

Ionization potential of the lithiumlike $1s^2 2s$ states from lithium to neon

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The ionization potentials of the $1s^2 2s$ states are calculated for $Z=3$ to 10 with a method of full core plus correlation using multiconfiguration interaction wave functions. Relativistic and mass polarization effects are included using first-order perturbation theory. The QED contributions to the ionization potential are calculated using effective nucleus charges. The results of this work generally agree with those of experiments. For example, our predicted ionization potentials for Li I and Be II are 43 487.15(9) and 146 883.03(18) cm^{-1} in comparison with the experimental results of 43 487.15 and 146 882.86 cm^{-1} , respectively. The predicted nonrelativistic energies in this work agree with those of King [Phys. Rev. A **40**, 1735 (1989); **38**, 6017 (1988)]. Our results show that the higher-order relativistic perturbation tends to reduce the ionization potential. It becomes appreciable for $Z \geq 7$, increases from less than 1 cm^{-1} for carbon to about 14 cm^{-1} for Ne. Although the agreement between our predictions and experiments is good for most systems, there is a clear discrepancy of more than 1 cm^{-1} in the case of boron. The reason for this discrepancy is not understood at this time.

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I. INTRODUCTION

The multiconfiguration wave-function approach to the atomic structure problem has the advantage that it can be applied to many-electron systems easily. This type of wave function has been used effectively in multiconfiguration Hartree-Fock (MCHF) calculations [1]. The multiconfiguration-interaction (CI) approach is also powerful. For some core-excited systems, highly accurate results have been obtained using this method [2]. However, for systems with a $1s^2$ core, it is difficult to obtain an accurate energy with CI wave functions. This is because the large contribution to the $1s^2$ core coming from the high-angular-momentum components makes the convergence slower [3]. Here the correlated-coordinate (Hylleraas-type) wave function becomes very effective [4], even though the convergence rate is still quite slow. However, it is difficult to extend the correlated-coordinate approach to a general many-particle system. For this reason, it is of interest to know whether accurate CI predictions are possible for systems with a $1s^2$ core, in spite of the inherent shortcomings. We will use the ionization potential (IP) for lithiumlike $1s^2 2s$ states as a test case and compare our results with high-precision experiments.

The method adopted in this work is to use a large CI $1s^2$ -core wave function which is sufficiently saturated in its radial correlation for each angular component. The large wave function is then used as a single entity in the total three-electron wave function. The relaxation of the core and other correlation effects are accounted for by adding another large CI function. By comparing the three-electron energy and the two-electron energy of the core, the IP can be predicted. The basic concept of this approach is perhaps as old as quantum mechanics itself. It is the advance of computer technology and the availa-

bility of computing resources that allow us to carry this old concept to its potential.

In this work, we calculate the IP for $1s^2 2s^2 S$ states from $Z=3$ to 10. The relativistic effects are calculated using first-order perturbation theory. The mass-polarization effect is included. To make a definitive comparison with the experiment, the radiative correction is calculated using the equation in Bethe and Salpeter [5].

The computation carried out in this work and the results presented are mostly in atomic units (a.u.). It is a convenient unit to use in computing different theoretical results. However, accurate experimental data are mostly given in cm^{-1} or eV. Therefore, to make a definitive comparison with the experiment, our IP's are converted into cm^{-1} using the reduced Rydberg constant. The corresponding nuclear mass is taken from Wapstra and Audi [6]. The isotopes used in this work are ^7Li , ^9Be , ^{11}B , ^{12}C , ^{14}N , ^{16}O , ^{19}F , and ^{20}Ne . The reduced Rydberg constants agree with those of Pekeris [7] to eight digits. The conversion factor from cm^{-1} to eV in this work is 0.000 123 984 24 [8]. This is very close to the value 0.000 123 985 used in Kelly [9] but different from the 0.000 123 95 used in Moore [10].

II. THEORY

The LS coupling scheme is used in the present work. The nonrelativistic Hamiltonian is given by (in a.u.)

$$H_0 = \sum_{i=1}^3 \left[-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right] + \sum_{\substack{i,j=1 \\ i < j}} \frac{1}{r_{ij}}. \quad (1)$$

The relativistic and mass-polarization perturbation operators are

$$H' = H_1 + H_2 + H_3 + H_4 + H_5, \quad (2)$$

where

$$H_1 = -\frac{1}{8c^2} \sum_{i=1}^3 \mathbf{P}_i^4 \quad (3)$$

(correction to kinetic energy),

$$H_2 = \frac{Z\pi}{2c^2} \sum_{i=1}^3 \delta(\mathbf{r}_i) \quad (4)$$

(Darwin term),

$$H_3 = -\frac{\pi}{c^2} \sum_{\substack{i,j=1 \\ i < j}} (1 + \frac{8}{3} \mathbf{s}_i \cdot \mathbf{s}_j) \delta(\mathbf{r}_{ij}) \quad (5)$$

(electron-electron contact term),

$$H_4 = -\frac{1}{M} \sum_{\substack{i,j=1 \\ i < j}} \nabla_i \cdot \nabla_j \quad (6)$$

(mass polarization),

$$H_5 = -\frac{1}{2c^2} \sum_{\substack{i,j=1 \\ i < j}} \frac{1}{r_{ij}} \left[\mathbf{P}_i \cdot \mathbf{P}_j + \frac{\mathbf{r}_{ij}(\mathbf{r}_{ij} \cdot \mathbf{P}_i) \cdot \mathbf{P}_j}{r_{ij}^2} \right] \quad (7)$$

(orbit-orbit interaction), where M is the nuclear mass. For the two-electron core, we use the wave function

$$\Phi_{1s1s}(\mathbf{r}_1, \mathbf{r}_2) = A \sum_{k,n,l} c_{knl} r_1^k r_2^n e^{-\beta_l r_1 - \rho_l r_2} \times Y_l(1,2) \chi(1,2), \quad (8)$$

where A is the antisymmetrization operator and $\chi(1,2)$ represents the singlet spin function. The angular component is given by

$$Y_l(1,2) = \sum_m \langle l, m, l, -m | 0, 0 \rangle Y_{lm}(\theta_1, \phi_1) Y_{l, -m}(\theta_2, \phi_2). \quad (9)$$

The nonlinear parameters β_l and ρ_l are individually optimized in the energy minimization process. The total wave function of the three-electron system is given by

$$\Psi(1,2,3) = A \left[\Phi_{1s1s}(1,2) \sum_i d_i r_3^i e^{-\beta r_3} \chi(3) + \sum_i C_i \Phi_{n(i),l(i)}(1,2,3) \right]. \quad (10)$$

