Regularized perturbative series for the ionization potential of atomic ions

Gabriel Gil and Augusto Gonzalez
Institute of Cybernetics, Mathematics and Physics, Calle E 309, Vedado, Havana, Cuba

We study \( N \)-electron atoms with nuclear charge \( Z \). It is well known that, in the cationic \((Z > N)\) high-\( Z \) region, the atom behaves as a weakly interacting system. The anionic \((Z < N)\) regime, on the other hand, is characterized by an instability threshold at \( Z \lesssim N - 1 \) below which the atom spontaneously emits an electron. We construct a regularized perturbative series (RPS) for the ionization potential of ions in an isoelectronic sequence that exactly reproduces both, the large \( Z \) and the \( Z \) near \( Z_c \) limits. The large-\( Z \) expansion coefficients are analytically computed from perturbation theory, whereas the slope of the energy curve at \( Z = N - 1 \) is computed from a kind of zero-range forces theory that uses as input the electron affinity and the covalent radius of the neutral atom with \( N - 1 \) electrons. Relativistic effects at the level of first-order perturbation theory in the one-particle Hamiltonian are considered. Our RPS results are compared with numbers from the NIST database.

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I. INTRODUCTION

Since the foundation of Quantum Mechanics, a huge amount of data on energy levels, linewidths and other properties of atoms have been recorded. Very often, such compilations are still waiting for a qualitative analysis, based on simple models. In the present paper, we suggest an analytical expression for the ionization energy of atomic ions and compare its predictions with the numbers provided by the NIST database.

Our expression is a regularized perturbative series (RPS), previously employed in other contexts. We use perturbation theory in \( 1/Z \) in order to compute the first two coefficients of the energy series in the large-\( Z \) region. Additionally, we require our RPS to reproduce the value of the ionization potential at \( Z = N - 1 \) (i.e. the electron affinity) and the slope of the curve at this point. The latter is computed from a kind of zero-range forces theory that uses as input the electron affinity and the covalent radius of the neutral atom with \( N - 1 \) electrons. The RPS continuously interpolates between the \( Z \approx N - 1 \) and large-\( Z \) limits for a given isoelectronic sequence.

We test our RPS against the numbers in the NIST compilation. In four isoelectronic sequences we point out experimental and computed values, contained in the database, that noticeably deviate from the expected behaviour.

II. ATOMS NEAR THE ANIONIC INSTABILITY THRESHOLD

It is well known that, for large \( Z \), the attraction of the electrons by the nucleus is stronger than electron-electron repulsion. On the contrary, for the neutral atom both contributions are more or less balanced, and in the anionic domain this balance may even be broken at a given \( Z_c \lesssim N - 1 \), where the atom spontaneously autoionizes.

First-principle calculations and some extrapolations indicate that \( Z_c \) is indeed very close to \( N - 1 \), excluding the possibility of doubly ionized atoms. A recent result by Gridnev on the other hand, rigorously states that the wave function is normalized at threshold. If we combine this result with perturbation theory, we get that the binding energy exhibits a linear dependence on \( Z \) near \( Z_c \).

In a previous paper, we compute the slope of the curve not at \( Z_c \) but at \( Z = N - 1 \). At this value of \( Z \) the outermost electron weakly interacts with the neutral core and the interaction is short-ranged. It can be shown that conditions are fulfilled for the application of zero-range forces theory. The slope of the curve may be computed from:

\[
 s = 2\kappa e^2 \frac{2}{\kappa R} \int_{R}^{\infty} d\rho e^{-2\kappa \rho / R},
\]

where \( \kappa = \sqrt{2E_a} \) and \( E_a \) is the electron affinity of the neutral system with \( N - 1 \) electrons. Atomic units are to be used everywhere in the paper. \( R \) is related with the size of core, containing nuclear charge \( Z \) and \( N - 1 \) electrons. For computational purposes, we use the covalent radius of the \( N - 1 \) electrons atom as an estimation of \( R \).

Eq. (1) will be used in Sect. IV, where we construct a RPS for the ionization potential.

