Charge density at the nucleus and radial behavior of ground state for lithium-like ions with $Z = 21$ to 30*

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By using the full-core plus correlation (FCPC) type wave functions, the accurate charge densities $\rho(0)$ at the nucleus and the radial expectation values of the ground states for the lithium-like systems with $Z = 21$ to 30 are obtained. The determinantal conditions and the electron-nucleus cusp condition are used to calculate the inequalities of the upper and the lower bounds to $\rho(0)$ with two or more expectation values. These inequalities, derived by Angulo and Dehesa [*Phys. Rev.* A **44** 1516 (1991)], are verified to be also valid for these ions with higher nuclear charge. The present results show that the wave functions used in this paper are satisfactory in the whole configuration space for these ions with higher nuclear charge.

Keywords: electron density, radial expectation values, upper and lower bounds, full core plus correlation method

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1. Introduction

Lithium and lithium-like ions are the most fundamental few-body systems. During the past two decades, some advances in high-precision calculations for these systems have been made.[1−5] The efforts of these calculations have been mainly focused on the energy levels, including the corrections from relativistic and quantum electrodynamic (QED) effects. Information about the charge density in the ground state is very important for the atomic structure and the properties in the density functional theory framework.[6,7] Some rigorous results, such as the lower and the upper bounds to the electron densities at the nucleus in the case of neutral atoms with $Z = 1$ to 54, have been obtained.[8−10] For the ground states of the lithium-like systems with $Z = 3$ to 10, King *et al.*[11,12] used the Hylleraas-type wave functions to study the radial electronic charge densities.

As is known, one of the important features of the ion with the higher nuclear charge lies in the fact that its electron density distribution is obviously compressed into the space near the nucleus. Therefore the study on the electronic charge density at the nucleus should be considered as a probe into the quality of the wave functions over the whole configuration space, especially, in the region near the nucleus, for these ions. Chung[13] has developed an elegant and complete variation approach, namely, the full-core plus correlation (FCPC) method. In a series of papers,[14−26] this method has been successfully applied to calculate ionization potential, transition energy, and oscillator strength for three-electron systems with a $1s^2$ core.

In this paper, we choose the ground states of the lithium-like systems with $Z = 21$ to 30 as our focus, and calculate their electron densities at the nucleus $\rho(0)$ and the radial expectation values $\langle r^\alpha \rangle$ $(-2 \leq \alpha \leq 10)$ by using the FCPC-type wave functions. Based on these results, the famous tight upper bound to the electron density at the nucleus (which was derived by Hoffmann-Ostenhof *et al.*[27] by assuming an infinite nuclear mass) and the lower bound are calculated. Finally, some inequalities involving two and three radial expectation values for these systems are investigated. We aim to further examine the quality of our FCPC wave functions over the whole configuration space, especially, in the region near the nu-

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cleus, for these systems with higher nuclear charge.

2. Theory

The electron density is given by

$$\rho(r) = N \int_0^{\pi} \int_0^{2\pi} \mathrm{d}\Omega_1 \int \Psi^*(x_1, x_2, \ldots, x_N) \times \Psi(x_1, x_2, \ldots, x_N) \mathrm{d}x_1 \mathrm{d}x_2 \cdots \mathrm{d}x_N, \tag{1}$$

where Ψ is a normalized position-space representation of the wave function, $\mathrm{d}\Omega_1 = \sin\theta_1 \mathrm{d}\theta_1 \mathrm{d}\phi_1$, and $x_i = (r_i, s_i)$ is a combined spatial and spin coordinate for the i-th electron. In this paper, the number of electrons in the system is $N = 3$.

The FCPC-type wave function of $1s^2 2s$ state for the lithium-like system is given by

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

where A is an antisymmetrization operator, and Φ_{1s1s} is a predetermined $1s^2$-core wave function.[13] The second term on the right-hand side describes the intrashell electron correlation and the relaxation of the core in the three-electron system. The basis function $\Phi_{n(i),l(i)}(1,2,3)$ is chosen to be

$$\Phi_{n(i),l(i)}(1,\,2,\,3) = \varphi_{n(i)}(R)\mathrm{Y}_{l(i)}^{LM}(\hat{R})\chi_{SM_S}. \tag{3}$$

