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Ground-state atomic ionization energies for $Z=2-18$ and up to 18 electrons

Neng Wu Zheng,* Tao Zhou, Tao Wang, Ru Yi Yang, Yu Jie Sun, Feng Wang, and Chao Guang Chen
Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

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Using the weakest-bound-electron potential model, an eight-parameter formula is derived for the 153 ionization potentials of atomic or ionic systems with $Z=2-18$, $N=2-18$ yielding results departing from experimental ones by no more than 0.65 eV.

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I. INTRODUCTION

Ionization energy has long been an important subject of many experimental and theoretical studies. Although ionization energies for a large number of atoms and ions are available experimentally, there are still many difficulties in determining the ionization energies for the highly stripped ions. Various theoretical methods, such as multiconfiguration Dirac-Fock method [1,2], relativistic configuration interaction method [3], relativistic many-body perturbation method (RMBPT) [4,5], relativistic coupled-cluster method [6,7], etc., have been used to investigate atomic ionization energies. However, these *ab initio* methods are mainly used to study the first-row atoms, and only a few calculations have been carried out with satisfactory accuracy for large systems except for alkali-metal atoms. It may be partially due to the increasing complexity of computations. Therefore, empirical and semiempirical methods are of interest when investigating complicated atoms.

The purpose of this paper is to study ground-state ionization energies along an isoelectronic sequence on the basis of the weakest-bound-electron potential model (WBEPM theory) [8]. In Sec. II, a brief review of WBEPM theory for calculating the ionization energy is given. In WBEPM theory, a single-electron effective potential is used to describe the behavior of the weakest bound electron that moves in a field generated by the atomic core composed of the nucleus and all the other electrons in an atom. In order to construct the model, some adjustable parameters are introduced, which are related to the screening effect, penetration effect, and polarization effect. Thus, the nonrelativistic ionization energy is approximated to a second-order polynomial in Z, and the parameters can be obtained by fitting it to the experimental data. In order to calculate ionization energies more accurately, a discussion about relativistic corrections, important for heavy atoms, is given in Sec. III. Conclusions are given in the last section.

II. THEORETICAL ANALYSIS

The ground-state ionization energy is defined as the energy required to completely remove the weakest bound electron from an atom or ion in its ground state so that the resulting ion is also in its ground state [9].

The experimental ionization energy for an N-electron atom with a nuclear charge of Z is given customarily by

$$I(N,Z)=-\Delta E(N,Z)=E(N-1,Z)-E(N,Z). \tag{1}$$

For light atoms, the total energy $E(N,Z)$ could be approximately decomposed into the nonrelativistic part and the relativistic part [10], i.e.,

$$E(N,Z)=E_{nr}(N,Z)+E_r(N,Z). \tag{2}$$

Combining Eq. (1) with Eq. (2), one has

$$\begin{aligned}I(N,Z)=&[E_{nr}(N-1,Z)-E_{nr}(N,Z)]+[E_r(N-1,Z)\\&-E_r(N,Z)]=I_{nr}(N,Z)+I_r(N,Z).\end{aligned} \tag{3}$$

The ground nonrelativistic ionization energies are available by (i) calculating the nonrelativistic total energies in the framework of *ab initio* approaches; (ii) subtracting the corresponding relativistic corrections from the experimental total energies or ionization energies; or (iii) modeling the interelectronic interaction with an effective Hamiltonian.

In principle, one can obtain the exact ground-state eigenvalue of the nonrelativistic Hamiltonian by solving the Schrödinger equation, but there are many difficulties in practical calculations. For example, configuration interaction [11,12] and multiconfiguration Hartree-Fock [13,14] are very effective for three- and four-electron systems, but the incompleteness of the set of configurations involved limits their more extensive application. Diagrammatic many-body perturbation theory (MBPT) [4,5] is also a very powerful approach to many-electron systems; however, it is necessary to consider higher-order perturbation terms, which become considerably complicated in neutral atoms. In all these *ab initio* methods there appear difficulties when the number of electrons increases. So people have made efforts to estimate relativistic corrections, and then the nonrelativistic total energies or ionization energies can be obtained by subtracting relativistic corrections from the experimental data. For example, Anno and Teruya [15] proposed a semiempirical formula for the relativistic effect on the total energies of atoms; Davidson *et al.* [10] estimated the relativistic corrections to the ground-state ionization energies of atoms with up to 18 electrons from the complete-valence-space multiconfiguration Dirac-Fock calculation. Another feasible approach is to model the interelectronic interaction with an effective Hamiltonian,