III. THE LARGE-\( Z \) LIMIT

In the following, we shall construct the large-\( Z \) series for the atomic energy. This is, in fact, a formal limit. In nature, atomic nuclei become unstable for large \( Z \) and there is a threshold for electron-positron pair production at \( Z \sim 137 \). Performing the scaling \( r_i \rightarrow r_i / Z \) in the non-relativistic Hamiltonian, we get:

\[
 \hat{H} = Z^2 \left\{ \sum_{i=1}^{N} \frac{p_i^2}{2} - \sum_{i=1}^{N} \frac{1}{r_i} + 1 \sum_{i<j} \frac{1}{|r_i - r_j|} \right\}.
\]
Notice that the expression inside brackets has a one-particle contribution (kinetic energy plus nuclear attraction) and the two-particle repulsion between electrons. The latter is of order $1/Z$. At large values of $Z$, the atom can be described as a system of non-interacting electrons in the central Coulomb field of the nucleus. The energy in this leading approximation is:

$$E_0 = - \sum_{i=1}^{N} \frac{Z^2}{2n_i^2}.$$  \hspace{1cm} (3)

Next, we shall include electron repulsions in first order perturbation theory. The energy is written as:

$$E = E_0 + Z \langle \Psi_0 \left| \sum_{i<j} \frac{1}{|\vec{r}_i - \vec{r}_j|} \right| \Psi_0 \rangle,$$  \hspace{1cm} (4)

where $\Psi_0$ is the Slater determinant made of hydrogenic functions. Corrections are explicitly given by:

$$E_1 = Z \sum_{i<j} \left\{ \langle ij \parallel ij \rangle - \langle ij \parallel ji \rangle \right\}.$$  \hspace{1cm} (5)

Note that the sum runs over the occupied orbitals $|i\rangle$ and $|j\rangle$ in the Slater determinant, and that $\langle ij \parallel ij \rangle$ and $\langle ij \parallel ji \rangle$ denote, respectively, direct and exchange two-particle Coulomb integrals involving orbitals $i$ and $j$. Their explicit expression can be found in Ref. [1].

Once we constructed a series for the total energy:

$$E = a_2 Z^2 + a_1 Z + \ldots,$$  \hspace{1cm} (6)

where $a_2 = E_0/Z^2$ and $a_1 = E_1/Z$, one can find also a similar expression for the binding energy, defined as $E_B(N,Z) = E(N,Z) - E(N-1,Z)$. We get:

$$E_B = b_2 Z^2 + b_1 Z + \ldots,$$  \hspace{1cm} (7)

where,

$$b_2 = - \frac{1}{2n_f^2},$$  \hspace{1cm} (8)

$$b_1 = \sum_{j=1}^{N} \left\{ \langle Nj \parallel Nj \rangle - \langle Nj \parallel jN \rangle \right\}.$$  \hspace{1cm} (9)

In these equations, $n_f$ is the principal quantum number of the last electronic shell, and $|N\rangle$ the last occupied orbital.

To end up this section, we shall stress that, in the large-$N$ limit:

$$b_2 = \frac{1}{2} \left( \frac{2}{3} \right)^{2/3} N^{-2/3} + \ldots,$$  \hspace{1cm} (10)

$$b_1 = -0.72 N^{1/3} + \ldots.$$  \hspace{1cm} (11)

Eq. (10) comes from analytical estimations, whereas Eq. (11) comes from a fit to the numerical results. These functional forms are consistent with the dependence $E_B \approx Z^2 N^{-2/3} f(N/Z)$, suggested by Thomas-Fermi theory.

A. Relativistic corrections

At large $Z$, a relativistic approach is required. In the leading approximation, one should solve the Dirac equation for an electron in a central Coulomb field. We choose a simpler approach in which relativistic corrections are computed in first order degenerate perturbation theory.

$$E_\lambda = E_\lambda^{(0)} + \langle \lambda | V_{rel} | \lambda \rangle,$$  \hspace{1cm} (12)

$$|\lambda\rangle = |\lambda\rangle + \sum_{j \in S_{\lambda}(\lambda)} \frac{|j\rangle \langle j| V_{rel} |\lambda\rangle}{E_\lambda^{(0)} - E_j^{(0)}}.$$  \hspace{1cm} (13)

Both $|\lambda\rangle$ and $|j\rangle$ are eigenstates of the non-relativistic one-electron Hamiltonian. Greek indices label states for which the total angular momentum (orbital plus spin) is a good quantum number. The relativistic perturbation, $V_{rel}$, includes the kinetic ($\sim p^4$), spin-orbit ($\sim \hat{L} \cdot \hat{S}$), and the Darwin term ($\sim \delta(\vec{r})$) terms. The sum in Eq. (13) runs over the space orthogonal to $|\lambda\rangle$.

