# Ionization potential for the lithiumlike $1s^2 2s$ states from Na IX to Ca XVIII

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The ionization potentials of lithiumlike $1s^2 2s$ states are calculated for systems with nuclear charge $Z=11$ to 20 using a full-core plus correlation method. The relativistic corrections are included using first-order perturbation theory. The QED contributions to the ionization potential are calculated using effective nuclear charge. These results are compared with data available in the literature.

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## I. INTRODUCTION

The full-core plus correlation method has been used for calculating the energies of the ground states [1] and excited states [2] of three-electron and four-electron [3] systems. In [1], the ionization potentials (IP) of the lithiumlike $1s^2 2s$ states are predicted to within 10 ppm of the experiment for all $Z$ from 3 to 10. The QED contribution to the IP is calculated from

$$\Delta E_{\rm QED}(n,0)=8Z_{\rm eff}^4\alpha^3\mathcal{R}\{\tfrac{19}{30}-2\ln(\alpha Z_{\rm eff}) -\ln[K(n,0)]\}/(3\pi n^3)\,, \quad (1)$$

where $n=2$, $Z_{\rm eff}$ is the effective nuclear charge affecting the $2s$ electron, and $\mathcal{R}$ is the Rydberg constant. However, we found recently that the contribution from the QED effect in [1] needs to be revised [4]. If we neglect the theoretical estimated uncertainty, the revised IP's agree with that of experiment [5] to about 1 ppm even for F VII and Ne VIII (see Table I). Except for B III where the comparison between prediction and experiment does not follow isoelectronic trend, the largest deviation of the predicted IP from that of Kelly [5] is for F VII. For F VII, the IP quoted in Kelly [5] is 1 493 629 $\rm cm^{-1}$ whereas our prediction is 1 493 630.4 $\rm cm^{-1}$. A recent experiment of Engström [6] gives 1 493 632±5 $\rm cm^{-1}$. In [1], the relativistic corrections are accounted for by using first-order perturbation theory. The contributions of this correction to the IP grow from 216.69 $\rm cm^{-1}$ in C IV to 2609.15 $\rm cm^{-1}$ in Ne VIII. In view of these large contributions, it is hard to assume that the higher-order relativistic effects make no contributions to the IP at all. Furthermore, the QED effects are calculated with a hydrogenlike formula using effective nuclear charge. This is also an approximation. In view of the exact agreement with experiment from $Z=3$ to 10 (except the discrepancy of 1.64 $\rm cm^{-1}$ in B III), it seems that the neglected parts in our approximation cancel out almost exactly. Whether the same cancellation will continue for higher-$Z$ systems is an interesting question. In the most recently compiled data tables [5,7], the IP's for the lithiumlike $1s^2 2s$ are only quoted to 100 $\rm cm^{-1}$ for $Z=11$ to 18 and to 1000 $\rm cm^{-1}$ for $Z=19$ and 20. If the cancellation of errors in our approximation continue as in the case of $Z=9$ and 10, it is likely that the theoretical prediction could be more reliable than the data available in the literature.

The purpose of the present work is twofold; to calculate the IP for lithiumlike $1s^2 2s$ using the full-core plus correlation method for $Z=11$ to 20 and to test whether the cancellation of errors in our approximation method continue for these systems. For this second purpose, we hope our result may stimulate some interest in precision measurements in the near future so that a more definitive conclusion can be made.

## II. COMPUTATION

The theoretical approach of the present work follows closely that of Ref. [1]. The method of extrapolation also follows that of [1]. These discussions will not be repeated. In [1], the exact nonrelativistic two-electron $1s^2$ energy of Pekeris [8] is used for extrapolation. For $Z=11$ to 20, we use those of Drake [9] where $1s^2$ results are calculated from the correlated-coordinate $Z$-expansion theory.

In the full-core plus correlation method, the total wave function for the three-electron system is given by

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

where $\Phi_{1s1s}$ is a predetermined two-electron core wave function. In this work, a 318-term core wave function is used. The three-electron wave function contains 1022 linear parameters (8 $d_i$'s and 1014 $C_i$'s). To avoid inaccuracy from linear dependence, all calculations in this work are carried out using quadruple precision ($R*16$) arithmetics. The energy convergence pattern is very similar to that of [1]. We summarize the nonrelativistic energy results in Table II.

The highest orbital angular momentum used for the wave functions in Table II is $l=6$. The angular components with $l>6$ which are not included in our calculation will also contribute to the IP. This contribution can be extrapolated using the method discussed in [1]. The IP values calculated in this work are quite large, ranging from $2.4\times10^6$ $\rm cm^{-1}$ for $Z=11$ to $9.3\times10^6$ $\rm cm^{-1}$ for

 

TABLE I. Ionization potential for the $1s^2 2s\ ^2S$ states of lithiumlike systems from Li I to Ne VIII with a revised QED correction (see Tables IV and V in [1]).

