On $1/Z$ expansion, critical charge for two-electron system and Reinhardt conjecture

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Abstract

The $1/Z$-expansion for the Coulomb system of infinitely massive center of charge $Z$ and two electrons (two electron ion) is discussed. Critical analysis of Baker et al, Phys. Rev. A41, 1247 (1990) is performed and its numerical deficiency, in particular, leading in the first coefficients of $1/Z$-expansion to unreliable decimal digits beyond 11-12th is indicated. Checking consistency it is shown that weighted sums of $1/Z$-expansion with Baker et al. coefficients reproduce the ground state energies of two-electron ions with $Z \geq 2$ with 12 decimal digits and sometimes up to one portion the 13th decimal. Ground state energies of two-electron ions $Z = 11$ ($Na^{9+}$) and $Z = 12$ ($Mg^{10+}$) are found with 12 decimal digits. It is demonstrated that the ground state energy behavior vs. $Z$ in vicinity of the critical charge \([Z_{cr} \div \frac{1}{2.5}]\) is described accurately by a terminated Puiseux expansion with integer and half-integer degrees being consistent with the critical charge and the linear slope found in Estienne et al. (2014). It suggests the existence of the square-root branch point at $Z_{cr}$ with exponent $3/2$. Close consistency of the Puiseux expansion with the higher order coefficients $e_{100,200}$ in $1/Z$-expansion, carried out by Baker et al. is indicated. It favors the Reinhardt conjecture about a connection between the radius of convergence $\lambda_{s}$ of $1/Z$-expansion and the critical charge, $\lambda_{s} = \frac{1}{Z_{cr}}$. 

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Two electron system with infinitely-massive charge center $Z$ is described by the Hamiltonian

$$
\mathcal{H} = -\frac{1}{2}(\Delta_1 + \Delta_2) - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}.
$$

(1)

A change of variables in (1), $\vec{r} \to \vec{r}/Z$, leads to a new form of the Hamiltonian

$$
\mathcal{H}_t = -\frac{1}{2}(\Delta_1 + \Delta_2) - \frac{1}{r_1} - \frac{1}{r_2} + \frac{\lambda}{r_{12}}, \quad \lambda = \frac{1}{Z},
$$

(2)

where the new energy $\tilde{E}(\lambda) = \frac{E(Z)}{Z^2}$, while $E(Z)$ is the ground state of (1). One of the important tools to study the spectra of (1) proposed in early days of quantum mechanics is to develop the perturbation theory in (2) in powers of $\frac{1}{Z}$ constructing the expansion of $\tilde{E}$,

$$
\tilde{E} = \sum_{n=0}^{\infty} e_n \lambda^n.
$$

(3)

The first two coefficients are found analytically, $e_0 = -1, e_1 = \frac{5}{8}$ while other coefficients can be found only approximately. The first attempt to calculate the next three of them was carried out by Hylleraas [1] and then many workers dedicated a plenty of efforts to find as many of these coefficients as possible with the highest possible accuracy (see [2] and [3] where extensive discussion with extended bibliography together with historical account is presented). A culmination of this story had happened at 1990 when Baker et al. [3] computed as many as $\sim 401$ coefficients of $1/Z$-expansion [3] essentially overpassing all previous calculations in both accuracy and the number of coefficients. It is worth mentioning that one of the main reasons of such an interest to $1/Z$-expansion from the point of theory: it is among very few convergent(!) expansions in quantum physics, thus, it was considered as a challenge to find its radius of convergency $\lambda_*$, the asymptotic behavior of coefficients.

Many years ago F. Stillinger [4] presented arguments that $\lambda_* > 1/Z_{cr}$ - the inverse critical charge for which the system $(Z, 2e)$ at $Z < Z_{cr}$ gets unbound, thus, $\tilde{E}(Z_{cr}) = -\frac{1}{2}$ and ionization energy is equal to zero. Later this statement was challenged by W. Reinhardt [5] who conjectured that the radius of convergency coincides with the inverse critical charge $\lambda_* = 1/Z_{cr}$ and there exists a singularity at $\lambda = \lambda_*$ (see for discussion [3] and references therein).

