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Atomic Ions Ionization Energy Values Assessment: Interpolative Empirical Analysis

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Abstract

In this paper, a novel ionization energy, IE, set theory-based organizational structure is suggested: (i) iso-protonic sets, ${}_{Z}IE$; (ii) iso-electronic sets, IE_s; and (iii) iso-ionic sets, IE^{i+}. A computational algorithm is proposed which was demonstrated on twenty-five iso-electronic IE_s-sets plotted vs. the nuclear charge, Z. The algorithm allows for: (i) the interpolative assessment of 162 new (not measured) IE values, with their uncertainties estimated by the Lagrange method, for ions from ${}_{30}$Zn to ${}_{41}$Nb; and (ii) effective atomic nuclear charge assessment. It is shown that the IE effective atomic nuclear charge assessment is strongly correlated with the Slater's effective charge and Pauling electronegativity scale.

Keywords: atoms; atomic ions; ionization energies; set theory

1. Introduction

Measuring, calculating, and utilizing the ionization energy values of atoms and atomic ions are an integral part of physical sciences, as outlined in the recent review by P. Lang [1]. The majority of the original atomic spectroscopic experimental work was done in the mid-20th century [2–4].

Today, 118 chemical elements are known, the first 94 (up to plutonium) of which occur naturally on Earth [5]. Each chemical element, with the nuclear charge (atomic number) Z, can be thought to represent a set consisting of one atom and $(Z-1)$ atomic ions, and with identical nuclei and varied number of electrons. Each member of the set has a well-defined, directly measurable ionization energy—IE. IE is defined as the energy required to extract the outermost electron from the ionic (atomic) shell. Thus, each chemical element can be associated with a set of Z number ionization energies. Thus, the 94 elements occurring naturally on Earth, have a total of 4465 $(94 \times 95/2)$ IE values, which can be organized and categorized by different criteria. The number of IE values of atoms and atomic ions included in the latest, 105th edition (2024) of the CRC Handbook of Chemistry and Physics [6] is 770. Thus, approximately 17% of the IEs have been measured. Currently, all ionization energies are measured up to ${}_{29}$Cu, and all ionization energies up to ion 29+ of two elements: ${}_{36}$Kr and ${}_{42}$Mo.

This study is inspired by the questions: Is there a way for more IE values, and effective nuclear charges [7], to be assessed empirically? Is it feasible to utilize the experimentally measured 770 IEs to estimate values not yet measured, bypassing the complicated quantum electrodynamical "bottom-up" approach in multielectron systems?

This study proposes a set theory-based—IE values—analysis. Set theory is a branch of mathematical logic concerned with the study of sets, which are collections of objects (called elements). The set elements herein are the IE values. Thus, 26 iso-electronic sets are

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considered in this study. The largest set has 29 elements, and the smallest has six elements. The analysis of sets with less than six elements is less reliable and it is not considered herein. Furthermore, we propose systematic, analytical, comparative investigation of robust quadratic correlations of each isoelectronic set, with the nuclear charge Z. The proposed investigation assesses 162 new (not measured) IE values via interpolation, with estimated uncertainties, for 11 chemical elements from $_{30}$Zn to $_{41}$Nb. For 13 chemical elements, IE values of one-electron ions, $\geq$12 keV, are assessed via extrapolation.

In addition, the iso-electronic analysis offers purely energy derived assessment of the effective nuclear charge, ζ, allowing the reliable estimation of the uncertainty up to $_{35}$Br. The proposed IE derived effective nuclear charge values revealed strong linear correlation for the 2nd and 3rd period of the periodic table, with the Slater effective nuclear charge [8] and the Pauling electronegativity scale [9].

2. Proposed Novel Set Theory-Based Ionization Energy (IE) Organization

Traditionally, the IE values are designated by roman numerals called the order of ionization: I, II, III, IV, etc. Where the ionization energy of: an atom is I; a singly ionized atom (1+) ion—II; (2+) ion—III; (3+)—IV, etc. The first ionization energy was measured for all chemical elements up to Z = 108 [10]. Out of the 108 values, the smallest value is 4.07 eV (Z = 87) and the largest value is 24.59 eV (Z = 2). Usually the first ionization energies are presented as a function of the nuclear charge, where the pattern of increasing IE values along the periods can be noticed, with the maximum at the noble gases, followed by a drop at the first group elements [7].