| | | | Ionization potential | | |
|---|---|---|---|---|---|
| | $1s1s$ | $1s^2 2s$ | (a.u.) | ($cm^{-1}$) | (eV) |
| | | $Z=3$ | | | |
| From [1][a] | −7.280 382 6 | −7.478 540 5 | 0.198 157 9(4) | 43 487.22(8) | 5.3917 |
| Revised QED correction | | | −0.000 000 4 | −0.08(1) | 0.0000 |
| IP this work | | | 0.198 157 5(4) | 43 487.14(9) | 5.3917 |
| Kelly [5], Bashkin and Stoner [7] | | | | 43 487.15(2) | 5.3917 |
| IP(theory)-IP(expt) | | | | −0.01(9) | |
| Moore [12] | | | | 43 487.19(2) | |
| Blundell *et al.* [17] | | | 0.198 158 4(5) | | |
| | | $Z=4$ | | | |
| From [1][a] | −13.657 604 4 | −14.326 896 7 | 0.669 292 3(6) | 146 883.73(13) | 18.2113 |
| Revised QED correction | | | −0.000 003 5(2) | −0.78(5) | −0.0001 |
| IP this work | | | 0.669 288 7(8) | 146 882.95(18) | 18.2112 |
| Kelly [5], Bashkin and Stoner [7] | | | | 146 882.86 | 18.2112 |
| IP(theory)-IP(expt) | | | | 0.09(18) | |
| Moore [12] | | | | 146 881.7 | |
| Blundell *et al.* [17] | | | 0.669 293(1) | | |
| | | $Z=5$ | | | |
| From [1][a] | −22.036 621 6 | −23.430 621 7 | 1.394 000 1(8) | 305 932.41(18) | 37.9308 |
| Revised QED correction | | | −0.000 013 5(9) | −2.95(21) | −0.0004 |
| IP this work | | | 1.393 986 7(17) | 305 929.46(39) | 37.9304 |
| Kelly [5], Bashkin and Stoner [7], Moore [12] | | | | 305 931.1 | 37.9306 |
| IP(theory)-IP(expt) | | | | −1.64(39) | |
| | | $Z=6$ | | | |
| From [1][a] | −32.418 825 2 | −34.789 074 2 | 2.370 249 0(10) | 520 185.72(23) | 64.4948 |
| Revised QED correction | | | −0.000 035 0(24) | −7.67(54) | −0.0010 |
| IP this work | | | 2.370 214 0(34) | 520 178.05(77) | 64.4939 |
| Kelly [5], Bashkin and Stoner [7] | | | | 520 178.4 | 64.4939 |
| IP(theory)-IP(expt) | | | | −0.35(77) | |
| Moore [12] | | | | 520 177.8 | |
| | | $Z=7$ | | | |
| From [1][a] | −44.805 884 1 | −48.403 496 6 | 3.597 612 5(12) | 789 553.71(25) | 97.8922 |
| Revised QED correction | | | −0.000 073 4(48) | −16.1(11) | −0.0020 |
| IP this work | | | 3.597 539 1(60) | 789 537.6(14) | 97.8902 |
| Kelly [5] | | | | 789 537.2 | 97.8902 |
| IP(theory)-IP(expt) | | | | 0.4(14) | |
| Moore [12], Bashkin and Stoner [7] | | | | 789 532.9 | |
| | | $Z=8$ | | | |
| From [1][a] | −59.199 740 4 | −64.275 839 9 | 5.076 099 6(13) | 1 114 036.84(28) | 138.1230 |
| Revised QED correction | | | −0.000 134 4(92) | −29.5(21) | −0.0037 |
| IP this work | | | 5.075 965 2 | 1 114 007.4(23) | 138.1194 |
| Kelly [5], Bashkin and Stoner [7] | | | | 1 114 008. | 138.1194 |
| IP(theory)-IP(expt) | | | | −0.6(23) | |
| Moore [12] | | | | 1 113 999.5 | |
| | | $Z=9$ | | | |
| From [1][a] | −75.602 653 7 | −82.408 554 7 | 6.805 901 1(14) | 1 493 679.45(30) | 185.1927 |
| Revised QED correction | | | −0.000 224(16) | −49.1(34) | −0.0061 |
| IP this work | | | 6.805 678(17) | 1 493 630.4(37) | 185.1866 |
| Kelly [5], Bashkin and Stoner [7] | | | | 1 493 629 | 185.1865 |
| IP(theory)-IP(expt) | | | | 1.4(37) | |
| Engström [6] | | | | 1 493 632(5) | |
| Moore [12] | | | | 1 493 656 | |

TABLE I. (*Continued*).

| | | | Ionization potential | | |
|---|---|---|---|---|---|
| | $1s1s$ | $1s^22s$ | (a.u.) | ($cm^{-1}$) | (eV) |
| | | $Z=10$ | | | |
| From [1][a] | −94.017 193 9 | −102.804 504 1 | 8.787 310 2(15) | 1 928 538.69(32) | 239.1084 |
| Revised QED correction | | | −0.000 347(24) | −76.1(53) | −0.0094 |
| IP this work | | | 8.786 964(25) | 1 928 462.6(56) | 239.0990 |
| Kelly [5], Bashkin and Stoner [7] | | | | 1 928 462 | 239.0989 |
| IP(theory)-IP(expt) | | | | 0.6(56) | |

[a]Results quoted from Tables IV and V in [1].

TABLE II. Energy convergence of the $1s1s\ ^1S$ core and the $1s^22s\ ^2S$ states of lithiumlike systems (in a.u., for notation see Ref. [1] and Table I therein).

