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The NIST compilation of ionization potentials revisited (I): From He-like to Xe-like ions

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The National Institute of Standards and Technology (NIST) database on ionization potentials for neutral atoms and ions is examined. For each isoelectronic sequence, we construct a regularized perturbative series based on the large- Z and $Z \approx N - 1$ behaviors. Comparison of the NIST data with this series allows the identification of problematic values in the reported data.

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Physics is indeed a mature science. Large amounts of data, of very different kinds, have been accumulated along decades. Sometimes, a fresh look at these compilations, on the basis of simple -physically meaningful models, leads to a qualitative understanding of the data.

In previous papers^{1,2}, on the basis of the scaling characteristic of Thomas-Fermi theory³, we have shown that both the NIST data on ionization potentials of atomic ions⁴, and the correlation energies of atomic ions can be accommodated along single universal curves.

Recently, we went a step further and develop a simple model allowing the identification of problematic isolated reported values for the ionization potentials in a particular isoelectronic sequence.⁷ In the present account, we systematically revisit the NIST ionization potential database in light of the new model. Because of the fact that the compilation is very often used for different purposes, indications of which data could be wrong and should be re-examined is of great importance. For instance, as commented in Refs. [5] and [6], accurate description of the spectra is useful in order to model some dynamical features of stellar sources, and also to interpret astronomical data.

Our model for the ionization potential is a smooth interpolation that matches both the large- Z (heavy ion) and the $Z \approx N - 1$ (anion) regions.⁷ We call it the “regularized perturbation theory” (RPT). In our previous work, Ref. [7], the model is explained in detail and applied to the analysis of a few isoelectronic sequences, $N = 10, 28, 29$ and 60 . Within this article, we analyze sequences from $N = 2$, He-like ions, to 54 , Xe-like ions.

We have used similar approaches in order to compute the energy of relatively large quantum dots,⁸ atomic ions in a harmonic trap,⁹ neutral atoms in traps,¹⁰ and Rydberg-like impurity levels in a quantum well.¹¹

The RPT series for the ionization potential of an N -electron atomic ion with nuclear charge Z is written as (atomic units are used everywhere):^{7,12}

$$I_p = a_2 Z^2 + a_1 Z + a_0 + a_{-1}/Z. \quad (1)$$

Coefficients a_2 and a_1 are obtained from the large- Z limit.⁷ a_2 comes from the leading term (free electrons in the nuclear field), whereas a_1 is computed in the next-to-leading approximation, where Coulomb repulsion between electrons is perturbatively treated. Relativistic corrections should be included because the NIST data span the range of nuclear charges up to very heavy ions, i.e., $N \leq Z \leq 110$.

The next two terms of the series have the functional form suggested by higher-order perturbation theory on the Coulomb repulsion. However, in order to determine them, we shall follow a different strategy. We force expression (1) to match the expected value and the slope at $Z = N - 1$.⁷ In this sense, it is a “regularized perturbative series”. These conditions are written as follows:

$$\begin{aligned} I_p|_{Z=N-1} &= E_a, \\ \frac{dI_p}{dZ}|_{Z=N-1} &= s = \frac{\int_R^\infty dr e^{-2\kappa r}/r}{\int_R^\infty dr e^{-2\kappa r}}. \end{aligned} \quad (2)$$

E_a is the electron affinity of the neutral atom with $N - 1$ electrons.¹³ The slope s , on the other hand, is computed in terms of E_a and R , the latter is a characteristic radius of the $(N - 1)$ -electron system, which we estimate as the covalent radius.¹² Note that $\kappa = \sqrt{2E_a}$. The expression of the slope makes use of the fact that, at $Z = N - 1$, the outer electron interacts with a neutral core. Thus, the interaction is short-ranged and the wave function at large distances is solely determined by the binding energy, i.e. E_a . We use this function in order to perturbatively compute the residual Coulomb interaction of the outer electron with the core, when Z is slightly displaced from $N - 1$. The explicit expression for s was derived earlier in Ref. [12].

Once the coefficients in Eq. (1) are determined, our RPT series provides an interpolation for intermediate values of Z . We show in Fig. 1, in quality of example, the series for F-like ions ($N = 9$) along with the corresponding NIST data.

FIG. 1. (Color online) F-like ions ($N = 9$). Upper panel: I_p taken from the NIST compilation along with our nonrelativistic (discontinuous, blue) and relativistically corrected (continuous, red) RPT predictions *vs.* Z . Curves are smooth at any scale. Lower panel: The difference between I_p values reported by NIST and those stemming from the relativistic RPT series *vs.* Z . Reported error bars are shown. A 5-points running average curve (blue line) is used to identify problematic points. Inconsistencies at $Z = 27$ and 74 are noticed. The jump at $Z = 50 - 51$ lies within error bars.

Some comments should be added to this figure. First, NIST and RPT values are relatively close even though no fitting parameters are used. The latter means that the RPT model contains the main contributions to I_p .

Second, the dependence of I_p on Z seems smooth in the upper panel. It is difficult to distinguish a problematic point in the sequence, even if we change the scale. The reason is that there are large contributions to I_p . The nuclear potential, for example, provides a term proportional to Z^2 , and electron-electron repulsions a term proportional to Z . If we compute the difference NIST - RPT, such contributions are subtracted and problematic points should become apparent. In principle, if RPT were an exact model, the mean value of NIST - RPT would be zero, and deviations from zero could only be related to experimental or computational uncertainties. Any point far from zero beyond error bars should be re-examined.

Our model is not exact, thus we shall expect a smooth NIST - RPT dependence, as shown in the lower panel.

Problematic points are identified by comparison with a smoothed curve, which we construct by means of a 5-points running average.

We notice that an abrupt change in I_p could only be related to a rearrangement of the occupied electronic levels. This may take place as Z is increased. However, for $Z > N + 5$ or so, as may be verified also in the NIST compilation, the large- Z ordering of levels (free electrons in the field of the nucleus) is established. Thus, every jump or deviation beyond error bars in the smoothed NIST-RPT, not coinciding with a spectrum rearrangement point, can be taken as a signature of a possible problem.

