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Energy of $1s^2ns$ ($n=3$, 4, and 5) states for the lithium isoelectronic sequence

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The nonrelativistic energies of the lithiumlike $1s^2ns$ ($n=3$, 4, and 5) states for $Z=3$ to 10 are calculated by using a full-core-plus-correlation method with multiconfiguration-interaction wave functions. Relativistic and mass-polarization effects on the energy are evaluated as the first-order perturbation corrections. The quantum-electrodynamic (QED) correction to the energy is included using effective nuclear charge. Our results are compared with the experimental data in the literature. For $Z<8$ systems, the discrepancies are about 1 cm^{-1} or less in most cases. Our nonrelativistic energies are also compared with previous theoretical results in the literature.

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I. INTRODUCTION

It is easier to apply the Slater-type multiconfiguration-interaction (CI) wave function than the correlation-coordinate (r_{ij}) wave function to many-electron atomic systems. For some core-excited lithiumlike systems, highly accurate results have been obtained by using this CI method [1,2]. However, for systems with $1s^2$ core (e.g., $1s^2ns$), high-precision results are difficult to obtain with CI wave functions. This is because the large contributions from the high-angular-momentum components in the wave function make the energy convergence slow.

Recently, a full-core-plus-correlation method was used successfully to calculate the ionization potentials (IP's) of the lithiumlike ground states, $1s^22s$, from $Z=3$ to 10 [3], and from $Z=11$ to 20 [4]. In Ref. [3], the IP's of the ground states from Li I to Ne VIII are predicted to within 10 ppm of the experiment. An improved calculation [4] reduced this discrepancy to within 1 ppm. The main difference of this method from the usual CI method is that the wave function of the core is frozen as one single term in the three-electron wave function. The effect of valence electron is accounted for by multiplying the core wave function with a linear combination of single-particle Slater orbitals. The relaxation of the core and the intrashall electron-electron interaction are described by another large CI wave function. This method has been applied to the ground states. A natural extension is to test this method on the excited atomic systems. In this work, we calculate the ionization potentials and the excitation energies of the $1s^2ns$ ($n=3$, 4, and 5) states for the lithium isoelectronic sequence from Li I to Ne VIII. The relativistic and the mass-polarization corrections to the energies are evaluated by using first-order perturbation theory. In order to make a definitive comparison with experimental data in the literature, the correction to the nonrelativistic upper bound from the neglected higher-l angular momentum components is included by using the same extrapolaration procedure as in Ref. [3], and the QED correction is estimated by using the formula in Bethe and Salpeter [5]. The values of the Bethe logarithms $K(n,0)$ are taken from Drake and Swainson [6].

Computation in the present work are carried out in atomic units (a.u.). For excited state, most of the precision data in the literature are given by its excitation energy in cm^{-1}. The excitation energy of a three-electron atomic system is the energy above the ground state $1s^22s$. We convert our excitation energy into cm^{-1} using the reduced *Rydberg* constants in Ref. [3]. These constants agree with those of Pekeris [7] to eight digits.

The theoretical method of the present work follows closely that of Ref. [3]. These presentations will not be repeated. In Sec. II the computation in this work is presented. The calculated results and discussion are given in Sec. III. A conclusion is given in Sec. IV.

II. COMPUTATION

We extend the full-core-plus-correlation method to calculate the energies of the lithiumlike $1s^2ns$ ($n=3$, 4, and 5) states. The wave function of the three-electron system is given by

$$\Psi(2,3,4)=A\left[\Phi_{1s1s}(1,2)\sum_i d_i r_3^i e^{-\beta r_3}\chi(3)+\sum_i C_i\Phi_{n(i),l(i)}(1,2,3)\right], \quad (1)$$

where A is an antisymmetrization operator. Φ_{1s1s} is a predetermined $1s^2$ core wave function. The second term on the right side of Eq. (1) describes the relaxation of the core and other possible correlations.