| Angular | No. of | $-\Delta E$ (a.u.) | | | |
|---|---|---|---|---|---|
| component | terms | $Z=13$ | $Z=14$ | $Z=15$ | $Z=16$ |
| (0,0) | 64 | 161.000 747 42 | 187.375 176 08 | 215.750 689 07 | 246.125 665 57 |
| (1,1) | 56 | 0.025 845 01 | 0.025 892 13 | 0.025 932 80 | 0.025 968 26 |
| (2,2) | 49 | 0.003 631 91 | 0.003 650 87 | 0.003 667 31 | 0.003 681 71 |
| (3,3) | 42 | 0.000 979 02 | 0.000 985 36 | 0.000 990 85 | 0.000 995 66 |
| (4,4) | 36 | 0.000 362 76 | 0.000 365 32 | 0.000 367 55 | 0.000 369 51 |
| (5,5) | 36 | 0.000 162 56 | 0.000 163 76 | 0.000 164 80 | 0.000 165 72 |
| (6,6) | 35 | 0.000 082 88 | 0.000 083 52 | 0.000 084 07 | 0.000 084 56 |
| Total | 318 | 161.031 811 6 | 187.406 857 0 | 215.781 896 5 | 246.156 931 0 |
| core+2$s$ | 8 | 177.231 900 25 | 206.583 871 82 | 238.185 875 30 | 272.037 904 55 |
| [(0,0)0,0] | 66 | 0.000 741 03 | 0.000 757 01 | 0.000 771 08 | 0.000 783 48 |
| [(0,1)1,1] | 283 | 0.004 715 38 | 0.004 779 01 | 0.004 834 08 | 0.004 882 18 |
| [(0,2)2,2] | 217 | 0.000 489 12 | 0.000 498 10 | 0.000 505 91 | 0.000 512 77 |
| [(0,3)3,3] | 156 | 0.000 110 56 | 0.000 112 96 | 0.000 115 03 | 0.000 116 84 |
| [(0,4)4,4] | 84 | 0.000 037 43 | 0.000 038 31 | 0.000 039 09 | 0.000 039 77 |
| [(0,5)5,5] | 84 | 0.000 016 99 | 0.000 017 42 | 0.000 017 80 | 0.000 018 14 |
| [(0,6)6,6] | 84 | 0.000 008 89 | 0.000 009 16 | 0.000 009 36 | 0.000 009 55 |
| [(1,2)1,1] | 20 | 0.000 001 66 | 0.000 001 45 | 0.000 001 28 | 0.000 001 14 |
| [(1,2)1,1] | 10 | 0.000 000 30 | 0.000 000 26 | 0.000 000 23 | 0.000 000 20 |
| [(2,3)1,1] | 10 | 0.000 000 21 | 0.000 000 18 | 0.000 000 16 | 0.000 000 14 |
| Total | 1022 | 177.238 021 8 | 206.590 085 7 | 238.192 169 3 | 272.044 268 8 |
| | | $Z=17$ | $Z=18$ | $Z=19$ | $Z=20$ |
| (0,0) | 64 | 278.500 644 92 | 312.875 626 64 | 349.250 610 34 | 387.625 595 72 |
| (1,1) | 56 | 0.025 999 46 | 0.026 027 11 | 0.026 051 79 | 0.026 073 96 |
| (2,2) | 49 | 0.003 694 43 | 0.003 705 73 | 0.003 715 85 | 0.003 724 97 |
| (3,3) | 42 | 0.000 999 91 | 0.001 003 70 | 0.001 007 09 | 0.001 010 29 |
| (4,4) | 36 | 0.000 371 24 | 0.000 372 78 | 0.000 374 16 | 0.000 375 41 |
| (5,5) | 36 | 0.000 166 53 | 0.000 167 26 | 0.000 167 90 | 0.000 168 49 |
| (6,6) | 35 | 0.000 084 98 | 0.000 085 37 | 0.000 085 71 | 0.000 086 02 |
| Total | 318 | 278.531 961 5 | 312.906 988 6 | 349.282 012 9 | 387.657 034 7 |
| core+2$s$ | 8 | 308.139 955 03 | 346.492 022 09 | 387.094 103 76 | 429.946 197 44 |
| [(0,0)0,0] | 66 | 0.000 794 37 | 0.000 804 29 | 0.000 813 10 | 0.000 821 07 |
| [(0,1)1,1] | 283 | 0.004 924 47 | 0.004 962 13 | 0.004 995 70 | 0.005 025 90 |
| [(0,2)2,2] | 217 | 0.000 518 82 | 0.000 524 24 | 0.000 529 08 | 0.000 533 45 |
| [(0,3)3,3] | 156 | 0.000 118 46 | 0.000 119 92 | 0.000 121 21 | 0.000 122 38 |
| [(0,4)4,4] | 84 | 0.000 040 37 | 0.000 040 91 | 0.000 041 39 | 0.000 041 84 |
| [(0,5)5,5] | 84 | 0.000 018 44 | 0.000 018 70 | 0.000 018 94 | 0.000 019 16 |
| [(0,6)6,6] | 84 | 0.000 009 71 | 0.000 009 87 | 0.000 010 01 | 0.000 010 13 |
| [(1,2)1,1] | 20 | 0.000 001 01 | 0.000 000 91 | 0.000 000 83 | 0.000 000 75 |
| [(1,2)1,1] | 10 | 0.000 000 18 | 0.000 000 16 | 0.000 000 14 | 0.000 000 13 |
| [(2,3)1,1] | 10 | 0.000 000 12 | 0.000 000 12 | 0.000 000 10 | 0.000 000 10 |
| Total | 1022 | 308.146 381 10 | 346.498 503 3 | 387.100 634 3 | 429.952 772 3 |

$Z=20$. The extrapolated higher-$l$ contribution to the IP is only about $5.1\pm0.5$ cm$^{-1}$. It is comparably less important. However, this extrapolated result allows us to obtain a more reliable nonrelativistic $1s^2 2s$ energy which is of interest to many theoreticians. For this reason, we made an analysis of the convergence using the same technique as in [1]. The results are shown in Table III.