This study proposes the following nomenclature for the ionization of energy values ${}_{Z}IE_{s}^{i+}$. The term suggests an *IE* value for a chemical element with the nuclear charge Z (lower left index), the number of screening electrons, s (lower right index), and the ionic charge i+ (upper right index). For example, the third ionization energy of Na III can be designated by the term: ${}_{11}IE_{8}^{2+}$. Na is a chemical element with $Z = 11$; an electron is removed from an ion with the charge $i = 2+$ and the number of the screening electrons $s = 8$.

This study develops a set theory-based IE values analysis. All IE values from the periodic table can be grouped in one of three types of sets: (i) iso-protonic, ${}_{Z}IE$; (ii) iso-ionic,IE^{i+}; and (iii) iso-electronic, IE_s. The iso-protonic and iso-ionic sets are described in Supplementary Materials S1. This study proceeds by illustrating the utility of the iso-electronic sets, yielding assessment of the unmeasured IE values and the effective atomic nuclear charge value.

The members of the IE_s sets have identical numbers of screening electrons, s. For example, the *IE* value set associated with ions with two screening electrons, $s = 2$, can be presented as:

$$IE_2 = \left\{ {}_{3}IE_{2}^{0}, {}_{4}IE_{2}^{1+}, {}_{4}IE_{2}^{2+}, \ldots, {}_{N}IE_{2}^{(N-2)+} \right\} \quad (1a)$$

A generalized IE_s-set can be written:

$$IE_s = \left\{ {}_{s+1}IE_{s}^{0}, {}_{s+2}IE_{s}^{1+}, \ldots, {}_{s+i+1}IE_{s}^{i+}, \ldots, {}_{N}IE_{s}^{(N-s-1)+} \right\} \quad (1b)$$

The first member of an IE_s-set is the *IE* value associated with an atom $(i = 0)$ with the nuclear charge: $Z = s + 1$, ${}_{s+1}IE_{s}^{0}$. The number of IE_s-sets that can be constructed is equal to the chemical elements in the periodic table, N, and $|IE_s| = N - s$.

This study investigates the correlation of the members of IE_s-sets with the nuclear charge, Z.

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3. Methodology and Outcome for Extrapolative Assessment of 13 New IE Values of Hydrogen-like Ions

First, we consider the IE_s-set of all known IE values of the hydrogen atom and 28 hydrogen-like ions, ${}_ZIE_0^{(Z-1)+}$ [5], up to ${}_{29}IE_0^{28+}$, Cu, which are plotted vs. the nuclear charge Z:

$$IE_0 = \left\{ {}_1IE_0^0, {}_2IE_0^{1+}, {}_3IE_0^{2+}, \ldots, {}_{29}IE_0^{28+} \right\} \tag{1c}$$

The data suggests that the quadratic fit of the experimental values ${}_ZIE_0^{(Z-1)+}$ might be deemed satisfactory up to ${}_9IE_0^{8+}$. The parabolic fitting function is in agreement with Zener [10,11]. At Z = 9, the difference between the experimental value and Equation (2a) $\left({}_9IE_0^{8+} - 13.60Z^2\right)$ is ≈1 eV. Overall, it is noted that the experimental values are consistently larger than the values assessed by Equation (2a), and the difference, $\left({}_ZIE_0^{(Z-1)+} - 13.60Z^2\right)$ increases with Z, reaching 125 eV for Cu, ${}_{29}IE_0^{28+}$. We further investigated the difference vs. Z, plotted in Figure 1a.