We stress that the NIST reported values are experimental points only when Z is very close to N . For larger Z , data come from calculations or interpolations and we may expect relatively high errors, as the reported error bars confirm.

Remarkable deviations at $Z = 74$ (e.g., in Fig. 1) are clear indications of points in the data that would require a further examination by the NIST team. Notably, the latter deviation is recurrent in 30 of the 43 isoelectronic sequences considered here (all coming from Ref. [14]). The abrupt jump at $Z = 50 - 51$,¹⁵ albeit not problematic for F-like ions as confirmed in Fig. 1, is indeed inconsistent for 5 isoelectronic sequences. The dispersion of the points for very heavy ions is also intriguing, although it may be related to rounding of the original data according to the estimated error bars.

In the appendices, we examine 43 isoelectronic sequences (five rows of the Mendeleev Table), from He-like to Xe-like ions. In this range, only the sequences which do not have a stable singly charged anion are excluded. Heavier ions, from Ba-like to Th-like, are to be analyzed in a subsequent paper¹⁶.

We hope that the present analysis will be helpful in order to improve the reference data.

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Appendix A: The He-like sequence ($N = 2$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.5 + 0.125 (Z/137.036)^2, \\ a_1 &= -0.625 - 0.0989536 (Z/137.036)^2, \\ a_0 &= 0.368987, \\ a_{-1} &= -0.216282. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(\text{H}) &= 0.0277063, \\ s &= 0.59129. \end{aligned} \quad (\text{A1})$$

The slope was computed from $E_a(\text{H})$ and $R_{cov}(\text{H}) = 0.604712$. Here, and in the analysis below, data for E_a and R_{cov} are taken from Ref. [13].

FIG. A.1. (Color online) He-like ions ($N = 2$). The difference between I_p values reported by NIST and those stemming from the relativistic RPT series *vs.* Z . Error bars are very small and can not be seen in the scale of the figure. No inconsistencies were detected.

Discussion:

Let us comment on some features of the I_p data for the He-like sequence shown in Fig. A.1. In the range $2 \leq Z \leq 60$, the difference between our RPT series and the reported values is very well behaved. In the intermediate region, the maximum relative error is around 0.15%.

When $Z > 56$, NIST-RPT rises. NIST ionization potentials in the $12 \leq Z \leq 100$ range come mainly from *ab initio* Quantum Electrodynamics calculations by Artemyev et al.,¹⁷ which include finite nuclear-size effects. Our perturbative treatment of relativity cannot reproduce their results for very large Z .

Appendix B: Second row elements

1. The Be-like sequence ($N = 4$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.125 + 0.0390625 (Z/137.036)^2, \\ a_1 &= -0.548196 - 0.0952831 (Z/137.036)^2, \\ a_0 &= 0.675679, \\ a_{-1} &= -0.400253. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(\text{Li}) &= 0.0227050, \\ s &= 0.246343. \end{aligned} \quad (\text{B1})$$

The slope was computed from $E_a(\text{Li})$ and $R_{cov}(\text{Li}) = 2.456644$.

FIG. B.1. (Color online) Be-like ions ($N = 4$). The abrupt jump at $Z = 50 - 51$ can be, however, accommodated within error bars.

Discussion:

The comparison between NIST and RPT I_p values for the Be-like sequence shows an abrupt jump of 0.28 a.u. at $Z = 50 - 51$ (see Fig. B.1). These are numbers based on Dirac-Fock calculations of I_p computed by different groups. For $Z \leq 50$, data come from Ref. [18], whereas for $Z \geq 51$ almost all reported numbers come from Rodrigues et al.¹⁵. We notice that, in Ref. [18], a formula like Eq. (1) is used as a fit to correct the computed values.

The observed jump is consistent with the natural dispersion of points, as suggested by the reported error bars. Thus, no inconsistency is detected.

2. The C-like sequence ($N = 6$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.125 + 0.0390625 (Z/137.036)^2, \\ a_1 &= -0.945089 - 0.241928 (Z/137.036)^2, \\ a_0 &= 0.0390625, \\ a_{-1} &= 0.643271. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(\text{B}) &= 0.0102761, \\ s &= 0.279379. \end{aligned} \quad (\text{B2})$$

The slope was computed from $E_a(\text{B})$ and $R_{cov}(\text{B}) = 1.58737$.

FIG. B.2. (Color online) C-like ions ($N = 6$). An inconsistency at $Z = 74$ and an abrupt jump at $Z = 50 - 51$ are noticed.

Discussion:

The analysis of NIST-RPT data for the C-like sequence (Fig. B.2) also shows an abrupt jump of nearly 0.43 a.u. at $Z = 50 - 51$. As in the Be-like case, this jump is associated to changes in the calculation methodology. However, the jump exactly equals the reported error bars. Thus, we recommend revision of this data.

In addition, an apparent deviation in the ionization potential is noticed at $Z = 74$. This number, corresponding to a tungsten heavy ion (W^{+68}), was collected by NIST compilers Kramida and Reader with the help of a semi-empirical approach¹⁴. Comparison with the average curve suggests that the reported value for W^{+68} is overestimated in 1.577 a.u.

3. The N-like sequence ($N = 7$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.125 + 0.0078125 (Z/137.036)^2, \\ a_1 &= -1.10915 - 0.152346 (Z/137.036)^2, \\ a_0 &= 2.26192, \\ a_{-1} &= -0.356612. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(C) &= 0.0463657, \\ s &= 0.400642. \end{aligned} \quad (B3)$$

The slope was computed from $E_a(C)$ and $R_{cov}(C) = 1.417295$.

FIG. B.3. (Color online) N-like ions ($N = 7$). Deviations at $Z = 26$ and 74 are noticed.