In [1], we have studied the contributions to the binding energy $\Delta E(l)$ from each $(0,l,l)$ and $(l,l)$ angular component; the rates of convergence for the three-electron $1s^2 2s$ and the two-electron $1s^2$ are about the same. Since we know the precise result for the $1s^2$, this allows us to extrapolate for the $1s^2 2s$ energy using the $\Delta E(l)$ from $l=4$, 5, or 6. In fact, we found that the extrapolated result remains the same whichever $l$ is used. However, for $Z \geq 10$, there is a small but noticeable rate increase in the contribution from $(0,l,l)$ as compared with $(l,l)$ for $l>4$. For example, in Table III, the $\Delta E(6)/\Delta E(5)$ is 0.510 for most $1s^2$ but it ranges from 0.515 to 0.528 for $1s^2 2s$. This means that if we still assume the same rate of convergence, our extrapolated three-electron result based on the information from $1s^2$ will most likely be too small. We also note from Table III that the extrapolated results from different $l$ are no longer identical with slightly larger results coming from the larger $l$. This implies that the true $1s^2 2s$ energy will probably be lower than the extrapolated results suggested in Table III. For this reason, we used the $l=6$ results in Table III as an upper limit together with a 9% uncertainty. Take $Z=11$ as an example; the result from $l=6$ is $-19.08$ $\mu$a.u., this gives a total extrapolated energy of $-20.8(17)$ $\mu$a.u. Again, this is very small in comparison with the IP of this system.

The relativistic contributions to the energies are calculated using the Pauli-Breit approximation [10]. The explicit expressions of the operators are given in [1]. In ad-

TABLE III. Convergence study and extrapolation of higher-$l$ contributions to the ionization potential. For notation see Ref. [1] [$E$(Drake) are from [9]].

| | $l=4$ | $l=5$ | $l=6$ | $l=4$ | $l=5$ | $l=6$ |
|---|---|---|---|---|---|---|
| | | Na IX | | | S XIV | |
| $\Delta E(l)/\Delta E(l-1)$—$1s\,1s$ | 0.370 | 0.448 | 0.509 | 0.371 | 0.448 | 0.510 |
| $\Delta E(l)/\Delta E(l-1)$—$1s\,1s2s$ | 0.338 | 0.452 | 0.515 | 0.340 | 0.456 | 0.526 |
| $\delta E_l(1s\,1s)$ ($\mu$a.u.) | −429.0 | −269.5 | −188.2 | −445.8 | −280.1 | −195.5 |
| $R_l$ | 1.204 | 1.689 | 2.316 | 1.206 | 1.690 | 2.312 |
| Extrapolated energy ($\mu$a.u.) | −18.38 | −18.76 | −19.08 | −20.29 | −21.11 | −22.07 |
| $E$(Drake) | | −114.281 883 8 a.u. | | | −246.157 126 5 a.u. | |
| | | Mg X | | | Cl XV | |
| $\Delta E(l)/\Delta E(l-1)$—$1s\,1s$ | 0.370 | 0.448 | 0.510 | 0.371 | 0.449 | 0.510 |
| $\Delta E(l)/\Delta E(l-1)$—$1s\,1s2s$ | 0.338 | 0.453 | 0.524 | 0.341 | 0.457 | 0.527 |
| $\delta E_l(1s\,1s)$ ($\mu$a.u.) | −433.6 | −272.4 | −190.3 | −448.1 | −281.6 | −196.6 |
| $R_l$ | 1.205 | 1.690 | 2.316 | 1.207 | 1.691 | 2.314 |
| Extrapolated energy ($\mu$a.u.) | −18.74 | −19.22 | −20.03 | −20.59 | −21.47 | −22.46 |
| $E$(Drake) | | −136.656 948 3 a.u. | | | −278.532 158 1 a.u. | |
| | | Al XI | | | Ar XVI | |
| $\Delta E(l)/\Delta E(l-1)$—$1s\,1s$ | 0.371 | 0.448 | 0.510 | 0.372 | 0.449 | 0.510 |
| $\Delta E(l)/\Delta E(l-1)$—$1s\,1s2s$ | 0.339 | 0.454 | 0.523 | 0.341 | 0.457 | 0.528 |
| $\delta E_l(1s\,1s)$ ($\mu$a.u.) | −436.9 | −274.3 | −191.4 | −450.1 | −282.9 | −197.5 |
| $R_l$ | 1.204 | 1.688 | 2.310 | 1.208 | 1.691 | 2.314 |
| Extrapolated energy ($\mu$a.u.) | −19.20 | −19.78 | −20.54 | −20.82 | −21.76 | −22.85 |
| $E$(Drake) | | −161.032 003 0 a.u. | | | −312.907 186 1 a.u. | |
| | | Si XII | | | K XVII | |
| $\Delta E(l)/\Delta E(l-1)$—$1s\,1s$ | 0.371 | 0.448 | 0.510 | 0.372 | 0.449 | 0.510 |
| $\Delta E(l)/\Delta E(l-1)$—$1s\,1s2s$ | 0.339 | 0.455 | 0.526 | 0.341 | 0.458 | 0.528 |
| $\delta E_l(1s\,1s)$ $\mu$a.u. | −440.2 | −276.5 | −193.0 | −451.9 | −284.0 | −198.3 |
| $R_l$ | 1.205 | 1.688 | 2.310 | 1.208 | 1.692 | 2.314 |
| Extrapolated energy ($\mu$a.u.) | −19.58 | −20.26 | −21.16 | −21.04 | −22.04 | −23.15 |
| $E$(Drake) | | −187.407 050 0 a.u. | | | −349.282 211 2 a.u. | |
| | | P XIII | | | Ca XVIII | |
| $\Delta E(l)/\Delta E(l-1)$—$1s\,1s$ | 0.371 | 0.448 | 0.510 | 0.372 | 0.449 | 0.511 |
| $\Delta E(l)/\Delta E(l-1)$—$1s\,1s2s$ | 0.340 | 0.456 | 0.526 | 0.342 | 0.458 | 0.528 |
| $\delta E_l(1s\,1s)$ $\mu$a.u. | −443.2 | −278.4 | −194.3 | −453.6 | −285.1 | −199.1 |
| $R_l$ | 1.206 | 1.689 | 2.312 | 1.208 | 1.692 | 2.315 |
| Extrapolated energy ($\mu$a.u.) | −19.96 | −20.71 | −21.65 | −21.26 | −22.30 | −23.44 |
| $E$(Drake) | | −215.782 090 8 a.u. | | | −387.657 233 8 a.u. | |