The second term on the right-hand side (rhs) accounts for the three-electron correlation and the relaxation of the core. The basis function is given by

$$\Phi_{n(i),l(i)}(1,2,3) = \varphi_{n(i)}(R) Y_{l(i)}^{LM}(\hat{\mathbf{R}}) \chi_{S_z}, \quad (11)$$

where R represents the radial parts of \mathbf{r}_1 , \mathbf{r}_2 , and \mathbf{r}_3 and $\hat{\mathbf{R}}$ represents their angular part. S_z is the Z component of spin S . The radial function is

$$\varphi_{n(i)}(R) = \prod_{j=1}^3 r_j^{n_j} \exp(-\alpha_j r_j), \quad (12)$$

and the orbital angular momentum function is

$$Y_{l(i)}^{LM}(\hat{\mathbf{R}}) = \sum_{m_j} \langle l_1 m_1 l_2 m_2 | l_{12} m_{12} \rangle \times \langle l_{12} m_{12} l_3 m_3 | LM \rangle \prod_{j=1}^3 Y_{l_j m_j}(\Omega_j). \quad (13)$$

For simplicity, we denote the angular component as

$$l(i) = ((l_1, l_2) l_{12}, l_3), \quad (14)$$

where l_{12} and l_3 couple into L is implicitly implied. Using this notation, the spin-angular-momentum functions become

$$\chi_{SS_z} = ((s_1, s_2) S_{12}, s_3). \quad (15)$$

There are two spin doublets,

$$\chi_1 = ((s_1, s_2) 1, s_3), \quad (16)$$

$$\chi_2 = ((s_1, s_2) 0, s_3). \quad (17)$$

The nonrelativistic energies of the $1s^2$ core and $1s^2 2s$ state are calculated by minimizing the expectation value

$$\delta E_0 = \delta \langle H_0 \rangle = \delta \frac{\langle \Psi | H_0 | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \quad (18)$$

The correction due to relativistic and mass-polarization perturbation are given by

$$\Delta E = \langle \Psi | H_1 + H_2 + H_3 + H_4 + H_5 | \Psi \rangle. \quad (19)$$

The total energy (excluding the radiative correction) becomes

$$E_{\text{tot}} = E_0 + \Delta E. \quad (20)$$

To calculate the ionization potential, we use

$$E_{\text{IP}} = E_{\text{tot}}(1s^2 1S) - E_{\text{tot}}(1s^2 2s^2 S) - \Delta E_{\text{QED}}(2s). \quad (21)$$

The last term on the rhs represents the contribution of the radiative correction to the ionization potential due to the $2s$ electron. We are not aware of any accurate QED calculation for the low- Z $1s^2 2s$ system. However, it is reasonable to assume that the QED effects of the core cancel out in the ionization potential and the net effect of the radiative correction comes from the valence $2s$ electron. This effect can be calculated using an effective nucleus charge Z_{eff} in the accurate formula [5]

$$\Delta E_{\text{QED}}(n, 0) = 8Z_{\text{eff}}^4 \alpha^3 R \left\{ \frac{19}{30} - 2 \ln(\alpha Z_{\text{eff}}) - \ln[K(n, 0)] \right\} / (3\pi n^3), \quad (22)$$

where R is the Rydberg constant. n is the principle quantum number which equals 2 in our case. $K(2, 0)$ has been accurately calculated [11] to be 16.6398. Z_{eff} can be calculated using the equation

$$E_{\text{nonrel}}(1s^2 2s) - E_{\text{nonrel}}(1s^2) = -Z_{\text{eff}}^2 / 8. \quad (23)$$

III. COMPUTATIONAL ASPECT

Most of the computations are carried out with double-precision ($R * 8$) arithmetic on an IBM 6000/320

workstation with 16 megabytes of RAM memory. The limited memory prevents us from extending the size of our matrix beyond 975×975 . The final calculations with 1017×1017 matrices are computed with quadruple precision ($R * 16$) on a mainframe computer. In calculating the core wave function, we attempt to saturate the radial

basis functions for each l in Eq. (8). However, too many terms in the same (l, l) angular component may lead to numerical instability. Although this numerical instability can be avoided with $R * 16$ precision, our workstation cannot perform such a calculation at present. Our resources on the mainframe computers are more restrict-

TABLE I. Energy convergence of the $1s 1s {}^1S$ core and the $1s^2s {}^2S$ states of lithiumlike systems. [In the 2S calculations, the spinor from Eq. (16) is adopted except for the core plus $2s$ and the last two angular components.]

Angular component	No. of terms	$-\Delta E$ (a.u.)			
		$Z=3$	$Z=4$	$Z=5$	$Z=6$
(0,0)	64	7.252 486 89	13.626 853 88	22.001 508 04	32.376 289 95
(1,1)	56	0.023 396 65	0.024 250 23	0.024 734 17	0.025 045 93
(2,2)	49	0.002 772 30	0.003 045 62	0.003 212 63	0.003 325 08
(3,3)	42	0.000 705 27	0.000 789 65	0.000 842 45	0.000 878 50
(4,4)	36	0.000 253 34	0.000 286 27	0.000 307 88	0.000 321 20
(5,5)	36	0.000 111 71	0.000 127 26	0.000 137 01	0.000 143 25
(6,6)	35	0.000 056 21	0.000 064 18	0.000 069 46	0.000 072 82
Total	318	7.279 782 38	13.655 417 10	22.030 811 64	32.406 076 73
core plus $2s$	8	7.476 009 95	14.321 361 36	23.420 369 04	34.770 708 34
((0,0)0,0)	66	0.000 136 62	0.000 293 87	0.000 408 28	0.000 492 25
((0,1)1,1)	283	0.001 604 34	0.002 636 07	0.003 249 33	0.003 653 12
((0,2)2,2)	217	0.000 124 53	0.000 228 67	0.000 298 55	0.000 347 49
((0,3)3,3)	141	0.000 023 98	0.000 046 91	0.000 063 26	0.000 075 08
((0,4)4,4)	84	0.000 007 61	0.000 015 15	0.000 020 76	0.000 024 85
((0,5)5,5)	84	0.000 003 17	0.000 006 40	0.000 009 02	0.000 010 92
((0,6)6,6)	84	0.000 001 55	0.000 003 26	0.000 004 50	0.000 005 52
((1,2)1,1)	20	0.000 009 57	0.000 009 65	0.000 007 82	0.000 006 21
((1,2)1,1)	20	0.000 002 69	0.000 001 87	0.000 001 32	0.000 000 94
((2,3)1,1)	10	0.000 001 06	0.000 001 07	0.000 000 88	0.000 000 71
Total	1017	7.477 925 06	14.324 604 29	23.424 432 77	34.775 325 44
		$Z=7$	$Z=8$	$Z=9$	$Z=10$
(0,0)	64	44.751 139 85	59.126 030 52	75.500 946 62	93.875 880 76
(1,1)	56	0.025 263 52	0.025 424 00	0.025 547 28	0.025 644 92
(2,2)	49	0.003 405 95	0.003 466 84	0.003 514 36	0.003 552 51
(3,3)	42	0.000 904 68	0.000 924 55	0.000 940 17	0.000 952 69
(4,4)	36	0.000 332 69	0.000 340 65	0.000 346 13	0.000 351 98
(5,5)	36	0.000 148 54	0.000 152 26	0.000 155 20	0.000 157 57
(6,6)	35	0.000 075 48	0.000 077 36	0.000 079 01	0.000 080 00
Total	318	44.781 270 71	59.156 416 18	75.531 528 76	93.906 620 43
core plus $2s$	8	48.371 691 52	64.223 030 09	82.324 587 47	102.676 290 41
((0,0)0,0)	66	0.000 555 19	0.000 604 06	0.000 642 81	0.000 674 48
((0,1)1,1)	283	0.003 938 66	0.004 151 07	0.004 315 20	0.004 445 75
((0,2)2,2)	217	0.000 383 88	0.004 411 54	0.000 433 46	0.000 451 01
((0,3)3,3)	141	0.000 083 89	0.000 090 92	0.000 096 42	0.000 100 90
((0,4)4,4)	84	0.000 027 97	0.000 030 44	0.000 032 54	0.000 034 14
((0,5)5,5)	84	0.000 012 38	0.000 013 57	0.000 014 51	0.000 015 32
((0,6)6,6)	84	0.000 006 28	0.000 006 90	0.000 007 43	0.000 007 88
((1,2)1,1)	20	0.000 005 12	0.000 004 18	0.000 003 45	0.000 002 89
((1,2)1,1)	20	0.000 000 55	0.000 000 41	0.000 000 32	0.000 000 26
((2,3)1,1)	10	0.000 000 57	0.000 000 47	0.000 000 39	0.000 000 33
Total	1017	48.376 706 02	64.228 343 65	82.330 133 99	102.682 023 38