The first order correction to $b_1$ can be obtained by replacing the non-relativistic states $|j\rangle$ and $|N\rangle$ in Eq. (13) by the expression (13), yielding:

$$b_1 = \sum_{\lambda \neq \sigma} \left\{ \langle \sigma\lambda \parallel \sigma\lambda \rangle - \langle \sigma\lambda \parallel \lambda\sigma \rangle \right\} +$$
+ 2 \sum_{\lambda \neq \sigma, k \in S^{(0)}_\lambda} \frac{\langle \sigma \lambda | k \lambda \rangle - \langle \sigma \lambda | \lambda k \rangle}{E^{(0)}_\sigma - E^{(0)}_k} \langle k | V_{\text{rel}} | \sigma \rangle + 2 \sum_{\lambda \neq \sigma, k \in S^{(1)}_\lambda} \frac{\langle \sigma \lambda | \sigma k \rangle - \langle \sigma \lambda | k \sigma \rangle}{E^{(0)}_\lambda - E^{(0)}_k} \langle k | V_{\text{rel}} | \lambda \rangle ,

(14)

where $|\sigma\rangle$ is the last occupied state.

The $b_2$ coefficient must be changed also in accordance with (12). The final expression for $b_2$ reads:

$$b_2 = \frac{1}{2n_f^2} \left[ 1 + \frac{(Z\alpha)^2}{n_f^2} \left( \frac{n_f}{j_f + 1/2} - \frac{3}{4} \right) \right] ,

(15)$$

where $j_f$ is the total angular momentum quantum number of the last occupied state and $\alpha \approx 1/137$ is the fine structure constant.

A summary of matrix elements $\langle k | V_{\text{rel}} | \lambda \rangle$ is given in the Appendix. Details on the derivation of $\langle \lambda | V_{\text{rel}} | \lambda \rangle$ can be found in Ref. [13].

IV. REGULARIZING THE PERTURBATIVE SERIES

Once described the region near the anionic threshold and the large-Z limit, one may try to find an interpolation between them. To this end, we use a regularization of the perturbative series, Eq. (14). The next two terms of the series

$$E_B = b_2 Z^2 + b_1 Z + b_0 + \frac{b_{-1}}{Z} ,

(16)$$

are used to force that, at $Z = N - 1$, $E_B = -E_a$ and $dE_B/dZ = -s$. That is:

$$-E_a = b_2 (N - 1)^2 + b_1 (N - 1) + b_0 + \frac{b_{-1}}{(N - 1)} ,

- s = 2b_2 (N - 1) + b_1 - \frac{b_{-1}}{(N - 1)^2} .

(17)$$

We get a linear system of two equations and two variables ($b_0$ and $b_{-1}$), yielding:

$$b_0 = -E_a - 3b_2 (N - 1)^2 - (2b_1 + s)(N - 1) ,

b_{-1} = 2b_2 (N - 1)^2 + (b_1 + s)(N - 1)^2 .

(18)$$

V. RESULTS AND DISCUSSION

We would like to show that Eq. (16) provide reasonable results for the ionization potential ($I_p = -E_B$) of atomic ions. We use the data from the extensive NIST compilation as a comparison. In what follows, we plot these data along with our RPS for four isoelectronic systems (Fig. 1-3). An exhaustive revision will be published elsewhere.

It is worth noticing that, in the large-Z region, the closed shell systems are not always inert gases because of the restructuration of the energy spectra. That is the case of $N = 28$ (Ni-like) and $N = 60$ (Nd-like), for example, which have close shells at large $Z$, but not when $Z = N$. We also show in Fig. 2 the Cu-like systems ($N = 29$), which have only one electron outside closed shells at large $Z$.