TABLE IV. Ionization potential for the $1s^2 2s\ ^2S$ states of lithiumlike systems from Na IX to P XIII (for notation see [1]).

| | | | Ionization potential | | |
|---|---|---|---|---|---|
| | $1s1s$ | $1s^2 2s$ | a.u. | $cm^{-1}$ | eV |
| | | $Z=11$ | | | |
| Nonrelativistic | −114.281 695 6 | −125.283 980 5 | 11.002 284 9 | 2 414 664.72 | 299.380 37 |
| $\langle H_1+H_2\rangle$ | −0.171 622 8 | −0.190 570 3 | 0.018 947 5 | 4 158.39 | 0.515 57 |
| $\langle H_3\rangle$ | 0.007 488 5 | 0.008 059 6 | −0.000 571 1 | −125.34 | −0.015 54 |
| $\langle H_5\rangle$ | −0.000 456 9 | −0.000 490 2 | 0.000 033 3 | 7.30 | 0.000 91 |
| $\langle H_4\rangle$ | 0.000 032 3 | 0.000 036 8 | −0.000 004 4 | −0.97 | −0.000 12 |
| Higher $l$ | | 0.000 020 8 | 0.000 020 8(17) | 4.56(38) | 0.000 57 |
| Subtotal | −114.446 254 5 | −125.466 965 3 | 11.020 710 8 | 2 418 708.66 | 299.881 8 |
| QED correction | | | −0.000 508 6 | −111.6(78) | −0.013 8 |
| IP this work | | | 11.020 202 2 | 2 418 597.04 | 299.867 9 |
| Kelly [5], Bashkin and Stoner [7] | | | | 2 418 700 | 299.88 |
| Moore [12] | | | | 2 418 520 | |
| Martin and Zalubas [13] | | | | 2 418 570 | |
| Other theory: Knight and Sanders [19] | | | 11.020 15 | | |
| Johnson *et al.* [18] | | | 11.020 755 | | |
| | | $Z=12$ | | | |
| Nonrelativistic | −136.656 758 0 | −150.135 983 7 | 13.479 225 7 | 2 958 280.35 | 366.780 14 |
| $\langle H_1+H_2\rangle$ | −0.245 621 3 | −0.273 629 6 | 0.028 008 3 | 6 146.97 | 0.762 13 |
| $\langle H_3\rangle$ | 0.009 862 0 | 0.010 632 6 | −0.000 770 6 | −169.12 | −0.020 97 |
| $\langle H_5\rangle$ | −0.000 550 0 | −0.000 591 1 | 0.000 041 0 | 9.00 | 0.001 12 |
| $\langle H_4\rangle$ | 0.000 034 1 | 0.000 038 8 | −0.000 004 8 | −1.04 | −0.000 13 |
| Higher $l$ | | −0.000 021 8 | 0.000 021 8(18) | 4.79(40) | 0.000 59 |
| Subtotal | −136.893 033 3 | −150.399 554 8 | 13.506 521 5 | 2 964 270.95 | 367.522 9 |
| QED correction | | | −0.000 714 7 | −156.86 | −0.019 4 |
| IP this work | | | 13.505 806 8 | 2 964 114.10 | 367.503 4 |
| Kelly [5], Bashkin and Stoner [7] | | | | 2 964 400 | 367.54 |
| Moore [12] | | | | 2 963 810 | |
| Martin and Zalubas [14] | | | | 2 963 970(250) | |
| Other theory: Knight and Sanders [19] | | | 13.508 84 | | |
| | | $Z=13$ | | | |
| Nonrelativistic | −161.031 811 6 | −177.238 021 8 | 16.206 210 3 | 3 556 779.61 | 440.984 62 |
| $\langle H_1+H_2\rangle$ | −0.341 323 1 | −0.381 296 2 | 0.039 973 1 | 8 772.90 | 1.087 70 |
| $\langle H_3\rangle$ | 0.012 690 5 | 0.013 702 3 | −0.001 011 8 | −222.05 | −0.027 53 |
| $\langle H_5\rangle$ | −0.000 6518 6 | −0.000 701 4 | 0.000 049 6 | 10.88 | 0.001 35 |
| $\langle H_4\rangle$ | 0.000 033 0 | 0.000 037 7 | −0.000 004 7 | −1.03 | −0.000 13 |
| Higher $l$ | | −0.000 022 4 | 0.000 022 4(18) | 4.91(41) | 0.000 61 |
| Subtotal | −161.361 063 0 | −177.606 301 9 | 16.245 238 9 | 3 565 345.23(41) | 442.0466 |
| QED correction | | | −0.000 969 3 | −212.73 | −0.0264 |
| IP this work | | | 16.244 269 6 | 3 565 132.49 | 442.0202 |
| Kelly [5], Bashkin and Stoner [7] | | | | 3 565 600 | 442.08 |
| Moore [12] | | | | 3 564 900 | |
| Martin and Zalubas [15] | | | | 3 565 000 | |
| Other theory: Knight and Sanders [19] | | | 16.244 42 | | |
| Johnson *et al.* [18] | | | 16.245 406 | | |
| | | $Z=14$ | | | |
| Nonrelativistic | −187.406 857 0 | −206.590 085 7 | 19.183 228 6 | 4 210 149.36 | 521.992 17 |
| $\langle H_1+H_2\rangle$ | −0.462 605 9 | −0.518 022 6 | 0.055 416 7 | 12 162.32 | 1.507 94 |
| $\langle H_3\rangle$ | 0.016 014 0 | 0.017 312 5 | −0.001 298 5 | −284.99 | −0.035 33 |
| $\langle H_5\rangle$ | −0.000 762 2 | −0.000 821 2 | 0.000 059 0 | 12.95 | 0.001 61 |
| $\langle H_4\rangle$ | 0.000 034 4 | 0.000 039 4 | −0.000 005 0 | −1.09 | −0.000 13 |
| Higher $l$ | | −0.000 023 1 | 0.000 023 1 | 5.06(42) | 0.000 63 |
| Subtotal | −187.854 176 7 | −207.091 600 6 | 19.237 423 9 | 4 222 043.61 | 523.466 9 |
| QED correction | | | −0.001 276 2 | −280.10 | −0.034 7 |
| IP this work | | | 19.236 144 7 | 4 221 763.51 | 523.432 1 |
| Kelly [5], Bashkin and Stoner [7] | | | | 4 222 400 | 523.52 |
| Moore [12] | | | | 4 221 460 | |
| Other theory: Knight and Sanders [19] | | | 19.236 46 | | |