Its radial and angular parts are

$$\varphi_{n(i)}(R) = \prod_{j=1}^{3} r_j^{n_j} \exp(-\beta_j r_j) \tag{4}$$

and

$$\mathrm{Y}_{l(i)}^{LM}(\hat{R}) = \sum_{m_j} \langle l_1 m_1 l_2 m_2 | l_{12} m_{12}\rangle \langle l_{12} m_{12} l_3 m_3 | LM\rangle \times \prod_{j=1}^{3} \mathrm{Y}_{l_j m_j}(\Omega_j), \tag{5}$$

respectively, where $l(i)$ represents the set of l_1, l_2, l_{12}, and l_3, R represents the radial parts of r_1, r_2, and r_3, $\hat{R}$ represents their angular parts, and M_S is the z-component of the total spin S. The linear and the nonlinear parameters in Eq. (1) are determined by using the Rayleigh–Ritz variation method.[13]

A theorem of Stieltjes[28] shows that if $f_m^{(k)}(r) = (-1)^k \rho^{(k)}(r) r^m$ is a function, then the moments of function $\nu_\alpha(k,m)$ can be defined by

$$\nu_\alpha(k,m) = \int_0^{\infty} r^\alpha f_m^{(k)}(r)\mathrm{d}r = \begin{cases} (-1)^{k-\alpha-m-1}\rho^{(k-\alpha-m-1)}(0)\,(\alpha+m)!, & (\alpha = -m, -m-1, \ldots, k-m-1), \\ \frac{\Gamma(\alpha+m+1)}{4\pi\,\Gamma(\alpha+m-k+1)}\langle r^{\alpha+m-k-2}\rangle, & (\alpha > k-m-1), \end{cases} \tag{6}$$

where $\rho^n(0)$ is the n-th order derivative of the electron density at the nucleus, and the radial expectation values $\langle r^\alpha\rangle$ is defined by

$$\langle r^\alpha\rangle = 4\pi \int r^{\alpha+2}\rho(r)\mathrm{d}r. \tag{7}$$

Its moments satisfy the following determinant inequalities:

$$\Delta_j^{(0)} \geq 0, \quad \Delta_j^{(1)} \geq 0, \quad j = 0, 1, \ldots, \tag{8}$$

where the symbols denote the Hadamard determinants

$$\Delta_j^{(i)} = \begin{vmatrix} \nu_i & \nu_{i+1} & \cdots & \nu_{i+j} \\ \nu_{i+1} & \nu_{i+2} & \cdots & \nu_{i+j+1} \\ \vdots & \vdots & \ddots & \vdots \\ \nu_{i+j} & \nu_{i+j+1} & \cdots & \nu_{i+2j} \end{vmatrix}. \tag{9}$$

On the other hand, a good wave function not only is able to give the variational energy that is close to the true eigenvalue, but also should satisfy the famous cusp condition introduced by Kato and Steiner,[29,30] which states that

$$\rho(0) + \frac{\rho'(0)}{2Z} = 0. \tag{10}$$

Now we will only show the positive values of determinants $\Delta_1^{(0)}$ and $\Delta_1^{(1)}$, because they are physically interesting, nontrivial, and simple.

For $m = k-1$, the non-negativity values of determinant $\Delta_1^{(1)}$ together with the moment values (6) produce the lower bound to the electron density at the nucleus

$$\rho(0) \geq \frac{1}{4\pi}\frac{k}{k+1}\frac{\langle r^{-2}\rangle^2}{\langle r^{-1}\rangle}, \quad k = 1, 2, \ldots. \tag{11}$$

This is the so-called Angulo and Dehesa inequality of electron density at the nucleus.[8] The lower bounds are naturally improved when higher values of k are used in Eq. (11).

For $m = k-2$ and $m = k+n$ $(n > -1)$, these two conditions lead to Angulo and Dehesa's first derivative of the single-particle density at the origin, and the inequalities of the radial expectation values[8] have the

following forms respectively:

$$-\rho'(0) \geq 4\pi \frac{k-1}{k} \frac{[\rho(0)]^2}{\langle r^{-2} \rangle}, \quad k = 2, 3, \ldots, \tag{12}$$

$$\langle r^n \rangle \langle r^{n-2} \rangle \geq \frac{(k+n+1)(n+2)}{(k+n+2)(n+1)} \langle r^{n-1} \rangle^2, \quad n > -1, \quad k = 0, 1, \ldots. \tag{13}$$

Obviously, Eq. (13) depends on the radial expectation values $\langle r^\alpha \rangle$ with $\alpha = n$, $n-1$, and $n-2$.