ed. The memory and precision are two factors which prevent us from obtaining much higher accuracy at this time. For this reason, we limit the k and n to about 14 or 15 in Eq. (8) and l to 6. It should be pointed out that, with regard to energy, we can obtain much lower upper bounds by simply increasing l . However, it is more important for us to saturate the radial correlations to learn the convergence of energy in terms of l such that a reliable extrapolation procedure can be found for higher l .

In the present work, the ionization potential is obtained from the energy difference calculated with Eqs. (8) and (10). Hence, it is crucially important that Φ_{1s1s} is sufficiently saturated so that $\Phi_{n(i),l(i)}$ does not contain a part which actually comes from the core. This implies that if the largest l used in Eq. (8) is 6, the maximum l 's in Eq. (13) will also be 6.

For the $1s1s$ core states, we used 318 terms in the seven l components. The convergence in energy is given in Table I. If we compare these results with those of Pekeris [7], the deficiency in energy ranges from

-0.0001310 a.u. in lithium to -0.0001861 a.u. in neon. Again, we emphasize that these energy values can easily be improved by including higher l 's in the wave function, but for our purpose, this is not as important as saturating the l 's radial functions already being used.

To calculate the $1s^22s$ energy, we use eight d_i terms in Eq. (10) and about 1009 terms in $\Phi_{n(i),l(i)}$; this implies that approximately one-half of 3553×3553 matrix elements are computed for each secular equation. The energy convergence in terms of increasing l for the 2S state is also given in Table I. In Sec. IV the binding energy coming from the $((0,5)5,5)$ and $((0,6)6,6)$ angular terms will be used to extrapolate the contribution from higher l . It is important to know that these energies are well converged. When we increase the number of terms in $((0,5)5,5)$ from 56 to 84, $-\Delta E$ changes from 3.087 to 3.172 micro-atomic-units ($\mu\text{a.u.}$) for lithium and from 15.16 to 15.32 $\mu\text{a.u.}$ for neon. The improvement is about 2.7% to 1.1%. Similarly, for $((0,6)6,6)$, they change from 1.493 to 1.545 $\mu\text{a.u.}$ for lithium and 7.727 to 7.883

TABLE II. Convergence study and extrapolation of the higher- l contributions to the ionization potential. [E (Pekeris) are from Ref. [7].]

	$l=4$	$l=5$	$l=6$	$l=4$	$l=5$	$l=6$	
		Li II				N V	
$\Delta E(l)/\Delta E(l-1)$ for $1s1s$	0.359	0.441	0.503	0.368	0.446	0.508	
$\Delta E(l)/\Delta E(l-1)$ for $1s^22s$	0.317	0.417	0.487	0.333	0.443	0.507	
$\delta E_l(1s1s)$ ($\mu\text{a.u.}$) [Eq. (24)]	-298.9	-187.2	-131.0	-398.4	-249.9	-174.4	
R_l [Eq. (25)]	1.180	1.676	2.331	1.198	1.682	2.310	
Extrapolated energy ($\mu\text{a.u.}$)	-4.26	-3.77	-3.60	-14.84	-14.55	-14.50	
E (Pekeris)		-7.279 9134 a.u.			-44.781 445 1 a.u.		
		Be II				O VI	
$\Delta E(l)/\Delta E(l-1)$ for $1s1s$	0.363	0.445	0.504	0.368	0.447	0.508	
$\Delta E(l)/\Delta E(l-1)$ for $1s^22s$	0.323	0.423	0.510	0.335	0.446	0.509	
$\delta E_l(1s1s)$ ($\mu\text{a.u.}$) [Eq. (24)]	-340.5	-213.3	-149.1	-408.5	-256.3	-178.9	
R_l [Eq. (25)]	1.190	1.676	2.323	1.199	1.683	2.313	
Extrapolated energy ($\mu\text{a.u.}$)	-8.36	-7.46	-7.58	-16.03	-15.93	-15.97	
E (Pekeris)		-13.655 566 2 a.u.			-59.156 595 1 a.u.		
		B III				F VII	
$\Delta E(l)/\Delta E(l-1)$ for $1s1s$	0.365	0.445	0.507	0.368	0.448	0.509	
$\Delta E(l)/\Delta E(l-1)$ for $1s^22s$	0.328	0.434	0.499	0.337	0.446	0.512	
$\delta E_l(1s1s)$ ($\mu\text{a.u.}$) [Eq. (24)]	-366.4	-229.4	-160.0	-417.7	-262.5	-183.5	
R_l [Eq. (25)]	1.190	1.675	2.303	1.207	1.692	2.323	
Extrapolated energy ($\mu\text{a.u.}$)	-11.20	-10.60	-10.36	-17.33	-17.12	-17.26	
E (Pekeris)		-22.030 971 6 a.u.			-75.531 712 3 a.u.		
		C VI				Ne III	
$\Delta E(l)/\Delta E(l-1)$ for $1s1s$	0.366	0.446	0.508	0.369	0.448	0.508	
$\Delta E(l)/\Delta E(l-1)$ for $1s^22s$	0.331	0.440	0.506	0.338	0.449	0.514	
$\Delta E_L(1s1s)$ ($\mu\text{a.u.}$) [Eq. (24)]	-385.9	-242.7	-169.9	-423.6	-266.1	-186.1	
R_l [Eq. (25)]	1.202	1.694	2.333	1.204	1.689	2.326	
Extrapolated energy ($\mu\text{a.u.}$)	-13.42	-12.98	-12.88	-17.89	-17.99	-18.33	
E (Pekeris)		-32.406 246 6 a.u.			-93.906 806 5 a.u.		