The nonrelativistic upper bounds of the $1s^2$ core and the $1s^2ns$ ($n=3$, 4, and 5) states are calculated by minimizing the expectation value of the nonrelativistic Hamiltonian whose explicit expression is given in Ref. [3]. In predicting the accurate nonrelativsitc energies of three-electron systems, two kinds of corrections should be added to the upper bounds. The first one is the core correction which is the deficiency of our core energy in comparison with the corresponding result of Pekeris [7]. Another correction is the contribution coming from the higher-l angular components which are not included in our wave function. This correction can be calculated by comparing the energy convergence with that of the $1s^22s$ and utilizing the extrapolated results from Ref. [3]. For $1s^2ns$ states with $n \geq 3$, the higher-l contributions are very small. The largest correction is the -5.2 μa.u. for the Ne VIII $1s^23s$. It is about 1.1 cm^{-1}.

The relativistic and mass-polarization effects on the energies are calculated using first-order perturbation theory. The explicit expressions of these operators are given in Ref. [3]; they will not be repeated here. In this work the nuclear mass for the mass-polarization effect is taken from Wapstra and Audi [8]. The isotopes used are ^{7}Li, ^{9}Be, ^{11}B, ^{12}C, ^{14}N, ^{16}O, ^{19}F, and ^{20}Ne.

The ionization potential E_{IP} is given by the sum of the energy expectation value differences between the core and the three-electron system. Although the core wave function we used is not exact, the error due to the approximation in the core essentially canceled in the IP calculation. The QED effect on the IP is estimated with a hydrogenic formula using effective nuclear charge [3,5].

To compare with the experimental "excitation energy" (T), we use the following definition:

$$T(1s^2ns)=E_{\text{IP}}(1s^22s)-E_{\text{IP}}(1s^2ns) \ . \tag{2}$$

For $E_{\text{IP}}(1s^22s)$, we use the experimental data in Kelly [9] for all Z except B III. For B III, the value 305 929.46 cm^{-1} [3,4] is used rather than the 305 931.1 cm^{-1}.

III. RESULTS AND DISCUSSION

For the $1s^2$ core wave function we used a total of 222 terms in the seven l components. Though the number of the terms is less than that of the terms used in Ref. [3], for our purpose this does not lead to a substantial effect on our results, because the IP is determined by the difference of the $1s^2ns$ energy with that of the core, as mentioned in Sec. II. The number of terms in the $\Phi_{n(i),l(i)}$ of Eq. (1) ranges from 364 terms to 669 terms. As expected, in order to obtain a more accurate upper bound the number of terms increases as Z becomes larger for a given principal quantum number n. They decrease with increasing n for a given Z due to less correlation. The energy convergence patterns of the lithiumlike systems from $Z=3$ to 10 are very similar wit each other. The energy convergence of these wave functions will be sent to the interested reader upon request.

The highest orbital-angular-momentum quantum number used in the wave function in this work is $l=6$. The contribution coming from the angular components with l higher than 6 should be taken into account. Since the precise energies of the $1s^2$ core for these systems are known [7], and the rates of convergence for the three-electron $1s^2ns$ and the two-electron $1s^2$ are basically the same, these permit us to extrapolate for the $1s^2ns$ energies using the contributions to the binding energy from $l=4$, 5, or 6, as discussed in detail in Ref. [3]. The extrapolated results are shown in Table I, where they are given in the column of "higher l." The extrapolated result for $3s$ is about one-fourth of that of $2s$. It is about one-sixth for $4s$ and one-twelfth for $5s$.

In Table I we give the nonrelativistic energies of the lithiumlike $1s^2ns$ ($n=3$, 4, and 5) states from $Z=3$ to 10, by including the upper bounds, the core corrections, the "higher-l" contributions and the total nonrelativistic energies. The recent results of King [10] are also given in this table for comparison. The results of King are more accurate than other theoretical calculations in the literature [11–15]. Our nonrelativistic energy results are substantially lower than the upper bounds in Ref. [10]. In Ref. [10], some empirical estimates are also quoted for the $1s^2ns$ states. Our results for lithium -7.354098, -7.318530, and -7.303551 a.u. agree well with the empirical estimated results of -7.354099, -7.318530, and -7.303550 a.u. However, substantial differences exist for other systems. Based on the close agreement between our results and the experimental data (see comparison below), these empirical estimates could be less accurate than the results given in Table I.

