequence are obtained by using the variation method.[10–15]

The following function can be defined through Eq.(2)

$$f(r) = \rho(r) + \frac{\rho'(r)}{2Z}, \tag{13}$$

where Z is the number of nuclear charge in the system. For atoms or ions in their ground state, the function $f(r)$ has the following property:

$$f(r) \geq 0, \tag{14}$$

which has been verified by March.[19]

By using the positivity of the function $f(r)$, several inequalities among moments of this function can be found. These moments are related to those of $\rho(r)$ by

$$\gamma_n = \int_0^{\infty} r^n f(r)\mathrm{d}r = \frac{< r^{-2} >}{4\pi} - \frac{\rho(0)}{2Z}, \quad (n = 0), \tag{15}$$

$$\gamma_n = \int_0^\infty r^n f(r)\mathrm{d}r$$
$$= \frac{1}{4\pi}\left[< r^{n-2} > - \frac{n}{2Z} < r^{n-3} > \right], \quad (n > 0), \quad (16)$$

where $\rho(0)$ is the electron density at the nucleus,

$$\rho(0) = \int_0^\infty \delta(r) D_0(r)\mathrm{d}r; \quad (17)$$

the radial expectation value $< r^n >$ is defined through Eq.(1) as

$$< r^n > = \int_0^\infty r^n D_0(r)\mathrm{d}r. \quad (18)$$

The Hadamard determinants[8] can be given by means of moments γ_n of $f(r)$

$$\Delta_m^{(n)} = \begin{vmatrix} \gamma_n & \gamma_{n+1} & \cdots & \gamma_{n+m} \\ \gamma_{n+1} & \gamma_{n+2} & \cdots & \gamma_{n+m+1} \\ \vdots & \vdots & \vdots & \vdots \\ \gamma_{n+m} & \gamma_{n+m+1} & \cdots & \gamma_{n+2m} \end{vmatrix}, \quad (19)$$

the application of the Stieljes theorem[20] to moments γ_n will lead to the positivity of Eq.(19) for any $n \geq 0$, and $m \geq 0$.

From the positivity of $\Delta_0^{(n)}(\gamma_n)$, we obtain the following relations:

(1) For n=0,

$$\rho(0) \leq \frac{Z < r^{-2} >}{2\pi} \equiv U_0^0. \quad (20)$$

(2) For $n > 0$,

$$< r^{n-3} > \leq \frac{2Z}{n} < r^{n-2} > \equiv U_0^n. \quad (21)$$

From the positivity of $\Delta_m^{(0)}$ we can improve Eq.(20) by including more expectation values (increasing the value of m). If we denote the determinant of the adjoint matrix in Eq.(19) by $adj(\gamma_j)$ corresponding to the element γ_{n+j} of the first row, when n=0, we obtain

$$\rho(0) \leq \frac{Z}{2\pi}\left[< r^{-2} > + 4\pi \frac{\sum_{j=1}^{m} \gamma_j adj(\gamma_j)}{adj(\gamma_0)} \right] \equiv U_m^0. \quad (22)$$

This is Gálvez and Porras' inequality of the electron density at the nucleus.[8] The second term on the right-hand side of Eq.(22) is a quantity smaller than zero for every m, and it depends on radial expectation values from $< r^{-2} >$ up to $< r^{2m-2} >$. For every $m > 0$, Eq.(22) gives an upper bound sharper than that given by Eq.(20).

The application of the positivity of Eq.(19), for a fixed value of $n > 0$, allows us to obtain upper bounds to $< r^{n-3} >$ in terms of other radial expectation values of high orders. The condition which leads to Gálvez and Porras' inequality of radial expectation values,[8] is of the form

$$< r^{n-3} > \leq \frac{2Z}{n}\left[< r^{n-2} > + 4\pi \frac{\sum_{j=1}^{m} \gamma_{n+j} adj(\gamma_{n+j})}{adj(\gamma_n)} \right] \equiv U_m^n, \quad (23)$$

where the second term on the right-hand side is a negative term too, which will improve the bounds defined in Eq.(21). Obviously, it depends on all the radial expectation values from $< r^{n-2} >$ up to $< r^{n+2m-2} >$.

Equations (22) and (23) can be verified by using all the radial expectation values calculated from our FCPC wavefunction determined above for the lithium isoelectronic sequence.

3. Results and discussion

In this paper, the same seven-angular-component 222 terms are used in the wavefunction for the $1s^2$-core. For the ground state in Li I, we choose the wavefunction with nine d_i terms and 650 terms in the $\Phi_{n(i),l(i)}$ of Eq.(3). Similarly, we choose the wavefunction with the same number of terms for d_i and about 300–600 terms in the $\Phi_{n(i),l(i)}$ of Eq.(3) for the other Z systems. The linear and nonlinear parameters are individually optimized in the energy minimization process. The electron density at the nucleus, $\rho(0)$, and radial expectation values $< r^n >$ $(-2 \leq n \leq 10)$ of the ground state for the lithium isoelectronic sequence from Z=3 to 10 are calculated from Eqs.(17) and (18) by using our FCPC wavefunctions obtained above. These theoretical results are given in Tables 1 and 2. King and Dressel[21] have also calculated these expectation values of the same atomic systems using Hylleraas approaches, most of their results agree with our calculation to five digits.