$\mu\text{a.u.}$ for neon. The improvement is about 3.6% to 2.0%. This suggests that a further increase in the number of terms will not change ΔE substantially.

IV. EXTRAPOLATION PROCEDURE

Comparing the convergence of $1s^2 2s^2 S$ and $1s 1s^1 S$ in Table I, it is apparent that the contribution to the binding energy of 2S from higher $(0, l, l)$ components is smaller than the (l, l) contribution to the core by more than an order of magnitude. However, for $l \geq 4$, the ‘‘rate’’ of convergence is about the same. This can be seen by comparing the ratio of $\Delta E(l)/\Delta E(l-1)$ for both states for the entire isoelectronic sequence. This comparison is given in Table II. We see that this rate for the 2S is almost the same as that of the core. From the results of Pekeris [7], we can compute the deficiency of the core. Most of this deficiency comes from the neglected higher- l angular components. If we define

$$\begin{aligned} \delta E_l(1s 1s^1 S) &= \sum_{l'=l+1}^{\infty} \Delta E_{l'}(1s 1s^1 S) \\ &= E(\text{Pekeris}) - E_l(1s 1s^1 S), \end{aligned} \quad (24)$$

where $E_l(1s 1s^1 S)$ is the energy of the wave function in which (l, l) is the highest angular component, and $\Delta E_l(1s 1s^1 S)$ represents the binding energy contribution from the (l, l) term, the ratio

$$R_l = \delta E_l(1s 1s^1 S) / \Delta E_l(1s 1s^1 S) \quad (25)$$

is stable for the entire isoelectronic sequence for $l > 3$. Table II shows that R_6 falls in the range 2.318 ± 0.015 and R_5 falls in the range 1.684 ± 0.010 . Since the ‘‘rate’’ of convergence for $1s^2 2s^2 S$ is about the same as that of $1s^2 1S$ (see Table II), it is reasonable to assume that this same convergence behavior will continue for higher l . Thus, a $\delta E_l(1s^2 2s^2 S)$ can be obtained from

$$\delta E_l(1s^2 2s^2 S) = R_l \Delta E_l(1s^2 2s^2 S), \quad (26)$$

where $\Delta E_l(1s^2 2s^2 S)$ represent the binding energy coming from the $(0, l, l)$ angular term. Obviously, if this empirical procedure is valid, then it is necessary that the extrapolated result must satisfy the relation

$$\delta E_l(1s^2 2s^2 S) = \delta E_{l-1}(1s^2 2s^2 S) - \Delta E_l(1s^2 2s^2 S). \quad (27)$$

This means that for sufficiently high l , the correction to our calculated upper bound should be the same for all l . The different corrections to the upper bound extrapolated from $l=4, 5$, and 6 are also given in Table II. One can see from this table that results for the $l=5$ and 6 are extremely close. The largest deviation is for neon where it is $0.35 \mu\text{a.u.}$, or 1.8% of the extrapolated energy. The total extrapolated energy ranges from $3.6 \mu\text{a.u.}$ for lithium to $18.3 \mu\text{a.u.}$ to neon. Since this procedure is not rigorous, we assign a 10% uncertainty to the extrapolat-

ed results for $Z=3$ and 8% for other Z . This error bar is probably sufficient. Using these results and the method in the following paragraph, we can predict a nonrelativistic energy for the $1s^2 2s$ states. We find that the results so obtained agree excellently with those from King [12] in all cases even if we reduce these estimated error bars by a factor of 2.

The computation mentioned above is relevant in obtaining an accurate IP. Another interesting question is whether one can also obtain an accurate $1s^2 2s^2 S$ nonrelativistic energy by adding $\delta E_l(1s 1s^1 S)$, i.e.,

$$\begin{aligned} E_{\text{nonrel}}(1s^2 2s^2 S) &= E_l(1s^2 2s^2 S) + \delta E_l(1s 1s^1 S) \\ &\quad + \delta E_l(1s^2 2s^2 S). \end{aligned} \quad (28)$$

Here the $E_l(1s^2 2s^2 S)$ is the upper bound calculated here. The validity of this equation would imply that the interaction energy coming from the neglected higher- l components in the core with other parts of the three-electron wave function must be small. This is difficult to prove in general. However, it can be studied empirically by successively adding (l, l) terms to the core and comparing the change of the three-electron energies to the corresponding change in the core energies. To illustrate, carbon is used as an example. The $(4, 4)$ angular component contribution to the binding energy of the two-electron core is $321.21 \mu\text{a.u.}$, but its contribution to the three-electron energy is $323.35 \mu\text{a.u.}$ The difference is $2.15 \mu\text{a.u.}$ This difference reduces to $0.54 \mu\text{a.u.}$ for $(5, 5)$ and $0.28 \mu\text{a.u.}$ for $(6, 6)$. Similar results are also obtained for lithium. Therefore, it may be reasonable to assume that for higher l this discrepancy will be further reduced, and the error bar introduced by such an approximation should be less than $0.5 \mu\text{a.u.}$ The total error bar in E_{nonrel} is given by the sum of the uncertainty on the rhs of Eq. (28). Using this E_{nonrel} , an accurate effective nuclear charge can be calculated for the $2s$ electron with Eq. (23).

V. RESULTS AND DISCUSSION

To obtain an accurate IP, the relativistic and mass-polarization effects must be included. Equation (19) is calculated for both the $1s 1s$ core and the $1s^2 2s$. These results are given in Table III. The relativistic effects to the core states have been calculated by Pekeris [7]. In comparison with the results in Ref. [7], we note that for most perturbations the discrepancies are less than 1% except for the electron-electron contact term which range from 4.9% in lithium to 1.4% in neon. These discrepancies should not cause an inaccuracy in the IP result, because exactly the same core is used in $1s^2 2s$. The errors due to the core should essentially cancel in the IP calculation. We may also improve our relativistic-perturbation results by adding the deficiency in the core. The reliability of this procedure can be seen from the results of mass polarization. For lithium, Pekeris [7] gives 4.95972 cm^{-1}

TABLE III. Relativistic and mass-polarization (MP) corrections for $1s^2 2s$ states (in a.u.) and comparison of $1s 1s$ core states with those of Pekeris (Ref. 7).