In Table II IP's of the $1s^2ns$ ($n=3$, 4, and 5) states are given from Li I to Ne VIII. Here "nonrel." represents the nonrelativistic upper bound which is obtained by using the wave function in Eq. (1). $\langle H_1+H_2 \rangle$ is the sum of the relativistic kinetic-energy correction and Darwin term. $\langle H_3 \rangle$ is the electron-electron contact term. $\langle H_5 \rangle$ is the orbit-orbit interaction. $\langle H_4 \rangle$ is the mass-polarization correction. The explicit expression of these operators is given in Ref. [3]. The QED correction to the IP is estimated with a hydrogenic formula using effective nuclear charge. The method of finding the effective charge is discussed in Ref. [3]. The entries in column 3 are the corresponding contribution to the IP obtained by the differences between column 2 and the $1s1s$ core expectation values. The entries in columns 5 and 7 are obtained in a similar manner. The IP values of $1s^23s$ states for Li I and Be II from the recent many-body perturbation theory calculation [16] are also given for comparison. If we scale the results of Ref. [16] into the atomic unit used in this work, they agree excellently with those of the present work.

The results in Table II reveal some interesting physics about the relativistic correction terms. From the solution to the one-particle Dirac equation for a Coulomb potential, the functional dependence of the one-particle operator $\langle H_1+H_2 \rangle$ on the nuclear charge Z and the principal quantum number n is well known [5]. However, H_3, H_4, and H_5 are two-body operators. If we consider the lithiumlike ^2S systems as a one-particle system moving under the influence of an effective nucleus charge, the functional dependence of $\langle H_3 \rangle$, $\langle H_4 \rangle$, and $\langle H_5 \rangle$ on n and on the effective nuclear charge Z_{eff} can be studied. Define

$$\langle H_r \rangle_{ns} = \langle H_r \rangle_{1s^2} - \langle H_r \rangle_{1s^2ns} \tag{3}$$

where $r=3$ 4, and 5, and the results of $\langle H_3 \rangle_{ns}$ show a $(Z_{\text{eff}}/n)^3$ dependence. If we plot the ratio

$$R=\frac{\langle H_3 \rangle_{ns}}{(Z_{\text{eff}}/n)^3} \tag{4}$$

as a function of the nuclear charge Z, R appears to approach a constant rather quickly (see Fig. 1). Both $\langle H_4 \rangle_{ns}$ and $\langle H_5 \rangle_{ns}$ also exhibit this $1/n^3$ dependence. $\langle H_5 \rangle_{ns}$ is approximately proportional to $(Z_{\text{eff}})^2$. The specific mass-polarization effect, i.e., the product of

TABLE I. Nonrelativistic energies of Li-like $1s^2ns$ states from $Z=3$ to 10 (in a.u.).

