Research Article

Relativistic Corrections for Calculating Ionization Energies of One- to Five-Electron Isoelectronic Atomic Ions

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Received 20 August 2012; Accepted 1 October 2012

Academic Editors: A. M. Fonseca, A. Karadag, and Z. Wu

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We have previously proposed a simple empirical equation to reproduce the literature values of the ionization energies of one-electron to four-electron atomic ions with very good agreement. However, we used a potential energy approach in our equation, which has no theoretical basis. This paper discusses an alternative kinetic energy expression for one to five electrons with simple corrections for relativistic and Lamb shift effects and for two- to-five electron ions additional effects including electron relaxation and residual interactions. For calculated values of one-electron (hydrogen-like) and two electron (helium like) atomic ions, the difference with the literature values is typically 0.001% or less. Agreement with the literature values for three-, four-, and five-electron ions is 99% or better. First electron affinities calculated by our expression also agree fairly well with generally recommended values. These results show that there is strong evidence that our methodology can be developed to reliably predict, with fairly good accuracy, ionization energies of multielectron atomic ions that have not been measured.

1. Introduction

A knowledge of ionization energies is essential for understanding the chemistry of the elements and other fundamental concepts, such as lattice energies of inorganic solids.

With the development of quantum theory, the two-particle problem can be solved exactly and the kinetic energy of the electron in a hydrogen atom can be calculated using the Schrödinger equation. Since the Schrödinger equation does not take account of relativistic effects, Dirac [1] produced an equation which included a relativistic correction for the electron energy levels. However, Lamb and Retherford [2–4] in a series of experiments showed that there is a small shift in the energy levels of the hydrogen atom not accounted for by the Dirac equation. This energy shift is now commonly called the Lamb shift. Theoretical atomic energy levels were calculated from a nonrelativistic model, and then relativistic and quantum electrodynamic effects were accounted for by treating them as perturbation corrections.

General availability of powerful computers allowed highly complicated theoretical calculations of the energy

levels and ionization energies of hydrogen [5] and helium-like ions [6] to be performed. These sophisticated equations for one- and two-electron atomic ions, which need complex computer routines to compute, include corrections for the variation of mass with velocity, reduced mass, mass polarization, and Lamb shift, and for two-electron ions, corrections for interactions between the two electrons. Values computed by these equations are quoted to cm^{-1} (wave number) level or small fractions of a cm^{-1} . Updated theoretical ionization energies and Lamb shifts for one-electron [7] and two-electron [8] atomic ions have been published more recently and are generally accepted as very accurate. These recent results differ very little from the earlier computed values of Garcia and Mack [5] or Midtdal and Aashamar [6].

We have previously devised a simple empirical equation to reproduce literature values for the ionization energies of one-electron [9] and two-electron [10] atomic ions with very good agreement. More recently, we extended calculations to three- and four-electron isoelectronic ions [11], which reproduced literature values with good agreement. However, this equation is based on a potential energy approach (when the

potential energy is maximum, the kinetic energy approaches zero, that is, zero velocity, and relativistic correction for the variation of mass with velocity is not required) and has no theoretical basis. In this paper we use a kinetic energy expression with a relativistic correction, which has theoretical justification to calculate the ionization energies of one- to five-electron atomic ions. Besides applying a relativistic and a Lamb shift correction, we have also made a few hypotheses on factors that influence the size of the ionization energy. To maintain our aim of simplicity and ease of computation, the equations only contain fundamental constants or values derived from fundamental constants and simple numbers.

2. Sources of Data

The extensive publications by Moore [12–15] contain detailed tables of atomic energy levels in reciprocal wavelengths or wave numbers (cm^{-1}), ionization reciprocal wavelengths (in cm^{-1}), and values converted from wave numbers to electron volts (eV) for atoms and atomic ions with estimated experimental errors and references to original work. This remains the most extensive survey of ionization energies. Recently, the *CRC Handbook of Chemistry and Physics* [16] presented extensive authoritative data of ionization energies with reference to Moore and other up-to-date works. Andersen et al. [17] provided an extensive compilation of first electron affinities (binding energies of single negative ions) based on both theory and experiment. The majority of compilations of ionization energy data are now available on the National Institute of Standards and Technology web site (<http://www.nist.gov/srd/>). These compilations include values of ionization energies that are accurately measured as well as crude estimates.

On closer examination of many of the original papers and compilations, we have found that, in general, the first few ionization energies are most reliably measured, experimental errors increase across the higher members of a series, and some results have errors of over one eV. For example, the ionization energy of Sc_{XVII} (five-electron boron series) is $1094 \pm 2 \text{ eV}^{18}$. Hence, we consider that when comparisons are made, agreement with the first few members of a series is more relevant than with higher members of a series. There is no reason to doubt the reliability of the values published in the *CRC Handbook of Chemistry and Physics* of all fundamental constants and ionization energies. Values of all fundamental constants used for calculation in this work and ionization energies for comparison purposes are taken directly from it. Table 1 shows the symbols, elementary constants and conversion factors used in this work.