$${}_ZIE_0^{(Z-1)+} = 13.60Z^2 \tag{2a}$$

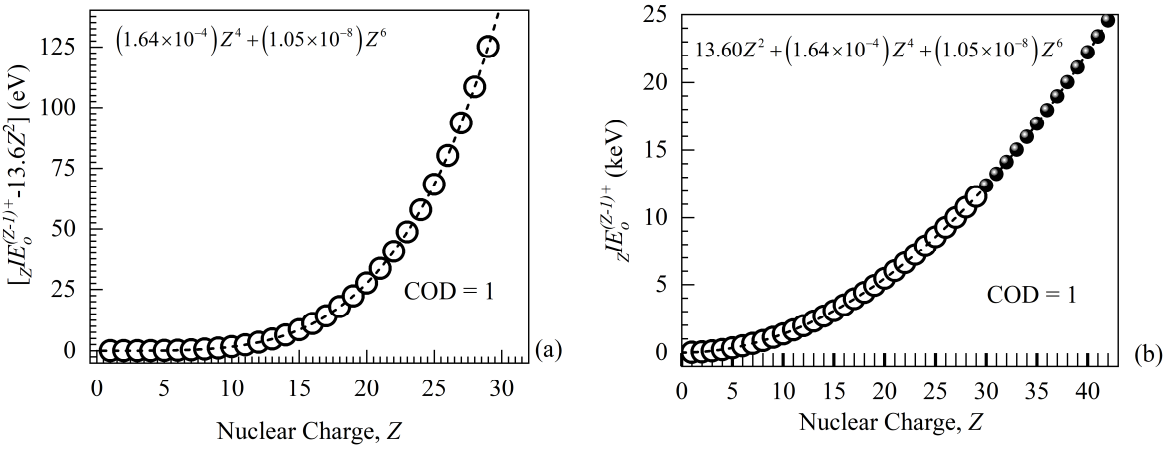


Figure 1. (**a**) The difference between the experimental[5] and Equation (2a) values plotted vs. Z. (**b**) The known (open circles) and the assessed new values (bullet points) of ${}_ZIE_0^{(Z-1)+}$-set plotted vs. Z. The fitting functions and the coefficients of determination COD are listed.

Based on the function of the difference data, Figure 1a, Equation (2b) yields much better accuracy with the experimental data.

$${}_ZIE_0^{(Z-1)+} = 13.60Z^2 + \left(1.64\times10^{-4}\right)Z^4 + \left(1.05\times10^{-8}\right)Z^6 \tag{2b}$$

Most importantly, the fourth and the sixth power terms are in agreement with the relativistic kinetic energy corrections to the hydrogen-like ions [11]. The inclusion of the sixth power allows for better absolute value accuracy, ≈0.7 eV, for the highest experimentally measured value of the hydrogen-like ion, Cu, ${}_{29}IE_0^{28+}$.

Finally, the open circles in Figure 1b summarize all known single-electron ion values, ${}_ZIE_0^{(Z-1)+}$ plotted vs. the nuclear charge, Z fitted with Equation (2b). A robust coefficient of determination, COD = 1 (>14 nines), allows us to assess 13 new values—${}_{30}IE_0^{29+}$ to ${}_{42}IE_0^{41+}$—which are plotted in Figure 1b with black bullet points. The extrapolated, numerical values are listed in Table 1. For further extrapolation of IE values, Z > 42, more expansion coefficients might be needed.

Table 1. Chemical element; nuclear charge, Z; extrapolated, hydrogen-like ions ${}_{Z}IE_{o}^{(Z-1)+}$ values (keV); total of 13 IE values, Equation (2b), with uncertainties ≈ 1 eV.

	Zn	Ga	Ge	As	Se	Br	Kr	Rb	Sr	Y	Zr	Nb	Mo
Z	30	31	32	33	34	35	36	37	38	39	40	41	42
keV	12.388	13.239	14.119	15.029	15.968	16.938	17.937	18.967	20.028	21.119	22.241	23.395	24.580

4. Methodology and Outcome for Interpolative Assessment of 162 New IE Values of Multielectron Ions

In addition to the above-discussed IE_0-set, 462 IE data points, ref [2], grouped in 25 iso-electronic IE_s-sets, Equation (3a), are discussed. There are two important outcomes when analyzing IE_s-sets: (i) unknown IE values can be assessed through interpolation and (ii) atomic effective nuclear charge can be evaluated.