Z	State	Upper bound	Core correction	Higher l	Total	King [10]
3	$1s^23s$	−7.353 938 0	−0.000 159 3	−0.000 000 7	−7.354 098 0	−7.354 076
	$1s^24s$	−7.318 370 7	−0.000 159 3	−0.000 000 3	−7.318 530 3	−7.318 315
	$1s^25s$	−7.303 391 4	−0.000 159 3	−0.000 000 1	−7.303 550 8	−7.301 943
4	$1s^23s$	−13.922 604 8	−0.000 181 6	−0.000 002 2	−13.922 788 6	−13.922 764
	$1s^24s$	−13.798 532 1	−0.000 181 6	−0.000 000 7	−13.798 714 4	−13.798 662
	$1s^25s$	−13.744 448 7	−0.000 181 6	−0.000 000 3	−13.744 630 6	−13.744 577
5	$1s^23s$	−22.603 552 2	−0.000 195 9	−0.000 003 0	−22.603 751 1	−22.603 724
	$1s^24s$	−22.341 633 5	−0.000 195 9	−0.000 001 8	−22.341 831 2	−22.341 779
	$1s^25s$	−22.225 638 1	−0.000 195 9	−0.000 000 8	−22.225 834 8	
6	$1s^23s$	−33.396 005 9	−0.000 205 6	−0.000 003 7	−33.396 215 2	−33.396 188
	$1s^24s$	−32.947 363 1	−0.000 205 6	−0.000 002 2	−32.947 570 9	−32.947 524
	$1s^25s$	−32.746 840 3	−0.000 205 6	−0.000 001 0	−32.747 046 9	
7	$1s^23s$	−46.299 747 6	−0.000 212 0	−0.000 004 1	−46.299 963 7	−46.299 936
	$1s^24s$	−45.615 643 2	−0.000 212 0	−0.000 002 2	−45.615 857 4	−45.615 809
	$1s^25s$	−45.308 039 7	−0.000 212 0	−0.000 001 1	−45.308 252 8	
8	$1s^23s$	−61.314 690 7	−0.000 217 6	−0.000 004 4	−61.314 912 7	−61.314 886
	$1s^24s$	−60.346 444 2	−0.000 217 6	−0.000 002 5	−60.346 664 3	−60.346 614
	$1s^25s$	−59.909 238 9	−0.000 217 6	−0.000 001 2	−59.909 457 7	
9	$1s^23s$	−78.440 797 8	−0.000 222 1	−0.000 004 9	−78.441 024 8	−78.440 999
	$1s^24s$	−77.139 756 9	−0.000 222 1	−0.000 002 8	−77.139 981 8	−77.139 930
	$1s^25s$	−76.550 424 7	−0.000 222 1	−0.000 001 3	−76.550 648 1	
10	$1s^23s$	−97.678 051 1	−0.000 225 8	−0.000 005 2	−97.678 282 1	−97.678 256
	$1s^24s$	−95.995 575 2	−0.000 225 8	−0.000 002 9	−95.995 803 9	−95.995 752
	$1s^25s$	−95.231 601 8	−0.000 225 8	−0.000 001 4	−95.231 829 0	

TABLE II. Ionization potential for the $1s^2ns\ ^2S$ states ($n=3,4,5$) of lithiumlike systems from Li I to Ne III (in a.u.).

	$1s^23s$		$1s^24s$		$1s^25s$	
	E	IP	E	IP	E	IP
			$Z=3$			
Nonrel.	−7.353 938 0	0.074 183 9	−7.318 370 7	0.038 616 6	−7.303 391 4	0.0236 374
$\langle H_1+H_2\rangle$	−0.000 696 8	0.000 003 5	−0.000 694 7	0.000 001 4	−0.000 694 0	0.000 000 7
$\langle H_3\rangle$	0.000 094 3	−0.000 000 4	0.000 094 0	−0.000 000 1	0.000 094 0	−0.000 000 1
$\langle H_5\rangle$	−0.000 023 0	0.000 000 1	−0.000 023 0	0.000 000 1	−0.000 023 0	0.000 000 1
$\langle H_4\rangle$	0.000 022 9	−0.000 000 2	0.000 022 8	−0.000 000 1	0.000 022 7	0.000 000 0
Higher l	−0.000 000 7	0.000 000 7	−0.000 000 3	0.000 000 3	−0.000 000 1	0.000 000 1
Subtotal	−7.354 541 3	0.074 187 6	−7.318 971 9	0.038 618 2	−7.303 991 8	0.023 638 1
QED corr.		−0.000 000 1		0.000 000 0		0.000 000 0
IP this work		0.074 187 5		0.038 618 2		0.023 638 1
Ref. [16]		0.074 187 4				
			$Z=4$			
Nonrel.	−13.922 604 8	0.267 220 2	−13.798 532 1	0.143 147 5	−13.744 448 7	0.089 064 1
$\langle H_1+H_2\rangle$	−0.002 460 3	0.000 031 0	−0.002 442 1	0.000 012 8	−0.002 435 9	0.000 006 6
$\langle H_3\rangle$	0.000 267 0	−0.000 002 6	0.000 265 4	−0.000 001 0	0.000 264 9	−0.000 000 5
$\langle H_5\rangle$	−0.000 047 4	0.000 000 4	−0.000 047 2	0.000 000 2	−0.000 047 1	0.000 000 1
$\langle H_4\rangle$	0.000 026 2	−0.000 000 5	0.000 025 9	−0.000 000 2	0.000 025 8	−0.000 000 1
Higher l	−0.000 002 2	0.000 002 2	−0.000 000 7	0.000 000 7	−0.000 000 3	0.000 000 3
Subtotal	−13.924 821 5	0.267 250 7	−13.800 730 8	0.143 160 0	−13.746 641 3	0.089 070 5
QED corr		−0.000 000 9		−0.000 000 3		−0.000 000 2
IP this work		0.267 249 8		0.143 159 7		0.089 070 3
Ref. [16]		0.267 250 7				
			$Z=5$			
Nonrel.	−22.603 552 2	0.572 776 5	−22.341 633 5	0.310 857 8	−22.225 638 1	0.194 862 4
$\langle H_1+H_2\rangle$	−0.006 447 0	0.000 120 4	−0.006 377 7	0.000 051 1	−0.006 352 9	0.000 026 3

