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Ionization potential for ground states of berylliumlike systems

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The $1s^22s^2$ ground-state energies of berylliumlike systems are calculated with a full-core plus correlation method. A partial saturation of a basis-function method is used to extrapolate a better nonrelativistic energy. The $1s^22s^2$ ionization potentials are calculated by including the relativistic corrections, mass polarization, and QED effects. These results are compared with the existing theoretical and experimental data in the literature. The predicted Be I, C III, N IV, and O V ionization potentials are within the quoted experimental error. Our result for F VI, 1 267 606.7 cm^{-1}, supports the recent experiment of Engström [Phys. Scr. **31**, 379 (1985)], 1 267 606(2) cm^{-1}, over the datum in the existing data tables. The predicted specific mass polarization contribution to the ionization potential for Be I, 0.006 88 a.u., agrees with the 0.006 74(100) a.u. from the experiment of Wen *et al.* [Phys. Rev. A **37**, 4207 (1988)]. The calculated relativistic correction to the double ionization of Be I, −0.000 135 0 a.u., also agrees with the recent result, −0.000 135 a.u., of Lindroth *et al.* [Phys. Rev. A **45**, 1493 (1992)]. Using the calculated results of $Z=4-10$, 15, and 20, we extrapolated the results for other Z systems up to $Z=25$ for which the ionization potentials are not explicitly computed.

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I. INTRODUCTION

Extensive efforts have been expended in the study of the Be I $1s^22s^2$ system by theorists [1–9] in the past. These efforts were accelerated in the last few years [10–17], partly due to the improvement of computation resources. The most accurate nonrelativistic energy of the Be I $1s^22s^2$ state was calculated by Bunge [5] to be −14.667 358(28) a.u. Recently, using the multiconfiguration Hartree-Fock method with full configuration interaction (CI), Olsen and Sundholm [11] obtained an energy of −14.667 37(3) a.u.

The relativistic contribution to the Be I energy has been studied by Liu and Kelly [15], and Lindroth *et al.* [16]. Lindroth *et al.* has done a careful study of the relativistic corrections to the double ionization of Be I. By subtracting the relativistic, the mass polarization, and the QED contributions from the experimental data, they obtain an "experimental" nonrelativistic energy of −14.667 353(2) a.u. Compared with the result of Olson and Sundholm [11], they concluded that "an accurate calculation of a nonrelativistic energy for Be thus remains a challenge to be pursued." A similar sentiment is also expressed in the recent work of Mårtensson-Pendrill *et al.* [14].

Most of the recent work on Be I uses the multiconfiguration Hartree-Fock method (MCHF), multiconfiguration Dirac-Fock method (MCDF), or many-body perturbation theory (MBPT). These methods clearly have the potential in extending the application to very complicated systems. For smaller systems such as Be I, the CI method is still quite effective. This is illustrated in the work of Bunge [5]. Hence, if we can use a CI method to obtain an accurate energy for Be I, this result will show precisely where the correlation energy comes from. This information could be useful to the workers in MBPT in deciding which type of Feynman diagrams should be included in the perturbation expansion.

The improvement in experimental techniques has also led to more interests on the mass polarization effect of atomic systems. Recently, Wen *et al.* [18] used high-resolution multiphoton-resonance-ionization mass spectroscopy to measure the isotope shift of the Be I states. They have also calculated the shift for the ground state with a MCHF method; the result strongly disagrees with their experiment. They noted the lack of reliable theoretical data in this important area and remarked "accurate *ab initio* calculation of this quantity poses a challenge to theory which to our knowledge, has not yet been met."

Recently, Chung and collaborators use a full-core plus correlation method (FCPC) to calculate the ionization energies for the ground and excited states of three-electron systems [19–21]. Accurate results are obtained. This method uses CI wave functions in the *LS* coupling scheme. The correlation effects are accounted for by the inclusion of various angular components. For three-electron systems the basis functions in the angular components can be saturated. This is much harder to accomplish for a four-electron system. In the first application of FCPC to the four-electron system, Chung and Fullbright [22] estimated the contributions from the saturation of basis functions for Li^-. This is acceptable for Li^- because the estimated contributions are very small for this negative ion. For neutral species and positive ions, these contributions are much larger. A more reliable method is therefore needed to calculate these contributions. In this work, we will use a method of partial saturation of angular components to improve the nonrelativistic energy. This method is similar to the extrapolation method used by Bunge [5].

The ionization potential (IP) results in Chung [20] agree with the available experimental data to about 1 ppm for $Z=3$ to 10 [23–25] except B III. This precise agreement raises some interesting questions. Since the relativistic effects are calculated with first-order perturbation theory and this correction is already very large for $Z\geq 8$, one would ask why the higher-order relativistic effect does not contribute to the IP [26]. Furthermore, the QED effects in Chung [20] are calculated using a hydrogenlike formula with an effective nuclear charge. These results are smaller than those of McKenzie and Drake [27] where a more elaborated approach is used. One possibility for the precise agreement in Chung [20] is that it could be the result of an accidental cancellation of errors. In this regard, it would be most interesting to see whether the same precision agreement between theory and experiment can be repeated for four-electron systems.

In this work we will use the full-core plus correlation method to calculate the IP of $1s^2 2s^2$ systems. These results will be compared with the data in the literature. In Sec. II, a brief account of the theory will be given. The method of partial saturation of angular component will be given in Sec. III and the method of energy extrapolation will be given in Sec. IV. The IP and mass polarization results will be presented in Sec. V together with the comparison with experiments. Section VI is a summary and conclusion.

II. THEORY

The zeroth-order nonrelativistic Hamiltonian is given by (in a.u.)

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

The perturbation operators are

$$H'=H_1+H_2+H_3+H_4+H_5 \ , \tag{2}$$

where

$$H_1=-\frac{1}{8c^2}\sum_{i=1}^{N}\mathbf{p}_i^4 \tag{3}$$

is the correction to kinetic energy,

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

is the Darwin term,

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

is the electron-electron contact term,

$$H_4=-\frac{1}{M}\sum_{\substack{i,j=1\\ i<j}}^{N}\nabla_i\cdot\nabla_j \tag{6}$$

is the mass polarization,

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

is the orbit-orbit interaction, and M is the nuclear mass.