It is not difficult to see that inequalities (11)–(13) are optimal in the completely monotonic case, i.e., for $k = \infty$. In this case, we can obtain the following rigorous inequalities:

$$\rho(0) \geq \frac{1}{4\pi} \frac{\langle r^{-2} \rangle^2}{\langle r^{-1} \rangle}, \tag{14}$$

$$-\rho'(0) \geq 4\pi \frac{[\rho(0)]^2}{\langle r^{-2} \rangle}, \tag{15}$$

and

$$\langle r^n \rangle \langle r^{n-2} \rangle \geq \frac{(n+2)}{(n+1)} \langle r^{n-1} \rangle^2, \quad n > -1. \tag{16}$$

Some particular cases of Eq. (16) are

$$N \langle r^{-2} \rangle \geq 2 \langle r^{-1} \rangle, \tag{17}$$

$$\langle r^{-1} \rangle \langle r \rangle \geq \frac{3}{2} N^2, \tag{18}$$

$$N \langle r^{-2} \rangle \geq \frac{4}{3} \langle r \rangle^2, \tag{19}$$

where we have made use of $\langle r^0 \rangle = N$.

3. Results and discussion

In our calculations, the seven-angular-component 222 terms are used in the $1s^2$-core wavefunctions, and atomic units are used in this paper. For the ground states of the lithium-like ions, we choose the wavefunction with nine d_i terms and 1013 terms in $\Phi_{n(i),l(i)}$ of Eq. (2). The linear and the nonlinear parameters in Eq. (2) are individually optimized in the process of minimizing the energy of the system. The electron densities at the nucleus, $\rho(0)$, and radial expectation values, $\langle r^\alpha \rangle$ ($-2 \leq \alpha \leq 10$), for the ground states of lithium isoelectronic sequence with $Z = 21$ to 30 are calculated by using our FCPC wave functions determined above. The results are given in Tables 1 and 2. It is seen from Table 1 that as Z increases along the isoelectronic sequence, the electron density at the nucleus rapidly increases. Figure 1 shows the variation of the electron density at the nucleus with Z, which is not difficult to understand. In fact, the reduction in the size of an ion with Z increasing from 21 to 30, as shown by the $\langle r \rangle$ values listed in Table 1, results in the compression of the wave function. Hence the electron density at the nucleus monotonously increases with Z. Figures 2 and 3 give the radial expectation values $\langle r^{-2} \rangle$ and $\langle r^2 \rangle$ for the ground states of these systems, respectively. As nuclear charge Z increases, the electronic orbits are gradually localized at the regions near the nuclei, and the amplitudes of the wave functions for these systems obviously increase in these regions. The radial expectation values , $\langle r^\alpha \rangle$ ($\alpha < 0$, $\alpha = -1, -2$), mainly depend on the radial behavior of the wave functions in the region near to the nucleus. Thus these expectation values increase as nuclear charge Z increases. On the other hand, the radial expectation values, $\langle r^\alpha \rangle$ ($\alpha > 0$, $\alpha = 1, 2, \ldots, 10$), mainly depend on the behavior of the wave functions in the region far away from the nucleus. For the same reason mentioned above, as nuclear charge Z increases, the amplitudes of the wave functions in the region far away from the nucleus reduce gradually. Thus the radial expectation values $\langle r^\alpha \rangle$ ($\alpha > 0$, $\alpha = 1, 2, \ldots, 10$) also reduce gradually with the increasing Z.

Table 1. Electron density at the nucleus $\rho(0)$ and radial expectation values $\langle r^\alpha \rangle$ ($-2 \leq \alpha \leq 4$) of the ground state for the lithuim isoelectronic sequence.

Z	$\rho(0)/10^3$	$\langle r^{-2} \rangle/10^3$	$\langle r^{-1} \rangle/10$	$\langle r \rangle/10^{-1}$	$\langle r^2 \rangle/10^{-2}$	$\langle r^3 \rangle/10^{-2}$	$\langle r^4 \rangle/10^{-3}$
21	6.017461	1.812691	4.6227136	4.4945998	12.184965	4.4649350	19.297566
22	6.931331	1.992470	4.8477140	4.2806405	11.043028	3.8500541	15.832358
23	7.933332	2.180748	5.0727136	4.0861399	10.054485	3.3431205	13.111321
24	9.027588	2.377527	5.2977148	3.9085592	9.1930346	2.9214450	10.950670
25	10.21843	2.582812	5.5227147	3.7457799	8.4377828	2.5678293	9.2174469
26	11.50880	2.796581	5.7477119	3.5960260	7.7719563	2.2690687	7.8139790
27	12.90395	3.018861	5.9727160	3.4577887	7.1819625	2.0149255	6.6678077
28	14.40772	3.249641	6.1977138	3.3297941	6.6567155	1.7973714	5.7243291
29	16.02384	3.488919	6.4227131	3.2109402	6.1870645	1.6100465	4.9419734
30	17.75657	3.736699	6.6477151	3.1002821	5.7654385	1.4478859	4.2889116

Table 2. Radial expectation values $\langle r^{\alpha}\rangle$ $(5 \leq \alpha \leq 10)$ of the ground state for the lithium isoelectronic sequence.