Discussion:

The N-like sequence (Fig. B.3) presents noticeable jumps at $Z = 26$ and, once more, at $Z = 74$.

The ionization potential for $Z = 26$ was taken from the paper by Sugar and Corliss.¹⁹ According to our procedure, an overestimation of 0.051 a.u. is noticed.

The $Z = 74$ case is again taken from Ref. [14]. It seems to be an inconsistent point, underestimated by 1.395 a.u.

Data for $Z = 42 - 50$ come from the Dirac-Fock calculations by Biémont et al.¹⁸ The reported large uncertainties in the data, of around 1.5 a.u., are consistent with the observed deviations.

Notice, that error bars are remarkably high (from 2.0 to 20 a.u.) for $Z > 74$.

4. The F-like sequence ($N = 9$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.125 + 0.0078125 (Z/137.036)^2, \\ a_1 &= -1.4654 - 0.181681 (Z/137.036)^2, \\ a_0 &= 2.79034, \\ a_{-1} &= 7.91836. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(O) &= 0.0536759, \\ s &= 0.410681. \end{aligned} \quad (B4)$$

The slope was computed from $E_a(O)$ and $R_{cov}(O) = 1.417295$.

Discussion:

In the F-like sequence (see Fig. 1), large deviations are noticed for $Z = 27$ and 74 . I_p for $Z = 27$ comes from Ref. [19], the very same paper by Sugar and Corliss cited in the N-like case. According to our Fig., it seems to be overestimated in 0.183 a.u.

On the other hand, $Z = 74$ belongs to the case of tungsten ions (W^{+65}), and the I_p value is, once more, taken from Ref. [14]. In this case, an underestimation of 1.071 a.u. is apparent.

Finally, the observed jump at $Z = 50 - 51$ is consistent with the reported error bars. It is also worth mentioning the large error bars accompanying the data for $Z \geq 80$.

5. The Ne-like sequence ($N = 10$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.125 + 0.0078125 (Z/137.036)^2, \\ a_1 &= -1.63649 - 0.195621 (Z/137.036)^2, \\ a_0 &= 4.13824, \\ a_{-1} &= 5.3556. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(F) &= 0.124985, \\ s &= 0.547149. \end{aligned} \quad (B5)$$

The slope was computed from $E_a(F)$ and $R_{cov}(F) = 1.13384$.

FIG. B.4. (Color online) Ne-like ions ($N = 10$). Inconsistencies at $Z = 21, 22, 27, 74$, and the abrupt jump at $Z = 50 - 51$ are noticed. A version of this figure was printed as part of Fig. 1 in Ref. [7].

Discussion:

In the Ne-like sequence (Fig. B.4), deviations at $Z = 21, 22$, and 27 are noticed. Points are related to Ref. [19]. We suggest correcting these values in $-0.034, +0.012$ and $+0.036$ a.u., respectively.

The $Z = 74$ case,¹⁴ is also clearly inconsistent. The ionization potential seems to be underestimated in 1.077 a.u.

The previously discussed abrupt jump at $Z = 50 - 51$, should be revised by the NIST team because the jump is greater than the data uncertainty.

Ne-like ions were considered in Ref. [7] and are shown here for completeness.

Appendix C: Third row elements

1. The Mg-like sequence ($N = 12$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.0555556 + 0.0138889 (Z/137.036)^2, \\ a_1 &= -0.931477 - 0.0906944 (Z/137.036)^2, \\ a_0 &= 2.62996, \\ a_{-1} &= 10.0077. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(Na) &= 0.0201287, \\ s &= 0.209421. \end{aligned} \quad (C1)$$

The slope was computed from $E_a(Na)$ and $R_{cov}(Na) = 3.023562$.

FIG. C.1. (Color online) Mg-like ions ($N = 12$). Inconsistencies at $Z = 23, 24, 25, 27$ and 28 , and a jump at $Z = 50 - 51$ are apparent.

Discussion:

The Mg-like sequence (Fig. C.1) shows clear deviations at $Z = 23, 24, 25, 27$ and 28 .¹⁹ The figure suggests corrections of $-0.015, -0.013, +0.026, -0.008$ and -0.016 a.u. to these points, respectively. In principle, also the value at $Z = 22$ qualifies as problematic, but once a smoother average curve is considered (e.g., based on 7 points instead of 5), it is no longer meeting our criterion (not shown).

The jump at $Z = 50 - 51$ was discussed above. It is clearly not consistent with error bars, thus we suggest revision of these data.

2. The Si-like sequence ($N = 14$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.0555556 + 0.0138889 (Z/137.036)^2, \\ a_1 &= -1.13489 - 0.148767 (Z/137.036)^2, \\ a_0 &= 4.44303, \\ a_{-1} &= 12.1396. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(\text{Al}) &= 0.0159006, \\ s &= 0.239636. \end{aligned} \quad (\text{C2})$$

The slope was computed from $E_a(\text{Al})$ and $R_{cov}(\text{Al}) = 2.343260$.

FIG. C.2. (Color online) Si-like ions ($N = 14$). Deviations at $Z = 21 - 26$ and $Z = 74$ are remarkable.

Discussion:

In the Si-like sequence (Fig. C.2), a group of four points, $Z = 23 - 26$, seems to be out of the general trend. Thus, we use a 7-points running average (instead of 5-points) in order to create a smooth curve. We suggest using the top of the error bars as values for $Z = 21 - 22$, and the bottom of the error bars for $Z = 23 - 26$.

The $Z = 74$ point, on the other hand, should be corrected in -0.329 a.u.

3. The P-like sequence ($N = 15$)

RPT coefficients:

$$a_2 = 0.0555556 + 0.00462963 (Z/137.036)^2,$$

$$\begin{aligned} a_1 &= -1.19956 - 0.109484 (Z/137.036)^2, \\ a_0 &= 5.24386, \\ a_{-1} &= 10.0615. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(\text{Si}) &= 0.0510817, \\ s &= 0.304873. \end{aligned} \quad (\text{C3})$$

The slope was computed from $E_a(\text{Si})$ and $R_{cov}(\text{Si}) = 2.154288$.