	$\langle H_1 + H_2 \rangle$ (units of 10^{-1})	$\langle H_3 \rangle$ (units of 10^{-3})	$\langle H_5 \rangle$ (units of 10^{-4})	Mass polarization	
				This work (units of 10^{-5})	Ref. 12 (units of 10^{-5})
$R = 109\,728.733 \text{ cm}^{-1}$					
$1s 1s$ this work ($Z=3$)	-0.006 934 5	0.093 484	-0.229 22	2.2630	
$1s 1s$ Pekeris	-0.006 953 9	0.089 298	-0.227 92	2.2600	
Deviation from Pekeris	0.000 019 5	0.004 186	-0.001 30	0.0030	
Discrepancy in %	-0.280	4.687	0.572	0.133	
$1s 1s 2s$ this work	-0.007 074 8	0.095 340	-0.233 31	2.3635	
Corrected for discrepancy	-0.007 094 2	0.091 154	-0.232 01	2.3605	3.2605
$R = 109\,730.633 \text{ cm}^{-1}$					
$1s 1s$ this work ($Z=4$)	-0.024 296 1	0.263 595	-0.469 60	2.5633	
$1s 1s$ Pekeris	-0.024 338 4	0.254 789	-0.467 97	2.5604	
Deviation from Pekeris	0.000 042 3	0.008 806	-0.001 63	0.0029	
Discrepancy in %	-0.174	3.456	0.349	0.115	
$1s 1s 2s$ this work	-0.025 373 7	0.273 551	-0.486 26	2.7603	
Corrected for discrepancy	-0.025 416 0	0.264 745	-0.484 63	2.7574	2.758(7)
$R = 109\,731.845 \text{ cm}^{-1}$					
$1s 1s$ this work ($Z=5$)	-0.063 271 5	0.569 210	-0.796 18	2.7578	
$1s 1s$ Pekeris	-0.063 341 5	0.554 178	-0.794 54	2.7549	
Deviation from Pekeris	0.000 070 0	0.015 032	-0.001 65	0.0029	
Discrepancy in %	-0.111	2.712	0.207	0.104	
$1s 1s 2s$ this work	-0.067 228 8	0.597 386	-0.833 57	3.0235	
Corrected for discrepancy	-0.067 298 8	0.582 354	-0.831 93	3.0206	3.0207
$R = 109\,732.296 \text{ cm}^{-1}$					
$1s 1s$ this work ($Z=6$)	-0.137 097 7	1.050 806	-1.209 14	3.1366	
$1s 1s$ Pekeris	-0.137 209 7	1.027 403	-1.207 71	3.1340	
Deviation from Pekeris	0.000 112 2	0.023 403	-0.001 43	0.0027	
Discrepancy in %	-0.082	2.278	0.118	0.085	
$1s 1s 2s$ this work	-0.147 544 5	1.111 312	-1.275 41	3.4788	
Corrected for discrepancy	-0.147 656 5	1.087 909	-1.273 99	3.4762	3.4760
$R = 109\,733.014 \text{ cm}^{-1}$					
$1s 1s$ this work ($Z=7$)	-0.262 220 9	1.747 417	-1.708 38	3.2085	
$1s 1s$ Pekeris	-0.262 381 0	1.714 396	-1.707 56	3.2060	
Deviation from Pekeris	0.000 160 1	0.033 021	-0.000 83	0.0025	
Discrepancy in %	-0.061	1.926	0.048	0.079	
$1s 1s 2s$ this work	-0.284 889 9	1.858 215	-1.811 66	3.5872	
Corrected for discrepancy	-0.285 050 0	1.825 195	-1.810 83	3.5847	3.5846
$R = 109\,733.549 \text{ cm}^{-1}$					
$1s 1s$ this work ($Z=8$)	-0.458 272 1	2.699 754	-2.294 02	3.2651	
$1s 1s$ Pekeris	-0.458 473 9	2.655 124	-2.294 07	3.2624	
Deviation from Pekeris	0.000 201 7	0.044 630	0.000 05	0.0026	
Discrepancy in %	-0.044	1.681	-0.002	0.080	
$1s 1s 2s$ this work	-0.501 556 5	2.882 836	-2.442 41	3.6721	
Corrected for discrepancy	-0.501 758 2	2.838 206	-2.442 46	3.6695	3.6696
$R = 109\,734.144 \text{ cm}^{-1}$					
$1s 1s$ this work ($Z=9$)	-0.748 071 6	3.947 526	-2.966 02	3.1332	
$1s 1s$ Pekeris	-0.748 345 7	3.889 420	-2.967 30	3.1307	
Deviation from Pekeris	0.000 274 2	0.058 106	0.001 28	0.0024	
Discrepancy in %	-0.037	1.494	-0.043	0.078	
$1s 1s 2s$ this work	-0.823 508 9	4.228 788	-3.167 69	3.5397	
Corrected for discrepancy	-0.823 783 1	4.170 682	-3.168 97	3.5375	3.5374

TABLE III. (Continued).

	$\langle H_1 + H_2 \rangle$ (units of 10^{-1})	$\langle H_3 \rangle$ (units of 10^{-3})	$\langle H_5 \rangle$ (units of 10^{-4})	Mass polarization	
				This work (units of 10^{-5})	Ref. 12 (units of 10^{-5})
		$R = 109\,734.301 \text{ cm}^{-1}$			
1s1s this work ($Z = 10$)	-1.157 650 5	5.530 620	-3.724 44	3.3427	
1s1s Pekeris	-1.158 015 4	5.457 300	-3.727 20	3.3403	
Deviation from Pekeris	0.000 364 9	0.073 320	0.002 75	0.0024	
Discrepancy in %	-0.032	1.344	-0.074	0.072	
1s1s2s this work	-1.280 414 1	5.939 890	-3.987 44	3.7900	
Corrected for discrepancy	-1.280 779 0	5.866 569	-3.990 20	3.7876	3.7876

which is $0.030 \mu\text{a.u.}$ less than our result. If we correct our $1s^2s$ result by this amount, we get $23.605 \mu\text{a.u.}$ which is exactly the result of King [12]. Close agreement with King is also reached for other members of the isoelectronic sequence. Perhaps one should not take these agreements too seriously because of rounding errors, but it does seem to suggest that the corrected relativistic results are reliable.

