On $1/Z$ expansion for two-electron systems

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Abstract

The $1/Z$-expansion for the Coulomb system of infinitely massive center of charge Z and two electrons is discussed. Numerical deficiency in Baker et al, Phys. Rev. A41, 1247 (1990) is indicated which continue to raise doubts in correctness of their calculations of the higher order coefficients in $1/Z$-expansion expressed in Refs.[4-5]. It is shown that a minor modification of a few first coefficients found in Ref.[3] allows to calculate the ground state energies at $Z = 1, 2, \ldots, 10$ (as well as at $Z > 10$) with a portion of 15th decimal digit in comparison with highly accurate calculations by C. Schwartz and by Nakashima-Nakatsuji. Ground state energies of two-electron ions $Z = 11$ ($Na^{9+}$) and $Z = 12$ ($Mg^{10+}$) are found with 14 decimal digits.

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Two electron system with infinitely-massive charge center $Z$ is described by the Hamiltonian
\[ H = -\frac{1}{2}(\Delta_1 + \Delta_2) - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{ab}}. \] (1)

A change of variables in (1), $\vec{r} \to \vec{r}/Z$, leads to a new form of the Hamiltonian
\[ H_t = -\frac{1}{2}(\Delta_1 + \Delta_2) - \frac{1}{r_1} - \frac{1}{r_2} + \frac{\lambda}{r_{ab}}, \quad \lambda = \frac{1}{Z}, \] (2)
where the new energy $\tilde{E}(\lambda) = \frac{E(Z)}{Z^2}$. One of the important tools to study the spectra of (2) is to develop the perturbation theory 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, $E_0 = -1, E_1 = 5/8$ 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 are 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 one of the main reasons of such an interest to $1/Z$-expansion: it is among very few convergent(!) expansions in quantum physics, thus, it was considered as a challenge to find the radius of convergency $\lambda_*$. Furthermore, it was conjectured that the radius of convergency coincides with inverse critical charge $\lambda_* = 1/Z_{cr}$, for which the system $(Z, 2e)$ at $Z < Z_{cr}$ gets unbound (see [3] and references therein).

We are not aware about any studies of $1/Z$-expansion performed, after the paper of Baker et al, [3] was published, for about twenty years. In 2010 the results of [3] were challenged [4]. It was shown that the asymptotic behavior of the coefficients $e_n$ at $n$ tends to infinity 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 of the order $10^{-16}$. In [5] it was considered as an indication that the computational accuracy at [3] is exaggerated, in particular, the
proclaimed quadruple precision arithmetics did not really work (or insufficient), at least, for calculation of the first significant digits in the higher order coefficients. In [5] it was also constructed the Puiseux expansion (in fractional degrees) of the ground state energy near the critical charge $Z_{cr}$. It was shown that the asymptotic behavior of the $e_n$ coefficients found in [3] is incompatible (slightly) with one derived from the Puiseux expansion, hence, the Reinhardt conjecture $\lambda^*_r = 1/Z_{cr}$ fails.

The goal of this short Note is to check compatibility of the ground state energies at $Z = 1, 2, 3, \ldots, 10$ found perturbatively, in particular, using the coefficients $e_n$ obtained (and published) in [3] with highly accurate results for the ground state energies of two-electron ions obtained in [6] and [7]. All calculations were made and checked in three different multiple precision arithmetics: (i) ifort q-precision real*16 (quadruple precision), (ii) Maple Digits=30 in Maple 13 and (iii) Charles Schwartz multiple precision arithmetic package.

The first observation is that we do not confirm the statement from Baker et al, [3] (p.1254):

\textit{The sum of the $e_n$’s for $n$ running from 0 to 401 is}

$$-0.527751016544266$$

\textit{which at the time we did our calculations was the most accurate estimate of the energy for the ground state of $H^-$}. Our result using $e_n$ published in [3]

$$-0.527751016544160$$

differs in the last three decimal digits. It gives us a chance to suspect that the quadruple precision arithmetics used by the authors of [3] did not really work and, probably, was downgraded to double precision arithmetics, or was insufficient to go beyond 12 decimal digits. Thus, we can not trust decimal digits in coefficients $e_n$ beyond 12th digit and, in particular, all $e_n$ for $n > 135$ (when the (rounded) coefficients are of the order -12 and less, see [3], Table III) are unreliable. Probably, they are random numbers ranging from 0 to 9.