In Figs. 1-3 we plot the non-relativistic and the relativistic RPS along with the NIST data. The lower panels

FIG. 1. (Color online) The case of Ne-like ions. Upper panel: Ionization potential taken from the NIST compilation along with our nonrelativistic (discontinuous, blue) and relativistically corrected (continuous, red) RPS predictions versus atomic number. Curves are smooth at any scale. Lower panel: Absolute value of the difference between the RPS relativistic curve and the NIST reported values versus atomic number. We have drawn a 5-points running average curve (continuous, blue) as a reference for deviations. The inconsistencies detected ($Z = 21, Z = 27, Z = 74$ and the abrupt jump for $Z \geq 51$) are marked with red arrows. We point out as well the great dispersion of the data for $Z > 100$ (discontinuous red ellipse).

N=10
show the absolute error $|NIST - RPS|$. First we shall notice that relativistic corrections are important at very large $Z$, specially for one-valence electron systems (Fig. 2 right panel). The latter statement comes from the well known fact that relativistic corrections are larger for lower angular momentum states.$^{13}$

It is also interesting to compare relativistic corrections in leading order ($\sim N^4Z^2\alpha^2$) with the main contribution coming from Coulomb repulsion between electrons ($\sim N^2Z$). The inequality $Z < N^{1/3}/\alpha^{2/3} \approx 27N^{1/3}$ gives the $Z$ range in which Coulomb interactions are more important than relativistic corrections. When $N = 10$, for example, the inequality is written as $Z < 58$, whereas for $N = 60$ it is $Z < 105$.

The dependence of the error, $|NIST - RPS|$, on $Z$ as given in Fig. 2 for $N = 29$, for example, is what one expects. That is, it goes to zero when $Z \rightarrow N - 1$ and for large values of $Z$ because both limits are respected by the RPS. It may grow in the intermediate region up to a few percents of $I_p$. The fact that the error grows for large $Z$ in the $N = 10$ and 60 systems may have multiple causes. On one hand, we are not exactly treating relativity, but only in first order of perturbation theory. On the other hand, the NIST data for large $Z$ usually comes from theoretical...
calculations and extrapolations.

In spite of the relatively large errors, our simple scheme allows us to identify points or regions which are not consistent with the rest of the data. In Fig. 1 for example, we draw arrows in these points (Sc XI, Co XVII and W LXIV). The uncertainties reported for Sc XI and W LXIV cannot account for these inconsistencies (see Table I). There is a noticeable jump at $Z = 50$ and a dispersion of points for $Z > 100$ that, undoubtedly, requires further attention from the NIST team.

Noticeable deviations are also seen in the $N = 28$, 29 and 60 isoelectronic sequences (Fig. 2 and 3). We shall stress that, for Nd-like ions, there is only one measured $I_p$, the rest of the points contained in the NIST database correspond to theoretical calculations or interpolated values.

The coefficients in our RPS, Eq. (16), come from first-principle considerations. One may relax this condition and fit the data by using Eq. (16) with free parameters. In Table II we show the root mean square errors of both out relativistic RPS and this reference fit. Notice that, for the reference fit, the rms error is greatly reduced.

| $N$ | RMSE Ref. fit | RMSE RPS |
|-----|--------------|----------|
| 10  | 1.19788      | 3.55392  |
| 28  | 0.113157     | 3.40226  |
| 29  | 0.827368     | 2.34635  |
| 60  | 0.249875     | 1.00877  |

TABLE II. Root mean square error of the RPS and of a reference fit (both based on Eq. (16)), as models for the NIST data, in the isoelectronic sequences considered in the paper.

VI. CONCLUSIONS

The main result of the present paper is an analytical expression for the ionization energies of $N$-electron ions ($Z \geq N - 1$) based on first-principles. This formula is exact in $Z = N - 1$ and large $Z$ regions. In the transition region, the error is only a few percents of the total ionization potential.

We show that our RPS expression may help identifying problems in a large database, such as the NIST compilation. Research along this line is still in progress.