Ionization energies are presented in electron volts (eV) in the *Handbook of Chemistry and Physics* and eV is a more commonly used unit, so, as with our previous work, ionization energies are presented here in eV and rounded to four decimal places (please note that 0.0001 eV is equivalent to 0.8 cm^{-1} .) We consider that this is sufficiently precise, since some literature values are quoted only to one or two decimal places or less because the levels of uncertainty/experimental error for some ionization energies can be of the order of an eV

TABLE 1: Symbols, conversion factors, and constants (to 9 significant figures).

Symbol/constant	Value/comment/definition
α	0.00729735254
I	Number of electrons remaining after ionization
k	$01.23984180 \times 10^{-4}$
n	Principal quantum number
v	Electron velocity
Q	Number of residual electron-electron interactions
A	Mass number
μ	Reduced mass (see Table 8 column 6 for individual values)
S	Screening constant for the ionizing electron
S_1	Screening for the remaining electron(s) after ionization
S_2	Screening for the remaining electron(s) before ionization
Z	Proton number (nuclear charge)
c	Velocity of light $2.99792458 \times 10^8 \text{ ms}^{-1}$
m_e	Electron rest mass $9.10938215 \times 10^{-31} \text{ kg}$
m_p	Proton rest mass $1.67262164 \times 10^{-27} \text{ kg}$
q	Electron charge $1.60217649 \times 10^{-19} \text{ C}$
h	Planck's constant $6.62606896 \times 10^{-34} \text{ Js}$
ε_0	$8.85418782 \times 10^{-12} \text{ Fm}^{-1}$

or more. For comparison purposes, values that are originally presented in cm^{-1} are converted to eV with the conversion factor k in Table 1. Results are presented up to atomic number 20 for the following two reasons. Firstly, uncertainties of the ionization energies of those elements with atomic number 21 or more (for an isoelectronic sequence) are usually much higher than the differences between the calculated values produced by our expression and literature values for elements with atomic number below 21. Secondly, our results are compared with ionization energies computed by Garcia and Mack [5] and Midtdal and Aashamar [6] who presented their results up to atomic number 20.

3. Contributions to the Electron Energy

The kinetic energy of an electron in an isolated atom or atomic ion is not simply $(1/2)m_0v^2$ because it is moving at high speed. When there is more than one electron in the system, it is logical to assume that the attractive energy between the nucleus and remaining electron(s) changes because of the change in screening experienced by the remaining electron(s) before and after ionization. The energy released by the electron relaxation or transition needs to be taken into account as well as the Lamb shift correction when calculating the ionization energy. There may be residual electron interactions because of the finite size of the electron. Hence, we assume that the ionization energy of an electron

can be considered to contain the following components in a multielectron system:

$$E_i = \frac{1}{n^2} \mu (J_k - J_l - J_t) \pm \mu E_r = E_k - E_l - E_t \pm \mu E_r, \quad (1)$$

where E_i is the ionization energy, J_k is the kinetic energy term, J_l is the Lamb shift term, J_t is the relaxation/transition energy term, and E_r represents residual electron interaction energy term. n is the principal quantum number and μ is the reduced mass [18] (because the nucleus and electron being ionized, both revolve around the centre of mass). E_k, E_l , and E_t represent J_k, J_l, J_t multiplied by $1/n^2$, respectively, because ionization occurs in energy level n , where n is the principal quantum number. Values of ionization energy calculated by our expression are converted to eV by dividing them with the elementary electron charge (given in Table 1).

4. Kinetic Energy and the Relativistic Correction

The maximum velocity of the electron moving in a Bohr orbit [19] can be calculated from the relationship:

$$\frac{m_0 v_0^2}{a_0} = \frac{q_1 q_2}{(4\pi\epsilon_0 a_0^2)}, \quad (2)$$

where m_0 is the electron rest mass, v_0 is the velocity of the electron, $q_1 q_2$ stand for the charges of the electron and nucleus, ϵ_0 is the permittivity of a vacuum, and a_0 , the Bohr radius, is $\epsilon_0 h^2 / \pi m_e c^2$. The velocity v_0 of the electron in the hydrogen atom can be calculated from (2) and is equal to 2.18769125×10^6 m/sec. The velocity v of the electron in successive atoms of the one-electron series increase by Z times, where Z is the atomic/proton number or $v = v_0 Z$. When there is more than one electron in the system, the velocity of the electron increases by $(Z - S)$, where S is the screening constant for that electron. A common interpretation of relativity theory [20] shows the total energy of a particle of mass m_0 and velocity v is

$$E = m_0 c^2 + \frac{1}{2} m_0 v^2 + \frac{(3/8) m_0 v^4}{c^2} + \frac{(5/16) m_0 v^6}{c^4} + \dots \quad (3)$$

and the kinetic energy of the particle is then

$$E_k = \frac{1}{2} m_0 v^2 + \frac{(3/8) m_0 v^4}{c^2} + \frac{(5/16) m_0 v^6}{c^4} + \dots \quad (4)$$