Table 1. The electron density at the nucleus $\rho(0)$ and radial expectation values $< r^n >$ $(n = -2 - 4)$ of the ground state for the lithium isoelectronic sequence.

Z	$\rho(0)$	$< r^{-2} >$	$< r^{-1} >$	$< r >$	$< r^2 >$	$< r^3 >$	$< r^4 >$
3	13.84223	30.24106	5.718046	4.989676	18.35581	92.61083	550.1345
4	35.10746	56.99613	7.973816	3.101452	6.508194	18.68781	63.22546
5	71.45828	92.26166	10.22547	2.282877	3.398179	6.902842	16.52786
6	126.9694	136.0334	12.47616	1.812811	2.098835	3.309338	6.151840
7	205.6789	188.3061	14.72650	1.505329	1.428085	1.842314	2.802402
8	311.6626	249.0814	16.97670	1.287832	1.035570	1.131081	1.456806
9	448.9721	318.3571	19.22682	1.125618	0.785726	0.744321	0.831512
10	621.6691	396.1336	21.47690	0.999884	0.616745	0.515897	0.508929

Table 2. The radial expectation values $< r^n >$ (n=5–10) of the ground state for the lithium isoelectronic sequence.

Z	$< r^5 >$	$< r^6 >$	$< r^7 >$	$< r^8 >$	$< r^9 >$	$< r^{10} >$
3	3.70505(3)[a)]	2.77310(4)[a)]	2.29198(5)[a)]	2.07159(6)[a)]	2.03304(7)[a)]	2.15291(8)[a)]
4	2.41357(2)[a)]	1.02224(3)[a)]	4.75578(3)[a)]	2.41184(4)[a)]	1.32487(5)[a)]	7.84046(5)[a)]
5	4.45957(1)[a)]	1.33257(2)[a)]	4.36579(2)[a)]	1.55660(3)[a)]	6.00262(3)[a)]	2.49025(4)[a)]
6	1.28799(1)[a)]	2.98292(1)[a)]	7.56714(1)[a)]	2.08720(2)[a)]	6.22154(2)[a)]	1.99369(3)[a)]
7	4.798952	9.085893	1.88293(1)[a)]	4.24012(1)[a)]	1.03132(2)[a)]	2.69540(2)[a)]
8	2.111789	3.383111	5.929655	1.12887(1)[a)]	2.32047(1)[a)]	5.12398(1)[a)]
9	1.045299	1.451754	2.205191	3.637212	6.475968	1.23842(1)[a)]
10	0.564882	0.692522	0.928321	1.350904	2.121598	3.577839

[a)] The notation (n) signifies $\times 10^n$.

Using the data in Tables 1 and 2, we can examine several inequalities derived by Gálvez and Porras for the lithium-like systems. According to the ratios $R_m = \rho(0)/U_m^0$ defined by Gálvez and Porras, we can study the accuracy of the upper bounds given by Eq.(22) for the lithium isoelectronic sequence. The test of the upper bounds to the electron density at the nucleus, $\rho(0)$, is listed in Table 3. From this table we can see that the values of R_m approximate rapidly to 1 when m increases for the same row and increases gradually as Z increases for the same column. In order to see clearly the regularity of the data listed in Table 3, we plot these data in Fig.1.

Many inequalities among radial expectation values for the lithium isoelectronic sequence can be obtained through Eq.(23). We will test the upper bounds given by Eq.(23) to $< r^a >$ $(-2 \leq a \leq 2)$ using the ratios $R_m =< r^n > /U_m^n$. The radial expectation values used in the calculation are obtained from Tables 1 and 2. These tested results are listed in Tables 4–7. It can also be found from these tables that the regularities exhibited in the data of each table are analogous to those in Table 3. All of them follow a well-behaved isoelectronic trend.

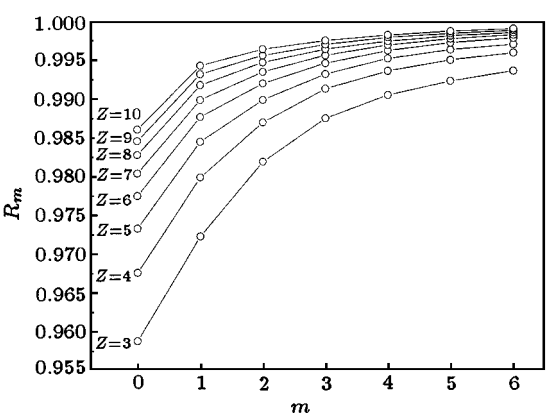


Fig.1. Comparison of the upper bounds to the electron density at the nucleus $\rho(0)$ of the ground state for the lithium isoelectronic sequence.

Table 3. Test of the upper bounds to the electron density at the nucleus $\rho(0)$ of the ground state for the lithium isoelectronic sequence.