FIG. C.3. (Color online) P-like ions ($N = 15$). A big jump at $Z = 50 - 51$, and a noticeable deviation at $Z = 74$ are apparent.

Discussion:

For the P-like sequence (Fig. C.3), we suggest a revision of the data near $Z = 50$, and correcting the $Z = 74$ value in $+0.247$ a.u.

4. The S-like sequence ($N = 16$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.0555556 + 0.00462963 (Z/137.036)^2, \\ a_1 &= -1.26711 - 0.114919 (Z/137.036)^2, \\ a_0 &= 4.83765, \\ a_{-1} &= 25.569. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(\text{P}) &= 0.0274519, \\ s &= 0.286207. \end{aligned} \quad (\text{C4})$$

The slope was computed from $E_a(\text{P})$ and $R_{cov}(\text{P}) = 2.0598015$.

FIG. C.4. (Color online) S-like ions ($N = 16$). The only detected inconsistency is the deviation at $Z = 74$.

Discussion:

Although error bars are relatively high for S-like ions (Fig. C.4), we suggest a correction of $+0.249$ a.u. to the $Z = 74$ value of I_p .

5. The Cl-like sequence ($N = 17$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.0555556 + 0.00462963 (Z/137.036)^2, \\ a_1 &= -1.34042 - 0.121136 (Z/137.036)^2, \\ a_0 &= 5.81594, \\ a_{-1} &= 23.9212. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(\text{S}) &= 0.0763283, \\ s &= 0.344289. \end{aligned} \quad (\text{C5})$$

The slope was computed from $E_a(\text{S})$ and $R_{cov}(\text{S}) = 1.965315$.

Discussion:

Error bars are also relatively large for the Cl-like sequence (Fig. C.5). However, we suggest a revision of the data near $Z = 50$, which show a jump of 0.216 a.u., and using in the $Z = 74$ case the top value of the error bar.

6. The Ar-like sequence ($N = 18$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.0555556 + 0.00462963 (Z/137.036)^2, \\ a_1 &= -1.40796 - 0.12657 (Z/137.036)^2, \\ a_0 &= 6.30212, \\ a_{-1} &= 29.2914. \end{aligned}$$

FIG. C.5. (Color online) Cl-like ions ($N = 17$). The jump at $Z = 50 - 51$, and the deviation at $Z = 74$ are noticeable.

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(\text{Cl}) &= 0.132775, \\ s &= 0.380045. \end{aligned} \quad (\text{C6})$$

The slope was computed from $E_a(\text{Cl})$ and $R_{cov}(\text{Cl}) = 1.889726$.

FIG. C.6. (Color online) Ar-like ions ($N = 18$). In this case, we distinguish only the deviation at $Z = 74$.¹⁴

Discussion:

In spite of the relatively large error bars for the Ar-like sequence (Fig. C.6), we suggest using the top of the error bar as the $Z = 74$ value of I_p .

Appendix D: Four row elements

1. The Ca-like sequence ($N = 20$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.0555556 + 0.00462963 (Z/137.036)^2, \\ a_1 &= -1.70312 - 0.200236 (Z/137.036)^2, \\ a_0 &= 7.96996, \\ a_{-1} &= 83.4702. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(\text{K}) &= 0.0184220, \\ s &= 0.176307. \end{aligned} \quad (\text{D1})$$

The slope was computed from $E_a(\text{K})$ and $R_{cov}(\text{K}) = 3.779452$.

FIG. D.1. (Color online) Ca-like ions ($N = 20$). Only the $Z = 74$ point is distinguished.

Discussion:

The Ca-like sequence (Fig. D.1) is the first with a rearrangement of the electronic spectrum with the increase of Z . For $Z \approx N$ the last two electrons occupy the 4s subshell, whereas for larger Z they move to the 3d orbital. The observed jump at $Z = 20 - 21$ is surely related to this fact.

On the other hand, we suggest using for I_p at $Z = 74$ the bottom of its error bar.

2. The Sc-like sequence ($N = 21$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.0555556 + 0.00462963 (Z/137.036)^2, \\ a_1 &= -1.79098 - 0.209669 (Z/137.036)^2, \\ a_0 &= 7.18837, \\ a_{-1} &= 129.196. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(\text{Ca}) &= 0.000901924, \\ s &= 0.107729. \end{aligned} \quad (\text{D2})$$

The slope was computed from $E_a(\text{Ca})$ and $R_{cov}(\text{Ca}) = 3.288123$.

FIG. D.2. (Color online) Sc-like ions ($N = 21$). Only the $Z = 74$ point is distinguished.

Discussion:

Sc-like sequence (Fig. D.2) is very similar to Ca-like case. We suggest correcting I_p at $Z = 74$ in -0.224 a.u.

3. The Ti-like sequence ($N = 22$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.0555556 + 0.00462963 (Z/137.036)^2, \\ a_1 &= -1.87158 - 0.218161 (Z/137.036)^2, \\ a_0 &= 8.87906, \\ a_{-1} &= 125.803. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(\text{Sc}) &= 0.00690650, \\ s &= 0.175933. \end{aligned} \quad (\text{D3})$$

The slope was computed from $E_a(\text{Sc})$ and $R_{cov}(\text{Sc}) = 3.004665$.

Discussion:

Ti-like sequence (Fig. D.3) is also very similar to the previous cases (Ca- and Sc-like). We suggest correcting I_p at $Z = 74$ in -0.205 a.u.

FIG. D.3. (Color online) Ti-like ions ($N = 22$). Only the $Z = 74$ point is distinguished.

4. The V-like sequence ($N = 23$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.0555556 + 0.00154321(Z/137.036)^2, \\ a_1 &= -1.95847 - 0.154589(Z/137.036)^2, \\ a_0 &= 8.95387, \\ a_{-1} &= 160.08. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(\text{Ti}) &= 0.00290230, \\ s &= 0.156499. \end{aligned} \quad (\text{D4})$$

The slope was computed from $E_a(\text{Ti})$ and $R_{cov}(\text{Ti}) = 2.796794$.