TABLE IV. (*Continued*).

| | | | Ionization potential | | |
|---|---|---|---|---|---|
| | $1s1s$ | $1s^2 2s$ | a.u. | $cm^{-1}$ | eV |
| | | $Z=15$ | | | |
| Nonrelativistic | −215.781 896 5 | −238.192 169 3 | 22.410 272 9 | 4 918 399.12 | 609.803 98 |
| $\langle H_1+H_2\rangle$ | −0.613 670 6 | −0.688 618 4 | 0.074 947 9 | 16 448.87 | 2.039 40 |
| $\langle H_3\rangle$ | 0.019 872 6 | 0.021 507 5 | −0.001 634 9 | −358.81 | −0.044 49 |
| $\langle H_5\rangle$ | −0.000 881 2 | −0.000 950 4 | 0.000 069 2 | 15.18 | 0.001 88 |
| $\langle H_4\rangle$ | 0.000 033 5 | 0.000 038 4 | −0.000 004 9 | −1.07 | −0.000 13 |
| Higher $l$ | | −0.000 023 6 | 0.000 023 6 | 5.18(42) | 0.000 64 |
| Subtotal | −216.376 542 2 | −238.860 215 9 | 22.483 673 8 | 4 934 508.47 | 611.801 3 |
| QED correction | | | −0.001 638 7 | −359.65 | −0.044 6 |
| IP this work | | | 22.482 035 0 | 4 934 148.82 | 611.756 7 |
| Kelly [5], Bashkin and Stoner [7] | | | | 4 935 000 | 611.9 |
| Moore [12] | | | | 4 933 060 | |
| Other theory: Knight and Sanders [19] | | | 22.482 56 | | |
| Johnson *et al.* [18] | | | 22.484 105 | | |

TABLE V. Ionization potential for the $1s^2 2s\ ^2S$ states of lithiumlike systems from S XIV to Ca XVIII (for notation see [1]).

| | | | Ionization potential | | |
|---|---|---|---|---|---|
| | $1s1s$ | $1s^2 2s$ | a.u. | $cm^{-1}$ | eV |
| | | $Z=16$ | | | |
| Nonrelativistic | −246.156 931 0 | −272.044 268 8 | 25.887 337 8 | 5 681 516.26 | 704.418 48 |
| $\langle H_1+H_2\rangle$ | −0.799 036 5 | −0.898 267 0 | 0.099 230 6 | 21 778.22 | 2.700 16 |
| $\langle H_3\rangle$ | 0.024 306 2 | 0.026 331 0 | −0.002 024 8 | −444.38 | −0.055 10 |
| $\langle H_5\rangle$ | −0.001 008 9 | −0.001 089 1 | 0.000 080 2 | 17.60 | 0.002 18 |
| $\langle H_4\rangle$ | 0.000 034 7 | 0.000 039 8 | −0.000 005 1 | −1.12 | −0.000 14 |
| Higher $l$ | | −0.000 024 1 | 0.000 024 1 | 5.28(44) | 0.000 65 |
| Subtotal | −246.932 635 4 | −272.917 278 1 | 25.984 642 7 | 5 702 871.86 | 707.066 2 |
| QED correction | | | −0.002 059 1 | −451.92 | −0.056 0 |
| IP this work | | | 25.982 583 6 | 5 702 419.94 | 707.010 2 |
| Kelly [5], Bashkin and Stoner [7] | | | | 5 703 600 | 707.16 |
| | | $Z=17$ | | | |
| Nonrelativistic | −278.531 961 5 | −308.146 381 0 | 29.614 419 5 | 6 499 511.65 | 805.837 01 |
| $\langle H_1+H_2\rangle$ | −1.023 542 6 | −1.152 521 0 | 0.128 978 4 | 28 307.04 | 3.509 63 |
| $\langle H_3\rangle$ | 0.029 354 6 | 0.031 826 7 | −0.002 472 1 | −542.55 | −0.067 27 |
| $\langle H_5\rangle$ | −0.001 145 2 | −0.001 237 2 | 0.000 092 0 | 20.20 | 0.002 50 |
| $\langle H_4\rangle$ | 0.000 033 8 | 0.000 038 9 | −0.000 005 0 | −1.10 | −0.000 14 |
| Higher $l$ | | −0.000 024 5 | 0.000 024 5 | 5.37(44) | 0.000 67 |
| Subtotal | −279.527 260 8 | −309.268 298 1 | 29.741 037 3 | 6 527 300.61 | 809.282 4 |
| QED correction | | | −0.002 539 1 | −557.26 | −0.069 1 |
| IP this work | | | 29.738 498 2 | 6 526 743.35 | 809.213 3 |
| Kelly [5], Bashkin and Stoner [7] | | | | 6 528 300 | 809.41 |
| Johnson *et al.* [18] | | | 29.742 006 | | |
| | | $Z=18$ | | | |
| Nonrelativistic | −312.906 988 6 | −346.498 503 3 | 33.591 514 7 | 7 372 383.90 | 914.059 41 |
| $\langle H_1+H_2\rangle$ | −1.292 347 1 | −1.457 302 2 | 0.164 955 1 | 36 202.96 | 4.488 60 |
| $\langle H_3\rangle$ | 0.035 058 1 | 0.038 038 8 | −0.002 980 7 | −654.19 | −0.081 11 |
| $\langle H_5\rangle$ | −0.001 290 1 | −0.001 394 8 | 0.000 104 7 | 22.97 | 0.002 85 |
| $\langle H_4\rangle$ | 0.000 031 5 | 0.000 036 2 | −0.000 004 7 | −1.03 | −0.000 13 |
| Higher $l$ | | −0.000 024 9 | 0.000 024 9 | 5.47(45) | 0.000 68 |
| Subtotal | −314.165 536 3 | −347.919 150 3 | 33.753 614 0 | 7 407 960.07 | 918.470 3 |
| QED correction | | | −0.003 079 3 | −675.82 | −0.0838 |
| IP this work | | | 33.737 534 7 | 7 407 284.26 | 918.3865 |
| Kelly [5], Bashkin and Stoner [7] | | | | 7 404 400 | 918.04 |