TABLE II. (*Continued*).

	$1s^23s$		$1s^24s$		$1s^25s$	
	E	IP	E	IP	E	IP
$\langle H_3 \rangle$	0.000 578 2	−0.000 007 4	0.000 573 7	−0.000 002 9	0.000 572 3	−0.000 001 5
$\langle H_5 \rangle$	−0.000 080 7	0.000 001 0	−0.000 080 1	0.000 000 4	−0.000 079 9	0.000 000 2
$\langle H_4 \rangle$	0.000 028 4	−0.000 000 7	0.000 028 0	−0.000 000 3	0.000 027 8	−0.000 000 1
Higher l	−0.000 003 0	0.000 003 0	−0.000 001 8	0.000 001 8	−0.000 000 8	0.000 000 8
Subtotal	−22.609 476 3	0.572 892 8	−22.347 491 4	0.310 907 9	−22.231 471 6	0.194 888 1
QED corr.		−0.000 003 5		−0.000 001 4		−0.000 000 7
IP this work		0.572 889 3		0.310 906 5		0.194 887 4
$Z=6$						
Nonrel.	−33.396 005 9	0.989 965 0	−32.947 363 1	0.541 322 2	−32.746 840 3	0.340 799 4
$\langle H_1+H_2 \rangle$	−0.014 036 8	0.000 327 3	−0.013 850 9	0.000 141 4	−0.013 783 5	0.000 074 0
$\langle H_3 \rangle$	0.001 069 1	−0.000 016 2	0.001 059 4	−0.000 006 5	0.001 056 1	−0.000 003 2
$\langle H_5 \rangle$	−0.000 122 8	0.000 001 9	−0.000 121 8	0.000 000 9	−0.000 121 4	0.000 000 5
$\langle H_4 \rangle$	0.000 032 4	−0.000 000 9	0.000 031 8	−0.000 000 3	0.000 031 7	−0.000 000 2
Higher l	−0.000 003 7	0.000 003 7	−0.000 002 2	0.000 002 2	−0.000 001 0	0.000 001 0
Subtotal	−33.409 067 7	0.990 280 8	−32.960 246 8	0.541 459 9	−32.759 658 4	0.340 871 5
QED corr.		−0.000 009 4		−0.000 003 8		−0.000 001 9
IP this work		0.990 271 4		0.541 456 1		0.340 869 6
$Z=7$						
Nonrel.	−46.299 747 6	1.518 514 5	−45.615 643 2	0.834 410 1	−45.308 039 7	0.526 806 6
$\langle H_1+H_2 \rangle$	−0.026 947 0	0.000 725 4	−0.026537 5	0.000 315 9	−0.026387 2	0.000 165 6
$\langle H_3 \rangle$	0.001 780 6	−0.000 029 9	0.001 762 8	−0.000 012 1	0.001 756 7	−0.000 006 0
$\langle H_5 \rangle$	−0.000 173 8	0.000 002 9	−0.000 172 1	0.000 001 2	−0.000 171 5	0.000 000 6
$\langle H_4 \rangle$	0.000 033 3	−0.000 001 1	0.000 032 6	−0.000 000 4	0.000 032 4	−0.000 000 2
Higher l	−0.000 004 1	0.000 004 1	−0.000 002 2	0.000 002 2	−0.000 001 1	0.000 001 1
Subtotal	−46.325 058 6	1.519 215 9	−45.640 559 6	0.834 716 9	−45.332 810 4	0.526 967 7
QED corr.		−0.000 020 1		−0.000 008 2		−0.000 004 1
IP this work		1.519 195 8		0.834 708 7		0.526 963 6
$Z=8$						
Nonrel.	−61.314 690 7	2.158 313 2	−60.346 444 2	1.190 066 7	−59.909 238 9	0.752 861 4