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*Author to whom correspondence should be addressed. Email address: nwzheng@ustc.edu.cn

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such as the model potential methods [16], density-functional theory [17], etc. The present work emphasizes on the Z expansion of the ground-state ionization energies, which is derived from an effective one-electron Hamiltonian based on WBEPM theory.

WBEPM theory originated from early works by Zheng [8,18]. In the later years it has been developed continuously and applied to calculate various atomic properties, such as atomic energy levels, transition probabilities, oscillator strength, lifetime of excited states, electronegativity scale, ionization energy, electron affinity, etc. [19,20]. According to the definition of the ionization energy [9], one can derive the concept that the so-called weakest bound electron (WBE) in a given atom or ion is the one excited or ionized most easily in the system. So, WBE in a given system differs from other electrons in behavior, and it can be treated separately. Some properties of a many-electron system may be referred to as its behavior. According to the WBEPM theory, the potential field generated by the nucleus and the nonweakest bound electrons (NWBE) is (in a.u.)

$$V(r)=\frac{A}{r}+\frac{B}{r^2}, \tag{4}$$

$$A=-Z', \tag{5}$$

$$B=\frac{d(d+1)+2dl}{2}, \tag{6}$$

where r is the distance between WBE and the nucleus, the effective nuclear charge Z' is nonintegral, and d is an adjustable parameter. In Eq. (4), the first term is related to the penetration effect and screening effect, and the second term represents the dipole potential produced by the polarization effect that the WBE polarizes the atomic core formed by nucleus and the NWBE. Thus, the nonrelativistic one-electron Schrödinger equation of the WBE is derived as

$$\left[-\frac{1}{2}\nabla^2+\frac{A}{r}+\frac{B}{r^2}\right]\varphi=\varepsilon\varphi. \tag{7}$$

By solving Eq. (7), one can obtain the radial wave function of WBE as follows:

$$R_{n'l'}(r)=Ne^{-Z'r/n'}r^{l'}L_{n'-l'-1}^{2l'+1}\left(\frac{2Z'r}{n'}\right) \tag{8}$$

in which, $L_{n'-l'-1}^{2l'+1}(2Z'r/n')$ is the general Laguerre polynomial.

And the eigenvalue of the one-electron effective Hamiltonian of the WBE is

$$\varepsilon=-\frac{Z'^2}{2n'^2}. \tag{9}$$

In Eqs. (8) and (9), n' is the effective principal quantum number, and l' is the effective angular quantum number of WBE. n' and l' are related to the parameter d:

$$n'=n+d, \tag{10}$$

$$l'=l+d. \tag{11}$$

TABLE I. The first-order and second-order differences of experimental ionization energies (in eV) for F I sequence. $\Delta I_{\rm expt}$ represents the first-order difference of ionization energies, and $\Delta^2 I_{\rm expt}$ represents second-order difference of ionization energies. The experimental ionization energies $I_{\rm expt}$ are taken from Ref. [24]. The datum marked with asterisk gives abnormal $\Delta^2 I_{\rm expt}$ and is not used to fit.

Z	$I_{\rm expt}$	$\Delta I_{\rm expt}$	$\Delta^2 I_{\rm expt}$
9	17.422 82		
10	40.963 28	23.540 46	
11	71.6200	30.656 72	7.116 26
12	109.2655	37.6455	6.988 78
13	153.825	44.5595	6.9140
14	205.27	51.445	6.8855
15	263.57	58.30	6.855
16	328.75	65.18	6.88
17	400.06	71.31	6.13
18	478.69	78.63	7.32
19	564.7	86.01	7.38
20	657.2	92.5	6.49
21	756.7	99.5	7.0
22	863.1	106.4	6.9
23	976	112.9	6.5
24	1097	121	8.1
25	1224	127	6
26	1358	134	7
27	1504.6*	146.6	12.6
28	1648	143.4	−3.2
29	1804	156	12.6