In reality, only the first three terms (in (4)) are significant as shown in the expression, and all other terms are minute and can be ignored. In an equilibrium situation, the energy of the electron is exactly half potential and half kinetic. Assuming that an electron is ionized in an equilibrium condition, only half the relativistic correction should be included, that is, the relativistic correction for a one-electron atom is then

$$0.5 \left(\frac{(3/8) m_0 v^4}{c^2} + \frac{(5/16) m_0 v^6}{c^4} \right). \quad (5)$$

For a hydrogen-like ion, there is no relaxation energy and no residual electron interactions, and the ionization energy is then represented by

$$E = \mu \left(\frac{1}{2} m_0 v^2 + 0.5 \left(\frac{(3/8) m_0 v^4}{c^2} + \frac{(5/16) m_0 v^6}{c^4} \right) - E_l \right). \quad (6)$$

Columns 2, 3, 5, and 6 of Table 2 list the nonrelativistic kinetic energy, the relativistic correction calculated by (5), the Lamb shift, and the ionization energy as calculated by (6), respectively. However, as shown below, values calculated by (6) for one-electron atoms are too large when compared to generally accepted values.

We consider that, as theory of relativity points out, the mass m of a moving particle is given by the expression $m_0 / (\sqrt{1 - v^2/c^2})$, where m_0 is the rest mass of particle. Expansion of this expression gives

$$m = m_0 \left(1 + \frac{(1/2) v^2}{c^2} + \frac{(3/8) v^4}{c^4} + \frac{(5/16) v^6}{c^6} + \dots \right). \quad (7)$$

Therefore, it follows that $(1/2) m v^2 = (1/2) m_0 v^2 (1 + (1/2) v^2/c^2 + (3/8) v^4/c^4 + (5/16) v^6/c^6 + \dots)$.

This expression for total kinetic energy can be simplified to:

$$\frac{1}{2} m_0 v^2 + \frac{(1/4) m_0 v^4}{c^2} + \frac{(3/16) m_0 v^6}{c^4} + \dots, \quad (8)$$

and the relativistic correction for a one electron atom at the equilibrium position is then

$$0.5 \left(\frac{(1/4) m_0 v^4}{c^2} + \frac{(3/16) m_0 v^6}{c^4} \right). \quad (9)$$

The ionization energy of a one-electron atom is then

$$I = \mu \left(\frac{1}{2} m_0 v^2 + 0.5 \left(\frac{(1/4) m_0 v^4}{c^2} + \frac{(3/16) m_0 v^6}{c^4} \right) - E_l \right). \quad (10)$$

Columns 4 and 7 of Table 2 list the relativistic corrections calculated by (9) and the ionization calculated by (10), respectively. As described below, when expression (9) is used, the ionization energies calculated have excellent agreement with values calculated by complex computer routines and other generally accepted literature values.

5. The Lamb Shift

The Lamb Shift is usually considered as a quantum electrodynamic effect (see e.g., Garcia and Mack [5] or Johnson and Soff [7]) and is computed by complex formulas.

We have made a number of assumptions (without theoretical justification) that the Lamb shift is a secondary relativistic effect. We assume that the Lamb shift is caused by a combination of effects related to mass and size and the whole

TABLE 2: Kinetic energy with two different relativistic and Lamb shift corrections for ionization energies of one-electron atomic ions (eV).

Z	(2) $\mu(1/2)m_0v^2$	(3) Corr (4)	(4) Corr (7)	(5) E_1	(6) I_1 (5)	(7) I_1 (9)
1	13.5983	0.0003	0.0002	0.0000	13.5985	13.5984
2	54.4153	0.0043	0.0029	0.0005	54.4192	54.4177
3	122.4416	0.0220	0.0147	0.0022	122.4615	122.4541
4	217.6778	0.0696	0.0464	0.0060	217.7414	217.7182
5	340.1253	0.1700	0.1133	0.0131	340.2823	340.2256
6	489.7825	0.3527	0.2351	0.0241	490.1111	489.9935
7	666.6528	0.6537	0.4357	0.0415	667.2651	667.0470
8	870.7344	1.1160	0.7438	0.0666	871.7838	871.4416
9	1102.0292	1.7890	1.1922	0.1028	1103.7154	1103.1187
10	1360.5319	2.7289	1.8185	0.1465	1363.1143	1362.2039
11	1646.2494	3.9992	2.6647	0.2082	1650.0404	1648.7060
12	1959.1748	5.6698	3.7774	0.2789	1964.5657	1962.6733
13	2299.3152	7.8179	5.2081	0.3748	2306.7584	2304.1485
14	2666.6634	10.5280	7.0126	0.4809	2676.7105	2673.1951
15	3061.2265	13.8917	9.2520	0.6204	3074.4978	3069.8581
16	3482.9974	18.0078	11.9917	0.7708	3500.2345	3494.2184
17	3931.9834	22.9829	15.3026	0.9642	3954.0021	3946.3218
18	4408.1838	28.9312	19.2601	1.2104	4435.9046	4426.2335
19	4911.5858	35.9744	23.9451	1.4269	4946.1332	4934.1039
20	5442.2023	44.2423	29.4434	1.6957	5484.7489	5469.9500