To implement the FCPC method for a four-electron system, it is best to take the $1s^2$ two-electron system as the "core." Hence, the IP calculated in this work would be the double-electron IP of the four-electron system. The single-electron IP of the four-electron system is obtained by subtracting the $1s^2 2s$ IP. The wave function for the four-electron system can be written as

$$\Psi(1,2,3,4)=A\left[\Phi_{1s1s}(1,2)\Phi_{2s2s}(3,4)+\sum_i C_i\Phi_{n(i),l(i)}(1,2,3,4)\right] . \tag{8}$$

A is the antisymmetrization operator. The $\Phi_{1s1s}(1,2)$ is a predetermined $1s^2$ core wave function. It is given by

$$\Phi_{1s1s}(1,2)=A\sum_{k,n,l}c_{knl}r_1^k r_2^n \exp(-\beta_l r_1-\rho_l r_2)\times Y_l(\Omega_1,\Omega_2)\chi(1,2) \ . \tag{9}$$

The angular part is given by

$$Y_l(\Omega_1,\Omega_2)=\sum_m \langle l,l,m,-m|0,0\rangle\times Y_{l,m}(\Omega_1)Y_{l,-m}(\Omega_2) \ . \tag{10}$$

χ is a two-electron singlet spin function. The constants c_{knl}, β_l, and ρ_l are determined by optimizing the energy of the two-electron core. $\Phi_{2s2s}(3,4)$ represents the wave function of the two $2s$ electrons which is given by

$$\Phi_{2s2s}(3,4)=A\sum_{k,n,l}d_{knl}r_3^k r_4^n \exp(-\lambda_l r_3-\eta_l r_4)\times Y_l(\Omega_3,\Omega_4)\chi(3,4) \ . \tag{11}$$

Since the $2s$ electrons also form a ^1S complex, their angular function $Y_l(\Omega_3,\Omega_4)$ is similar to Eq. (10). In principle, the l summation in Eq. (11) should include all l. However, the computation resources needed for such a wave function would be prohibitive. In this work, we only sum l from 0 to 1, the contribution from all other l's is included in $\Phi_{n(i),l(i)}(1,2,3,4)$. This latter wave function also includes the intershell correlation as well as the relaxation of the core. It is given by

$$\Phi_{n(i),l(i)}(1,2,3,4)=\phi_{n(i),l(i)}(R)Y_{l(i)}^{LM}(\Omega)\chi_{SSz} \tag{12}$$

where

$$\phi_{n(i),l(i)}(R)=\prod_{j=1}^{4}r_j^{n_j}\exp(-\alpha_j r_j) \ . \tag{13}$$

A different set of α_j is used for each $l(i)$. The angular part is

$$Y_{l(i)}^{LM}(\Omega)=\sum_{m_j}\langle l_1 l_2 m_1 m_2|l_{12}m_{12}\rangle\times\langle l_{12}l_3 m_{12}m_3|l_{123}m_{123}\rangle\times\langle l_{123}l_4 m_{123}m_4|LM\rangle\prod_{j=1}^{4}Y_{l_j m_j}(\Omega_j) \ . \tag{14}$$

To simplify notation, this angular function is denoted as

$$l(i)=[(l_1,l_2)l_{12},l_3]l_{123},l_4 \ . \tag{15}$$

In this expression it is implicitly implied that l_{123} and l_4 couple into a wave function of total orbital angular momentum L and azimuthal component M. In this work $L=0$ and $M=0$. The four-electron spin wave function can also be represented in this notation as

$$\chi_{SS_z}=[(s_1,s_2)s_{12},s_3]s_{123},s_4 \ . \tag{16}$$

There are two possible spin functions for the ^1S system. Namely

$$\chi_1=[(s_1,s_2)0,s_3]\tfrac{1}{2},s_4 \ , \tag{17}$$

$$\chi_2=[(s_1,s_2)1,s_3]\tfrac{1}{2},s_4 \ . \tag{18}$$

The linear parameters C_i, d_{knl} and the nonlinear parameters α_j, λ_l, and η_l in Eqs. (8), (11), and (13) are determined in the energy optimization processes.

The nonrelativistic energies of the $1s^2$ core and the $1s^22s^2$ state are calculated using the Rayleigh-Ritz variation method,

$$\delta E_{\text{nonrel}}=\delta\langle H_0\rangle=\delta\frac{\langle\Psi|H_0|\Psi\rangle}{\langle\Psi|\Psi\rangle} \ . \tag{19}$$

The relativistic and mass polarization corrections are given by

$$\begin{aligned}\Delta E&=\langle\Psi|H_1+H_2|\Psi\rangle+\langle\Psi|H_3+H_4+H_5|\Psi\rangle\\&=\Delta E_1+\Delta E_2 \ ,\end{aligned} \tag{20}$$

where ΔE_1 is the first-order energy from the one-particle perturbation operators and ΔE_2 is from the two-particle operators. The total energy, which is accurate to first order, becomes

$$E_{\text{tot}}=E_{\text{nonrel}}+\Delta E \ . \tag{21}$$

To obtain an accurate ionization potential for the $1s^22s^2$ system, the quantum electrodynamic effect (QED) cannot be neglected. It would be very difficult to carry out a complete QED calculation for the four-electron system. In Chung [19], the contribution of the QED to the IP of the $1s^22s$ system is estimated using the hydrogenic formula from Bethe and Salpeter [28]. A more precise formula has been given in Erickson and Yennie [29] and in Drake [30]. For an s-electron with principal quantum number n, we have

$$\begin{aligned}\Delta E_{\text{QED}}(n,0)=4Z_{\text{eff}}^4\alpha^3\{&\tfrac{19}{30}-2\ln(\alpha Z_{\text{eff}})-\ln[K(n,0)]+7.214\alpha Z_{\text{eff}}\\&-(Z_{\text{eff}}\alpha)^2[3\ln^2(Z_{\text{eff}}\alpha)+8.695\ln(Z_{\text{eff}}\alpha)+19.081]\}/(3\pi n^3) \ .\end{aligned} \tag{22}$$

This equation is also used in Edlén [31] for the IP of lithiumlike ground states with $Z_{\text{eff}}=Z-1.6$. In this work, we will treat the $2s2s$ electrons as two hydrogenic electrons. The effective nuclear charges Z_{eff} for the two electrons are estimated by two methods: In the first method, we assume the Z_{eff} of the two electrons are the same. The energy eigenvalue of the one-electron Dirac equation (excluding the rest mass energy) for a Coulomb potential is [28]

$$E_{\text{Dirac}}(Z)=\frac{1}{\alpha^2}\left[1+\left[\frac{\alpha Z}{n-k+\sqrt{k^2-\alpha^2Z^2}}\right]^2\right]^{-1/2}-\frac{1}{\alpha^2} \ , \tag{23}$$

where k is related to the total angular momentum j of the hydrogenic electron by $k=j+\frac{1}{2}$. To order of α^2Z^4, E_{Dirac} reduces to

$$E^{(1)}(Z)=-\frac{Z^2}{2n^2}\left[1+\frac{\alpha^2Z^2}{n}\left[\frac{1}{k}-\frac{3}{4n}\right]\right] \ . \tag{24}$$

Since we have calculated the energy of the $2s$ valence electron to order of α^2Z^4 with Eqs. (19) and (20), we can define a Z_{eff} by

$$\begin{aligned}&E_{\text{nonrel}}(1s^22s^2)+\Delta E_1(1s^22s^2)-E_{\text{nonrel}}(1s^2)\\&\quad-\Delta E_1(1s^2)=-\frac{Z_{\text{eff}}^2}{n^2}\left[1+\frac{\alpha^2Z_{\text{eff}}^2}{n}\left[\frac{1}{k}-\frac{3}{4n}\right]\right] \ .\end{aligned} \tag{25}$$

Using this Z_{eff}, an approximate $\Delta E_{\text{QED}}(2,0)$ for the $2s$ electron can be estimated from Eq. (22). In addition, we can also use this Z_{eff} to estimate the higher-order relativistic contribution from

$$\Delta E_{\text{higher order}}=2E_{\text{Dirac}}(Z_{\text{eff}})-2E^{(1)}(Z_{\text{eff}}) \ . \tag{26}$$