Concluding, we note that both above numbers coincide up to 12 decimal digits with accurate result given by [7] for $Z = 1$

$$-0.527751016544377$$

but differ from it in 13th and subsequent decimal digits. It is the explicit indication that $e_n$ calculated in [3] beyond 12 decimal digits are wrong.
Taking all 401 $e_n$ coefficients from [3] we calculated the weighted sums (3) for $Z = 1, \ldots, 10$ and compared with the energies found in [6] at $Z = 2$ and [7]. They coincided up to 12 decimal digits. We consider it as an indication that 12 decimal digits in coefficients $e_n$ in [3], Table III might be correct. Taking $e_2$ from [12] and making a ”minimal” modification of the coefficients $e_3, e_4, e_5, e_6$, see Table II we obtain a substantial improvement in the agreement between energies found perturbatively through (3) and ones from [6] and [7]: for all $Z = 1 \ldots 10$ they differ in a portion of 15th decimal digit (see Table II). 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 14 of the correct decimal digits should be obtained for larger $Z > 10$. As an example, 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, known up to date to the present authors, by [8], they differ from them in the sixth decimal digit.

\begin{verbatim}
$e_0 = -1$
$e_1 = +5/8$
$e_2 = -0.157 666 429 469 15^*$
$e_3 = +0.008 699 031 527 90 8 -$
$e_4 = -0.000 888 707 284 23 (-)
$e_5 = -0.001 036 371 848 05 (- -)
$e_6 = -0.000 612 940 520 53 (-)
$e_7 = -0.000 372 175 576 5$
$e_8 = -0.000 242 877 973 2
$e_9 = -0.000 165 661 054 7
$e_{10} = -0.000 116 179 202 6
\end{verbatim}

TABLE I: List of the first perturbation coefficients $e_n$, some of them are modified in comparison with ones found in [3], modification is marked by bold, non-modified (original) digits from [3] are shown in brackets, dash means that digit was not present in original coefficient; * $e_2$ found by C Schwartz [12]: the difference with $e_2$ from [3] in 14th decimal digit, 4 is replaced by 5.

Concluding we want to state that independent calculation of coefficients of $1/Z$-expansion
Z | $E$ (a.u.) from (3) | $E$ (a.u.) from Refs. [6], [7]
---|------------------|------------------
1  | -0.527 751 016 544 380 | -0.527 751 016 544 377 |
2  | -2.903 724 377 034 122 | -2.903 724 377 034 119 |
3  | -7.279 913 412 669 304 | -7.279 913 412 669 305 |
4  | -13.655 566 238 423 584 | -13.655 566 238 423 586 |
5  | -22.030 971 580 242 778 | -22.030 971 580 242 781 |
6  | -32.406 246 601 898 527 | -32.406 246 601 898 530 |
7  | -44.781 145 148 772 701 | -44.781 145 148 772 704 |
8  | -59.156 595 122 757 921 | -59.156 595 122 757 925 |
9  | -75.531 712 363 959 486 | -75.531 712 363 959 491 |
10 | -93.906 806 515 037 544 | -93.906 806 515 037 549 |
11 | -114.281 883 776 072 717 | -114.281 879 (*) |
12 | -136.656 948 312 646 925 | -136.656 944 (*) |

TABLE II: Left column: perturbatively found energies $E(Z)$ from $[3]$ with coefficients $e_{3,4,5,6}$, see Table I and others from $[3]$. Right column: rounded results from Refs. $[6]$ ($Z = 2$) and $[7]$, the results from Ref. $[8]$ marked by (*)

is needed. From one side, it can be repeated the same calculation as in $[3]$ but with reliable multiple precision package. From another side, much more accurate trial functions, than one used in $[3]$, are now available like one by Korobov $[9]$, or by Drake et al. $[10]$, or by Schwartz $[6]$ (see Notes added), or by Nakashima-Nakatsuji $[7]$ among others. It seems any of these trial functions can be taken as entry in the procedure elaborated in $[3]$. Such a calculation can eventually allows to find the asymptotic behavior $e_n$ coefficients, radius of convergency of $1/Z$-expansion (a value of critical charge) and reveal a structure of singularity. Besides that we feel a need to develop analytical approach for finding the asymptotic behavior of coefficients, probably, similar to dispersion relations in a coupling constant for anharmonic oscillators due to Bender and Wu $[11]$.

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*Note added. I. (Sept.22, 2013).* When the article was submitted for publication, C. Schwartz informed us that he carried out a direct calculation of $e_2$ with 25 decimal digits [12]

$$e_2 = -0.1576664294691509410566793$$

It does not confirm the 14th decimal digit found in [3]. Thus, it provides one more indication that the accuracy reported in [3] was exaggerated and the results presented there are not reliable. We used the $e_2$ reported in [12] for our analysis, see Table I.

*Note added. II. (Nov.21, 2013).* When the article was under consideration, C. Schwartz informed us that he carried out a direct calculation of the coefficients $e_3 - e_{20}, e_{30}, e_{40}, e_{50}$ [13]. It was used the $F$-function method [6] with basis set length up to 3091 terms [14] in 58-digit arithmetics. It was shown that the 12th decimal digit (and next ones when available) of $e_3 - e_{20}$ calculated in [3] are found systematically wrong which is in agreement with main conclusion of this paper. Furthermore, the number of correct significant digits reduces gradually with $n$ and becomes for $e_{50}$ equal to 5 out of 12 decimal digits. If such a tendency will continue there will be no correct significant digits found in $e_n$ for $n \geq 130$.

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