system in motion. The energy reduction is approximated to the following expression:

$$E_l = \frac{m_e}{(m_e + m_p)} \times \left[\left(\frac{\alpha}{2^{0.667}} \right) \left(\left(\frac{1}{2} \right) m_0 v_0^2 \right) (Z - S)^{3.2} A^{1/3} \right], \quad (11)$$

where m_e is the electron mass, m_p is the proton mass, where the factor for the reduced mass correction for hydrogen is $m_e/(m_e + m_p)$. α is the fine structure constant and $(\alpha/2^{0.667})$ is a crude approximation of the square root of the ratio of nuclear to atomic size for hydrogen. A is the mass number of the atom. S is the screening constant and in a one-electron system S is zero. The size of the nucleus increases [21] roughly in proportion to $A^{1/3}$. As shown in Table 3, the Lamb shift values calculated using this simple equation agree well with those computed by Johnson and Soff [7] for the one-electron system. For the two-electron system, the values calculated by (11) are higher than those computed by Midtdal and Aashamar [6], but they compare well with those computed by Drake [8], which are more recent and probably more accurate.

6. Electron Relaxation Energy

After an electron is ionized, one or more of the remaining electron(s) is/are attracted more closely to the nucleus. The attractive energy between the nucleus and remaining electron(s) changes because of the change in screening experienced by the remaining electron(s) before and after

ionization. This relaxation or transition energy is proportional to

$$\frac{n^2}{4} \times \left[\left(\frac{1}{2} \right) m_0 (v_0 (Z - S_1))^2 - \left(\frac{1}{2} \right) m_0 (v_0 (Z - S_2))^2 \right], \quad (12)$$

where S_1 is the screening constant for remaining electron(s) after ionization and S_2 is the screening constant for the remaining electron(s) before ionization.

In the helium system, there are two electrons and both occupy the 1s orbital. Since each electron occupies half of the space and each is repelled by only one other electron (here we have assumed that the two electrons act as in a two-particle problem and are equivalent), the screening constant is a half (0.5). After ionization, there is only one electron in the system and so there is zero screening.

In the lithium series, the electron that is ionized occupies a higher (2s) orbital and is shielded by two 1s electrons, and the screening increases by 1 to 1.5. The extra screening experienced by the two inner electrons in the 1s orbital increases to 0.625, which is an increase by 1/8 or 0.125 rather than 0.5 because the third electron occupies a different orbital and in a different electron shell (i.e., 0.5 of 0.5 of 0.5). After ionization, only two electrons are left in the system and the screening reduces to just 0.5.

In the beryllium series, the electron that is ionized occupies the 2s orbital. Since there are four electrons and each moving in an elliptical orbit, each may at any time interact differently with the other three electrons. We suppose that the screening of the fourth electron increases by a half to 2 and the other electron in the 2s orbital experiences a

TABLE 3: Comparison of Lamb shifts for one, and two-electron atomic ions (eV).

Z	(2) One electron (this work)	(3) One electron (Johnson and Soff)	(4) Two electron (this work)	(5) Two electron (Drake)	(6) Two electron (Midtdal et al.)
1	0.00003	0.00003			
2	0.0005	0.0004	0.0002	0.0002	0.0002
3	0.0022	0.0020	0.0012	0.0011	0.0010
4	0.0060	0.0056	0.0039	0.0037	0.0034
5	0.0131	0.0126	0.0093	0.0091	0.0081
6	0.0241	0.0243	0.0182	0.0186	0.0164
7	0.0415	0.0422	0.0328	0.0336	0.0292
8	0.0666	0.0678	0.0541	0.0557	0.0475
9	0.1208	0.1028	0.0856	0.0864	0.0724
10	0.1465	0.1489	0.1243	0.1275	0.1047
11	0.2082	0.2079	0.1793	0.1806	0.1453
12	0.2789	0.2817	0.2434	0.2476	0.1948
13	0.3748	0.3720	0.3305	0.3303	0.2538
14	0.4809	0.4808	0.4280	0.4306	0.3226
15	0.6204	0.6101	0.5565	0.5504	0.4013
16	0.7708	0.7620	0.6962	0.6916	0.4900
17	0.9642	0.9383	0.8762	0.8562	0.5883
18	1.2104	1.1414	1.1058	1.0461	0.6957
19	1.4269	1.3724	1.3099	1.2634	0.8116
20	1.6957	1.6346	1.5634	1.5101	0.9348

TABLE 4: Screening constants.