The analysis procedure is illustrated with the two IE_s-sets: (i) two-electron ions (one screening electron, $s = 1$), IE_1, which are plotted as orange symbols in Figure 2:

$$IE_1 = \left\{ {}_2IE_1^0, {}_3IE_1^{1+}, {}_4IE_1^{2+}, \ldots, {}_{29}IE_1^{27+} \right\} \quad (3a)$$

and (ii) 10-electron ions (9 screening electrons, $s = 9$) IE_9, which are plotted as black symbols in Figure 2:

$$IE_9 = \left\{ {}_{10}IE_9^0, {}_{11}IE_9^{1+}, {}_{12}IE_9^{2+}, \ldots, {}_{36}IE_9^{26+} \right\} \quad (3b)$$

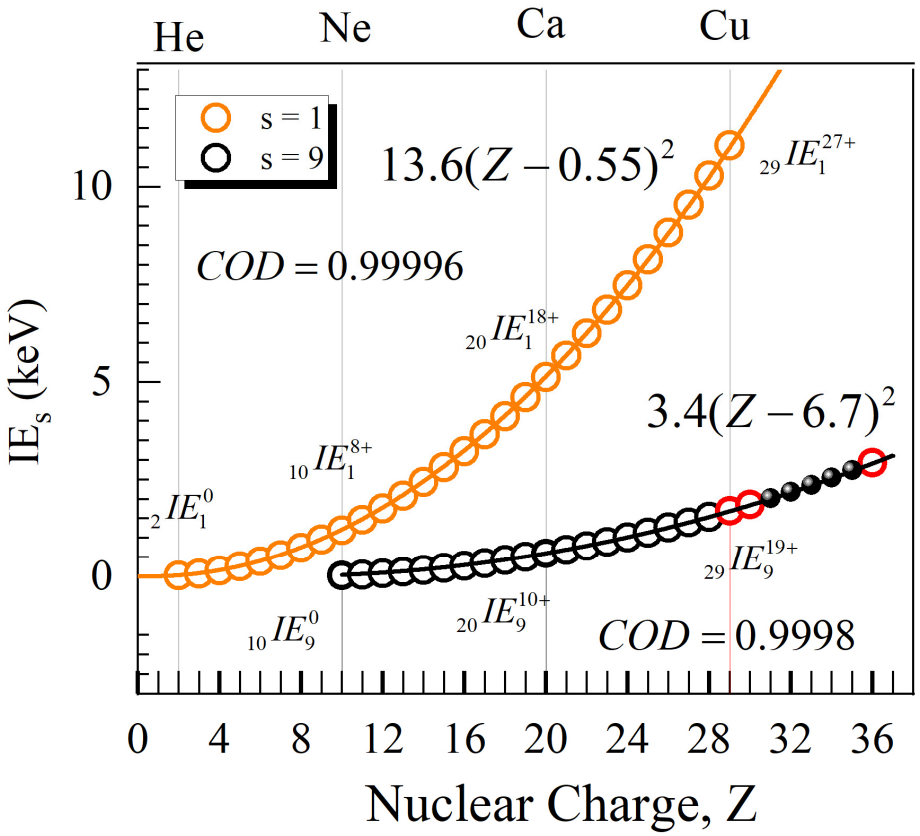


Figure 2. IE values [2] correlated with the nuclear charge, Z for IE_1-set, Equation (3a)—orange open symbols and IE_9-set, Equation (3b)—black/red open symbols. Parabolic fit analytic expression for each series is listed. The atoms, and atomic ions IE notations of He, Ne, Ca, and Cu are listed for clarity.

Each series starts with the ionization energy of a neutral atom, first ionization energy, ${}_2IE_1^0$ (He) and ${}_{10}IE_9^0$ (Ne). The last known ionization energy in this set is the XXVIII ionization energy of Cu-${}_{29}IE_1^{27+}$. All energies listed in the IE_1 set are known (measured). However, there are five unmeasured values in the IE_9-set namely: ${}_{31}IE_9^{21+}$, ${}_{32}IE_9^{22+}$, ${}_{33}IE_9^{23+}$, ${}_{34}IE_9^{24+}$, ${}_{35}IE_9^{25+}$.