The QED contribution is expected to be substantial for the $1s1s$ core, but the contribution coming from the $2s$ valence electron is expected to be much smaller. It is difficult to carry out a complete three-electron calculation for this radiative correction. An approximation method will be adopted. The QED calculation for the hydrogenlike systems have been well studied in the literature [5,11]. An accurate formula for QED shifts for the hydrogenlike $2s$ state is available. If we use Eq. (22) with the effective nucleus charge calculated earlier, the QED contribution to the ionization potential can be estimated. This is obviously an approximation. Therefore, we assign a $\pm 7\%$ error bar to the value obtained. In quoting the IP, the error bars from extrapolation and from QED are added.

If we add the QED correction to the nonrelativistic and relativistic effects, final IP results are obtained. These results are given in Tables IV and V. The experimental IP quoted in the tables are from Moore [10], Bashkin and Stoner [13], and Kelly [9]. Moore did not give the IP for Ne VIII. The data from Moore have been revised in Kelly except for B III. Most of the lithiumlike IP in Bashkin and Stoner [13] are identical to that of Kelly [9] except for N V. To compare with experiment, we convert the atomic-unit results into cm^{-1} using the reduced Rydberg constant. In the case of Li I, both IP experimental data are within the uncertainty quoted in this work. But for all other systems, our results show a clear preference for the new Kelly's [9] data rather than that of Moore [10]. Most of the IP in Moore comes from the spectroscopy analysis of Edlen (see Ref. [10]).

The Be II IP datum in Kelly agrees with this work. However, starting from C IV, a small discrepancy between our result and that of Kelly begins to show. In C IV, the deviation is $0.68(69) \text{ cm}^{-1}$. It increases steadily to $2.8(12)$, $4.1(20)$, $9.9(31)$, and $14.8(47) \text{ cm}^{-1}$ for N V, O VI, F VII and Ne VIII, respectively (see Table V). If we divide these by $(Z\alpha)^2$ times the first-order relativistic contribution to the IP, the ratios are 1.64, 2.24, 1.31, 1.43, and 1.06 from C IV to Ne VIII. Hence, we attribute

this deviation to the higher-order relativistic perturbation. It is interesting to note that while the first-order relativistic effect increases the IP, this higher-order relativistic effect tends to reduce IP. The leading higher-order relativistic contribution for a $1s$ hydrogenlike ion is shown to be $8Z^5\alpha^3/3\pi$ in Kissel-Phillip and Schwarz [14]. However, our result seems to suggest that for the $2s$ electron in the lithiumlike ions, it could still be proportional to $Z^6\alpha^4$ as suggested by the perturbation theory.

Recently, the IP for the Li I and Be II $1s^2s$ states have been calculated to high accuracy [15,16]. These results are compared in Table IV. Our Li I IP, $0.198\,158 \text{ a.u.}$, agrees extremely well with the $0.198\,154(3) \text{ a.u.}$ of Lindgren [16]. However, our calculated relativistic contribution is $11.5 \mu\text{a.u.}$ whereas it is $16 \mu\text{a.u.}$ in Lindgren [16].

Although the discrepancy between theory and experiment from C IV to Ne VIII may be explained by higher-order relativistic effects, we cannot explain the $-1.29(36) \text{ cm}^{-1}$ discrepancy in boron. The higher-order relativistic effect for this system is of the order of 0.1 cm^{-1} , which increases the discrepancy to approximately $-1.39(36) \text{ cm}^{-1}$. We note that the IP for B III in Moore [10], Bashkin and Stoner [13], and Kelly [9] are the same. Moore made the following comment in her table: "The terms are from Edlen. The absolute values are based on the assumption that n^* for $5g^2G$ equals that of the corresponding term in C IV where $5g^2G - 6h^2H^o$ has been observed. The precision of this term in B III is estimated to be within $\pm 1 \text{ cm}^{-1}$. The series are well represented by a Ritz formula." Because of the approximation used in the present work, our result is not conclusive evidence that Edlen's result is off by more than 1 cm^{-1} . Nevertheless, our result does emphasize the need to take a closer look at this IP value. As other IP values are revised from Moore [10] to Kelly [9], it is possible that this B III IP could be slightly revised also.

Using the extrapolation procedure discussed in Sec. IV, we tabulated the nonrelativistic energy using Eq. (28). These results and their comparisons with other theories [17-29] are given in Table VI. Recently, the nonrelativistic energies of the lithiumlike $1s^2s$ states have been calculated for Li I to Ne VIII by King [12]. Our results agree with those of King in each case. This is interesting because the nonrelativistic energies of Li I have been empirically estimated by Bunge to be $-7.478\,073$ [17], $-7.478\,071(5)$ [26], and $-7.478\,062\,47(7) \text{ a.u.}$ [27]. Other estimates are $-7.478\,068 \text{ a.u.}$ [19] and $-7.478\,069 \text{ a.u.}$

TABLE IV. Ionization potential for the $1s^2 2s^2 S$ states of lithiumlike systems from Li I to C IV.

	$1s1s$	$1s^2 2s$	a.u.	cm ⁻¹	eV
Z = 3					
Nonrel.	-7.279 782 4	-7.477 925 1	0.198 142 7	43 483.89	5.391 32
$\langle H_1 + H_2 \rangle$	-0.000 693 4	-0.000 707 5	0.000 014 0	3.08	0.000 38
$\langle H_3 \rangle$	0.000 093 5	0.000 095 3	-0.000 001 9	-0.41	-0.000 05
$\langle H_5 \rangle$	-0.000 022 9	-0.000 023 3	0.000 000 4	0.09	0.000 01
$\langle H_4 \rangle$	0.000 022 6	0.000 023 6	-0.000 001 0	-0.22	-0.000 03
Higher l		0.000 003 6(4)	0.000 003 6(4)	0.79(8)	0.000 10
Subtotal	-7.280 382 6	-7.478 540 5	0.198 157 9(4)	43 487.22	5.391 7
QED corr.			-0.000 000 3	-0.07(1)	0.000 0
IP this work			0.198 157 5(4)	43 487.15(9)	5.391 7
Kelly, ^a Bashkin and Stoner ^b				43 487.15(2)	5.391 7
Moore ^c				43 487.19(2)	
Other theory; Lindgren ^a			0.198 154(3)		
Blundell <i>et al.</i> ^e			0.198 1429(5) ^f		
Z = 4					
Nonrel.	-13.655 417 1	-14.324 604 3	0.669 187 2	146 860.67	18.208 41
$\langle H_1 + H_2 \rangle$	-0.002 429 6	-0.002 537 4	0.000 107 8	23.65	0.002 93
$\langle H_3 \rangle$	0.000 263 6	0.000 273 6	-0.000 010 0	-2.18	-0.000 27
$\langle H_5 \rangle$	-0.000 047 0	-0.000 048 6	0.000 001 7	0.37	0.000 05
$\langle H_4 \rangle$	0.000 025 6	0.000 027 6	-0.000 002 0	-0.43	-0.000 05
Higher l		-0.000 007 6(6)	0.000 007 6(6)	1.66(13)	0.000 21
Subtotal	-13.657 604 4	-14.326 896 7	0.669 292 3(6)	146 883.73(13)	18.211 3
QED correction			-0.000 003 2(2)	-0.69(5)	-0.000 1
IP this work			0.669 289 1(8)	146 883.03(18)	18.211 2
Kelly, ^a Bashkin and Stoner ^b				146 882.86	18.211 2
IP(theory)—IP(expt.)				0.17(18)	
Moore ^c				146 881.7	
Other theory; Blundell <i>et al.</i> ^e			0.669 252(3) ^f		
Z = 5					
Nonrel.	-22.030 811 6	-23.424 432 8	1.393 621 1	305 849.23	37.920 48
$\langle H_1 + H_2 \rangle$	-0.006 327 1	-0.006 722 9	0.000 395 7	86.85	0.010 77
$\langle H_3 \rangle$	0.000 569 2	0.000 597 4	-0.000 028 2	-6.18	-0.000 77
$\langle H_5 \rangle$	-0.000 079 6	-0.000 083 4	0.000 003 7	0.82	0.000 10
$\langle H_4 \rangle$	0.000 027 6	0.000 030 2	-0.000 002 7	-0.58	-0.000 07
Higher l		-0.000 010 4(8)	0.000 010 4(8)	2.27(18)	0.000 28
Subtotal	-22.036 621 6	-23.430 621 7	1.394 000 1(8)	305 932.41(18)	37.930 8
QED correction			-0.000 011 8(8)	-2.60(18)	-0.000 3
IP this work			1.393 988 3(16)	305 929.81(36)	37.930 5