$\langle H_1+H_2 \rangle$	−0.047 233 3	0.001 406 8	−0.046 442 9	0.000 616 4	−0.46 148 8	0.000 322 3
$\langle H_3 \rangle$	0.002 754 0	−0.000 049 9	0.002 724 3	−0.000 020 2	0.002 714 3	−0.000 010 2
$\langle H_5 \rangle$	−0.000 233 7	0.000 004 3	−0.000 231 2	0.000 001 8	−0.000 230 3	0.000 000 9
$\langle H_4 \rangle$	0.000 033 9	−0.000 001 1	0.000 033 2	−0.000 000 4	0.000 033 0	−0.000 000 2
Higher l	−0.000 004 4	0.000 004 4	−0.000 002 5	0.000 002 5	−0.000 001 2	0.000 001 2
Subtotal	−61.359 374 2	2.159 677 7	−60.390 363 3	1.190 666 8	−59.952 871 9	0.753 175 4
QED corr.		−0.000 037 3		−0.000 015 3		−0.000 007 7
IP this work		2.159 640 4		1.190 651 5		0.753 167 7
$Z=9$						
Nonrel.	−78.440 797 8	2.909 307 6	−77.139 756 9	1.608 266 7	−76.550 424 7	1.018 934 5
$\langle H_1+H_2 \rangle$	−0.077 283 9	0.002 477 1	−0.075 899 2	0.001 092 4	−0.075 381 6	0.000 574 8
$\langle H_3 \rangle$	0.004 030 2	−0.000 077 2	0.003 984 4	−0.000 031 4	0.003 968 7	−0.000 015 7
$\langle H_5 \rangle$	−0.000 302 4	0.000 005 8	−0.000 299 1	0.000 002 5	−0.000 297 9	0.000 001 3
$\langle H_4 \rangle$	0.000 032 6	−0.000 001 2	0.000 031 9	−0.000 000 5	0.000 031 7	−0.000 000 3
Higher l	−0.000 004 9	0.000 004 9	−0.000 002 8	0.000 002 8	−0.000 001 3	0.000 001 3
Subtotal	−78.514 326 2	2.911 717 0	−77.211 941 7	1.609 332 5	−76.622 105 1	1.019 495 9
QED corr.		−0.000 062 8		−0.000 025 8		−0.000 013 0
IP this work		2.911 654 2		1.609 306 7		1.019 482 9
$Z=10$						
Nonrel.	−97.678 051 1	3.771 470 5	−95.995 575 2	2.088 994 6	−95.231 601 8	1.325 021 2
$\langle H_1+H_2 \rangle$	−0.119 832 9	0.004 069 1	−0.117 563 2	0.001 799 4	−0.116 708 3	0.000 944 5
$\langle H_3 \rangle$	0.005 650 4	−0.000 112 9	0.005 583 5	−0.000 046 0	0.005 560 7	−0.000 023 2
$\langle H_5 \rangle$	−0.000 380 0	0.000 007 6	−0.000 375 7	0.000 003 3	−0.000 374 1	0.000 001 7
$\langle H_4 \rangle$	0.000 034 8	−0.000 001 3	0.000 034 1	−0.000 000 6	0.000 033 8	−0.000 000 3
Higher l	−0.000 005 2	0.000 005 2	−0.000 002 9	0.000 002 9	−0.000 001 4	0.000 001 4
Subtotal	−97.792 584 0	3.775 438 2	−96.107 899 2	2.090 753 6	−95.343 091 1	1.325 945 3
QED corr.		−0.000 098 2		−0.000 040 6		−0.000 020 5
IP this work		3.7753400		2.090 713 0		1.325 924 8