The fact that the last value ${}_{36}IE_9^{26+}$ (XXVII ionization energy of Kr) is measured plays an important role in our considerations. This allows for the interpolative assessment of the missing five values.

The set members in Equation (3a,b) are plotted vs. nuclear charge, Z, in Figure 2. Furthermore, the IE_1 and IE_9 sets are fitted with the quadratic form:

$$IE_s = a_s(Z - S_s)^2 \tag{4}$$

where a_s, and S_s are the two fitting parameters. a_s is in eV and S_s represents the screening charge produced by s number of electrons. For fitting the isoelectronic experimental IE values sets, IE_s [5], we used a simple quadratic expression, yielding a strongly satisfactory coefficient of determination value, COD > 0.9993. The author is unaware of an accepted methodology which accounts for the exchange and orbital energies, residual interactions, relativistic kinetic energy, spin–orbit coupling, Darwin term, and other quantum electrodynamic effects of the multielectron isoelectronic series [12]. Thus, further investigation of the physical plausibility of the quadratic form and the expected limit of its validity is outside of the scope of this study. We concur with published studies [12] suggesting a strong case for the implementation of a simple quadratic expression for the purposes of interpolative assessment of IE values neither calculated nor experimentally measured yet. Furthermore, uniform fitting of all 25 IE_s series allows for reliable comparative empirical assessment of the screening charge, S.

The values of the fitting parameters $S_1 = 0.55$, and $S_9 = 6.7$ are listed in Figure 2. The coefficient of determination, COD > 0.999 is included in Figure 2 as well. The COD values strongly support the appropriateness of the fitting Equation (4). Therefore, all members of a specific IE_s-set can be associated with one and the same screening charge. Furthermore, from S_s, a linear transformation is proposed for evaluating the effective nuclear charge ζ of the neutral atoms, vide infra.

This study proceeds with an interpolative assessment of the new IE values. For a more accurate numerical assessment of the new (unmeasured) IE values, three points bracketing the Z range were selected to be interpolated, e.g., the red bold open symbols in s = 9 trace in Figure 2.

For example, a quadratic fit was used for the local, three points bracketing the interpolation area, with the goal of producing a more accurate assessment of non-measured, ionization energies—as can be seen by the five black bullet points in the IE_9-set, Figure 2. Furthermore, the uncertainty of the interpolated values is determined via the Lagrange method [13]. The uncertainty in the last decimal place is presented in parenthesis after the value.

In general, utilizing Equation (4) it is possible to assess, via extrapolation, the ionization energies for atomic ions from the isoelectronic series discussed herein, with $Z \geq 42$. However, assessing the uncertainty might be difficult.

The analysis followed the procedure described above for the investigation 25 isoelectronic series, Figure 3. All isoelectronic series are fitted with parabolas, Equation (4).