TABLE IV. (Continued).

	$1s1s$	$1s^2s$	a.u.	cm ⁻¹	eV
Kelly, ^a Bashkin and Stoner ^b				305 931.1	37.9306
Moore ^c				-1.29(36)	
IP(theory) - IP(expt.)					
Z = 6					
Nonrel.	-32.4060767	-34.7753254	2.3692487	519 966.20	64.46761
$\langle H_1 + H_2 \rangle$	-0.0137098	-0.0147544	0.0010447	229.27	0.02843
$\langle H_3 \rangle$	0.0010508	0.0011113	-0.0000605	-13.28	-0.00165
$\langle H_5 \rangle$	-0.0001209	-0.0001275	0.0000066	1.45	0.00018
$\langle H_4 \rangle$	0.0000314	0.0000348	-0.0000034	-0.75	-0.00009
Higher l		-0.0000129(10)	0.0000129(10)	2.83(23)	0.00035
Subtotal	-32.4188252	-34.7890742	2.3702490(10)	520 185.72(23)	64.4948
QED correction			-0.0000303(21)	6.64(46)	-0.0008
IP this work			2.3702187(31)	520 179.08(69)	64.4940
Kelly, ^a Bashkin and Stoner ^b				520 178.4	64.4939
IP(theory) - IP(expt.)				0.68(69)	
Moore ^c				520 177.8	

^aReference [9].^bReference [13].^cReference [10].^dReference [16].^eReference [15].^fResults correspond to infinite nuclear mass.

TABLE V. Ionization potential for the $1s^2s^2S$ states of lithiumlike systems from N v to Ne VIII.

	Ionization potential				
	1s1s	$1s^2s$	a.u. cm ⁻¹ eV		
Z = 7					
Nonrel.	-44.781 270 7	-48.376 706 0	3.595 435 3	789 075.90	97.832 98
$\langle H_1 + H_2 \rangle$	-0.026 222&1	-0.028 489 0	0.002 266 9	497.51	0.061 68
$\langle H_3 \rangle$	0.001 747 4	0.001 858 2	-0.000 110 8	24.32	-0.003 01
$\langle H_5 \rangle$	-0.000 170 8	-0.000 181 2	0.000 010 3	2.27	0.000 28
$\langle H_4 \rangle$	0.000 032 1	0.000 035 9	-0.000 003 8	-0.83	-0.000 10
Higher <i>l</i>		-0.000 014 5(12)	0.000 014 5(12)	3.18(25)	0.000 39
Subtotal	-44.805 884 1	-48.403 496 6	3.597 612 5(12)	789 553.71(25)	97.892 2
QED correction			-0.000 062 6(43)	-13.74(96)	0.001 7
IP this work			3.597 549 9(55)	789 540.0(12)	97.890 5
Kelly ^a				789 537.2	97.890 2
IP(theory)—IP(expt.)				2.8(12)	
Moore ^b				789 532.9	
Z = 8					
Nonrel.	-59.156 416 2	-64.228 343 6	5.071 927 5	1 113 121.20	138.009 49
$\langle H_1 + H_2 \rangle$	-0.045 827 2	-0.050 155 6	0.004 328 4	949.95	0.117 78
$\langle H_3 \rangle$	0.002 699 8	0.002 882 8	-0.000 183 1	-40.18	-0.004 98
$\langle H_5 \rangle$	-0.000 229 4	-0.000 244 2	0.000 014 8	3.26	0.000 40
$\langle H_4 \rangle$	0.000 032 7	0.000 036 7	-0.000 004 1	-0.89	-0.000 11
Higher <i>l</i>		-0.000 016 0(13)	0.000 016 0(13)	3.50(28)	0.000 43
Subtotal	-59.199 740 4	-64.275 839 9	5.076 099 6(13)	1 114 036.84(28)	138.123 0
QED correction			-0.000 112 9(79)	-24.8(17)	-0.003 1
IP this work			5.075 986 7(92)	1 114 012.1(20)	138.119 9
Kelly, ^a Bashkin and Stoner ^c				1 114 008	138.119 4
IP(theory)—IP(expt.)				4.1(20)	
Moore ^b				1 113 999.5	
Z = 9					
Nonrel.	-75.531 528 8	-82.330 134 0	6.798 605 2	1 492 078.25	184.994 19
$\langle H_1 + H_2 \rangle$	-0.074 807 2	-0.082 350 9	0.007 543 7	1 655.61	0.205 27
$\langle H_3 \rangle$	0.003 947 5	0.004 228 8	-0.000 281 3	-61.73	-0.007 65
$\langle H_5 \rangle$	-0.000 296 6	-0.000 316 8	0.000 020 2	4.43	0.000 55
$\langle H_4 \rangle$	0.000 031 3	0.000 035 4	-0.000 004 1	-0.89	-0.000 11
Higher <i>l</i>		-0.000 017 3(14)	0.000 017 3(14)	3.79(30)	0.000 47
Subtotal	-75.602 653 7	-82.408 554 7	6.805 901 1(14)	1 493 679.45(30)	185.192 7
QED correction			-0.000 185(13)	-40.6(28)	-0.005 0
IP this work			6.805 716(14)	1 493 638.9(31)	185.187 7
Kelly, ^a Bashkin and Stoner ^c				1 493 629	185.186 5
IP(theory)—IP(expt.)				9.9(31)	
Moore ^b				1 493 656	

TABLE V. (Continued).