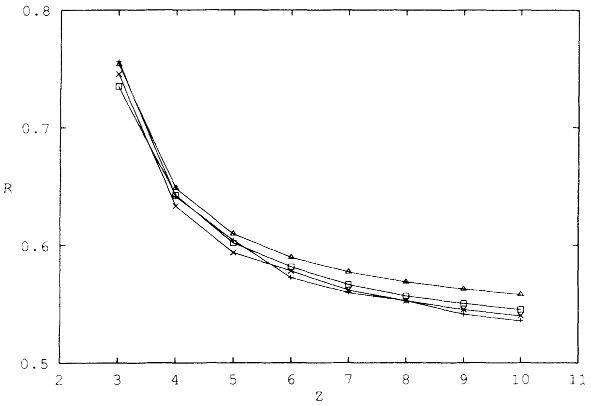

FIG. 1. The ratio $R=\langle H_3\rangle_{ns}/(Z_{\mathrm{eff}}/n)^3$ (in 10^{-5} a.u.) as a function of the nuclear charge Z. H_3 is the perturbation potential for the electron-electron contact term. The explicit expression of the operator is given in Ref. [3]. Z_{eff} is the effective nuclear charge seen by the ns electron. △, $n=2$; □, $n=3$; ×, $n=4$; and +, $n=5$.

$\langle H_4\rangle_{ns}$ and the nuclear mass, depend linearly on Z_{eff}. Even though this $\langle H_4\rangle_{ns}$ is small, the dependence on the nuclear mass contributes an isotope shift in the observed optical spectra. This shift can be measured in experiments.

In Table III we give the excitation energies of the $1s^2ns$ states for Li I to Ne VIII in cm^{-1}. These excitation energies are in reference to the experimental $1s^22s$ energies quoted in Kelly [9] except for B III. For B III, 305 929.46 cm^{-1} [4] is used. We expect these predicted results be accurate to within 1 cm^{-1} for $Z\leq 5$. The errors may become slightly larger for larger Z. The experimental data [9,17–20] and the other theoretical excitation energy results [21,22] are also listed in this table.

In comparing our $1s^2ns$ results with those of Kelly [9], we note that close agreements are obtained for Li I and Be II. The discrepancies are well within 0.5 cm^{-1}. For B III, our $1s^23s$ result, 180 201.06 cm^{-1}, is 0.7 cm^{-1} lower than the 180 201.8 cm^{-1} in Kelly [9]. Our $1s^24s$ and $1s^25s$ excitation energies are about 1.3 and 2.5 cm^{-1} higher than those of Kelly [9] and Moore [20], but they

TABLE III. Excitation energy of $1s^2ns$ ($n=3$, 4, and 5) states for lithiumlike systems from Li I to Ne VIII (in cm^{-1}).

					Other theory		
Z	State	This work	Kelly[a]	Other work	Ref. [22]	Ref. [21]	Ref. [16]
3	$1s^23s$	27 206.15	27 206.12			27 191	27 206.17
	$1s^24s$	35 012.12	35 012.06			35 043	
	$1s^25s$	38 299.57	38 299.50			38 335	
4	$1s^23s$	88 231.87	88 231.91	88 231.2[b]		88 221	88 231.68
	$1s^24s$	115 464.86	115 464.44	115 465.2[b]		115 491	
	$1s^25s$	127 335.38	127 335.19	127 336.1[b]		127 347	
5	$1s^23s$	180 201.06	180 201.8	180 202.09[c]		180 197	
	$1s^24s$	237 696.79	237 695.5	237 698.45[c]		237 701	
	$1s^25s$	263 158.74	263 156.2[b]	263 159.81[c]		263 159	
6	$1s^23s$	302 848.91	302 849.0	302 847.9[b]	302 858	302 850	
	$1s^24s$	401 347.96	401 348.1	401 346.7[b]	401 152	401 337	
	$1s^25s$	445 369.22	445 368.5	445 366.1[b]	445 221	445 362	
7	$1s^23s$	456 125.44	456 126.6	456 129.7[d]	456 147	456 134	
	$1s^24s$	606 347.00	606 348.8	606 347.7[d]	606 123	606 336	
	$1s^25s$	673 886.59	673 886.2	673 884.8[d]	673 721	673 881	
8	$1s^23s$	640 037.90	604 039.8		640 062	640 056	
	$1s^24s$	852 699.17	852 696		852 436	852 687	
	$1s^25s$	948 712.45	948.69×10^3		948 521	948 706	
9	$1s^23s$	854 613.24	854 625	854 621[e]	885 456	854 640	
	$1s^24s$	1 140 437.21	1 140 416	1 140 432[e]	1140.13×10^3	1 140 434	
	$1s^25s$	1 269 885.10	1 269 826	1 269 881[e]	1269.66×10^3	1 269 885	
10	$1s^23s$	1 099 893.93	1099.87×10^3		1 099 916	1 099 933	
	$1s^24s$	1 469 616.51	1469.64×10^3		1469.27×10^3	1 469 621	
	$1s^25s$	1 637 463.14	1637.41×10^3		1637.21×10^3	1 637 466	