Z	$\rho(0)$	R_0	R_1	R_2	R_3	R_4	R_5	R_6
3	13.84423	0.9588	0.9723	0.9819	0.9875	0.9905	0.9923	0.9936
4	35.10746	0.9676	0.9799	0.9870	0.9913	0.9936	0.9950	0.9959
5	71.46018	0.9733	0.9845	0.9899	0.9932	0.9952	0.9963	0.9970
6	126.9734	0.9775	0.9877	0.9920	0.9946	0.9962	0.9972	0.9978
7	205.6854	0.9804	0.9899	0.9935	0.9956	0.9969	0.9977	0.9982
8	311.6726	0.9828	0.9918	0.9947	0.9964	0.9974	0.9981	0.9985
9	448.9821	0.9846	0.9932	0.9956	0.9970	0.9979	0.9984	0.9988
10	621.6791	0.9861	0.9943	0.9964	0.9975	0.9982	0.9987	0.9990

Table 4. Test of the upper bounds to the radial expectation values $< r^{-2} >$ of the ground state for the lithium isoelectronic sequence.

Z	$< r^{-2} >$	R_0	R_1	R_2	R_3	R_4	R_5
3	30.24116	0.8815	0.9377	0.9589	0.9725	0.9814	0.9869
4	56.99613	0.8935	0.9549	0.9728	0.9825	0.9885	0.9921
5	92.26166	0.9023	0.9645	0.9799	0.9873	0.9917	0.9943
6	136.0334	0.9086	0.9707	0.9843	0.9902	0.9936	0.9957
7	188.3061	0.9133	0.9750	0.9873	0.9922	0.9949	0.9965
8	249.0814	0.9170	0.9782	0.9895	0.9937	0.9958	0.9972
9	318.3571	0.9199	0.9807	0.9912	0.9948	0.9966	0.9977
10	396.1336	0.9222	0.9827	0.9926	0.9957	0.9972	0.9981

Table 5. Test of the upper bounds to the radial expectation values $< r^{-1} >$ of the ground state for the lithium isoelectronic sequence.

Z	$< r^{-1} >$	R_0	R_1	R_2	R_3	R_4	R_5
3	5.718046	0.6353	0.8704	0.9312	0.9562	0.9706	0.9801
4	7.973816	0.6645	0.9012	0.9550	0.9741	0.9831	0.9893
5	10.22547	0.6817	0.9169	0.9660	0.9816	0.9888	0.9928
6	12.47616	0.6931	0.9265	0.9724	0.9859	0.9916	0.9947
7	14.72650	0.7013	0.9331	0.9766	0.9886	0.9934	0.9959
8	16.97670	0.7074	0.9378	0.9796	0.9906	0.9947	0.9967
9	19.22682	0.7121	0.9414	0.9818	0.9920	0.9956	0.9973
10	21.47690	0.7159	0.9443	0.9836	0.9931	0.9964	0.9978

Table 6. Test of the upper bounds to the radial expectation values $< r >$ of the ground state for the lithium isoelectronic sequence.

Z	$< r >$	R_0	R_1	R_2	R_3	R_4
3	4.989676	0.1812	0.6287	0.8755	0.9553	0.9788
4	3.101452	0.2383	0.7164	0.9170	0.9713	0.9876
5	2.282877	0.2687	0.7535	0.9327	0.9780	0.9910
6	1.812811	0.2879	0.7742	0.9410	0.9814	0.9928
7	1.505329	0.3012	0.7873	0.9461	0.9835	0.9938
8	1.287832	0.3109	0.7966	0.9496	0.9850	0.9945
9	1.125618	0.3184	0.8034	0.9522	0.9860	0.9950
10	0.999884	0.3242	0.8086	0.9541	0.9868	0.9954

Table 7. Test of the upper bounds to the radial expectation values $< r^2 >$ of the ground state for the lithium isoelectronic sequence.

Z	$< r^2 >$	R_0	R_1	R_2	R_3
3	18.35582	0.1652	0.6330	0.8930	0.9670
4	6.508194	0.2177	0.7173	0.9273	0.9787
5	3.398179	0.2461	0.7526	0.9399	0.9830
6	2.098836	0.2643	0.7723	0.9465	0.9853
7	1.428085	0.2768	0.7848	0.9506	0.9867
8	1.035570	0.2861	0.7935	0.9534	0.9875
9	0.785726	0.2932	0.7999	0.9553	0.9881
10	0.616745	0.2989	0.8048	0.9569	0.9887

In summary, we have examined and verified Gálvez and Porras' inequalities of the electron density at the nucleus $\rho(0)$ and radial expectation values $< r^a >$ $(-2 \leq a \leq 2)$ of the ground state for the lithium isoelectronic sequence from Z=3 to 10 by using the FCPC wavefunctions. The final results show that Gálvez and Porras' several accurate inequalities are valid for the lithium-like systems. It is also shown that our present FCPC wavefunction can give the reasonable and satisfactory results in full configuration space.

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