As pointed out in Ref. [21], the ionization potential is generally meaningless unless the states of the system studied are defined. According to the definition mentioned above, for a chosen isoelectronic sequence, if all the members lie in their ground states, the ionization potential of WBE equal the negative value of the eigenvalue ε in Eq. (9) approximately [because Eq. (7) is the nonrelativistic one-electron Schrödinger equation],

$$I=-\varepsilon=\frac{Z'^2}{2n'^2}. \tag{12}$$

As mentioned above, the parameter d is associated to the nonrigid structure of the core. The polarization effect of the WBE on the core drops off with the increase of Z because of the orbit contraction. Thus, d is a small quantity that decreases with the increase of Z, and for large Z, d approximates to a constant. So, in an isoelectronic sequence, the effective principal quantum number n' could be approximately treated as a constant for the purpose of simplification. This is confirmed by the following fact, i.e., for an isoelectronic sequence, the plot of $\Delta I_{\rm expt}$ the first-order differences

TABLE II. Our results (in eV) of ionization energies. The values for atoms or ions in various stages of ionization with Z up to 18 are calculated using Eq. (17).

	I		II		III		IV		V		VI	
Z	$I_{\rm cal}$	$I_{\rm expt}-I_{\rm cal}$	$I_{\rm cal}$	$I_{\rm expt}-I_{\rm cal}$	$I_{\rm cal}$	$I_{\rm expt}-I_{\rm cal}$	$I_{\rm cal}$	$I_{\rm expt}-I_{\rm cal}$	$I_{\rm cal}$	$I_{\rm expt}-I_{\rm cal}$	$I_{\rm cal}$	$I_{\rm expt}-I_{\rm cal}$
2	24.654 80	−0.067 39										
3	5.305 74	0.085 98	75.635 57	0.004 61								
4	9.232 22	0.090 48	18.235 22	−0.024 06	153.857 60	0.039 01						
5	8.229 85	−0.068 18	25.172 54	−0.017 70	37.980 61	−0.049 97	259.325 02	0.050 19				
6	11.160 62	−0.099 68	24.435 12	0.051 80	47.938 82	−0.051 02	64.544 37	−0.050 47	392.046 91	0.040 09		
7	14.280 80	0.253 34	29.632 92	0.031 62	47.504 63	0.055 39	77.531 40	−0.057 90	97.930 58	−0.040 38	552.037 35	0.034 45
8	13.406 87	0.211 19	35.182 43	−0.065 13	54.983 41	0.047 91	77.438 63	0.025 10	113.952 33	−0.053 33	138.144 95	−0.025 25
9	17.281 10	0.141 72	35.065 90	−0.095 08	62.874 92	−0.166 52	87.201 09	0.061 29	114.238 83	−0.003 97	157.205 43	−0.040 33
10	21.487 92	0.076 68	41.070 45	−0.107 17	63.616 66	−0.166 66	97.359 15	−0.239 15	126.277 86	0.067 86	157.908 46	−0.021 54
11	5.062 59	0.076 49	47.314 55	−0.028 15	71.768 81	−0.148 81	99.045 18	−0.135 18	138.638 21	−0.238 21	172.208 49	0.028 49
12	7.486 06	0.160 18	15.133 41	−0.098 13	80.177 13	−0.033 43	109.357 84	−0.092 34	141.340 76	−0.070 76	186.717 44	0.042 56
13	5.911 45	0.074 32	18.955 37	−0.126 81	28.507 28	−0.059 63	120.018 99	−0.026 99	153.823 12	0.001 88	190.495 93	−0.005 93
14	8.011 60	0.140 09	16.466 32	−0.120 47	33.642 24	−0.149 22	45.135 87	0.005 94	166.792 91	−0.025 91	205.154 15	0.115 85
15	10.380 18	0.106 51	19.953 10	−0.183 70	30.266 26	−0.063 56	51.528 41	−0.084 51	64.976 93	0.048 17	220.461 15	−0.040 15
16	10.322 96	0.037 05	23.433 45	−0.095 55	35.038 28	−0.248 28	47.289 87	−0.067 87	72.597 82	−0.003 32	87.994 23	0.058 77
17	12.976 89	−0.009 25	23.871 96	−0.057 96	39.869 05	−0.259 05	53.290 66	0.174 64	67.518 57	0.281 43	96.836 64	0.193 36
18	15.777 27	−0.017 65	27.661 81	−0.031 81	40.762 08	−0.022 08	59.606 11	0.203 89	74.727 63	0.292 37	90.936 55	0.072 45