We are not aware about any studies of $1/Z$-expansion coefficients performed, after the paper of Baker et al. [3] was published (and became canonical), for about twenty years. In 2010 the results of [3] were challenged in [6]. In this paper it was shown that the asymptotic
behavior of the coefficients $e_n$ at $n \to \infty$ derived from the analysis of the coefficients $e_n$, taken from $n = 13$ to $n = 19$, differs from one obtained from the analysis of the coefficients $e_n$ taken from $n = 25$ to $n = 401$. It leads to a significant deviation at large $n$ coefficients, e.g. at $n = 200$ the discrepancy in the leading significant digit is about 50% while $e_{200}$ is itself of the order $10^{-16}$ (see below Table 11). In [1] this result was considered as an indication that the computational accuracy at [3] is exaggerated, in particular, the quadruple precision arithmetics either does not work or might be insufficient, at least, for calculation of the first significant digits in the higher order coefficients. From another side in [8] it was indicated the sum of printed $e_n$-coefficients in [3] does not correspond to the number which was reported in 13-15 decimal digits. It was also shown that making a phenomenological analysis by fitting the coefficients $e_{2-6}$ allows to reproduce the ground state energies for $Z = 1 - 10$ found in [9] with 14 decimal digits. Those fitted coefficients $e_{2-6}$ coincided with ones from [3] in 12 decimal digits but usually differed in others. In particular, in $e_2$ the 14th decimal from the fit should be 5 instead of 4. All that was considered as an indication that $e_n$-coefficients found in [3] are doubtful beyond 12 decimal digits. Note that in [7] it was also constructed a terminated Puiseux expansion (in fractional degrees) as high accuracy interpolation of the ground state energy close and above the critical charge $Z_{cr}$. It was shown that the Puiseux expansion contains integer and half-integer degrees and the asymptotic behavior of the $e_n$ coefficients derived from that is incompatible with one found in [3]. Hence, the Reinhardt conjecture $\lambda_* = 1/Z_{cr}$ can fail. Also it was demonstrated that the critical charge derived from the Puiseux expansion coincides in three decimals with one found in [3] variationally.

The main goal of this paper is to check compatibility of the ground state energies at $Z = 1, 2, 3, \ldots, 10$ found perturbatively using the coefficients $e_n$ obtained (and printed) in [3] with highly accurate results for the ground state energies of two-electron ions obtained in [9]. Another goal is to make a perturbative calculation of the threshold energy $E_{th}$ which corresponds to the critical charge, thus, for which the ionization energy vanishes. In particular, we want to calculate the ground state energies at $Z = 11, 12$ perturbatively with maximal possible accuracy at present. All perturbation theory summations are made and checked in two different multiple precision arithmetics: (i) ifort q-precision real*16 (quadruple precision) and (ii) Maple Digits=30 in Maple 13. Eventually, the third goal is to construct a terminated Puiseux expansion from the critical charge reliably calculated at [11] checking a presence of a singularity.
We begin our presentation indicating three numerically incorrect statements from the canonical paper [3].

(I). The first observation is that we do not confirm the statement from [3] (p.1254) (see [8]):

*The sum of the $e_n$’s for $n$ running from 0 to 401 is

$$-0.527751016544266$$

which at the time we did our calculations was the most accurate estimate of the energy for the ground state of $H^-$. Our result of summation using $e_n$ printed in [3], Table III, in general, with ten significant figures but eventually presented with 12 decimals, at least, and sometimes more decimals (by adding zeroes afterwards, those digits were neither printed nor mentioned in [3] but needed to get (4))

$$-0.527751016544160$$

differs in the last three decimal digits. It gives us a chance to suspect that either the quadruple precision arithmetics used by the authors of [3] was insufficient due to accumulation of errors or the length of the trial function expansion (476 basis functions) was not enough or both factors together prevent to go beyond 12 decimal digits. Thus, we can not trust decimal digits beyond 12th in coefficients $e_n$. In particular, all $e_n$ for $n > 135$ (when the (rounded) coefficients are of the order $10^{-12}$ and less, see [3], Table III) may seem unreliable. Concluding, we have to note that both above numbers for energy at $Z = 1$ coincide up to 12 decimal digits with accurate result obtained in [9]

$$-0.527751016544377$$

but differ from it in 13th and subsequent decimal digits. It is the explicit indication that $e_n$ (all or some) calculated in [3] beyond 12 decimal digits are not trustful. Furthermore, making a comparison of the numbers (4) and (5) one can draw a conclusion that the results obtained in [3] remain doubtful even if we assume that more significant figures in $e_n$ were calculated, then for whatever reason not printed in [3] but used to obtain the sum (4).