FIG. D.4. (Color online) The V-like ions ($N = 23$). No inconsistencies were detected.

5. The Cr-like sequence ($N = 24$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.0555556 + 0.00154321(Z/137.036)^2, \\ a_1 &= -2.03885 - 0.15826(Z/137.036)^2, \\ a_0 &= 10.9246, \\ a_{-1} &= 153.618. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(\text{V}) &= 0.0192866, \\ s &= 0.223850. \end{aligned} \quad (\text{D5})$$

The slope was computed from $E_a(\text{V})$ and $R_{cov}(\text{V}) = 2.721206$.

FIG. D.5. (Color online) Cr-like ions ($N = 24$). An apparent deviation at $Z = 32$ is detected.

Discussion:

In the Cr-like sequence (Fig. D.5), we shall distinguish the problematic point at $Z = 32$, coming from the paper by Sugar and Musgrove²⁰. I_p is overestimated in 0.181 a.u.

6. The Mn-like sequence ($N = 25$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.0555556 + 0.00154321(Z/137.036)^2, \\ a_1 &= -2.12264 - 0.162119(Z/137.036)^2, \\ a_0 &= 12.0502, \\ a_{-1} &= 168.234. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(\text{Cr}) &= 0.0244666, \\ s &= 0.249254. \end{aligned} \quad (\text{D6})$$

FIG. D.6. (Color online) Mn-like ions ($N = 25$). No inconsistency is detected.

The slope was computed from $E_a(\text{Cr})$ and $R_{cov}(\text{Cr}) = 2.456644$.

7. The Co-like sequence ($N = 27$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.0555556 + 0.00154321 (Z/137.036)^2, \\ a_1 &= -2.29511 - 0.170117 (Z/137.036)^2, \\ a_0 &= 11.9833, \\ a_{-1} &= 266.793. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(\text{Fe}) &= 0.00554713, \\ s &= 0.195878. \end{aligned} \quad (\text{D7})$$

The slope was computed from $E_a(\text{Fe})$ and $R_{cov}(\text{Fe}) = 2.343260$.

Discussion:

In the Co-like sequence (Fig. D.7), I_p at $Z = 74$ is overestimated in 0.196 a.u.

8. The Ni-like sequence ($N = 28$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.0555556 + 0.00154321 (Z/137.036)^2, \\ a_1 &= -2.3755 - 0.173789 (Z/137.036)^2, \\ a_0 &= 14.2165, \\ a_{-1} &= 258.787. \end{aligned}$$

FIG. D.7. (Color online) Co-like ions ($N = 27$). The only detected inconsistency is at $Z = 74$.

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(\text{Co}) &= 0.0243196, \\ s &= 0.266002. \end{aligned} \quad (\text{D8})$$

The slope was computed from $E_a(\text{Co})$ and $R_{cov}(\text{Co}) = 2.229877$.

FIG. D.8. (Color online) Ni-like ions ($N = 28$). Inconsistencies are detected at $Z = 42$, 74 , and 79 . A version of this figure was printed as part of Fig. 2 in Ref. [7].

Discussion:

The Ni-like sequence (Fig. D.8) shows deviations at $Z = 42$, 74 and 79 , the latter coming from the paper by Tragin et al.²¹.

As suggested by the figure, I_p at $Z = 42$ is overestimated in 0.071 a.u. Corrections of -0.141 and -0.203 a.u. should be added to the points at $Z = 74$ and 79 , respectively.

Ni-like ions were considered in Ref. [7] and are shown here for completeness.

9. The Cu-like sequence ($N = 29$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.03125 + 0.00634766 (Z/137.036)^2, \\ a_1 &= -1.34713 - 0.0620302 (Z/137.036)^2, \\ a_0 &= 9.66505, \\ a_{-1} &= 96.9281. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(\text{Ni}) &= 0.0424673, \\ s &= 0.291495. \end{aligned} \quad (\text{D9})$$

The slope was computed from $E_a(\text{Ni})$ and $R_{cov}(\text{Ni}) = 2.210980$.

FIG. D.9. (Color online) Cu-like ions ($N = 29$). Small deviations at $Z = 70$ and 79 are noticed. A version of this figure was printed as part of Fig. 2 in Ref. [7].

Discussion:

In the Cu-like sequence (Fig. D.9), slight deviations at $Z = 70$ and 79 are apparent. The data come from Ref. [21]. Points seem to be overestimated in 0.064 and 0.097 a.u., respectively.

Cu-like ions were considered in Ref. [7] and are shown here for completeness.

10. The Zn-like sequence ($N = 30$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.03125 + 0.00634766 (Z/137.036)^2, \\ a_1 &= -1.3844 - 0.0677735 (Z/137.036)^2, \\ a_0 &= 9.2367, \\ a_{-1} &= 131.194. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(\text{Cu}) &= 0.0453693, \\ s &= 0.285562. \end{aligned} \quad (\text{D10})$$

The slope was computed from $E_a(\text{Cu})$ and $R_{cov}(\text{Cu}) = 2.305466$.

FIG. D.10. (Color online) Zn-like ions ($N = 30$). Inconsistencies are noticed at $Z = 35, 42, 45$ and 74 .

Discussion:

In the Zn-like sequence (Fig. D.10), the data for $Z = 35$ is taken from the Dirac-Fock calculation of Ref. [15], while the value for $Z = 42$ is due to Refs. [24] and [25]. These potentials should be corrected in $+0.076$ and -0.045 a.u., respectively.

On the other hand, $Z = 45$ ionization potential was collected from the relativistic multireference many-body perturbation theory calculations of Vilkas et al.²². It seems to be overestimated in 0.087 a.u.

The $Z = 74$ ionization potential comes from Ref. [14], as before. It is 0.103 a.u. higher than the average curve.