TABLE V. (*Continued*).

| | $1s1s$ | $1s^22s$ | Ionization potential a.u. | $cm^{-1}$ | eV |
|---|---|---|---|---|---|
| | | $Z=19$ | | | |
| Nonrelativistic | −349.282 012 9 | −387.100 634 3 | 37.818 621 4 | 8 300 110.90 | 1029.082 94 |
| $\langle H_1+H_2\rangle$ | −1.610 928 0 | −1.818 902 2 | 0.207 974 2 | 45 644.42 | 5.659 19 |
| $\langle H_3\rangle$ | 0.041 456 2 | 0.045 011 0 | −0.003 554 8 | −780.18 | −0.096 73 |
| $\langle H_5\rangle$ | −0.001 443 7 | −0.001 561 8 | 0.000 118 1 | 25.92 | 0.003 21 |
| $\langle H_4\rangle$ | 0.000 034 1 | 0.000 039 3 | −0.000 005 1 | −1.13 | −0.000 14 |
| Higher $l$ | | −0.000 025 2 | 0.000 025 2 | 5.54(46) | 0.000 69 |
| Subtotal | −350.852 894 3 | −388.876 073 3 | 38.023 179 0 | 8 345 005.47 | 1034.649 2 |
| QED correction | | | −0.003 679 4 | −807.51 | −0.100 1 |
| IP this work | | | 38.019 477 7 | 8 344 197.96 | 1034.549 0 |
| Kelly [5] | | | | 8 344 000 | 1033.4[a] |
| Bashkin and Stoner [7] | | | | 8 340 000 | 1034 |
| | | $Z=20$ | | | |
| Nonrelativistic | −387.657 034 7 | −429.952 772 3 | 42.295 737 6 | 9 282 713.73 | 1150.910 21 |
| $\langle H_1+H_2\rangle$ | −1.985 082 6 | −2.243 981 6 | 0.258 899 0 | 56 820.98 | 7.044 91 |
| $\langle H_3\rangle$ | 0.048 589 0 | 0.052 787 1 | −0.004 198 1 | −921.37 | −0.114 24 |
| $\langle H_5\rangle$ | −0.001 606 0 | −0.001 738 3 | 0.000 132 4 | 29.05 | 0.003 60 |
| $\langle H_4\rangle$ | 0.000 035 1 | 0.000 040 4 | −0.000 005 3 | −1.17 | −0.000 14 |
| Higher $l$ | | −0.000 025 5 | 0.000 025 5 | 5.61(46) | 0.000 70 |
| Subtotal | −389.595 099 1 | −432.145 690 2 | 42.550 591 1 | 9 338 646.83 | 1157.845 0 |
| QED correction | | | −0.004 338 0 | −952.07 | −0.118 0 |
| IP this work | | | 42.546 253 1 | 9 337 694.76 | 1157.727 0 |
| Kelly [5], Bashkin and Stoner [7] | | | | 9 332 000 | 1157.0 |
| Johnson *et al.* [18] | | | 42.553 336 | | |

[a]Should be 1034.52 eV if we use 1 $cm^{-1}$=0.000 123 984 24 eV.

dition to the relativistic corrections, the mass polarization effect is also calculated. The isotopes used in this calculation are $^{23}Na$, $^{24}Mg$, $^{27}Al$, $^{28}Si$, $^{31}P$, $^{32}S$, $^{35}Cl$, $^{39}K$, $^{40}Ar$, and $^{40}Ca$. The atomic masses of these isotopes are taken from Wapstra and Audi [11].

## III. RESULTS AND DISCUSSION

In the full-core plus correlation method, the IP is calculated from the difference of the relativistic $1s^22s$ energy with that of the core. Adding the extrapolated energy from the higher-$l$ angular components and the estimated QED contribution, the final IP is obtained. In Tables IV and V we give the IP's calculated in this work from Na IX to Ca XVIII. These results are compared with those from the atomic data tables such as those of Kelly [5], Bashkin and Stoner [7], and Moore [12].