The double-electron ionization potential becomes

$$\begin{aligned}E_{\text{dbIP}}=\ &E_{\text{tot}}(1s^2\,{}^1S)-E_{\text{tot}}(1s^22s^2\,{}^1S)\\&-\Delta E_{\text{higher order}}-2\Delta E_{\text{QED}}(2,0) \ .\end{aligned} \tag{27}$$

The $E_{\text{IP}}(1s^22s^2)$ is obtained by subtracting the $E_{\text{IP}}(1s^22s)$ from this result, i.e.,

$$E_{\text{IP}}(1s^22s^2)=E_{\text{dbIP}}-E_{\text{IP}}(1s^22s) \ . \tag{28}$$

The second method is to assume that there are two different Z_{eff}'s. They are obtained by solving the equations

$$\begin{aligned}&E_{\text{nonrel}}(1s^22s)+\Delta E_1(1s^22s)-E_{\text{nonrel}}(1s^2)-\Delta E_1(1s^2)\\&\quad=-\frac{Z_{\text{eff}1}^2}{2n^2}\left[1+\frac{\alpha^2Z_{\text{eff}1}^2}{n}\left[\frac{1}{k}-\frac{3}{4n}\right]\right] \ ,\end{aligned} \tag{29}$$

$$\begin{aligned}&E_{\text{nonrel}}(1s^22s^2)+\Delta E_1(1s^22s^2)-E_{\text{nonrel}}(1s^22s)\\&\quad-\Delta E_1(1s^22s)=-\frac{Z_{\text{eff}2}^2}{2n^2}\left[1+\frac{\alpha^2Z_{\text{eff}2}^2}{n}\left[\frac{1}{k}-\frac{3}{4n}\right]\right] \ .\end{aligned} \tag{30}$$

These Z_{eff}'s are substituted into Eq. (22) to find the total

QED contributions. This result is then compared with that from Eq. (25).

For small-Z systems, the nuclear size effect is negligible. It becomes appreciable for $Z>15$. If we assume a uniform spherical nuclear charge distribution with a cutoff radius R_{nu}, the perturbation potential is, for $r\leq R_{\mathrm{nu}}$,

$$H_{\mathrm{nu}}=\frac{Z}{r}-1.5\frac{Z}{R_{\mathrm{nu}}}+0.5\frac{Zr^2}{R_{\mathrm{nu}}^3} \tag{31}$$

since this is a very small effect. We estimated the contribution of H_{nu} to IP using the hydrogenic function with the Z_{eff} calculated earlier. The radii of the nuclei are taken from Johnson and Soff [32].

III. PARTIAL SATURATION OF ANGULAR COMPONENT BASIS FUNCTIONS

A four-electron calculation is much more time consuming than a three-electron calculation. In Chung [19], a 318-term wave function is used for the $1s1s$ core. If we use the same core wave function for this four-electron calculation, the computation resources needed will be very large. Recently, Chung and Fullbright [22] used a 159-term core wave function to calculate the electron affinity of lithium; an accurate result is obtained. We will also use a 159-term wave function for the $1s1s$ core in this work. The Φ_{2s2s} in Eq. (8) should be a correlated two-electron wave function similar to the Φ_{1s1s}. To save computer CPU time, we include only the (0,0) and (1,1) angular components in Φ_{2s2s}. All other correlations are included in the wave function $\Phi_{n(i),l(i)}(1,2,3,4)$. The intershell correlation effect is also included in this four-electron wave function.

Compared to the three-electron ground-state calculation [19], one obvious complication is that it is much harder to saturate a four-electron wave function. There are also far more angular coupling terms which may contribute to the binding energy of the four-electron system. It is impossible to saturate all these angular components simultaneously as in the case of Refs. [19] and [20]. Hence, we have adopted a method of partial saturation of angular components. The method is similar in spirit to the one used by Bunge [5].

We first choose a sufficiently accurate but not yet fully saturated wave function. The wave function has 25 and 20 terms in the (0,0) and (1,1) components of Φ_{2s2s}. In addition, we choose a 34-angular-component 868-term $\Phi_{n(i),l(i)}$. This forms a "basic" function of 913 terms. Due to the 159-term core, this implies that 8023×4012 matrix elements are calculated before they are reduced to a 913×913 secular equation.

In Table I we give the result for Be I from this basic function. The angular components and their number of radial basis functions are also listed. The energy upper bound from this wave function is −14.667 042 a.u. Although this result can be lowered very substantially if the core wave function is improved, it is the lowest upper bound for Be I in the literature, except perhaps for that of Olsen and Sundholm [11] who uses an extremely large wave function. It is obvious from Table I that the basis function in the angular components is far from saturated.

Next, we group the 34 angular components in Table I into 12 mutually orthogonal groups of different (l_1,l_2,l_3,l_4). In subsequent calculations, we increase the basis functions in the (l_1,l_2,l_3,l_4) components, one group at a time. The new upper bound is then compared with that of the 913-term basis function. The energy improvement is recorded. These results are shown in Table II. The total improvement is 40.3μa.u. We should mention that except in the [0000], [0011], or [0112] computations, when the basis functions of one group are saturated, the energy contributions from the other groups change very little from those of Table I. Even in these exceptional cases the changes are small mainly because a significant number of terms is already used in the basic function.

IV. EXTRAPOLATION TO HIGHER l

The wave function in Table I has only included the angular components with $l\leq 6$. The components with $l\geq 7$ will also contribute significantly to the energy. This contribution needs to be extrapolated. If we examine the energy contributions from the ($00ll$) components and compare them with the (l,l) contributions from the 318-term core wave function [19,20], it is interesting to note that the ratio of

$$R=\Delta E(l,l)/\Delta E(0,0,l,l) \tag{32}$$

is a constant for $l=4$, 5, and 6. This can be seen from the data in Table III. The constant ratio in this equation indicates that the $\Delta E(l,l)$ and $\Delta E(0,0,l,l)$ have the same pattern of angular convergence. The contribution from the higher l's to the core energy can be deduced from Pekeris [33] and Drake [34]. If we assume that the same ratio will continue for the higher-l components in the four-electron system, then the $l\geq 7$ contributions to the binding energy can be extrapolated. These extrapolated results are given in Table III.

In this work explicit calculations are carried out for $Z=4-10$, 15, and 20. Using the results from Tables II and III, we can compute the nonrelativistic energies for these systems. This result is given in Table IV. In the second column of this table, the upper bounds from the basic functions are given. With the corrections from the higher-l components, from the partial saturation of angular component basis functions, and from the core correction, a final nonrelativistic energy is obtained. This is given in the last column of Table IV.

V. RESULTS AND DISCUSSION

Using the wave function from the 159-term core and the 913-term basic function, we compute the relativistic perturbation contributions to the total energy and the double-electron IP. These results also allow us to compute the Z_{eff} for the QED and higher-order relativistic corrections. As mentioned in Sec. II, there are two ways to consider the screening of nuclear charge and the Z_{eff}'s. One way is to assume that the Z_{eff}'s for the two electrons are identical whereas the other assumes a successive screening. We find that these two approaches give essen-

TABLE I. Energy convergence of the $1s^2$ core and $1s^22s^2\,{}^1S$ state for the Be I basic (913-term) wave function.