Z	$\langle r^5\rangle/10^{-3}$	$\langle r^6\rangle/10^{-3}$	$\langle r^7\rangle/10^{-4}$	$\langle r^8\rangle/10^{-4}$	$\langle r^9\rangle/10^{-4}$	$\langle r^{10}\rangle/10^{-4}$
21	9.3791087	5.0297090	0.29457867	18.707521	12.807294	9.4046833
22	7.3213604	3.7355266	0.20815415	12.577106	8.1925880	5.7245111
23	5.7823207	2.8135822	0.1951297	8.6149819	5.3515190	3.5660852
24	4.6157203	2.1464922	0.1.0901130	6.0029780	3.5638331	2.2698051
25	3.7205629	1.6569004	8.0584769	4.2504014	2.4180225	1.4775311
26	3.0258174	1.2926603	6.0305785	3.0505070	1.6635276	0.97317747
27	2.4811171	1.0185224	4.5657356	2.2190586	1.1626329	0.65339636
28	2.0499635	0.80987068	3.4937194	1.6340372	0.82382071	0.44549315
29	1.7056447	0.64939076	2.6995792	1.2165776	0.59088922	0.30774998
30	1.4285212	0.52487784	2.1057923	0.91592586	0.42943059	0.21595380

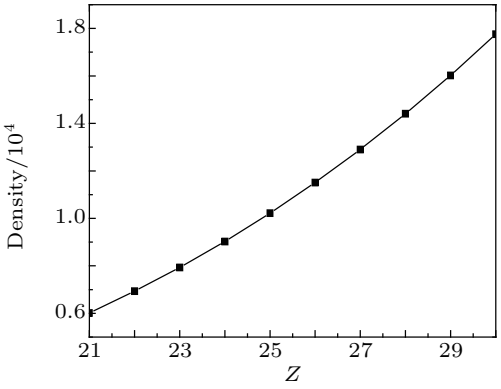


Fig. 1. Electron density at the nucleus of the ground state for the lithium isoelectronic sequence with $Z = 21$ to 30.

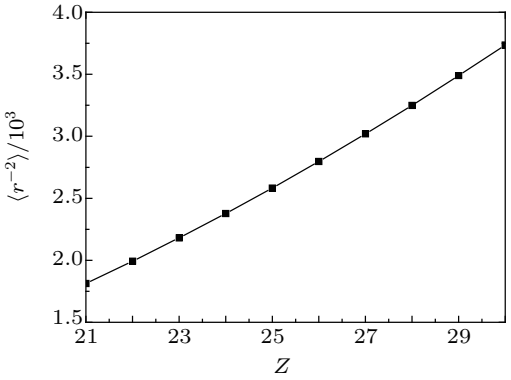


Fig. 2. Radial expectation value $\langle r^{-2}\rangle$ for the ground states of lithium-like systems ($Z = 21$–30).

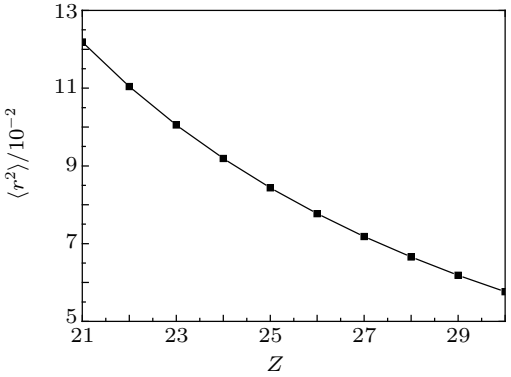


Fig. 3. Radial expectation value $\langle r^2\rangle$ for the ground states of lithium-like systems ($Z = 21$–30).

Using part of the data shown in Tables 1 and 2, we can examine the inequalities defined by Angulo and Dehesa to study the upper and the lower bounds to the electron density at the nucleus for the lithium-like systems with higher Z. Inequality (15) together with the electron-nucleus cusp condition[29,30] $\rho'(0) = -2Z\rho(0)$ produces the upper bound

$$\rho(0) \leq \frac{Z}{2\pi}\langle r^{-2}\rangle. \tag{20}$$

This is the famous upper bound to the electron density at the nucleus given by Hoffmann-Ostenhof *et al.*[27] Here it should be noted that Cioslowski[31] has found a three-moment approximate expression for $\rho(0)$, which coincides with this bound and has a higher accuracy. Inequality (14) gives a lower bound to $\rho(0)$.