	VII		VIII		IX		X		XI		XII	
Z	$I_{\rm cal}$	$I_{\rm expt}-I_{\rm cal}$	$I_{\rm cal}$	$I_{\rm expt}-I_{\rm cal}$	$I_{\rm cal}$	$I_{\rm expt}-I_{\rm cal}$	$I_{\rm cal}$	$I_{\rm expt}-I_{\rm cal}$	$I_{\rm cal}$	$I_{\rm expt}-I_{\rm cal}$	$I_{\rm cal}$	$I_{\rm expt}-I_{\rm cal}$
8	739.315 43	−0.025 43										
9	185.194 82	−0.008 82	953.905 18	0.006 02								
10	207.296 21	−0.020 31	239.089 14	0.009 76	1195.8356	−0.007 06						
11	208.452 20	0.047 80	264.231 95	0.018 05	299.838 49	0.025 51	1465.1408	−0.019 87				
12	224.990 64	−0.029 36	265.876 26	0.083 74	328.021 65	0.038 35	367.455 06	0.044 94	1761.8598	−0.054 84		
13	241.604 38	−0.115 62	284.624 87	−0.035 13	330.188 30	−0.058 30	398.676 03	0.073 97	441.952 70	0.047 30	2086.03 65	−0.056 55
14	246.506 43	−0.006 43	303.308 82	−0.231 18	351.114 61	−0.005 39	401.397 48	−0.027 48	476.207 56	0.152 44	523.346 84	0.073 16
15	263.344 38	0.225 62	309.371 28	0.228 72	371.842 74	−0.287 26	424.466 19	0.066 19	479.514 46	−0.054 46	560.630 45	0.169 55
16	280.995 42	−0.047 42	328.391 15	0.358 85	379.092 70	0.457 30	447.220 89	−0.279 61	504.688 82	−0.111 18	564.551 37	−0.111 37
17	114.157 63	0.038 17	348.376 92	−0.096 92	400.295 76	−0.235 76	455.676 18	−0.046 18	529.458 20	0.178 20	591.794 59	−0.195 41
18	124.233 27	0.089 73	143.443 04	0.016 96	422.596 28	−0.146 28	479.063 41	−0.373 41	539.130 42	−0.170 42	618.574 86	0.314 86

	XIII		XIV		XV		XVI		XVII		XVIII	
Z	$I_{\rm cal}$	$I_{\rm expt}-I_{\rm cal}$	$I_{\rm cal}$	$I_{\rm expt}-I_{\rm cal}$	$I_{\rm cal}$	$I_{\rm expt}-I_{\rm cal}$	$I_{\rm cal}$	$I_{\rm expt}-I_{\rm cal}$	$I_{\rm cal}$	$I_{\rm expt}-I_{\rm cal}$	$I_{\rm cal}$	$I_{\rm expt}-I_{\rm cal}$
14	2437.7199	−0.089 99										
15	611.654 56	0.085 44	2816.9641	−0.054 12								
16	651.960 62	0.239 38	706.894 56	0.115 44	3223.8278	−0.047 88						
17	656.521 83	0.188 17	750.215 75	−0.455 75	809.087 16	0.312 84	3658.3752	0.145 78				
18	685.798 49	−0.301 51	755.440 97	0.299 03	855.415 22	−0.645 22	918.254 31	−0.224 31	4120.6750	0.210 65		

of the experimental ionization energies, vs Z, is nearly linear, and the values of second-order differences are nearly constant.