	Angular component	No. of terms	$-\Delta E$ (a.u.)		Angular component	No. of terms	$-\Delta E$ (a.u.)
	(0,0)	36	13.626 840 80				
	(1,1)	30	0.024 234 29				
	(2,2)	25	0.003 028 74				
	(3,3)	20	0.000 776 52				
	(4,4)	16	0.000 275 37				
	(5,5)	16	0.000 120 37				
	(6,6)	16	0.000 059 99				
	Total	159	13.655 336 08				
	Core + (0,0)	25	14.620 403 65				
	Core + (1,1)	20	0.041 913 33				
1	[(1,1)0,0]0,0[a]	80	0.001 708 43	18	[(0,4)4,0]4,4	15	0.000 007 60
2	[(0,1)1,0]1,1	70	0.001 234 47	19	[(0,1)1,1]2,2[b]	11	0.000 007 86
3	[(0,0)0,2]2,2	50	0.000 597 68	20	[(1,1)0,2]2,2	16	0.000 007 24
4	[(0,1)1,1]2,2	46	0.000 296 83	21	[(2,2)0,0]0,0[a]	16	0.000 004 69
5	[(0,0)0,0]0,0[a]	30	0.000 282 08	22	[(0,1)1,3]4,4	15	0.000 004 40
6	[(0,0)0,3]3,3	50	0.000 166 20	23	[(0,5)5,0]5,5	15	0.000 003 71
7	[(0,2)2,0]2,2	70	0.000 150 21	24	[(3,3)0,0]0,0[a]	16	0.000 002 60
8	[(0,0)0,2]2,2	16	0.000 055 58	25	[(0,6)6,0]6,6	15	0.000 001 87
9	[(0,0)0,4]4,4	50	0.000 056 71	26	[(0,0)0,3]3,3	8	0.000 001 76
10	[(0,3)3,0]3,3	35	0.000 024 62	27	[(4,4)0,0]0,0[a]	8	0.000 001 62
11	[(0,0)0,5]5,5	50	0.000 023 89	28	[(0,1)1,3]4,4[a]	5	0.000 001 40
12	[(0,1)1,1]2,2[a]	24	0.000 018 46	29	[(0,1)1,4]5,5	5	0.000 001 31
13	[(0,1)1,2]3,3	15	0.000 017 70	30	[(0,1)1,0]1,1[b]	5	0.000 001 46
14	[(0,0)0,6]6,6	49	0.000 011 70	31	[(1,1)0,3]3,3	8	0.000 001 07
15	[(0,1)1,2]3,3[a]	15	0.000 011 49	32	[(1,2)1,1]2,2	5	0.000 000 91
16	[(0,0)0,0]0,0	16	0.000 011 76	33	[(2,2)0,2]2,2	8	0.000 000 86
17	[(0,1)1,0]1,1[a]	15	0.000 008 08	34	[(1,1)0,1]1,1	16	0.000 000 19
					Total	913	14.667 043 41

[a] In these angular components the spins of the first two electrons couple into a triplet.

[b] A repeated angular component with the same *l*'s but different set of nonlinear parameters.

TABLE II. Be I $1s^22s^2$ energy improvement over the basic (913-term) wave function by partial saturation of angular components (see the discussion in text).

Angular component expanded	No. of terms in the basic wave function	No. of terms increased	Total No. of terms	Upper bound energy E (a.u.)	ΔE (a.u.) improved
[0000]	46	157	1070	−14.667 047 35	−0.000 003 94
[0011]	170	214	1127	−14.667 050 53	−0.000 007 12
[0022]	152	152	1065	−14.667 046 91	−0.000 003 50
[0033]	109	169	1082	−14.667 047 21	−0.000 003 80
[0112]	81	225	1138	−14.667 050 41	−0.000 007 00
[0044]	73	165	1078	−14.667 047 14	−0.000 003 76
[0055]	64	208	1121	−14.667 046 18	−0.000 002 77
[0066]	64	210	1123	−14.667 045 10	−0.000 001 69
[0123]	30	214	1127	−14.667 046 24	−0.000 002 83
[0134]	20	168	1081	−14.667 044 39	−0.000 000 98
[0145][a]	5	309	1222	−14.667 044 63	−0.000 001 22
[0156][b]	0	155	1068	−14.667 044 70	−0.000 001 29
[1122]	21	103	1016	−14.667 043 76	−0.000 000 35
Total-energy improvement					−0.000 040 25

[a] Also including [0222] and [1113] angular components.

[b] Also including [0167] angular components.

TABLE III. Extrapolation of the higher angular component ($l > 6$) contribution to the binding energy of Be-like $1s^2 2s^2$ systems (in a.u.). The extrapolated ($l > 6$) contributions are based on the $l = 6$ results and their comparison with that of the $1s^2$ core [19,20]. See the discussion in text.

	$-\Delta E$ (a.u.)			$-\Delta E$ (a.u.)		
	$1s^2$	$1s^2 2s^2$	Ratio[a]	$1s^2$	$1s^2 2s^2$	Ratio[a]
	$Z=4$			$Z=9$		
$l=4$	0.000 286 3	0.000 069 7	4.108	0.000 346 1	0.000 201 7	1.716
$l=5$	0.000 127 3	0.000 030 4	4.190	0.000 155 2	0.000 090 2	1.720
$l=6$	0.000 064 2	0.000 015 2	4.206	0.000 079 0	0.000 045 6	1.735
$l>6$	0.000 149 1	0.000 035 4		0.000 183 5	0.000 105 8	
	$Z=5$			$Z=10$		
$l=4$	0.000 307 9	0.000 109 2	2.821	0.000 352 0	0.000 215 1	1.636
$l=5$	0.000 137 0	0.000 047 5	2.887	0.000 157 6	0.000 096 3	1.636
$l=6$	0.000 069 5	0.000 024 0	2.899	0.000 080 0	0.000 048 7	1.643
$l>6$	0.000 160 0	0.000 055 2		0.000 186 1	0.000 113 3	
	$Z=6$			$Z=15$		
$l=4$	0.000 321 2	0.000 139 8	2.297	0.000 367 6	0.000 259 0	1.419
$l=5$	0.000 143 3	0.000 061 0	2.348	0.000 164 8	0.000 117 4	1.404
$l=6$	0.000 072 8	0.000 030 5	2.387	0.000 084 1	0.000 059 7	1.408
$l>6$	0.000 169 9	0.000 071 2		0.000 194 3	0.000 138 0	
	$Z=7$			$Z=20$		
$l=4$	0.000 332 7	0.000 164 9	2.021	0.000 375 4	0.000 282 5	1.329
$l=5$	0.000 148 5	0.000 073 2	2.030	0.000 168 5	0.000 128 5	1.312
$l=6$	0.000 075 5	0.000 037 0	2.040	0.000 086 0	0.000 065 5	1.314
$l>6$	0.000 174 4	0.000 085 5		0.000 199 1	0.000 151 5	
	$Z=8$					
$l=4$	0.000 340 7	0.000 185 0	1.841			
$l=5$	0.000 152 3	0.000 082 5	1.846			
$l=6$	0.000 077 4	0.000 041 5	1.864			
$l>6$	0.000 178 9	0.000 096 0				

[a] The ratio is $\Delta E_{1s^2}(l,l)/\Delta E_{1s^2 2s^2}(00ll)$.

tially the same results for both the QED and the higher-order relativistic corrections, with the result from the latter approach being slightly larger. For example, the difference between the two sets of QED corrections is 0.08 cm^{-1} for $Z=4$. For $Z=20$, it increases to 1.49 cm^{-1} which is only 0.06% of the total QED contribution to the double-electron IP. Hence only one set of results (from successive screening Z_{eff}) is included in Table V.