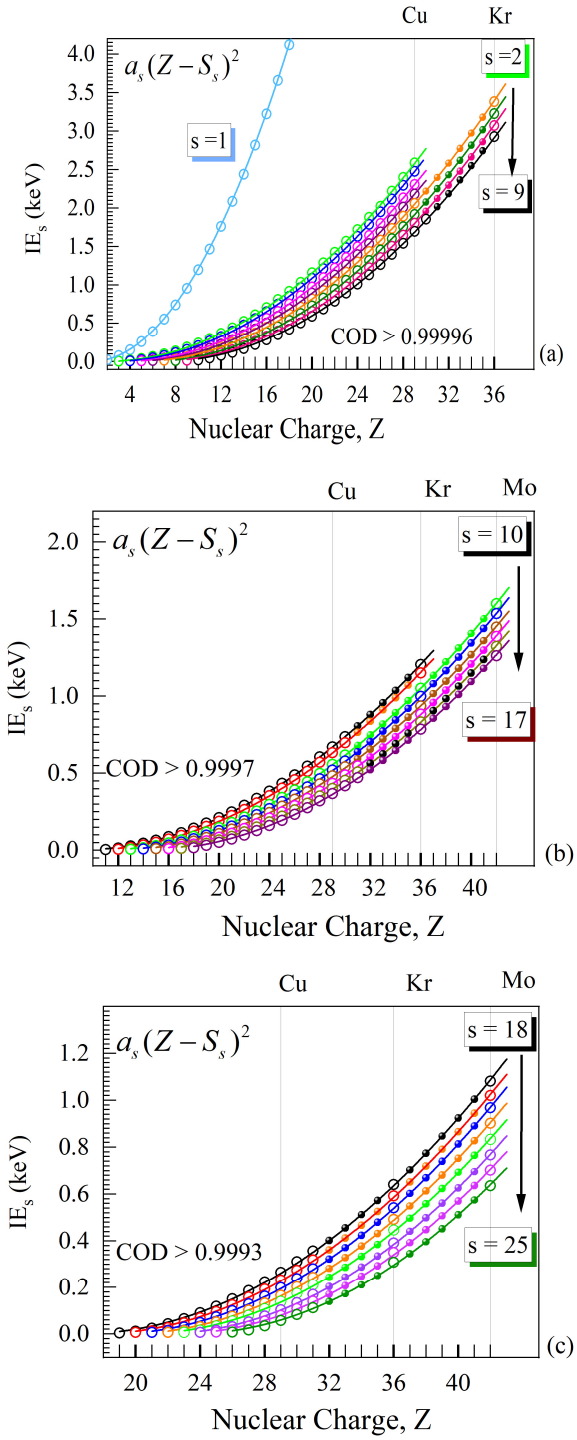


Figure 3. Ionization energies [2], keV, as a function of the nuclear charge, Z, of isoelectronic atomic ions series, s (known values, open circles) with: (**a**) $1 \leq s \leq 9$; (**b**) $10 \leq s \leq 17$; and (**c**) $18 \leq s \leq 25$; quadratic fit lines correspond to each isoelectronic series, the minimum coefficient of determination (COD) is listed; interpolated values are included (bullet points).

The two fitting coefficients in Equation (4), along with their uncertainties, *COD*, and the number of points in each parabolic fit, are listed in Table S1. The high coefficient determination of the fits, $0.9990 \leq COD \leq 0.999997$, allows for assessing the missing 162 IE values of 11 chemical elements—between $_{30}$Zn and $_{41}$Nb. The assessed new IE values are included in Figure 3 as bullet points, in the same color as the measured IE values. The numerical values, in eV, of the interpolated data points are listed in Tables S2–S5

with the uncertainty in parentheses after the last decimal place. The uncertainties of the interpolated values, indicated in Figure 4 are within the size of the bullet points.