	Ionization potential				
	$1s1s$	$1s^2s$	a.u.	cm^{-1}	eV
Z = 10					
Nonrel.	-93.906 620 4	102.682 023 4	8.775 402 9	1 925 925.42	238.784 40
$\langle H_1 + H_2 \rangle$	-0.115 765 0	-0.128 041 4	0.012 276 4	2694.28	0.334 05
$\langle H_3 \rangle$	0.005 530 6	0.005 939 9	-0.000 409 3	-89.82	-0.011 14
$\langle H_5 \rangle$	-0.000 372 4	-0.000 398 7	0.000 026 3	5.77	0.000 72
$\langle H_4 \rangle$	0.000 033 4	0.000 037 9	-0.000 004 5	-0.98	-0.000 12
Higher l		-0.000 018 3(15)	0.000 018 3(15)	4.02(32)	0.000 50
Subtotal	-94.017 193 9	-102.804 504 1	8.787 310 2(15)	1 928 538.69(31)	239.108 4
QED correction			-0.000 282(20)	-61.9(43)	-0.007 7
IP this work			8.787 028(22)	1 928 476.8(46)	239.100 7
Kelly ^a Bashkin and Stoner ^c				1 928 462	239.098 9
IP(theory) - IP(expt.)				14.8(47)	

^aReference [9].^bReference [10].^cReference [13].

[28]. Our result is $-7.478\,059\,7(9)$ a.u. which agrees with the $-7.478\,059\,53$ a.u. of King and Bergsbaken [12] and the $-7.478\,060\,32(1)$ of McKenzie [29]. For Be II, the nonrelativistic energy has been estimated to be $-14.324\,79$ a.u. in Weiss [18] and $-14.324\,807$ a.u. in Muszynska *et al.* [19]. Our result, $-14.324\,761\,0(11)$ a.u., again agrees with the $-14.324\,760$ a.u. of King. The agreement between theory and experiment obtained in this work could be considered a confirmation of King's result in the case of Be^+ . The predicted nonrelativistic results are compared with other theoretical results [20–29] in Table VI. The energy results with the first-order relativistic and mass-polarization corrections from Table III are also given. Since only the QED result of the $2s$ electron is calculated in this work, it is not included in this relativistic energy.

VI. SUMMARY

In this work, we used a CI approach with a method of full core plus correlation to calculate the ionization potentials of the lithiumlike ground states for $Z=3$ to 10. Most of our results support the experimental IP data in Kelly [9]. However, B III is an exception. We hope our result may stimulate more interest in taking a closer look at this IP value. This IP is important in establishing the correct term energy table and Grotrian diagrams. In the present work, the full core is frozen as one single term in the three-electron calculation. On the surface, the flexibility in the variation calculation is reduced, thus disallowing the possibility that the total energy might be lowered even more. However, there are a few distinctive advantages in this approach to an IP calculation. Namely, since (except for the Pauli-antisymmetry principle) the core is the same two-electron ground state considered in the IP calculation, the error due to the approximation in the core will essentially cancel out, which makes the IP result more reliable. We should emphasize the words "full core" if a highly reliable result is expected. We do not claim that this method can obtain the accuracy that may be possible with an extensive correlated-coordinate (Hylleraas-type) method. However, in the absence of the latter, what we obtained appears to be a good alternative.

There is also an advantage from a numerical aspect. As we mentioned in Sec. IV, our secular equation from Eq. (18) actually involves the computation of about one-half of the 3553×3553 matrix elements. To diagonalize such a matrix would certainly lead to numerical instability in our calculation, not to mention the huge RAM memory needed in our computer. By reducing the core wave function into a single term, this matrix size is reduced to 1017×1017 .

This method should also be useful in calculating transition processes where the participation of the core is weak, in, for example, the optical transition of $1s^2nl \rightarrow 1s^2n'l'$. Whether we are calculating transition energy or oscillator strength, the cancellation of the errors in the core function will likely assist in obtaining a more accurate result. In the case of Auger processes ($1s^2n_1l_1, n_2l_2 \rightarrow 1s^2n_1'l_1' + e$), the method could also be useful.

Note added in proof. I have just received a copy of unpublished work from McKenzie and Drake (Windsor).

TABLE VI. Nonrelativistic and relativistic energy ($-E$) of lithiumlike $1s^2s^2S$ states and comparison with other theories.

Z	Upper bound This work (a.u.)	Corrections		Nonrel. E This work (a.u.)	Other theory (a.u.)	Relativistic E This work (a.u.)
		Higher- l (0.1 μ a.u.)	Core (0.1 μ a.u.)			
3	7.477 925 1	36(4)	1310(5)	7.478 059 7(9)	7.478 059 53 ^a 7.478 025 ^b 7.478 062 4(7) ^c 7.477 160 ^d 7.478 060 32(1) ^e	7.478 677 5(9)
4	14.324 604 3	76(6)	1491(5)	14.324 761 0(11)	14.324 760 ^a 14.324 807 ^f 14.324 57 ^g 14.324 696 ^h 14.324 72 ⁱ 14.323 50 ^j	14.327 058 7(11)
5	23.424 432 8	104(8)	1600(5)	23.424 603 1(13)	23.424 604 ^a 23.432 481 ^d	23.430 803 6(13)
6	34.775 325 4	129(10)	1699(5)	34.775 508 2(15)	34.775 509 ^a 34.744 325 ^d	34.789 278 6(15)
7	48.376 706 0	145(12)	1744(6)	48.376 894 9(18)	48.376 896 ^a 48.375 668 ^d	48.4037 200(18)
8	64.228 343 6	160(13)	1789(6)	64.228 538 5(19)	64.228 540 ^a 64.227 273 ^d	64.276 083 7(19)
9	82.330 134 0	173(14)	1835(7)	82.330 334 8(21)	82.330 336 ^a 82.329 039 ^d	82.408 823 9(21)
10	102.682 023 4	183(15)	1861(7)	102.682 227 8(22)	102.682 229 ^a 102.680 905 ^d	102.804 800 3(22)

^aReference [12].^bReference [20].^cReference [27].^dReference [22].^eReference [29].^fReference [19].^gReference [23].^hReference [24].ⁱReference [25].^jReference [18].

Their QED results for the lithiumlike $1s^2s$ are very different from those of the present work. Assuming their results are accurate, these results imply that a substantial discrepancy exists between theory and experiment on the ionization potentials of Be II, B III, and C IV. Since the nonrelativistic energies of this work are accurate and the higher-order relativistic contributions are small for $Z=4$ to 6, the source of this discrepancy is not clear at this time.

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