Table V gives the IP results for $Z=4-10$ and for $Z=15$ and 20. The last two states are computed in order to extrapolate our results to higher-Z systems. In this table the results from the $1s1s$ core are given in the second column. The nonrelativistic energy of the core is corrected using Pekeris [33] and Drake [34]. Hence, the $1s1s$ energy is directly from Pekeris [33] and Drake [34]. The row of "Rel. corr." is the discrepancy of our first-order relativistic results with that of Pekeris. This correction does not affect the IP but it affects the four-electron relativistic energy. Most of this discrepancy comes from the electron-electron contact potential which is particularly large for the $1s^2$ core. This shows the weakness of the CI wave function in the case of the $1s$-$1s$ interaction. For the $1s$-$2s$ and $2s$-$2s$ interactions, the CI wave function works much better. The difference of

TABLE IV. Nonrelativistic energies of Be-like $1s^2 2s^2$ states (in a.u.).

Z	913 term Upper bound	Higher-l corr.	Corr. from partial wave saturation	Core corr.	Total
4	$-14.667\,043\,4$	$-0.000\,035\,4$	$-0.000\,040\,3$	$-0.000\,230\,1$	$-14.667\,349\,2$
5	$-24.348\,516\,1$	$-0.000\,055\,2$	$-0.000\,051\,4$	$-0.002\,247\,6$	$-24.348\,870\,3$
6	$-36.534\,435\,9$	$-0.000\,071\,2$	$-0.000\,055\,5$	$-0.000\,260\,0$	$-36.534\,822\,3$
7	$-51.222\,272\,0$	$-0.000\,085\,5$	$-0.000\,062\,7$	$-0.000\,268\,8$	$-51.222\,689\,0$
8	$-68.411\,074\,1$	$-0.000\,096\,0$	$-0.000\,071\,7$	$-0.000\,275\,8$	$-68.411\,517\,5$
9	$-88.100\,440\,8$	$-0.000\,105\,8$	$-0.000\,073\,9$	$-0.000\,281\,3$	$-88.100\,901\,9$
10	$-110.290\,158\,6$	$-0.000\,113\,3$	$-0.000\,071\,8$	$-0.000\,285\,9$	$-110.290\,629\,5$
15	$-258.741\,139\,4$	$-0.000\,138\,0$	$-0.000\,089\,0$	$-0.000\,300\,2$	$-258.741\,666\,6$
20	$-469.693\,640\,1$	$-0.000\,151\,5$	$-0.000\,093\,4$	$-0.000\,308\,0$	$-469.694\,193\,0$

TABLE V. Ionization potential for the $1s^22s^2$ states of beryllium-like systems (in a.u.).

			Ionization potential	
	$1s1s$	$1s^22s^2$	a.u.	cm^{-1}
$Z=4$				
Nonrel. (with core corr.)	−13.655 566 21	−14.667 349 19	1.011 782 98	222 047.17
$\langle H_1+H_2\rangle$	−0.002 429 60	−0.002 578 34	0.000 148 74	32.64
$\langle H_3\rangle$	0.000 265 31	0.000 279 74	−0.000 014 43	−3.17
$\langle H_5\rangle$	−0.000 047 03	−0.000 047 70	0.000 000 68	0.15
$\langle H_4\rangle$	0.000 025 72	0.000 028 11	−0.000 002 39	−0.52
Rel. corr.[a]	−0.000 014 65	−0.000 014 65		
Subtotal	−13.657 766 46	−14.669 682 04	1.011 915 6	222 076.28
QED corr.			−0.000 004 6	−1.02
Double IP (this work)			1.011 910 9	222 075.25
$1s^22s$ IP			0.669 289 3	146 883.08
$1s^22s^2$ IP (this work)			0.342 621 6	75 192.17
Expt.[b]			0.342 621 1	75 192.07
(theory)−(experiment)			0.000 000 5	0.10
$Z=5$				
Nonrel. (with core corr.)	−22.030 971 55	−24.348 870 27	2.317 898 72	508 694.61
$\langle H_1+H_2\rangle$	−0.006 327 03	−0.006 940 37	0.000 613 34	134.61
$\langle H_3\rangle$	0.000 572 36	0.000 618 49	−0.000 046 13	−10.12
$\langle H_5\rangle$	−0.000 079 70	−0.000 080 84	0.000 001 14	0.25
$\langle H_4\rangle$	0.000 027 67	0.000 029 78	−0.000 002 11	−0.46
Rel. corr.[a]	−0.000 025 18	−0.000 025 18		
Higher rel. corr.[c]		−0.000 000 10	0.000 000 1	0.02
Subtotal	−22.036 803 43	−24.355 268 49	2.318 465 1	508 818.90
QED corr.			−0.000 020 4	−4.47
Double IP (this work)			2.318 444 6	508 814.42
$1s^22s$ IP			1.393 987 6	305 929.67
$1s^22s^2$ IP (this work)			0.924 457 0	202 884.75
Expt.[d]			0.924 469 1	202 887.40
(theory)−(experiment)			−0.000 012 1	−2.65
$Z=6$				
Nonrel. (with core corr.)	−32.406 246 57	−36.534 822 33	4.128 575 76	906 076.19
$\langle H_1+H_2\rangle$	−0.013 709 88	−0.015 430 92	0.001 721 04	377.71
$\langle H_3\rangle$	0.001 055 31	0.001 160 14	−0.000 104 83	−23.01
$\langle H_5\rangle$	−0.000 121 00	−0.000 121 97	0.000 000 98	0.21
$\langle H_4\rangle$	0.000 031 47	0.000 032 78	−0.000 001 31	−0.29
Rel. corr.[a]	−0.000 038 90	−0.000 038 90		
Higher rel. corr.[c]		−0.000 000 56	0.000 000 56	0.12
Subtotal	−32.419 029 57	−36.549 221 76	4.130 192 2	906 430.95
QED corr.			−0.000 057 7	−12.65
Nuclear size			−0.000 000 1	−0.02
Double IP (this work)			4.130 134 5	906 418.27
$1s^22s$ IP			2.370 215 1	520 178.28
$1s^22s^2$ IP (this work)			1.759 919 4	386 239.99
Expt.[d]			1.759 924 0	386 241(2)
(theory)−(experiment)			−0.000 004 6	−1.01
$Z=7$				
Nonrel. (with core corr.)	−44.781 445 12	−51.222 689 03	6.441 243 91	1 413 634.21
$\langle H_1+H_2\rangle$	−0.026 222 70	−0.030 044 77	0.003 822 06	838.81
$\langle H_3\rangle$	0.001 754 07	0.001 953 09	−0.000 199 02	−43.68
$\langle H_5\rangle$	−0.000 170 92	−0.000 170 50	−0.000 000 42	−0.09
$\langle H_4\rangle$	0.000 032 19	0.000 032 09	0.000 000 10	0.02
Rel. corr.[a]	−0.000 055 04	−0.000 055 04		
Higher rel. corr.[c]		−0.000 002 07	0.000 002 07	0.45
Subtotal	−44.806 107 52	−51.250 976 23	6.444 868 7	1 414 429.73
QED corr.			−0.000 128 4	−28.18
Nuclear size			−0.000 000 2	−0.05
Double IP (this work)			6.444 740 1	1 414 401.51
$1s^22s$ IP			3.597 539 4	789 537.69
$1s^22s^2$ IP (this work)			2.847 200 7	624 863.82

TABLE V. (*Continued*).