(II). The second observation is that we do not confirm another statement from [3] (p.1254):

*For $Z = 2$ the corresponding weighted sum of coefficients … yields an estimate of

$$-2.9037243770341167$$

(6)
for the ground state energy of helium.... Our result using \( e_n \) printed in [3] with ten significant figures, in general, but with 12 decimals at least (by adding zeroes afterwards)

\[
-2.903\,724\,377\,034\,051\,9 \quad (\text{non-rounded})
\]
differs in the last four decimal digits. We have to note that both above numbers coincide up to 12 decimal digits (before rounding) with accurate result given by [9] for \( Z = 2 \)

\[
-2.903\,724\,377\,034\,119\,5 \quad (7)
\]
Even if we assume that more significant figures in \( e_n \) were calculated but not printed in [3], the result (6) differs from (7) in 15-16th decimal digits. It is the explicit indication that \( e_n \) calculated in [3] beyond 14th decimal digit are not trustful.

Following the above conclusions the number of trustable significant digits in \( e_n \) from [3] reduces gradually with increase of \( n \) and becomes for \( e_{40,50} \) equal to 5 out of 12 decimal digits. It leads to questioning the statement from [3] (p.1254):

(III). The results ... suggest that even our higher order \( e_n \)'s are accurate to a few parts in \( 10^{-5} \) and our high-order \( r_n \)'s (the ratio of subsequent coefficients) to a few parts in \( 10^{-6} \).

We are puzzled why the authors of [3] decided (and Physical Review A Editors agreed and permitted) to print in their Table III ten significant figures in higher order coefficients, say, \( n > 40 \) knowing in advance that their correctness is not guaranteed.

Taking into account coefficients \( e_n \) found in [3] (see Table III therein), we obtain an agreement between energies found perturbatively through (3) and ones [9] for all \( Z = 2 \ldots 10 \): they coincide up to 12th, even 13th decimal digits, see our Table III. Since a contribution of the higher order coefficients in the weighted sum [3] to the ground state energy decreases dramatically with the increase of the charge \( Z \), it is guaranteed that the same number 12 of correct decimal digits, at least, should be obtained for larger \( Z > 10 \). Based on that the ground state energies for two-electron ions \( Z = 11 \) (\( Na^{9+} \)) and \( Z = 12 \) (\( Mg^{10+} \)) are calculated perturbatively and presented in Table III. They essentially improve the most accurate results obtained in [10] long ago: they differ from them in the sixth decimal digit. However, for \( Z = 1 \) the agreement between energy found perturbatively through (3) and one from [9] occurs up to 12th decimal digit only (before rounding). We made an experiment by rounding the coefficients \( e_n \) from [3] to 12 decimals. It implies, in particular, that all \( e_n = 0, \; n > 135 \), and then calculated weighted sums. For \( Z = 2, \ldots, 12 \) the results for
weighted sums remain essentially unchanged up to 12 decimals, see Table III sometimes making a difference in one portion of $10^{-12}$. It implies that, in fact, decimals beyond 12th in $e_n$ do not give a contribution to the first 12 decimal digits in ground state energies for $Z = 2, \ldots, 12$. However, for $Z = 1$ the situation gets different: the sum is increased in such a way that a coincidence with the energy of [9] occurs up to 10th decimal digit only (after rounding), see Table III. It can be considered as an indication to a presence of incorrectly calculated decimal digits in [3] in coefficients $e_n, n > n_0$ beyond the first 10th decimals, where $n_0$ is some integer. It seems evident that $e_n$-coefficients should be recalculated beyond 10th decimal digits in order to get an agreement with the energy found in [9] for $Z = 1$.

Recently, Estienne et al. [11] (EBMD) in remarkable, high precision variational calculation with triple basis sets containing up to 2276 terms obtained highly accurate value for the critical charge

$$Z_{cr}^{EBMD} = 0.911 028 224 077 255 73 , \quad (8)$$

and for the linear slope of $E(\lambda)$ at the critical charge, 0.2451890639. This result (8) coincides in 5 decimals with one from [3] and in 3 decimals with [7] (after rounding). In spite of the Reinhardt conjecture claim that the $1/Z$ expansion diverges at $Z_{cr}$ we calculated the weighted sum [3] for such a critical charge using the coefficients from [3], see Table III.