[a] Reference [9].
[b] Reference [20].
[c] Reference [18].
[d] Reference [17].
[e] Reference [19].

are 1.7 and 1.1 cm^{-1} lower than those of Ølme [18]. For C IV, the agreement between our results and Kelly's [9] for the 3*s*, 4*s*, and 5*s* states are close to 1 cm^{-1} or less.

Most of the $1s^2ns$ excitation energy data in Kelly [9] and Bashkin and Stoner [17] are the same. N V is an exception. The N V data in Kelly [9] are mostly from Hallin [23]. Our N V results agree better with those of Kelly [9] than with those of Bashkin and Stoner [17]. The largest deviation is for $1s^24s$ where a discrepancy of 1.8 cm^{-1} is noted. In this case our predicted excitation energy, 606 347.0 cm^{-1}, agrees better with the 606 347.7 cm^{-1} of Bashkin and Stoner [17]. For $1s^23s$, however, our result is lower than that of Ref. [17] by about 4 cm^{-1}. We note that one of the 3*s*-4*p* transition wavelengths (624.75 Å) in the Grotrian Diagram [17] is incorrect. Whether this has affected their $1s^23s$ excitation energy is not clear.

For O VI, our $1s^23s$ result is lower than that of Kelly [9] by 1.9 cm^{-1}. For $1s^24s$, there is a discrepancy of 3.2 cm^{-1}. The excitation energy of the O VI $1s^25s$ in Kelly [9] has only been quoted to five digits. This is probably an indication that the experimental data is not very reliable. Our result seems to support his conclusion.

For F VII, our results deviate substantially from the data in Kelly [9]. A more recent experiment was carried out by Engström [19] on this system. The excitation energies obtained in Ref. [19] agree much better with the theoretical prediction. The discrepancies are less than 8 cm^{-1} for each of the three states. However, our $1s^23s$ is lower than the experiment by 7.7 cm^{-1} whereas the 4*s* and 5*s* are higher by 5.2 and 4.1 cm^{-1}, respectively. This is unexpected.

The three Ne VIII excitation energies in Kelly [9] are quoted to 10 cm^{-1} only. They deviate with the prediction by 24, −23, and 53 cm^{-1} for $1s^23s$, 4*s*, and 5*s*, respectively. It appears that these experimental data can be improved in the future.

It is interesting to note that for Be II, C IV, and N V, the $1s^2ns$ excitation energy data are revised from Moore [20] to Kelly [9]. In each case, the revised data agree much better with our prediction (see Table III). The B III, O VI, and F VII $1s^2ns$ excitation energies in Refs. [9,20] are identical. Our results suggests that a revision of some of these data may be needed.

IV. CONCLUSION

In this work, we aim at examining whether accurate prediction of excitation energies are possible for the exited $1s^2ns$ states of lithiumlike systems. The results indicate that our calculated excitation energies of the $1s^2ns$ ($n=3$, 4, and 5) for systems from $Z=3$ to 7 agree with the experimental data to about 1 cm^{-1} in most cases. Recently we have calculated the excitation energies and the fine structures of the $1s^2np$, $1s^2nd$ and $1s^2nf$ states for these systems using the same method. Highly accurate results are also obtained [24,25]. We have also calculated the transition wavelengths and oscillator strengths of these systems using our energies and CI wave functions. These results show that the full-core-plus-correlation method is effective for calculating the excited atomic systems with a $1s^2$-core.

For F VII and Ne VIII, the comparison between theory and experimental is less conclusive. We hope that more precise measurements can be carried out to make such a comparison.

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