			Ionization potential	
	$1s1s$	$1s^22s^2$	a.u.	cm^{-1}
Expt.[e]			2.847 210 6	624 866(3)
(theory) − (experiment)			−0.000 009 9	−2.18
$Z=8$				
Nonrel. (with core corr.)	−59.156 595 06	−68.411 517 53	9.254 922 47	2 031 150.98
$\langle H_1+H_2\rangle$	−0.045 828 18	−0.053 298 54	0.007 470 35	1 639.50
$\langle H_3\rangle$	0.002 708 74	0.003 045 13	−0.000 336 40	−73.83
$\langle H_5\rangle$	−0.000 229 47	−0.000 226 20	−0.000 003 26	−0.72
$\langle H_4\rangle$	0.000 032 75	0.000 031 06	0.000 001 69	0.37
Rel. corr.[a]	−0.000 072 88	−0.000 072 88		
Higher rel. corr.[c]		−0.000 006 07	0.000 006 07	1.33
Subtotal	−59.199 984 10	−68.462 045 03	9.262 060 9	2 032 717.63
QED corr.			−0.000 246 0	−53.98
Nuclear size			−0.000 000 5	−0.10
Double IP (this work)			9.261 814 5	2 032 663.54
$1s^22s$ IP			5.075 960 6	1 114 006.34
$1s^22s^2$ IP (this work)			4.185 853 9	918 657.20
Expt.[f]			4.185 853 0	918 657(4)
(theory) − (experiment)			0.000 000 9	0.20
$Z=9$				
Nonrel. (with core corr.)	−75.531 712 34	−88.100 901 88	12.569 189 54	2 758538.51
$\langle H_1+H_2\rangle$	−0.074 809 57	−0.088 038 68	0.013 229 10	2 903.37
$\langle H_3\rangle$	0.003 959 05	0.004 484 21	−0.000 525 16	−115.25
$\langle H_5\rangle$	−0.000 296 65	−0.000 288 43	−0.000 008 22	−1.80
$\langle H_4\rangle$	−0.000 031 43	0.000 028 19	0.000 003 24	0.71
Rel. corr.[a]	−0.000 094 84	−0.000 094 84		
Higher rel. corr.[c]		−0.000 015 11	0.000 015 11	3.32
Subtotal	−75.602 922 92	−88.184 826 54	12.581 903 6	2 761 328.85
QED corr.			−0.000 425 1	−93.30
Nuclear size			−0.000 001 0	−0.21
Double IP (this work)			12.581 477 6	2 761 235.34
$1s^22s$ IP			6.805 669 5	1 493 628.64
$1s^22s^2$ IP (this work)			5.775 808 0	1 267 606.70
Expt.[g]			5.775 804 8	1 267 606(2)
(theory) − (experiment)			0.000 003 2	0.70
$Z=10$				
Nonrel. (with core corr.)	−93.906 806 48	−110.290 629 51	16.383 823 03	3 595 734.75
$\langle H_1+H_2\rangle$	−0.115 769 18	−0.137 570 76	0.021 801 58	4 784.76
$\langle H_3\rangle$	0.005545 11	0.006 318 85	−0.000 773 75	−169.81
$\langle H_5\rangle$	−0.000 372 45	−0.000 356 82	−0.000 015 63	−3.43
$\langle H_4\rangle$	0.000 033 53	0.000 028 29	0.000 005 24	1.15
Rel. corr.[a]	−0.000 120 56	−0.000 120 56		
Higher rel. corr.[c]		−0.000 033 33	0.000 033 33	7.32
Subtotal	−94.017 490 04	−110.422 363 85	16.404 873 8	3 600 354.74
QED corr.			−0.000 681 5	−149.57
Nuclear size			−0.000 001 7	−0.38
Double IP (this work)			16.404 190 6	3 600 204.79
$1s^22s$ IP			8.786 952 4	1 928 460.16
$1s^22s^2$ IP (this work)			7.617 238 2	1 671 744.63
Expt.[d]			7.617 454 1	1 671 792.00
(theory) − (experiment)			−0.000 215 9	−47.37
$Z=15$				
Nonrel. (with core corr.)	−215.782 090 80	−258.741 666 60	41.959 575 80	9 428 369.80
$\langle H_1+H_2\rangle$	−0.613 692 47	−0.751 500 33	0.137 807 86	30 244.79
$\langle H_3\rangle$	0.019 908 22	0.023 101 63	−0.003 193 41	−700.86
$\langle H_5\rangle$	−0.000 880 94	−0.000 774 24	−0.000 106 70	−23.42
$\langle H_4\rangle$	0.000 033 47	0.000 018 85	0.000 014 62	3.21
Higher rel. corr.[c]		−0.000 597 59	0.000 597 59	131.15
Subtotal			43.094 695 8	9 458 024.68
QED corr.			−0.003 732 7	−819.22

TABLE V. (*Continued*).

			Ionization potential	
	$1s1s$	$1s^22s^2$	a.u.	cm^{-1}
Nuclear size			$-0.000\,012\,3$	-2.71
Double IP (this work)			43.090 950 7	9 457 202.75
$1s^22s$ IP			22.481 996 8	4 934 140.43
$1s^22s^2$ IP (this work)			20.608 953 9	4 523 062.32
Expt.[h]			20.608 669 9	4 523 000.00
(theory) − (experiment)			0.000 283 9	62.32
$Z=20$				
Nonrel. (with core corr.)	$-387.657\,233\,80$	$-469.694\,193\,03$	82.036 959 23	18 004 783.70
$\langle H_1+H_2\rangle$	$-1.985\,129\,30$	$-2.468\,931\,80$	0.483 802 50	106 180.91
$\langle H_3\rangle$	0.048 653 12	0.056 975 68	$-0.008\,322\,56$	$-1\,826.57$
$\langle H_5\rangle$	$-0.001\,605\,16$	$-0.001\,275\,14$	$-0.000\,330\,03$	-72.43
$\langle H_4\rangle$	0.000 035 12	0.000 009 61	0.000 025 51	5.60
Higher rel. corr.[c]		$-0.004\,173\,79$	0.004 173 79	916.03
Subtotal			82.516 308 4	18 109 987.25
QED corr.			$-0.011\,519\,8$	$-2\,528.26$
Nuclear size			$-0.000\,051\,3$	-11.26
Double IP (this work)			82.504 737 3	18 107 447.72
$1s^22s$ IP			42.546 775 3	9 337 809.37
$1s^22s^2$ IP (this work)			39.957 962 0	8 769 638.35
Expt.[d]			39.959 609 9	8 770 000.00
(theory) − (experiment)			$-0.001\,647\,8$	-361.65

[a] This is the total deviation of first-order corrections between our $1s^2$ core and those of Pekeris [33].