Surprisingly, this result being compared with the exact energy at threshold,

$$E_{th} = -\frac{(Z_{cr}^{EBMD})^2}{2} , \quad (9)$$

leads to a difference $\sim 10^{-7}$. The remainder in (3) is

$$\frac{e_{401}}{Z_{401}^{cr}} \sim -2 \times 10^{-9}.$$  

It indicates the singularity at $Z_{cr}$ if exists is pretty "weak". Recently, the value of the critical charge (8) was calculated in a direct solution of the Schroedinger equation for the Hamiltonian (1) using the Lagrange-mesh method [12]. It was found that for $Z = Z_{cr}^{EBMD}$ the lowest eigenvalue coincides with threshold energy $E_{th}$ in 11 decimal digits. That corresponds to the ionization energy $\sim 10^{-12}$.

With accurate knowledge of the critical charge (8) and linear slope of $E(\lambda)$ at the critical charge [11] (predicted in [13]) one can make the analysis of the behavior of the ground state energy $\tilde{E}(\lambda)$ in vicinity of the inverse critical charge at $\lambda \leq \lambda_{cr}$ fitting $\tilde{E}(\lambda)$ via the terminated Puiseux expansion (c.f. [7]). This time it is the interpolation of energy $E(Z)/Z^2$.
at eight points including the critical charge, $Z \in [Z_{EBMD}^{cr}, 0.95, 1., 1.05, 1.1, 1.15, 1.2, 1.25]$ taken the energies for $Z > Z_{EBMD}^{cr}$ calculated in [7]. It leads to the expansion
\[
\tilde{E}^{(fit)}(\lambda) = -\frac{1}{2} - 0.2451890639 \tilde{\lambda} - 0.0252309 \tilde{\lambda}^{3/2} - 0.5532438 \tilde{\lambda}^2 \\
+ 0.9729112 \tilde{\lambda}^{5/2} - 0.707285 \tilde{\lambda}^3 + \ldots ,
\] (10)
(c.f. [7]), where $\tilde{\lambda} = (\lambda_{EBMD}^{cr} - \lambda)$ and $\lambda_{EBMD}^{cr} = 1.09766083373855980$ [11]. The expression (10) reproduces 7 s.d. in energies at $Z$ close to the critical charge, e.g. at $Z = 0.95$ gradually deteriorating with the increase in $Z$ giving 3 s.d. at $Z = 1.25$, for an illustration see Table I. Note the coefficients in front of half-integer degrees are sufficiently large indicating impossibility to interpolate the above-mentioned energies using a terminated Taylor expansion in $\tilde{\lambda}$. The existence of the Puiseux expansion (10) leads to a conclusion that the energy $E(Z)$ (or $\tilde{E}(\lambda)$) has square-root singularity with exponent $3/2$ at the critical charge in agreement with [4], [6], [7]. Thus, it can be considered as an indication the validity of the Reinhardt conjecture about a connection between the radius $\lambda^*_{cr}$ of convergency of $1/Z$-expansion and the critical charge, $\lambda_c = \lambda_{cr}$. Physics meaning of this singularity is unclear: can it make sense as a point of level crossing.

The expression (10) provides a behavior of the energy near singularity at the critical charge in dominant and several subdominant orders. Thus, after expanding (10) in powers of $\lambda$, the expansion of the coefficients $e_n$ in powers $1/n$ should be generated. The dominant term of this expansion emerges from term $\sim (\tilde{\lambda})^{3/2}$, the subdominant one comes from $\sim (\tilde{\lambda})^{5/2}$ etc. In Table II the comparison of the calculated coefficients $e_{100,200}$ in [3] with ones found

| Z   | $E$   | $E^{(fit)}$ |
|-----|-------|------------|
| 1.3 | -0.609 406 309 | -0.609 9   |
| 1.25| -0.597 488 174 | -0.597 7   |
| 1.15| -0.571 655 437 | -0.571 68  |
| 1.00| -0.527 751 017 | -0.527 751 009 |
| 0.95| -0.512 049 529 | -0.512 049 511 |