Isoelectronic series	S	S ₁	S ₂
Helium series	0.5	0.0	0.5
Lithium series	1.5	0.5	0.625
Beryllium series	2.0	1.5	1.75
Boron series	3.0	2.0	2.25

screening of between 1.5 and 2 and is 1.75. After ionization of the fourth electron, the screening experienced by the third electron drops back to 1.5.

For the boron system, the outermost electron occupies a new orbital and the screening increases by 1 to 3. The screening of the fourth electron increases by 0.25 to 2.25 and after ionization the screening reduces back to 2. There is no reason to expect screening constants to be complicated numbers, and the screening constants used in the calculations are listed in Table 4.

7. Residual Electron Interaction

The reduced mass calculation implicitly assumes that the electron and nucleus are point charges, but the nucleus and the electron have a finite size [22]. We assume that when there is more than one electron in the atom/ion, the finite size of the electron generates two opposite and competing kinds of residual electron-electron interactions. The first type

is residual electron-electron repulsion because the electrons are not point charges (have a finite size) and are slightly closer to each other. This increases the electron-electron repulsion and reduces the energy required to ionize the electron. However, this reduction diminishes very rapidly with increasing number of protons as the electrons become much more tightly bound to the nucleus.

This residual electron-electron repulsion is directly proportional to the number of electron-electron interactions and an inverse function of proton-electron interactions. The number of electron-electron interactions Q_1 , before ionization, is 1, 3, and 6 when there are two, three, or four electrons and so on. The reduction in energy resulting from this interaction is approximated to

$$E_{r1} = \left(\frac{1}{2}m_0v_0^2\right)Q_1\sqrt{\frac{(r_e/r_B)}{(Z-(I-1))!}} \quad (13)$$

r_e , the electron radius, is $e^2/4\pi\epsilon_0m_e c^2$, r_B is the Bohr radius ($\epsilon_0 h^2/\pi m_e c^2$), and I is the number of electrons after ionization.

We assume that the second type of residual interaction, which is opposite to the first type and a competing type of electron-electron interaction, occurs when there are three or more electrons in the system before ionization. In a three-electron system, two electrons occupy the 1s orbital and one occupies the 2s orbital. The finite size of the two electrons causes them to repel each other slightly more and tend to

TABLE 5: Comparison of the ionization energies of one-electron atomic ions (eV).

Z	(2) This paper	(3) Johnson and Soff	(4) Garcia and Mack	(5) CRC	(6) Diff %
1	13.5984	13.5984	13.5984	13.5984	0.0001
2	54.4177	54.4178	54.4178	54.4178	0.0001
3	122.4541	122.4543	122.4543	122.4543	0.0001
4	217.7182	217.7185	217.7185	217.7187	0.0002
5	340.2256	340.2260	340.2259	340.2258	0.0001
6	489.9935	489.9931	489.9931	489.9933	0.0000
7	667.0470	667.0460	667.0459	667.0460	-0.0001
8	871.4116	871.4098	871.4095	871.4101	-0.0002
9	1103.1187	1103.1173	1103.1170	1103.1176	-0.0001
10	1362.2039	1362.1990	1362.1987	1362.1995	-0.0003
11	1648.7060	1648.7019	1648.7015	1648.7020	-0.0002
12	1962.6733	1962.6634	1962.6629	1962.6650	-0.0004
13	2304.1485	2304.1397	2304.1391	2304.1410	-0.0003
14	2673.1951	2673.1772	2673.1768	2673.1820	-0.0005
15	3069.8581	3069.8411	3069.8411	3069.8420	-0.0005
16	3494.2184	3494.1874	3494.1884	3494.1892	-0.0008
17	3946.3218	3946.2904	3946.2931	3946.2960	-0.0007
18	4426.2335	4426.2222	4426.2273	4426.2296	-0.0001
19	4934.1039	4934.0476	4934.0574	4934.0460	-0.0012
20	5469.9500	5469.8608	5469.8776	5469.8640	-0.0016

TABLE 6: Components of the ionization energies of two-electron atomic ions (eV).

Z	(2) E_k	(3) E_l	(4) E_t	(5) E_r	(6) I_2
1	3.3996	0.0000	2.5497	0.0993	0.7507
2	30.6094	0.0002	5.9517	0.0702	24.5874
3	85.0353	0.0012	9.3532	0.0405	75.6404
4	166.6840	0.0039	12.7546	0.0203	153.9053
5	275.5684	0.0093	16.1560	0.0091	259.3941
6	411.7027	0.0182	19.5573	0.0037	392.1235
7	575.1094	0.0328	22.9587	0.0014	552.1166
8	765.8109	0.0541	26.3601	0.0005	739.3961
9	983.8362	0.0856	29.7616	0.0002	953.9889
10	1229.2125	0.1243	33.1630	0.0001	1195.9253
11	1501.9819	0.1793	36.5644	0.0000	1465.2381
12	1802.1778	0.2434	39.9658	0.0000	1761.9686
13	2129.8508	0.3305	43.3673	0.0000	2086.1531
14	2485.0427	0.4280	46.7686	0.0000	2437.8461
15	2867.8127	0.5565	50.1701	0.0000	2817.0861
16	3278.2110	0.6962	53.5715	0.0000	3223.9433
17	3716.3056	0.8762	56.9729	0.0000	3658.4565
18	4182.1621	1.1058	60.3744	0.0000	4120.6818
19	4675.8384	1.3099	63.7758	0.0000	4610.7527
20	5197.4218	1.5634	67.1772	0.0000	5128.6812

TABLE 7: Comparison of ionization energies of two-electron atomic ions (eV).