[b] Reference [37].

[c] See Eq. (26) and the discussion in Sec. V.

[d] Reference [24].

[e] Reference [40].

[f] Reference [41].

[g] Reference [25].

[h] Reference [36].

columns two and three, together with the QED and higher-order relativistic correction, gives the double-electron IP of the $1s^22s^2$ state. If we subtract the IP of $1s^22s$ from this result, the single-electron IP of the $1s^22s^2$ system is obtained. For consistency, we subtract the theoretical $1s^22s$ IP results calculated in Chung [20] which are corrected by adding the higher-order relativistic effect and nuclear size effect. The QED contribution in Ref. [20] is also improved with Eq. (22). Some of these results are given in Chung [35]. For four-electron systems, the experimental data are taken from Kelly [24] for $Z=4$–8, 10, and 20. For *F* VI the more recent experimental IP datum of Engström [25] is used. For *P* XII, the IP datum of Martin, Zalubas, and Musgrove [36] is used for comparison.

The experimental IP for Be I from Johansson is 75 192.07(10) cm^{-1} [37]; it agrees well with the predicted result of 75 192.17 cm^{-1}. In view of the approximation in the QED calculation and the extrapolation methods used in the theory, this agreement is better than one would expect. The Be I IP quoted in Moore [38] is 75 192.29 cm^{-1}; it also agrees well with the theory.

Among the $1s^22s^2$ systems, the Be I is the most extensively studied in the literature. Before 1991, most of the theoretical efforts are expended on the calculation of nonrelativistic energy (see Table VI). Among these, the most accurate nonrelativistic energy is probably the $-14.667\,37(3)$ a.u. of Olsen and Sundholm [11]. Our result, $-14.667\,3492$ a.u., gives an order of magnitude improvement over their calculation. Recently, Lindroth *et al.* [16] deduced a semiempirical nonrelativistic energy by subtracting the relativistic and QED corrections from the experimental IP. Their result, $-14.667\,353(2)$ a.u., is different from this work by 4(2) μa.u. Most of the difference comes from the estimated QED contribution. It is interesting to note that in Table V the relativistic contribution to the Be I double IP (from H_1, H_2, H_3, and H_5) is 0.000 134 99 a.u. This agrees exactly with the 0.000 135 a.u. of Lindroth *et al.* [16]. In the recent work of Davidson *et al.* [17], they obtain 0.000 116 a.u. with the QED effect included. Their estimated $1s^22s^2$ nonrelativistic energies are lower than those obtained in this work. The discrepancy increases from 0.000 01 a.u. for Be I to 0.000 30 a.u. for Ne VII. For Ca XVII, the discrepancy is 0.000 59 a.u.

Recently, Wen *et al.* [18] has measured the contribution of the mass polarization effect to the Be $1s^22s^2$ IP. Their specific mass polarization contribution is

TABLE VI. Comparison of theoretical and experimental Be $1s^2 2s^2$ energies (in a.u.). The QED of the Be^{2+} $1s1s$ core is not included.

Ref.		Method	$-E_{\text{nonrel}}$	$-E_{\text{rel}}$
[1]	Kelly (1963)	MBPT	14.664 0	
[3]	Sims and Hagstrom (1971)	Hylleraas-CI	14.666 54	
[4]	Fischer and Saxena (1974)	MCHF	14.665 87	
[5]	Bunge (1976)	CI	14.667 358(28)	
[6]	Lindgren and Salomonson (1980)	MBPT (CC)	14.665 96	
[7]	Salomonson, Lindgren, and Mårtensson (1980)	MBPT (MCMS)	14.661 1	
[10]	Millack (1989)	*g*-Hartree	14.670	
[11]	Olsen and Sundholm (1989)	MCHF-full CI	14.667 37(3)	
[12]	Salomonson and Öster (1990)	MBPT (CC)	14.666 69	
[13]	Dietz and Hess (1990)	Gaussian-basis CI	14.657 843	
[14]	Mårtensson-Pendrill *et al.* (1991)	MCHF		14.669 67(3)
[15]	Liu and Kelly (1991)	MBPT (MCDF)		14.671 1
[17]	Davidson *et al.* (1991)	Estimated	14.667 36	
[16]	Lindroth *et al.* (1992)	Semiempirical	14.667 353(2)	
	This work	Full-core plus Corr.	14.667 349 2	14.669 677 4
[24]	Kelly[a]	Experiment		14.669 675 9
[38]	Moore[b]	Experiment		14.669 671 7

[a] Using Pekeris' [33] two-electron relativistic energy plus the ionization potentials 146 882.86 and 75 192.07 cm^{-1}.

[b] Using Pekeris' [33] two-electron relativistic energy plus the ionization potentials 146 881.7 and 75 192.29 cm^{-1}.

0.006 74(100) a.u. In this reference the authors remarked that their calculated result, $-0.001\,47$ a.u., disagrees with the experiment. They attributed this discrepancy to the lack of correlation in their calculation. Lindroth *et al.* [16] adopted the experimental data in their analysis. They did not make any calculation on this effect. For ^{9}Be, the experimental result of Wen *et al.* [18] corresponds to

$$\langle H_4\rangle_{1s^2 2s} - \langle H_4\rangle_{1s^2 2s^2} = -\frac{0.006\,74(100)}{1823\times 9.012\,182\,2} = -0.410(61)\ \mu\text{a.u.} \qquad (33)$$

In Table V the mass polarization contribution to the double-electron IP is -2.389 μa.u. Its contribution to the $1s^2 2s$ IP is found to be -1.970 μa.u. [19]. This implies that the contribution to the $1s^2 2s^2$ IP should be -0.419 μa.u., which is well within the experimental uncertainty.

In Table VI we make a comparison between the various results of Be I in the literature. Note that the experimental energies are obtained by adding the double-electron IP quoted in Kelly [24] and in Moore [38] to the $1s^2$ energy of Pekeris [33]. The $-14.669\,677\,4$ a.u. quoted in this table is the result of our relativistic energy plus the $2s2s$ QED effect. Although the $1s^2 2s^2$ IP of Moore agrees closely with our prediction, her $1s^2 2s$ IP disagrees with theory by more than 1 cm^{-1} [20]. This discrepancy is reflected in the comparison.

For C III, N IV, and O V, our predicted results are all within the quoted experimental uncertainty. These experimental data are quoted in Kelly [24] and Moore [39]. The C III IP quoted in these two references is 386 241(2) cm^{-1}. This agrees with the predicted result of 386 239.99 cm^{-1}. The N IV IP is predicted to be 624 863.82 cm^{-1}; it is within the experimental uncertainty of 624 866(3) cm^{-1} [40]. The O V IP is predicted to be 918 657.20 cm^{-1}; it also agrees with the experimental result of 918 657(4) cm^{-1} [41].

For F VI, the IP quoted in Kelly [24] is 1 267 622 cm^{-1}. No error bar is given for this datum. It differs from our prediction, 1 267 606.70 cm^{-1}, by 15 cm^{-1}. A more recent measurement on F VI has been reported by Engström [25]. His result, 1 267 606(2) cm^{-1}, agrees well with the prediction.

For the systems discussed above, the experiment and theory agree closely. However, there are cases where the predicted IP lies outside of the experimental uncertainty. B II is the most interesting case in question.