TABLE I: Ground state energy $E$ for two-electron ion for selected values of $Z$ found in [7] and corrected at [12] for $Z = 0.95$ where all displayed digits assumed to be correct and $E^{(fit)}$ from the fit (10).
| n     | [3]  | [6]  | [7]  | [11] |
|-------|------|------|------|------|
| 100   | -0.398e-10 | - | -0.689e-10 | -0.234e-10 |
| 200   | -0.301e-15 | -0.222e-15 | -1.065e-15 | -0.271e-15 |

TABLE II: Comparison the $e_n$-coefficients in the expansion (3) calculated in [3] (rounded to 3 s.d.), obtained in [6] and [7], and ones found by using the formula (10).

| $Z_{cr}^{EBMD}$ | $E$ (a.u.) from [3] | $E$ (a.u.) |
|-----------------|---------------------|------------|
| -0.414 986 047  | -0.414 986 212 532 679 |
| -0.414 978 381   | -0.414 986 212 53 [12] |
| -0.527 751 016 544 (2) | -0.527 751 016 544 377 |
| -0.527 751 016 499 (*) | -0.527 751 016 499 (*) |
| -2.903 724 377 034 (1) | -2.903 724 377 034 119 |
| -7.279 913 412 669 (3) | -7.279 913 412 669 305 |
| -13.655 566 238 423 (6) | -13.655 566 238 423 586 |
| -22.030 971 580 242 (8) | -22.030 971 580 242 781 |
| -32.406 246 601 898 (5) | -32.406 246 601 898 530 |
| -44.781 445 148 772 (7) | -44.781 445 148 772 704 |
| -59.156 595 122 757 (9) | -59.156 595 122 757 925 |
| -75.531 712 363 959 (4) | -75.531 712 363 959 491 |
| -93.906 806 515 037 (5) | -93.906 806 515 037 549 |
| -114.281 883 776 072 (7) | -114.281 879 (**) |
| -136.656 948 312 646 (9) | -136.656 944 (**) |

TABLE III: Perturbative Theory energies $E(Z)$ from (3) with coefficients $e_n$ from (3), (*) with reduced # of decimal digits (see text). Energies $E$ (rounded, right column) at the threshold, for $Z = 1$ (see text), from Ref. [9] for $Z > 1$; the results from [10] marked by (**) in re-expansion of [10] as well as in other approaches. It shows that even the very accurate interpolation of the energy on the level of 12 decimal digits where the point $Z_{cr}$ is not included which was performed in [7] leads to a certain inaccuracies at coefficients and the critical charge - it is determined with 3 s.d. only (see above). In turn, the fit (10) leads to
the agreement in coefficient $e_{100}$ in $\sim 50\%$ while the agreement in coefficient $e_{200}$ increases up to $\sim 10\%$ and even the first significant figure is reproduced! The reason of disagreement might be related with a existence of the square-root branch points in complex $\lambda$-plane due to level crossings and thus a contribution of them to $e_n$-coefficients. Since probably there are infinitely-many such branch points their contribution to coefficients of $1/Z$ expansion even of large order can be significant. It can create an obstacle to find the asymptotic behavior out of coefficients of finite order.

Concluding we state that the use the coefficients by Baker et al. ones in weighted sum (3) allow to reproduce up to 12 decimals in exact ground state energies for $Z = 1, \ldots, 10$. It seems crucial to recalculate $e_n$ with $n > 200$ and make a comparison with the coefficients obtained from (10). It will allow to check and probably establish the asymptotic behavior of the $e_n$-coefficients at $n \to \infty$.

We feel a necessity to develop an alternative, analytical approach for finding the asymptotic behavior of $e_n$-coefficients, probably, similar to one based on dispersion relations in a coupling constant for anharmonic oscillators due to Bender and Wu [14] or derived directly from path integral as is done in quantum field theory. A separate issue is to find level crossings in $\lambda$ complex plane closest (and close) to $\lambda_{cr}$ and its contribution to $e_n$ coefficients. It might be a subject to future work. Careful numerical analysis of the behavior of $E(\lambda)$ near $\lambda_{cr}$ using a finite number of terms in Puiseux expansion leads to degrees which are (very) close to integer and half-integer numbers. It was a natural assumption that these numbers are, in reality, integer and half-integer. It has to be justified rigorously. We do not think that without addressing above issues the validity of the Reinhardt conjecture can be established.

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