Z	(2) This work	(3) Drake	(4) Midtdal et al.	(5) CRC	(6) Diff %
1					
2	24.5874	24.5874	24.5874	24.5874	0.0001
3	75.6404	75.6401	75.6402	75.6400	-0.0005
4	153.9053	153.8962	153.8965	153.8966	-0.0057
5	259.3941	259.3743	259.3753	259.3752	-0.0073
6	392.1235	392.0905	392.0926	392.0870	-0.0093
7	552.1166	552.0673	552.0715	552.0718	-0.0081
8	739.3961	739.3267	739.3344	739.2900	-0.0144
9	953.9889	953.8979	953.9107	953.9112	-0.0081
10	1195.9253	1195.8077	1195.8278	1195.8286	-0.0081
11	1465.2381	1465.0983	1465.1286	1465.1210	-0.0080
12	1761.9686	1761.8038	1761.8475	1761.8050	-0.0093
13	2086.1531	2085.9754	2086.0365	2085.9800	-0.0083
14	2437.8461	2437.6558	2437.7388	2437.6300	-0.0089
15	2817.0861	2816.9054	2817.0154	2816.9100	-0.0063
16	3223.9433	3223.7762	3223.9187	3223.7800	-0.0051
17	3658.4565	3658.3380	3658.5187	3658.5210	0.0018
18	4120.6818	4120.6582	4120.8833	4120.8857	0.0049
19	4610.7527	4610.7978	4611.0728	4610.8000	0.0010
20	5128.6812	5128.8458	5129.1766	5128.8000	0.0023

move further from each other. This asymmetric distribution of electrons causes the 2s electron being screened slightly less from each of the 1s electrons. The result is that it is attracted to the nucleus a bit more than expected and hence increases amount of energy required to remove it from the atom/ion. The small increase in energy is a function of the number of electron-electron interactions, there are because the more electron-electron interactions, the further they are apart and the bigger will be the reduction in screening of the nucleus from the ionizing electron. This effect also increases as the number of protons increases (i.e., attraction between the nucleus and outermost electron(s) increases), and for a system with three or more electrons it is approximately

$$E_{r2} = \frac{1}{n^2} \left(\frac{1}{2} m_0 v_0^2 (Z - S)^2 \right) Q_{II} \sqrt{\frac{(r_e/r_B)}{2^2}}. \quad (14)$$

Q_{II} is the number of electron interactions after ionization and the total residual electron interaction energy change is

$$E_r = - \left(\frac{1}{2} m_0 v_0^2 \right) Q_I \sqrt{\frac{(r_e/r_B)}{(Z - (I - 1))!}} + \frac{1}{n^2} \left(\frac{1}{2} m_0 v_0^2 (Z - S)^2 \right) Q_{II} \sqrt{\frac{(r_e/r_B)}{2^2}}. \quad (15)$$

8. Ionization Energy of One-Electron Atoms

There is only one electron, n is 1, and the expression for calculating the ionization energy is

$$E = \mu \left(\frac{1}{2} m_0 v^2 + 0.5 \left(\frac{(1/4) m_0 v^4}{c^2} + \frac{(3/16) m_0 v^6}{c^4} \right) - \frac{m_e}{(m_e + m_p)} \times \left[\left(\frac{\alpha}{2^{0.667}} \right) \left(\left(\frac{1}{2} \right) m_0 v_0^2 \right) (Z)^{3.2} A^{1/3} \right] \right). \quad (16)$$

Column 2 of Table 2 shows the nonrelativistic kinetic energy $\mu((1/2)m_0v^2)$, for the purpose of comparison, column 3 shows the relativistic correction calculated by (5), column 4 shows the relativistic correction calculated by (9), column 5 shows the Lamb shift correction, column 6 shows the ionization energy calculated by expression (6), and column 7 shows the ionization energy calculated by expression (16) (which is equivalent to (10)).

The one-electron ionization energies calculated by (16) are shown in column 2 of Table 5. Ionization energies computed by Johnson and Soff [7] and Garcia and Mack [5] and values published in the *CRC Handbook* are shown in columns 3, 4, and 5, respectively. It is very clear that (9) is a much more appropriate expression than (5) to calculate the relativistic correction. Ionization energies calculated by expression (16) show exceptional agreement with values computed by complex formulas and with the latest accepted values. Compared to ionization energies published in the *CRC Handbook*, values calculated by (16) agree to 99.999% or differ by less than 0.001% (or <10 parts per million) in 18 out

of the 20 values as shown in column 6 of Table 5, the biggest absolute difference is 0.0860 eV from a calculated value of 5469.95 eV.