11. The Ge-like sequence ($N = 32$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.03125 + 0.00634766 (Z/137.036)^2, \\ a_1 &= -1.51951 - 0.0952627 (Z/137.036)^2, \\ a_0 &= 10.9568, \\ a_{-1} &= 185.117. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(\text{Ga}) &= 0.0157966, \\ s &= 0.240629. \end{aligned} \quad (\text{D11})$$

The slope was computed from $E_a(\text{Ga})$ and $R_{cov}(\text{Ga}) = 2.324363$.

FIG. D.11. (Color online) Ge-like ions ($N = 32$). Only the $Z = 74$ point is distinguished.

Discussion:

In the Ge-like sequence (Fig. D.11), I_p at $Z = 74$ is overestimated in 0.116 a.u.

12. The As-like sequence ($N = 33$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.03125 + 0.00244141 (Z/137.036)^2, \\ a_1 &= -1.55446 - 0.0829917 (Z/137.036)^2, \\ a_0 &= 12.6573, \\ a_{-1} &= 164.459. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(\text{Ge}) &= 0.0453118, \\ s &= 0.288928. \end{aligned} \quad (\text{D12})$$

The slope was computed from $E_a(\text{Ge})$ and $R_{cov}(\text{Ge}) = 2.267671$.

13. The Se-like sequence ($N = 34$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.03125 + 0.00244141 (Z/137.036)^2, \\ a_1 &= -1.59101 - 0.0853527 (Z/137.036)^2, \\ a_0 &= 11.7569, \\ a_{-1} &= 222.876. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(\text{As}) &= 0.0295464, \\ s &= 0.271227. \end{aligned} \quad (\text{D13})$$

FIG. D.12. (Color online) As-like ions ($N = 33$). No inconsistencies are detected.

The slope was computed from $E_a(\text{As})$ and $R_{cov}(\text{As}) = 2.267671$.

FIG. D.13. (Color online) Se-like ions ($N = 34$). Slight deviations at $Z = 39$ and 42 are apparent.

Discussion:

In the Se-like sequence (Fig. D.13), we detect inconsistencies at $Z = 39$ and 42 . I_p at $Z = 39$ seems to be overestimated in 0.033 a.u.

The number for I_p in Mo^{+18} (i.e. $Z = 42$, $N = 34$) comes from Refs. [23] and [24]. It seems to be 0.059 a.u. higher than the average curve.

14. The Br-like sequence ($N = 35$)

RPT coefficients:

$$a_2 = 0.03125 + 0.00244141 (Z/137.036)^2,$$

$$\begin{aligned}
 a_1 &= -1.63074 - 0.0881566 (Z/137.036)^2, \\
 a_0 &= 13.0595, \\
 a_{-1} &= 215.756.
 \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned}
 E_a(\text{Se}) &= 0.0742704, \\
 s &= 0.312415.
 \end{aligned} \tag{D14}$$

The slope was computed from $E_a(\text{Se})$ and $R_{\text{cov}}(\text{Se}) = 2.229877$.

FIG. D.14. (Color online) Br-like ions ($N = 35$). A smooth curve. No inconsistencies are detected.

15. The Kr-like sequence ($N = 36$)

RPT coefficients:

$$\begin{aligned}
 a_2 &= 0.03125 + 0.00244141 (Z/137.036)^2, \\
 a_1 &= -1.66728 - 0.0905176 (Z/137.036)^2, \\
 a_0 &= 13.5057, \\
 a_{-1} &= 234.611.
 \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned}
 E_a(\text{Br}) &= 0.123625, \\
 s &= 0.333943.
 \end{aligned} \tag{D15}$$

The slope was computed from $E_a(\text{Br})$ and $R_{\text{cov}}(\text{Br}) = 2.210980$.

FIG. D.15. (Color online) Kr-like ions ($N = 36$). No inconsistencies are detected.

Appendix E: Fifth row elements

1. The Sr-like sequence ($N = 38$)

RPT coefficients:

$$\begin{aligned}
 a_2 &= 0.03125 + 0.00244141 (Z/137.036)^2, \\
 a_1 &= -1.86543 - 0.136324 (Z/137.036)^2, \\
 a_0 &= 15.882, \\
 a_{-1} &= 388.488.
 \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned}
 E_a(\text{Rb}) &= 0.0178511, \\
 s &= 0.166529.
 \end{aligned} \tag{E1}$$

The slope was computed from $E_a(\text{Rb})$ and $R_{\text{cov}}(\text{Rb}) = 4.062911$.

FIG. E.1. (Color online) Sr-like ions ($N = 38$). An apparent deviation at $Z = 74^{14}$ is shown.

Discussion:

In the Sr-like sequence (Fig. E.1), I_p at $Z = 74$ is overestimated in 0.132 a.u.

2. The Y-like sequence ($N = 39$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.03125 + 0.00244141 (Z/137.036)^2, \\ a_1 &= -1.90897 - 0.139844 (Z/137.036)^2, \\ a_0 &= 14.2754, \\ a_{-1} &= 504.63. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(\text{Sr}) &= 0.00176347, \\ s &= 0.120083. \end{aligned} \quad (\text{E2})$$

The slope was computed from $E_a(\text{Sr})$ and $R_{cov}(\text{Sr}) = 3.590480$.

FIG. E.2. (Color online) Y-like ions ($N = 39$). The only detected inconsistency is at $Z = 74$ ¹⁴.

Discussion:

In the Y-like sequence (Fig. E.2), I_p at $Z = 74$ should be corrected in -0.148 a.u.

3. The Zr-like sequence ($N = 40$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.03125 + 0.00244141 (Z/137.036)^2, \\ a_1 &= -1.94905 - 0.142908 (Z/137.036)^2, \\ a_0 &= 16.4347, \\ a_{-1} &= 476.155. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(\text{Y}) &= 0.0112782, \\ s &= 0.179247. \end{aligned} \quad (\text{E3})$$

The slope was computed from $E_a(\text{Y})$ and $R_{cov}(\text{Y}) = 3.325918$.