In an earlier work [18], we proposed that the effective nuclear charge Z' can be expressed as

$$Z' = \sqrt{(Z-\sigma)^2 + g(Z-Z_0)}, \tag{13}$$

where Z_0 is the nuclear charge of the first member in an isoelectronic sequence, σ is the screening constant of the first member, and the parameter g, called relatively increase factor, indicates the effect on the effective nuclear charge due to the nuclear charge increase in the sequence.

Combining with Eq. (13), Eq. (12) becomes

$$I = \frac{(Z-\sigma)^2 + g(Z-Z_0)}{2n'^2}. \tag{14}$$

A parabolic relation in the form of Eq. (14) is adequate to describe the systemic behavior of the ground-state ionization energies along an isoelectronic sequence. It implies that second-order differences of the ionization energies for a sequence are nearly constant, which has been proved by the application of the Moseley's law [22] and the irregular-doublet law [23].

TABLE III. Comparison of ionization energies (in eV) for neutral atoms. The designations $I_{\mathrm{HF}(H)}$, $I_{\mathrm{HF,CR}}$, and I_{cal} refer to Huang *et al.* (Ref. [27]), Clementi and Roetti (Ref. [28]), and the present work. I_{expt} is the experimental data and taken from Ref. [24].

Z	$I_{\mathrm{HF}(H)}$	$I_{\mathrm{HF,CR}}$	I_{cal}	I_{expt}
3	5.33	5.34	5.305 74	5.391 72
4	7.99	8.05	9.232 22	9.3227
5	7.97	7.93	8.229 85	8.161 67
6	9.48	10.79	11.160 62	11.060 94
7	11.75	13.96	14.280 80	14.534 14
8	14.07	11.89	13.406 87	13.618 06
9	16.59	15.72	17.281 10	17.422 82
10	19.50	19.85	21.487 92	21.5646
11	4.86	4.95	5.062 59	5.139 08
12	6.57	6.61	7.486 06	7.646 24
13	5.51	5.50	5.911 45	5.985 77
14	6.78	7.66	8.011 60	8.151 69
15	8.53	10.04	10.380 18	10.486 69
16	10.26	9.03	10.322 96	10.360 01
17	12.54	11.79	12.976 89	12.967 64
18	14.76	14.77	15.777 27	15.759 62

It is appropriate to explain the effective nuclear charge in the form of Eq. (13). In the empirical formula of Rydberg [22], an integral effective nuclear charge, $Z' = Z - N + 1$, is used. It is suitable when the outer electron lies far enough from the core and full screening occurs. For lower-energy states, the penetration of the outer electron may lead to large deviations from Rydberg's formula. Moreover, assuming a linear dependence of the effective nuclear charge on Z, i.e., $g = 0$ for Eq. (14), one has

$$I = \frac{(Z-\sigma)^2}{2n'^2}, \tag{15}$$

which is similar to Hertz's formula [23] except for the nonintegral n'. In order to check the reliability of Eq. (15), we plot ΔI_{expt} the first-order difference of the experimental data in an isoelectronic sequence vs Z. The effective principal quantum number n' is then evaluated from the slope of the curve. The screening constant σ of the first member of the sequence can be determined by substituting n' and the corresponding experimental ionization energy I_{expt} into Eq. (15). Substituting σ and n' into Eq. (15) to calculate ionization energies I of the sequence, we find immediately a serious deviation between I and I_{expt}. For example, in the Na I sequence, the deviations between the ionization energies calculated with Eq. (15) and the experimental data obtained from Ref. [24] increase from 2.641 26 eV for $Z = 12$ to 76 eV for $Z = 36$. However, when using the effective nuclear charge in the form of Eq. (13), the situation is much better. Following the procedure described in Refs. [8,18,19], one can determine the parameters σ, g and n' in Eq. (14), and then calculate the ionization energy. For example, using Eq. (14), we calculated the ionization energies of C I and Al I sequences, and comparison with experimental data shows that the deviations are reduced to near 1 eV or better.