9. Ionization Energy of Two-Electron Atoms

The ionization energy of a two-electron system is $(E_k - E_l - E_t \pm E_r)$, where:

$$E_l = \mu \left(\frac{m_e}{(m_e + m_p)} \times \left[\left(\frac{\alpha}{2^{2/3}} \right) \left(\left(\frac{1}{2} \right) m_0 v_0^2 \right) (Z - 0.5)^{3.2} A^{1/3} \right] \right)$$

$$E_t = 0.25\mu \left(\frac{1}{2} m_0 (v_0(Z))^2 - \frac{1}{2} m_0 (v_0(Z - 0.5))^2 \right),$$

$$E_r = \left(- \left(\frac{1}{2} m_0 v_0^2 \right) Q_I \sqrt{\frac{(r_e/r_B)}{(Z)!}} \right).$$
(17)

Since, for simplicity, we have not applied a relativistic correction to E_t , we have made a crude approximation of reducing the relativistic correction in E_k by 5% to 0.45 (rather than 0.5) and where v is $(v_0(Z - 0.5))$, so it is

$$E_k = \mu \left(\frac{1}{2} m_0 v^2 + 0.45 \left(\frac{(1/4) m_0 v^4}{c^2} + \frac{(3/16) m_0 v^6}{c^4} \right) \right).$$
(18)

Columns 2, 3, 4, 5, and 6 of Table 6 show E_k, E_l, E_t, E_r separately and the calculated ionization energies of two-electron atoms, respectively. Table 7 is a comparison of the ionization energies calculated in this paper and those computed by Drake [8], Midtdal, and Aashamar [6] and values published in the *CRC Handbook*. As shown in the table, there is very good agreement with the other computed results. When compared to values published in the *CRC Handbook*, all values except one (atomic number 8) agree to better than 99.99% (or difference of less than 0.01% as shown in column 6), and the largest absolute difference is 0.2161 eV from a calculated value of 2437.8641 eV.

10. Ionization Energy of Three, Four, and Five Electron Atoms

The ionization energy of a three- to-five electron system is

$$(E_k - E_l - E_t \pm E_r),$$
(19)

where

$$E_k = 0.25\mu \left(\frac{1}{2} m_0 v^2 + 0.5 \left(\frac{(1/4) m_0 v^4}{c^2} + \frac{(3/16) m_0 v^6}{c^4} \right) \right),$$

$$E_l = 0.25\mu \left(\frac{m_e}{m_e + m_p} \left(\frac{\alpha}{2^{2/3}} \right) \left(\frac{1}{2} m_0 v_0^2 \right) (Z - S)^{3.2} A^{1/3} \right),$$

$$E_t = \mu \left(\frac{1}{2} m_0 (v_0(Z - S_1))^2 - \frac{1}{2} m_0 (v_0(Z - S_2))^2 \right),$$

$$E_r = \left(- \left(\frac{1}{2} m_0 v_0^2 \right) Q_I \sqrt{\frac{(r_e/r_B)}{(Z - (I - 1))!}} \right. \\ \left. + \frac{1}{n^2} \left(\frac{1}{2} m_0 v_0^2 (Z - S)^2 \right) Q_{II} \sqrt{\frac{(r_e/r_B)}{2^2}} \right).$$
(20)

The screening constants used are shown in Table 4, and Q_I , the number of electron-electron interactions before ionization, is 3, 6, and 10, respectively, for three-, four-, and five-electron systems. Columns 2, 3, and 4 of Table 8 list the calculated ionization energies, literature values, and the percentage differences of three-electron isoelectronic systems. The calculated ionization energies of four- and five-electron isoelectronic sequences are shown in columns 2 and 5; the corresponding literature values in columns 3 and 6 and their differences are shown in columns 4 and 7, respectively, in Table 9. The agreement with literature values is 99% or better in all cases (99.9% or better for a third of all values).

11. First Electron Affinities

First electron affinities calculated by our expression and recommended values are listed in Table 10. Our calculated value of the first electron affinity of helium differs from the generally accepted value by less than 0.5% which is an excellent agreement. There is also fairly good agreement between our other calculated values and recommended values.

12. Discussion

Johnson and Soff [7] used an approximate empirical formula as part of the set of expressions to calculate the finite nuclear size correction. Drake [8] reported that uncertainties of calculated Lamb shifts in some cases can be up to 10%. Our expression (19) is fairly simple and can be calculated quite easily as compared to the complex equations, which required computer routines to compute.