The upper bounds (UB) and the lower bounds (LB) to the electron densities at the nucleus for the ground states of the lithium-like systems with $Z = 21$ to 30, which are obtained from Eqs. (20) and (14), respectively, are given in Table 3. We notice from this table the following facts. Firstly, all of $\rho(0)$ values obtained in this paper lie between the upper bounds and the lower bounds, and the accuracy of both bounds is improved as the value of Z increases along the isoelectronic sequence. On the contrary, the ratios between $\rho(0)$ and the bounds decrease as nuclear charge Z increases for the neutral atomic systems in Ref. [8]. This difference arises from that the wave function of the three-electron ion with a $1s^2$-core becomes more localized as nuclear charge Z increases. Secondly, in comparison with the lower bounds, our $\rho(0)$ values are more closed to their upper bounds. Finally, in order to further examine the applicability of inequalities (17)–(19) for the ions with higher Z, we can define the

ratios of these inequalities as

$$R_0 = \frac{2}{N}\frac{\langle r^{-1}\rangle^2}{\langle r^{-2}\rangle}, \quad R_1 = \frac{3N^2}{2\langle r^{-1}\rangle\langle r\rangle},$$
$$R_2 = \frac{4}{3N}\frac{\langle r\rangle^2}{\langle r^2\rangle}. \tag{21}$$

Our results are given in Table 4. It is seen from this table that although the quality of inequality (17) is higher than that of the other two inequalities (18) and (19), the latter two inequalities can still be regarded as reasonable and accurate for all ions considered here.

Table 3. Comparison of the upper bound, $U = (Z/2\pi)\langle r^{-2}\rangle$, and the lower bound, $L = (Z/4\pi)(\langle r^{-2}\rangle^2/\langle r^{-1}\rangle)$, with the charge density at the nucleus, $\rho(0)$, for the lithium-like systems. Ratios between bounds and $\rho(0)$ are also given.

Z	$\rho(0)$	LB	UB	LB $\cdot\rho(0)^{-1}$ /%	UB $\cdot\rho(0)^{-1}$/%
21	6017.461	5656.409	6058.474	93.99992	99.32306
22	6931.331	6516.835	6976.452	94.01997	99.35324
23	7933.332	7460.378	7982.767	94.03839	99.38073
24	9027.588	8490.875	9081.484	94.05475	99.40652
25	10218.43	9612.211	10276.68	94.06740	99.43314
26	11508.80	10828.04	11572.33	94.08489	99.45100
27	12903.95	12142.40	12972.60	94.09831	99.47081
28	14407.72	13559.05	14481.50	94.10964	99.49052
29	16023.84	15081.81	16103.08	94.12106	99.50790
30	17756.57	16714.52	17841.42	94.13148	99.52440

Table 4. Ratios R_i $(i = 0, 1, 2)$ defined in text are given in percentage.

Z	R_0	R_1	R_2
21	78.59209	64.97492	73.68436
22	78.63048	65.05611	73.74740
23	78.66541	65.12988	73.80472
24	78.69742	65.19714	73.85705
25	78.72653	65.25877	73.90498
26	78.75377	65.31545	73.94908
27	78.77880	65.36773	73.98971
28	78.80185	65.41613	74.02735
29	78.82335	65.46107	74.06230
30	78.84341	65.50285	74.09476

It should be mentioned here that the consideration of the order $j \geq 2$ for determinantal inequalities (8) can lead to more accurate bounds. But by doing so, one needs to use much more radial expectation values, which will make the calculation more cumbersome.

4. Conclusion

In this paper, the electron densities at the nucleus, $\rho(0)$, and radial expectation values, $\langle r^\alpha\rangle$ $(-2 \leq \alpha \leq 10)$, of the ground states for the lithium-like ions with $Z = 21$ to 30 have been obtained by using the FCPC-type wave functions. The $\rho(0)$ monotonically increases with Z increasing along the isoelectronic sequence. For these ions with higher nuclear charge, the applicability of some inequalities derived by Angulo and Dehesa in the case of a neutral atom has been investigated. The reliabilities of these inequalities depend on the accuracy of the radial behavior for the wave function used in the calculations. The results show that Angulo and Dehesa' inequalities are also valid for these ions with higher nuclear charge, and our FCPC wave functions can give satisfactory results in the whole configuration space, including the region near the nucleus for these systems with higher nuclear charge.

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