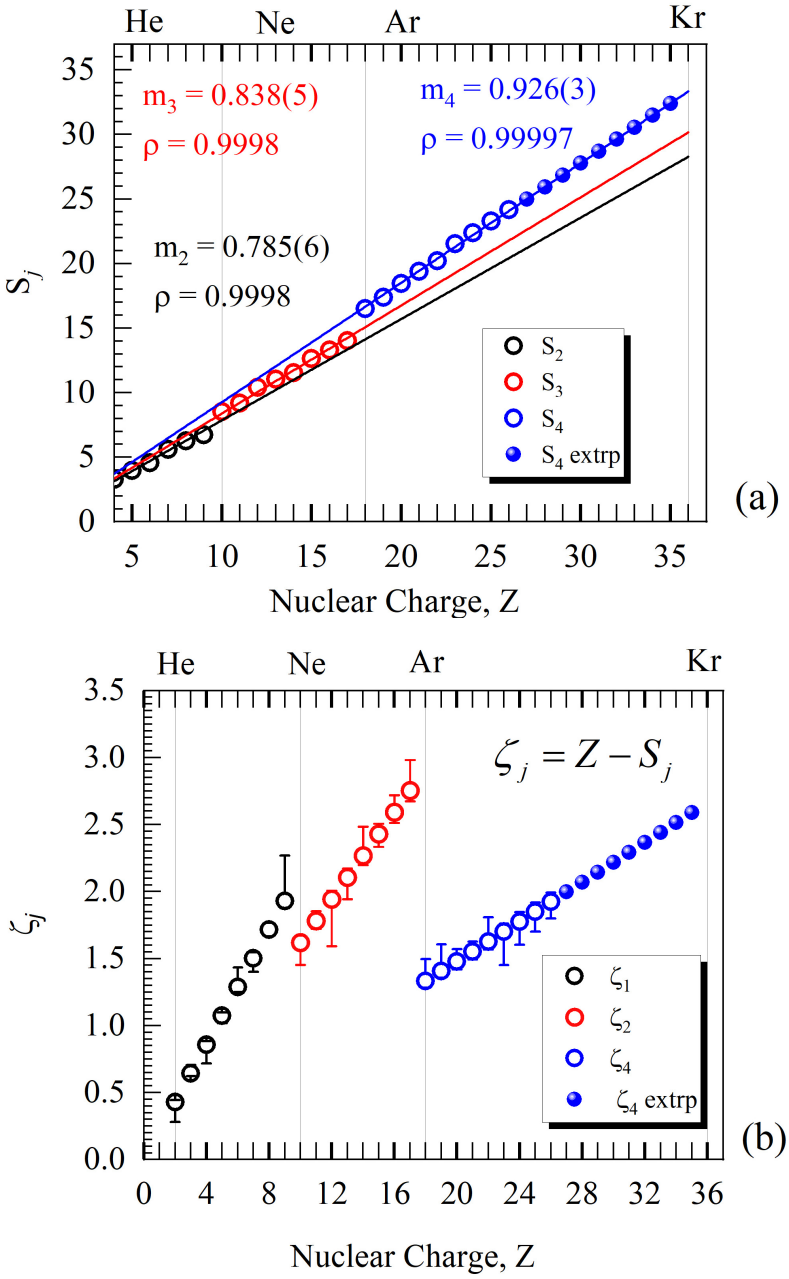


Figure 4. (**a**) Fitting parameter, S and (**b**) phenomenologically assessed atomic effective nuclear charge ζ, vs. the nuclear charge Z. All points are color coded by the period, (index j): black open circles—2nd period; red open circles—3rd period; blue open circles—4th period; the blue bullet points are linearly extrapolated values up to Kr.

Finally, we summarize the number of assessed IE values per chemical element. The number of known IE values [6] per chemical element are also listed for comparison, Table 2. Overall, 168 IE values are measured, while 162 IE values are assessed herein, $30 \leq Z \leq 41$.

Table 2. Chemical element, nuclear charge, number of interpolated IE values from this study, and known IE values [6].

	Zn	Ga	Ge	As	Se	Br	Kr	Rb	Sr	Y	Zr	Nb
Z	30	31	32	33	34	35	36	37	38	39	40	41
intrp	3	9	20	20	20	20	0	14	14	14	14	14
known	21	16	5	6	7	8	30	10	11	12	5	7

5. Methodology and Outcome for Phenomenological Effective Nuclear Charge Assessment

The 25 isoelectronic series fits yield 25 S_s values, Table S1. The first member of every IE_s-set is the first ionization energy of a neutral atom ${}_{s+1}IE_s^0$ with a nuclear charge $Z = s+1$. The S_s values are plotted vs. the nuclear charge, Z, in Figure 4a.

It was noted that the fitting parameter S_s was revealed to be linearly correlated with the atomic number, Z, with a robust Pearson's correlation factor, $\rho > 0.9997$, for 2nd, 3rd and 4th periods of the periodic table. The periods are color coded, and the period number is indicated by the subscript of the slope, m_j (m_2, m_3, m_4). As expected, the slope remains less than one. It can be projected that in higher number periods, the slope will asymptotically approach one. Overall, it can be suggested that, statistically, more electrons screen the nucleus more efficiently. The effective atomic nuclear charges, ζ_j, where the index j, indicates the period, is assessed herein from the linear fit values $S_j = m_j Z$ expressed in the effective nuclear charge definition: $\zeta_j = Z - S_j$, Figure 4b. The indicated larger uncertainty reflects the point's residue from the linear regression. Effective nuclear charge values are listed in Table S6. Extrapolated values are listed in Table S7.