For B II our predicted IP is about -2.65 cm^{-1} off from the 202 887.4(8) cm^{-1} quoted in Kelly [24] and Moore [39]. Moore attributes this datum to the unpublished work of Ölme. It is interesting to note that while most of the predicted $1s^2 2s$ IP agrees well with the experiment for $Z = 3$ to 10 [20]. The B III is also an exception. The predicted IP, 305 929.67 cm^{-1}, is 1.43 cm^{-1} smaller than the experimental result 305 931.1(6) cm^{-1}, also by Ölme [42]. Although the discrepancies between theory and experiment are not very large, they are definitely outside of the quoted uncertainty.

The agreement between theory and experiment is poorer for Ne VII, P XII, and Ca XVII. The discrepancy in Ne VII is 47 cm^{-1} based on the quoted IP in Kelly [24] and Moore [39]. This datum is from the unpublished data of Edlén. Judging from the agreement of the $1s^2 2s^2$ IP for $Z = 3$ to 9, it seems unlikely that our prediction for $Z = 10$ could be off by this amount.

As Z becomes larger than ten, the QED and higher-order relativistic effects increase quickly. In principle, the approximations we used in this work may cause the prediction to be less accurate. Unfortunately, for these systems, most of the "experimental" $1s^2 2s^2$ IP data in the data tables [39] do not give experimental uncertainty. For the very few cases where error bars are given, our predicted IP's are well within the quoted uncertainty.

For P XII, the IP quoted in Kelly [24] and Moore [39] is 4 520 100 cm^{-1}. This is very different from the 4 523 000 cm^{-1} given in Martin, Zalubas, and Musgrove [36]. Our predicted IP, 4 523 062 cm^{-1}, strongly favors the latter datum. For Ca XVII, the IP quoted in Moore [39] is 8 767 000 cm^{-1}. Our prediction, 8 769 628 cm^{-1}, favors the 8 770 000 cm^{-1} quoted in Kelly [24].

By making a least-squares fit for the IP with the data calculated in Table V, we can extrapolate for other Z systems. These results are given in Table VII for $Z=11$ to 25. These results allow us to make a comparison with experiment. Some of the IP data are compiled more recently by Martin and collaborators [43–47]. These compiled data are substantially closer to our prediction than those from Kelly [24]. For example, the predicted Na VIII IP is 343 cm^{-1} higher than that of Kelly, but it is well within the experimental uncertainty of 2 131 300(250) cm^{-1} of Martin and Zalubas [43]. Some of the predicted data are extremely close to the more recent experimental data. For Al X, the discrepancy is only 34 cm^{-1} and it is 62 cm^{-1} for P XII. Unfortunately, the uncertainties in these experimental data are not quoted. The significance of these agreements is not clear.

VI. CONCLUSION

In this work we use a full-core plus correlation method to calculate the ionization potential of the $1s^22s^2$ systems. CI wave functions are used. In order to obtain a more reliable energy, we adopted a method of partial saturation for the radial basis functions in the angular components. The relativistic corrections are first calculated with first-order perturbation theory. This is further corrected by estimating the QED and higher-order relativistic corrections using an effective nuclear charge. The contribution of the nuclear size effect to the IP is also estimated with hydrogenic functions by assuming a uniform spherical nuclear charge distribution. Explicit calculations are carried out for $Z=4$–10, 15, and 20. The IP results for other Z systems are obtained by a least-squares fit to the calculated data.

TABLE VII. $1s^22s^2$ ionization potential from a least-squares fit (in cm^{-1}).

Z	This work	Experiment[a]	Ref. No.
11	2 131 142.8	2 131 300(250)	[43]
12	2 645 871.7	2 646 000[b]	[44]
13	3 216 033.9	3 216 000	[45]
14	3 841 727.1	3 842 100	[46]
16	5 260 213.9	5 260 000	[47]
17	6 053 278.9	6 047 200	
18	6 902 434.5	6 894 200	
19	7 807 821.5	[7 810 000]	
21	9 788 076.7	[9 780 000]	
22	10 863 324.0	[10 860 000]	
23	11 995 599.1	[11 990 000]	
24	13 185 117.6	[13 180 000]	
25	14 432 130.7	[14 420 000]	

[a] Data for $Z=17$–25 are from Kelly [24]. The values in brackets are based on extrapolation rather than observation.

[b] It is remarked that the uncertainty should be several hundred cm^{-1}.

Judging from the comparison of our prediction with the available experimental data, the method appears to be reliable. With the exception of B II, the results we obtained are well within the experimental uncertainty quoted.

It should be pointed out that the Z_{eff} defined by Eq. (25) or by Eqs. (29) and (30) is only an approximation. Therefore, the QED, higher-order relativistic correction, and nuclear size effect are not calculated from first principles. The QED contribution calculated in this work is smaller than that of Lindroth *et al.* [16]. Equation (25) is not the only way the Z_{eff} can be defined. For example, we may define a Z_{eff} by using the first-order relativistic correction only. Hence, for the $2s$ electron in $1s^22s$, we have

$$\Delta E_1(1s^22s)-\Delta E_1(1s^2)=-\frac{\alpha^2 Z_{\text{eff}}^4}{2n^3}\left[\frac{1}{k}-\frac{3}{4n}\right] . \qquad (34)$$

This definition leads to a larger Z_{eff} for the $2s$ electron. The QED results calculated with this Z_{eff} agree excellently with the results of McKenzie and Drake [27] (see Table VIII) and the Be I result agrees with Lindroth *et al.* [16]. However, based on the available experimental data, the IP's calculated with these QED values give poorer agreement with experiment for both the three- and especially the four-electron systems for $Z=5$ to 9. We hope that more precision measurement on the IP's of these systems can be made. This may help us to decide unambiguously which Z_{eff} is physically more correct. We note that the definition of Eq. (34) runs into difficulty for some np electrons where the energy contribution of the relativistic effect is positive [17]. For low-Z systems, the approximation used in this work [i.e., using Eqs. (29) and (30)] seems to be justified by the exceptional agreement between theory and the existing experiment for both the three-electron [20] and four-electron systems. However, for

TABLE VIII. QED results using the Z_{eff} from Eq. (34) and comparison with those of Mckenzie and Drake [27] and with Lindroth *et al.* [16] (in 10 μa.u.).

			$2s$			
Z	4	5	6	7	8	9
Eq. (34)	0.62	2.05	4.94	10.0	17.8	29.2
Ref. [27]	0.68	2.21	5.26	10.5	18.6	30.3
Z	10	11	13	15	17	20
Eq. (34)	45.1	66.2	128	222	356	652
Ref. [27]	46.6	68.1	131	226	362	651
			$2s2s$			
Z	4	5	6	7	8	9
Eq. (34)[a]	0.88	3.23	8.27	17.0	31.1	51.9
Ref. [16]	1.0(1)					
Z	10	15	20			
Eq. (34)[a]	81.0	412	1229			

[a] The generalization of this equation for the case of $1s^22s^2$.

medium-Z systems, accurate experimental data are lacking. Whether this approximation will again be justified remains to be seen.

The method adopted in this work should be easily applicable to excited four-electron atomic systems. It could also be useful for five or more electron atomic systems.

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