The IP's quoted in Bashkin and Stoner [7] are identical to those of Kelly [5] except for $Z=7$ and 19. They differ substantially from those of Moore [12]. In [1], our calculated IP favors Kelly [5] over those of Moore [12]. This is particularly apparent in Table I. This is no longer true for systems with $Z>10$. Unlike the agreement obtained in Table I where the predicted IP agrees with that of Kelly [5] to about 1 $cm^{-1}$, we found the calculated results differ greatly with the existing data (see Tables IV and V). In Kelly [5], the IP's of the $1s^22s$ systems are quoted to 100 $cm^{-1}$ from $Z=11$ to 18 and to 1000 $cm^{-1}$ for $Z=19$ and 20. But the discrepancy between our result and that of Kelly [5] is larger than 100 $cm^{-1}$ for each of the ten systems considered in this work. Unlike Kelly [5], the IP's of $1s^22s$ are only quoted for $Z=11$ to 15 in Moore [12]. For each of these systems, our prediction is larger than that of Moore [12] but smaller than that of Kelly [5]. For $Z=11$, 13, and 14, our predictions lie much closer to Moore [12] than Kelly [5]. It appears that our results agree better with the more recent data of Martin and Zalubas [13–15] (see Table IV).

For K XVII, the IP datum is revised from 8 340 000 $cm^{-1}$ in Bashkin and Stoner [7] to 8 344 000 $cm^{-1}$ in Kelly [5]. It brings this IP much closer to our prediction of 8 344 197 $cm^{-1}$ (1034.549 eV). However, the eV number quoted in Kelly [5] is 1033.4 eV. Using 1 $cm^{-1}$=0.000 123 942 4 eV [16] the number should be 1034.52 eV.

From $Z=11$ to 17, the discrepancy between our prediction and that of Kelly grows smoothly from −103 to −1557 $cm^{-1}$. This discrepancy changes to 2884, 198, and 5694 $cm^{-1}$ for $Z=18$, 19, and 20. From a theoretical point of view, we expect our prediction to be consistently above or below the true IP. The discrepancy should grow uniformly with $Z$. The unusual comparison shown in Tables IV and V could be an indication that some of the existing data are not reliable.

Theoretically, the $1s^22s$ IP's for $Z=3$ and 4 are calculated by Blundell *et al.* [17] and for $Z=3$–92 by Johnson *et al.* [18]. The QED effect is not included in these references. If we convert their data with the infinite mass

TABLE VI. Nonrelativistic energy ($-E$) and Rydberg constants of lithiumlike $1s^2 2s$ states from $Z=11$ to 20.

| | Energy ($-E$) | | | | |
|---|---|---|---|---|---|
| $Z$ | Upper bound (a.u.) | Core correction ($\mu$a.u.) | Higher $l$ ($\mu$a.u.) | Total (a.u.) | Rydberg constant ($cm^{-1}$) |
| 11 | 125.283 980 5 | 188.2(5) | 20.8(17) | 125.284 189 4(22) | 109 734.694 |
| 12 | 150.135 983 7 | 190.3(5) | 21.8(18) | 150.399 533 0(23) | 109 734.803 |
| 13 | 177.238 021 8 | 191.4(5) | 22.4(18) | 177.238 235 7(23) | 109 735.081 |
| 14 | 206.590 085 7 | 193.0(5) | 23.1(19) | 206.590 301 7(24) | 109 735.161 |
| 15 | 238.192 169 3 | 194.3(5) | 23.6(19) | 238.192 387 3(24) | 109 735.369 |
| 16 | 272.044 268 8 | 195.5(5) | 24.1(20) | 272.044 488 3(25) | 109 735.430 |
| 17 | 308.146 381 0 | 196.6(5) | 24.5(20) | 308.146 602 1(25) | 109 735.591 |
| 18 | 346.498 503 3 | 197.5(5) | 24.9(21) | 346.498 725 8(26) | 109 735.806 |
| 19 | 387.100 634 3 | 198.3(5) | 25.2(21) | 387.100 857 8(26) | 109 735.768 |
| 20 | 429.952 772 3 | 199.1(5) | 25.5(21) | 429.952 997 0(26) | 109 735.806 |

Rydberg constant and compare them with the results of this work without the QED, the agreement between the present work with Ref. [17] is almost exact. The discrepancies between our results and Ref. [18] become more substantial after $Z=13$. However, they are much smaller than the discrepancies between theory and experiment. The IP's for the $Z=11$ to 18 $1s^2 2s$ systems have been calculated by Knight and Sanders [19] using a $Z$-dependent perturbation theory. The relativistic corrections are estimated in this reference. For some systems their result agrees rather well with our prediction, no QED contribution is considered in their calculation whereas QED contributed $-111.6$ to $-675.8$ $cm^{-1}$ to our IP data.

In Table VI, the nonrelativistic $1s^2 2s$ energies are given. We are not aware of the results from other accurate methods for these $Z$. The Rydberg constants used in this work are also given in this table.

## IV. CONCLUSION

The purpose of this work is to use a full-core plus correlation method to calculate the IP for lithiumlike $1s^2 2s$ from $Z=11$ to 20. The precision IP predictions for $Z=3$ to 10 using this method indicate a high degree of cancellation of errors in our approximation. This cancellation of errors may become incomplete as $Z$ increases, but we expect this to be gradual rather than sudden. For $Z=11$ to 20, the $1s^2 2s$ IP data in Kelly [5] and Bashkin and Stoner [7] are quoted to 100 $cm^{-1}$. A comparison of their data with our prediction gives a discrepancy which is much larger than 100 $cm^{-1}$. We noted that for $Z=19$, the revised IP from Bashkin and Stoner [7] to Kelly [5] reduces the discrepancy with our prediction drastically.

The lithiumlike $1s^2 2s$ IP is critically important in establishing the term diagram for the three-electron systems. It is also essential if one wishes to compare the calculated energy of a three-electron or four-electron system with experiment. One important question from a theoretical point of view is what $Z$ value the cancellation of errors may continue to in our approximation method. The current data in the literature are not sufficiently accurate to answer this question. We hope that more precision experimental measurements can be carried out in the near future so that a definitive answer can be obtained.

## ACKNOWLEDGMENTS

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