In a paper published in 1930, Slater proposed an assessment of the effective nuclear charge, $\zeta = Z - S$. Slater's study was based on different weights of the electron wave functions (s p, d, f) and on assigning a parameter called effective quantum number, n^* [8]. Thus, Slater's treatment can be considered a "bottom-up" approach, while the proposed herein IE_s-sets consideration is deemed "top-down" approach. Most importantly, there is a strong linear correlation between Slater's atomic effective nuclear charge, ζ_j, and the same parameter assessed independently from the IE_s-set analysis proposed herein, Figure 5a. In addition, the IE_s-set analysis exhibits a robust correlation with the Pauling relative electronegativity scale [14] for the 2nd and 3rd periods, Figure 5b.

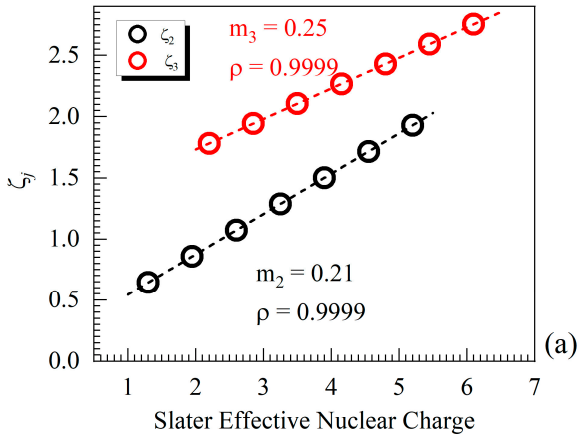


Figure 5. *Cont.*

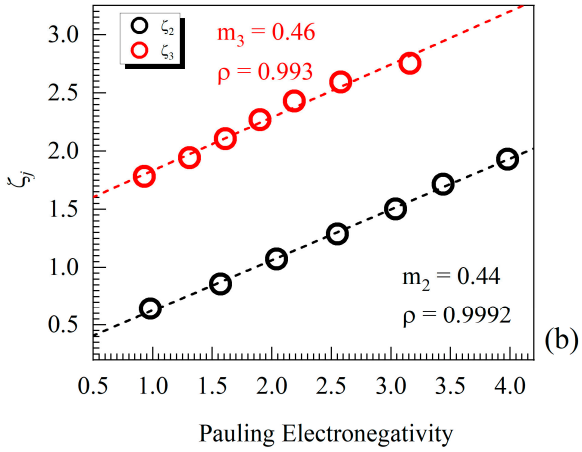


Figure 5. IE assessed parameter ζ_j, correlated (**a**) with Slater effective nuclear charge and (**b**) Pauling electronegativity scale; 2nd (black open circles) and 3rd (red open circles) period, solid symbols, not included in the linear fit (black and red dashed lines); slope and the Pearson's ρ are listed.

6. Conclusions

A novel, set theory-based ionization energy computational algorithm is proposed. The isoelectronic IE_s-sets are fitted with parabolic curves allowing for: (i) the interpolative assessment of 162 new IE values of ionization energies, with their uncertainties estimated by the Lagrange method—for ions from $_{30}$Zn to $_{41}$Nb. In addition, 13 values of single-electron ions $_Z IE_o^{(Z-1)+}$ are estimated via the extrapolation of a proposed expanded parabolic function. (ii) The phenomenologically assessed parameter ζ_j strongly correlates with the effective atomic nuclear charge, Slater's effective charge, and the Pauling electronegativity.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/atoms14030015/s1, Supplementary Materials S1 includes the proposed set theory-based ionization energy organization—iso-protonic and iso-ionic sets; its utilization is outside of the scope of the current study. Supplementary Materials S2 includes all numerical values with its uncertainties assessed in the discussion, systematized in eight tables: Table S1. The fitting parameters of the parabolic fits, Equation (4). The COD of each fit and number of the points used for fitting are also listed; Tables S2–S5: Interpolated IE values with their uncertainties assessed by the Lagrange method, Figures 2 and 3 bullet points. Table S6. IE effective charge, ζ_i values and the assessed uncertainties; Table S7. Extrapolated IE effective charge, ζ values, for 35 > Z > 26; Figure 4b.

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Data Availability Statement: The data that supports the findings of this study are available within the article and its Supplementary Material.

Conflicts of Interest: The author declares no conflict of interest.

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