In the process of determining the parameters, we find that there may be one or several abnormal experimental data for a well-established sequence. As an example of an abnormality, the first-order and second-order differences of ionization energies of F I sequence are given in Table I. We found that the experimental value of the 19th member gives abnormal second-order differences of ionization energies $\Delta^2 I_{\mathrm{expt}}$, i.e., 12.6, -3.2, and 12.6 eV, which deviate from a constant badly. This is partly because of the fact that several ionization energies listed in the compilation of Ref. [24] are obtained from theoretical extrapolations rather than from experimental measurements. Although the average of the abnormal $\Delta^2 I_{\mathrm{expt}}$ is 7.3 eV and approximates to those of other $\Delta^2 I_{\mathrm{expt}}$ large deviations would appear if the 19th member of the sequence is taken into account. We therefore choose data in accordance with $\Delta^2 I_{\mathrm{expt}}$ and those abnormal data are not used in our fitting.

III. EXPRESSION CONTAINING RELATIVISTIC EFFECTS

As is well known, the electron-electron Coulomb energies scale only as r^{-1} and therefore go as Z, the electron-nuclear Coulomb energies scale as $-2Z/r \propto Z^2$; and the kinetic energies scale as r^{-2} and thus also go as Z^2 [25,26]. However, the mass-velocity term, the Darwin term, and the spin-orbit term increase as the fourth power of Z. These relativistic contributions to the ionization energy cannot be properly taken into account with an expression with Z^2 as the highest power. In order to obtain more accurate results, relativistic corrections should be added to the ionization energy calculated from Eq. (14). In this paper, we fit the deviations $I_{\mathrm{expt}} - I_{\text{cal-nr}}$ to a fourth-order polynomial in Z, where the second-order polynomial Eq. (14) is used to calculate $I_{\text{cal-nr}}$. So the deviations can be presented using the following formula:

$$I_r = \sum_{i=0}^{4} a_i Z^i. \tag{16}$$

Thus, the relativistic expression of ionization energy for an isoelectronic sequence is

$$I = \frac{[\sqrt{(Z-\sigma)^2 + g(Z-Z_0)}]^2}{2n'^2} + I_r. \tag{17}$$

Using Eq. (17), we calculate some ionization energies I_{cal}, and the results are listed in Table II. Good agreement is seen in comparisons of the present results with the experimental data I_{expt} [24], and the deviations are very small. In Table III, the present results are compared with the results obtained from Hartree-Fock (HF) methods [27,28] and the experimental data [24] for neutral atoms. One finds from Table III that except for the Li atom, the present results are much closer to experimental data than HF values. Even for the Li atom, the deviation is small. For some atoms, such as Be, F, Ne, Mg, Ar, etc., the present results are considerably better than HF results.

The possibility of interpolation with Eq. (17) is investigated. We delete some data from those used to fit, and calculate the deleted values using the residual data. The results indicate that an interpolation of the known data using Eq. (17) is feasible and the deviations are generally small. The feasibility of extrapolation with Eq. (17) is also studied. We find that the deviations between the extrapolated values and experimental data are also small for the next several members, but large deviations may arise for the members with large Z.

IV. CONCLUSION

For an isoelectronic sequence, the ground-state ionization energy I is only a function of the nuclear charge Z. The relationship between I and Z can be represented by Eq. (17), i.e., the nonrelativistic approximation Eq. (14) and the relativistic correction I_r Eq. (16). Using the method proposed in Refs. [8,18,19], one can determine the parameters n', σ, and g in Eq. (14). Then the deviations $I_{\text{expt}}-I_{\text{cal-nr}}$ are fitted to a fourth-order polynomial in Z, and the expression of I_r in the form of Eq. (16) is obtained. The ionization energies calculated from Eq. (17) are in good agreement with the experimental data available in the literature.

It must be pointed out that because the experimental data have been used to determine n', σ, and g, $I_{\text{cal-nr}}$ obtained from Eq. (14) are not pure nonrelativistic ionization energies. Partial relativistic effects have been included in $I_{\text{cal-nr}}$. Similarly, I_r is not a pure relativistic correction. In fact, it represents the correction to ionization energies with a polynomial in Z with an order not higher than quartic, which relates to the relativistic effects.

This method can also be used to investigate the Z dependence of the ionization energies of excited atoms, which will be studied in our other papers.

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