FIG. E.3. (Color online) Zr-like ions ($N = 40$). The $Z = 74$ point is distinguished.

Discussion:

In the Zr-like sequence (Fig. E.3), I_p at $Z = 74$ shows an overestimation of 0.147 a.u.

4. The Nb-like sequence ($N = 41$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.03125 + 0.00113932 (Z/137.036)^2, \\ a_1 &= -1.99199 - 0.112623 (Z/137.036)^2, \\ a_0 &= 17.6019, \\ a_{-1} &= 492.881. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(\text{Zr}) &= 0.0156496, \\ s &= 0.198128. \end{aligned} \quad (\text{E4})$$

The slope was computed from $E_a(\text{Zr})$ and $R_{cov}(\text{Zr}) = 3.099151$.

Discussion:

In the Nb-like sequence (Fig. E.4), I_p at $Z = 74$ is overestimated in 0.116 a.u.

FIG. E.4. (Color online) Nb-like ions ($N = 41$). The only detected inconsistency is the $Z = 74$ point.¹⁴

5. The Mo-like sequence ($N = 42$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.03125 + 0.00113932 (Z/137.036)^2, \\ a_1 &= -2.03196 - 0.114317 (Z/137.036)^2, \\ a_0 &= 18.7868, \\ a_{-1} &= 503.25. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(\text{Nb}) &= 0.0336625, \\ s &= 0.229290. \end{aligned} \quad (\text{E5})$$

The slope was computed from $E_a(\text{Nb})$ and $R_{cov}(\text{Nb}) = 2.947973$.

FIG. E.5. (Color online) Mo-like ions ($N = 42$). The only inconsistent point is $Z = 74$.¹⁴

Discussion:

In the Mo-like sequence (Fig. E.5), I_p at $Z = 74$ should be corrected in -0.120 a.u.

6. The Tc-like sequence ($N = 43$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.03125 + 0.00113932 (Z/137.036)^2, \\ a_1 &= -2.07354 - 0.116109 (Z/137.036)^2, \\ a_0 &= 19.0013, \\ a_{-1} &= 556.886. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(\text{Mo}) &= 0.0274790, \\ s &= 0.233850. \end{aligned} \quad (\text{E6})$$

The slope was computed from $E_a(\text{Mo})$ and $R_{cov}(\text{Mo}) = 2.759000$.

FIG. E.6. (Color online) Tc-like ions ($N = 43$). Only the $Z = 74$ point is distinguished.¹⁴

Discussion:

In the Tc-like sequence (Fig. E.6), I_p at $Z = 74$ is overestimated in 0.123 a.u.

7. The Ru-like sequence ($N = 44$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.03125 + 0.00113932 (Z/137.036)^2, \\ a_1 &= -2.11747 - 0.118053 (Z/137.036)^2, \\ a_0 &= 19.1396, \\ a_{-1} &= 621.055. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(\text{Tc}) &= 0.0202049, \\ s &= 0.232165. \end{aligned} \quad (\text{E7})$$

The slope was computed from $E_a(\text{Tc})$ and $R_{cov}(\text{Tc}) = 2.607822$.

FIG. E.7. (Color online) Ru-like ions ($N = 44$). An inconsistency at $Z = 74$ is apparent.

Discussion:

In the Ru-like sequence (Fig. E.7), I_p at $Z = 74$ is overestimated in 0.136 a.u.

8. The Rh-like sequence ($N = 45$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.03125 + 0.00113932 (Z/137.036)^2, \\ a_1 &= -2.15904 - 0.119845 (Z/137.036)^2, \\ a_0 &= 20.2974, \\ a_{-1} &= 640.445. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(\text{Ru}) &= 0.0385732, \\ s &= 0.232165. \end{aligned} \quad (\text{E8})$$

The slope was computed from $E_a(\text{Ru})$ and $R_{cov}(\text{Ru}) = 2.570028$.

Discussion:

In the Rh-like sequence (Fig. E.8), I_p at $Z = 49$ is underestimated in 0.072 a.u., whereas the $Z = 74$ point is 0.136 a.u. higher than the average curve.

FIG. E.8. (Color online) Rh-like ions ($N = 45$). There are apparent inconsistencies at $Z = 49$ ¹⁵ and $Z = 74$ ¹⁴.

9. The Pd-like sequence ($N = 46$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.03125 + 0.00113932 (Z/137.036)^2, \\ a_1 &= -2.19902 - 0.121538 (Z/137.036)^2, \\ a_0 &= 20.4131, \\ a_{-1} &= 703.998. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(\text{Rh}) &= 0.0417692, \\ s &= 0.258127. \end{aligned} \quad (\text{E9})$$

The slope was computed from $E_a(\text{Rh})$ and $R_{cov}(\text{Rh}) = 2.532233$.

FIG. E.9. (Color online) Pd-like ions ($N = 46$). Inconsistencies at $Z = 55$ and $Z = 74$ are noticed.

Discussion:

In the Pd-like sequence (Fig. E.9), in addition to $Z = 74$, an apparent inconsistency at $Z = 55$ comes from the experimental work of Churilov et al.²⁶ The $Z = 55$ and 74 points are, respectively, 0.120 and 0.118 a.u. above the average curve.

10. The Ag-like sequence ($N = 47$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.03125 + 0.00113932 (Z/137.036)^2, \\ a_1 &= -2.41502 - 0.161518 (Z/137.036)^2, \\ a_0 &= 35.8484, \\ a_{-1} &= 446.393. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(\text{Pd}) &= 0.0206460, \\ s &= 0.263779. \end{aligned} \quad (\text{E10})$$

The slope was computed from $E_a(\text{Pd})$ and $R_{\text{cov}}(\text{Pd}) = 2.456644$.