Appendix A: Explicit matrix elements for relativistic corrections

We can write the relativistically corrected Hamiltonian as:

$$H = H_0 + V_{rel},$$

where the non-perturbed Hamiltonian is given by:

$$H_0 = -\frac{1}{2} \nabla^2 - \frac{Z}{r} = T + V,$$

and the perturbation is expressed as a sum of terms:

$$V_{rel} = H_1 + H_2 + H_3,$$

$$H_1 = \frac{\alpha^2}{2} T^2 = -\frac{\alpha^2}{2} \left( H_0 + \frac{Z}{r} \right)^2,$$

$$H_2 = \frac{Z \alpha^2}{2} \frac{1}{T^3} \vec{L} \cdot \vec{S} = \frac{Z \alpha^2}{4} \frac{1}{r^3} (J^2 - L^2 - S^2)(1 - \delta_{00}),$$

$$H_3 = \pi \frac{Z \alpha^2}{2} \delta(\vec{r}) \delta_{00}.$$
where $\alpha$ is the fine structure constant, and $l$ is the orbital angular momentum quantum number.

We consider first-order perturbative corrections due to $V_{\text{rel}}$. The relevant matrix element is $\langle i | V_{\text{rel}} | \lambda \rangle$, where $i$ is an eigenstate of $H_0$, $L^2$, $L_z$, $S^2$, $S_z$, and $| \lambda \rangle$ an eigenstate of $H_0$, $L^2$, $S^2$, $J^2$, $J_z$. Only states such that $\langle i | \lambda \rangle = 0$ enter Eq. (A3), thus we restrict ourselves to this case. We have:

$$\langle i | V_{\text{rel}} | \lambda \rangle = \frac{Z^4 \alpha^2}{2} \left[ -\langle i | 1/r | \lambda \rangle (\epsilon_n + \epsilon_{n'}) - \langle i | 1/r^2 | \lambda \rangle \right]$$

$$+ \langle i | 1/r^3 | \lambda \rangle \frac{1}{2} \left( j(j + 1) - l(l + 1) - \frac{3}{4} \right) + \pi \langle i | \delta(\vec{r}) | \lambda \rangle ,$$  \hspace{1cm} (A4)

where $j$ is the total angular momentum quantum number, and $|i\rangle$, $|\lambda\rangle$ are eigenstates of the Hydrogen ($Z = 1$) Hamiltonian. $\epsilon_n$ and $\epsilon_{n'}$ are also scaled energies.

Notice that $|\lambda\rangle$ states can be labelled by $n$ (principal quantum number), $l$, $j$ and $m_j$ (total angular momentum projection on $z$), whereas for $|i\rangle$ we need $n$, $l$, $m$ (orbital angular momentum projection on $z$), and $s_z$ (spin angular momentum projection on $z$). We can expand $|nljm_j\rangle$ in terms of $|nlms_z\rangle$ by means of the Clebsch-Gordan coefficients:

$$\langle nlsjm_j | nlsms_z \rangle \langle lsms_z | jm_j \rangle ,$$  \hspace{1cm} (A5)

$$\langle lsms_z | jm_j \rangle$$

are non-vanishing only for $|l - s| \leq j \leq l+s$, and $m_j = m + s_z$.

The matrix elements entering Eq. (A4) are explicitly written as:

$$\langle i | \delta(\vec{r}) | j \rangle = \delta_{l0} \delta_{l'0} \delta_{mm'} \delta_{ss_0} \frac{1}{\pi} \frac{1}{(nm')^{3/2}} ,$$  \hspace{1cm} (A6)

$$\langle i | 1/r | j \rangle = Z^4 \delta_{l0} \delta_{ll'} \delta_{ss} \delta_{ss_0} \theta(n' - 1 - l) 2^{2l+2} \frac{(nm')^{l-q+1}}{(n+n')^{2l+2-q+1}} \sqrt{(n - l - 1)!(n' - l - 1)!(n + l)!(n' + l)!}$$

$$\times \sum_{k=0}^{n-l-1} \sum_{k'=0}^{n'-l-1} k!k'!(n - l - k - 1)!(n' - l - k' - 1)!(2l + k + 1)!(2l + k' + 1)! \left( \frac{n}{(n+n')^{k+k'}} \right) \Gamma(k+k' + 2l+2 - q + 1) ,$$  \hspace{1cm} (A7)

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