We have only used the size of the (one-electron) hydrogen atom in the Lamb shift equation for one to five electrons. It is fairly remarkable that in the majority of cases agreement between our calculated values and the values computed by Johnson and Soff [7] and Drake [8] is 90% or better. The size of hydride ion (negative hydrogen ion) is different from the hydrogen atom, and obviously the sizes of the negative helium, lithium, and beryllium ions are as well. We have not applied any corrections to negative ions for the two- to five-electron systems, because the size of the hydride ion

TABLE 8: Ionization energies of three electron atom/atomic ions (eV).

Z	(2) This work	(3) CRC	(4) Diff %	(5) 1	(6) 0.999455717
2				2	0.999862962
3	5.3975	5.3917	-0.1075	3	0.999921837
4	18.2921	18.2111	-0.4445	4	0.999939160
5	37.9891	37.9306	-0.1540	5	0.999950207
6	64.4924	64.4939	0.0024	6	0.999954325
7	97.8161	97.8902	0.0757	7	0.999960870
8	137.9734	138.1197	0.1059	8	0.999965753
9	184.9757	185.1860	0.1136	9	0.999971178
10	238.8325	239.0989	0.1114	10	0.999972620
11	299.5532	299.8640	0.1036	11	0.999972620
12	367.1481	367.5000	0.0957	12	0.999977196
13	441.6271	442.0000	0.0844	13	0.999979768
14	523.0034	523.4200	0.0796	14	0.999980467
15	611.2877	611.7400	0.0739	15	0.999982367
16	706.4970	707.0100	0.0726	16	0.999982925
17	808.6426	809.4000	0.0936	17	0.999984398
18	917.7394	918.0300	0.0317	18	0.999986358
19	1033.8184	1033.4000	-0.0405	19	0.999986014
20	1156.8864	1157.8000	0.0789	20	0.999986372

TABLE 9: Ionization energies of four- and five-electron atom/atomic ions (eV).

Z	(2) This work (four electrons)	(3) CRC	(4) Diff %	(5) This work (five electrons)	(6) CRC	(7) Diff %
3						
4	9.2942	9.3227	0.3058			
5	24.9666	25.1548	0.7482	8.3121	8.2980	-0.1695
6	47.4641	47.8878	0.8849	24.2893	24.3833	0.3855
7	76.7925	77.4735	0.8791	47.1286	47.4492	0.6758
8	112.9756	113.8990	0.8107	76.8369	77.4135	0.7449
9	156.0359	157.1651	0.7185	113.4510	114.2428	0.6931
10	205.9899	207.2759	0.6204	157.0043	157.9300	0.5861
11	262.8503	264.2500	0.5297	207.5202	208.5000	0.4699
12	326.6286	328.0600	0.4363	265.0149	265.9600	0.3553
13	397.3348	398.7500	0.3549	329.5004	330.1300	0.1907
14	474.9817	476.3600	0.2893	400.9890	401.3700	0.0949
15	559.5797	560.8000	0.2176	479.4916	479.4600	-0.0065
16	651.1450	652.2000	0.1618	565.0208	564.4400	-0.1029
17	749.6888	749.7600	0.0095	657.5892	656.7100	-0.1339
18	855.2253	854.7700	-0.0533	757.2096	755.7400	-0.1945
19	967.7837	968.0000	0.0223	863.9076	861.1000	-0.3261
20	1087.3713	1087.0000	-0.0342	977.6915	974.0000	-0.3790

[23] is contentious and there is no accurate measurement of the size of the other negative ions. There are no reliable Lamb shift calculations for three- to five-electron systems, so a comparison with our results is not possible. Even though our assumptions and approximations are simple and straight forward, our results show excellent agreement with ionization energies published in the *CRC Handbook* as well as with

Johnson and Soff [7] and Garcia and Mack [5] for one-electron and Midtdal and Aashamar [6] and Drake [8] for two-electron ions.

We have found that, as shown by up-to-date publications [24], Moore is still quoted as a major source of experimental information. For some isoelectronic sequences, only the first five or six members are reliably measured and there may

TABLE 10: First electron affinities (eV).

(1) Element	(2) Hydrogen	(3) Helium	(4) Lithium	(5) Beryllium
Calculated	0.7507	-0.6667	0.5045	-0.4824
Recommended*	0.7542	<0	0.6180	<0

*Recommended values are from [16].

be many members somewhere along the sequence without any reliably measured ionization energies, and in these cases values are obtained by semiempirical interpolation or extrapolation formulas [25]. Recent papers [26, 27] also quoted ionization energies of some members of many isoelectronic sequences estimated by Lotz [28] in 1967. We have recently demonstrated [29, 30] that ionization energies and ionization pathways of some elements or sequences are fairly complicated. Hence, there is scope to update the measurements and calculations of ionization energies of isoelectronic sequences.

Although some of our hypotheses may be controversial and there is no proof that our interpretation of the relativistic correction for mass change is correct, there is no doubt that they form part of expressions that produce very precise values of the ionization energies of one- to five-electron isoelectronic sequences. This is good evidence that both expression (19) or our alternative potential energy approach can be developed to predict, with good accuracy, ionization energies of multi-electron atomic ions that have not been reliably measured.

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