FIG. E.10. (Color online) Ag-like ions ($N = 47$). The average curve is drawn (blue) in order to identify problematic points. Inconsistencies at $Z = 61$ and 74 are apparent. The $Z = 95$ point also distinguishes in spite of its huge error bar.

Discussion:

A qualitatively different picture appears in the Ag-like sequence (Fig. E.10). The maximum of $|\text{RPT} - \text{NIST}|$ diminished, as compared with the Pd-like sequence, but the dispersion of points has significantly increased.

The problematic point at $Z = 61$ comes from Ref. [15]. It seems to be 0.191 a.u. below the average curve. I_p at $Z = 74$, on the other hand, is underestimated in 0.275 a.u.

Data for $Z \geq 77$ is the entire responsibility of Carlson et al.²⁷, who employ a simple spherical shell model in order to compute the ionization potentials. The indicated error bars are very high.

11. The Cd-like sequence ($N = 48$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.03125 + 0.00113932 (Z/137.036)^2, \\ a_1 &= -2.46174 - 0.163993 (Z/137.036)^2, \\ a_0 &= 37.7704, \\ a_{-1} &= 449.257. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(\text{Ag}) &= 0.0478309, \\ s &= 0.265692. \end{aligned} \quad (\text{E11})$$

The slope was computed from $E_a(\text{Ag})$ and $R_{\text{cov}}(\text{Ag}) = 2.570028$.

FIG. E.11. (Color online) Cd-like ions ($N = 48$). Inconsistencies are detected at $Z = 61$ and 74.

Discussion:

In the Cd-like sequence (Fig. E.11), I_p at $Z = 74$ is underestimated in 0.431 a.u. The value at $Z = 61$, although having error bars near the 5-pts average, is deviating even more from an smoother 7-pts average curve (not shown).

12. The Sn-like sequence ($N = 50$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.03125 + 0.00113932 (Z/137.036)^2, \\ a_1 &= -2.56241 - 0.169401 (Z/137.036)^2, \\ a_0 &= 37.191, \\ a_{-1} &= 688.884. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(\text{In}) &= 0.0110208, \\ s &= 0.205786. \end{aligned} \quad (\text{E12})$$

The slope was computed from $E_a(\text{In})$ and $R_{cov}(\text{In}) = 2.683411$.

FIG. E.12. (Color online) Sn-like ions ($N = 50$). A deviation at $Z = 74$ ¹⁴ is apparent.

Discussion:

In the Sn-like sequence (Fig. E.12), I_p at $Z = 74$ shows a huge deviation of -0.720 a.u. We may notice also that, apparently, there are crossing points at $Z = 60$ and 64 . Thus the group of points in $Z = 61 - 63$ should be below the x axis. However, we do not have a precise way of estimating these potentials.

13. The Sb-like sequence ($N = 51$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.03125 + 0.00113932 (Z/137.036)^2, \\ a_1 &= -2.61122 - 0.172008 (Z/137.036)^2, \\ a_0 &= 40.6766, \\ a_{-1} &= 628.32. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(\text{Sn}) &= 0.0408532, \\ s &= 0.254716. \end{aligned} \quad (\text{E13})$$

The slope was computed from $E_a(\text{Sn})$ and $R_{cov}(\text{Sn}) = 2.645617$.

Discussion:

In the Sb-like sequence (Fig. E.13), I_p at $Z = 74$ is underestimated in -0.678 a.u. We have stressed previously the problem of $Z = 61 - 63$ ions for Sn-like case. A similar comment applies here.

FIG. E.13. (Color online) Sb-like ions ($N = 51$). The $Z = 74$ ¹⁴ point is distinguished.

14. The Te-like sequence ($N = 52$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.03125 + 0.00113932 (Z/137.036)^2, \\ a_1 &= -2.65793 - 0.174483 (Z/137.036)^2, \\ a_0 &= 41.4216, \\ a_{-1} &= 699.342. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(\text{Sb}) &= 0.0384262, \\ s &= 0.252618. \end{aligned} \quad (\text{E14})$$

The slope was computed from $E_a(\text{Sb})$ and $R_{cov}(\text{Sb}) = 2.645617$.

FIG. E.14. (Color online) Te-like ions ($N = 52$). A marked deviation at $Z = 74$ ¹⁴ is noticed.

Discussion:

In the Te-like sequence (Fig. E.14), I_p at $Z = 74$ is 0.668 a.u. below the average curve.

15. The I-like sequence ($N = 53$)

RPT coefficients:

$$\begin{aligned} a_2 &= 0.03125 + 0.000488281 (Z/137.036)^2, \\ a_1 &= -2.71192 - 0.133452 (Z/137.036)^2, \\ a_0 &= 44.5066, \\ a_{-1} &= 670.563. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(\text{Te}) &= 0.0724331, \\ s &= 0.278176. \end{aligned} \quad (\text{E15})$$

The slope was computed from $E_a(\text{Te})$ and $R_{cov}(\text{Te}) = 2.588925$.

FIG. E.15. (Color online) I-like ions ($N = 53$). An inconsistency is detected at $Z = 74$.

Discussion:**16. The Xe-like sequence ($N = 54$)**

RPT coefficients:

$$\begin{aligned} a_2 &= 0.03125 + 0.000488281 (Z/137.036)^2, \\ a_1 &= -2.75916 - 0.134776 (Z/137.036)^2, \\ a_0 &= 46.3287, \\ a_{-1} &= 694.4. \end{aligned}$$

Conditions at $Z = N - 1$:

$$\begin{aligned} E_a(\text{I}) &= 0.112416, \\ s &= 0.293706. \end{aligned} \quad (\text{E16})$$

The slope was computed from $E_a(\text{I})$ and $R_{cov}(\text{I}) = 2.570028$.

FIG. E.16. (Color online) Xe-like ions ($N = 54$). Only the $Z = 74$ point shows a clear inconsistency.

Discussion:

In the Xe-like sequence (Fig. E.16), I_p at $Z = 74$ is underestimated in 0.799 a.u.

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