Convergence study of the 1/Z expansion for the energy levels of two-electron atoms

J. Zamastil, J. Čížek, L. Skála, and M. Šimánek
Department of Applied Mathematics, University of Waterloo, Waterloo, Ontario, N2L 3G1, Canada, and Department of Chemical Physics and Optics, Charles University, Faculty of Mathematics and Physics, Ke Karlovu 3, CZ-121 16 Prague 2, Czech Republic

(Received 2 December 2009; published 22 March 2010)

We perform numerical analysis of the first 20 and 14 coefficients for $1\,^1S$ and $2\,^3S$ states of the $1/Z$ expansion of the energy of two-electron atoms, respectively. The radius of convergence and large-order behavior of the coefficients are determined. The results obtained are in disagreement with those given so far in the literature. We sum the terms of the series with known coefficients and the remainder of the series where we replace the actual coefficients by their large-order values. We show that inclusion of the remainder improves agreement with variational results by more than three orders of magnitude. We argue that the energy is at least three times and most likely infinitely degenerate at the singularity. Numerical result for the effective characteristic polynomial supports this conclusion.

DOI: 10.1103/PhysRevA.81.032118 PACS number(s): 03.65.Ge, 02.30.Lt

I. INTRODUCTION

The Schrödinger equation for two-electron atoms in atomic units reads

$$\left[-\frac{\nabla^2_{(1)}}{2}-\frac{\nabla^2_{(2)}}{2}-\frac{Z}{r_1}-\frac{Z}{r_2}+\frac{1}{r_{12}}\right]\psi=E(Z)\psi. \quad (1)$$

By scaling the coordinates of the electrons $\vec{x}^{(i)}\to Z^{-1}\vec{x}^{(i)}$, $i=1,2$, we get an equivalent equation

$$\left[-\frac{\nabla^2_{(1)}}{2}-\frac{\nabla^2_{(2)}}{2}-\frac{1}{r_1}-\frac{1}{r_2}+z\frac{1}{r_{12}}\right]\psi=E(z)\psi, \quad (2)$$

where $z=1/Z$ and $E(z)=E(Z)/Z^2$. Searching for the solution in the form of a series in the inverse powers of the nuclear charge one obtains the $1/Z$ expansion

$$E(z)=\sum_{n=0}^{\infty}K_n z^n, \quad (3)$$

which is subject of this paper.

This expansion and its generalization is one of the key tools in atomic physics calculations. It has been used, for example, for determination of the energy levels of the highly charged ions within the S-matrix approach [1], for calculation of the Hartree-Fock and correlation energies [2], energy levels, autoionization rates, and radiative transition probabilities for autoionizing states [3], for determining accurate energies and oscillator strengths for many-electron ions [4], for calculating the double photoeffect [5], and for estimation of the negative energy contributions to transitions amplitudes [6]. This list is far from being complete.

There has long been confusion, described in [7], about two points. First, what is the position z_0 and nature of the singularity closest to the point of expansion $z=0$? Second, what is the relation of z_0 to the critical value z_c for which there is a bound state with zero binding energy? The importance of these questions lies in the fact that the position and nature of the singularity determine the radius and rate of convergence of the series (3). This is of crucial importance for the practical use of the $1/Z$ expansion. Identification of z_0 with z_c then determines the nature of the resonances states (see, e.g., [8]).

This confusion seemed to be definitely settled in [7]. However, as we shall argue, part of the analysis made there is not correct. Namely, we find that the position and nature of the singularity are different than that given there.

To determine the position and nature of the singularity one has to know a sufficient number of the perturbation coefficients with sufficient accuracy. This problem has been only gradually appreciated over the years (see the discussion in [7]). What is especially disturbing is that one does not *a priori* know what is meant by a "sufficient number" and "sufficient accuracy."

We take the first 20 coefficients given in Table III of [7] for the $1\,^1S$ state and the first 14 coefficients given in Table IV of the same paper for the $2\,^3S$ state. For the coefficient K_2 for the $1\,^1S$ state we take the value given in the main text of the paper between Eqs. (45) and (46). These are the only coefficients given so far in the literature that meet both criteria of "sufficient number" and "sufficient accuracy."

We determine the position and nature of the singularity by the method developed in [9]. This yields precise knowledge of the large-order behavior of the coefficients K_n. For the $1\,^1S$ state we sum the first 20 coefficients and the remainder of the series where the actual coefficients are replaced by their large-order values. We show that inclusion of the remainder improves the agreement with variational results by more than three orders of magnitude. For the $2\,^3S$ state the results are even more impressive. This is the most important result of this paper. First, it shows how the performance of the perturbation method can be improved. Second, it provides support for the correctness of the analysis made here. Further, we analyze the characteristic polynomial in the vicinity of the singularity. We come to the conclusion that the energy is at the singularity at least three times and most likely infinitely times degenerate. We construct the effective characteristic polynomial [10] to verify this conclusion numerically.

II. THE METHOD

First we describe the method given in [9] for determination of the nature and position of the singularity closest to the point of the expansion. Second, we show how this knowledge can be used for improvement of the perturbation result.

Let us assume that the function $E(z)$ behaves at the neighborhood of the singularity z_0 as

$$E(z) = c_1\left(1-\frac{z}{z_0}\right)^{\alpha_1} + c_2\left(1-\frac{z}{z_0}\right)^{\alpha_2} + \cdots + d_0 + d_1\left(1-\frac{z}{z_0}\right) + d_2\left(1-\frac{z}{z_0}\right)^2 + \cdots, \quad (4)$$

where α_i are supposed to be rational and noninteger. The integer powers do not influence the large-order behavior of the series (3).

We show how from this assumption the large-order behavior of K_n coefficients can be deduced, or conversely, how we can determine parameters in Eq. (4) from the large-order of K_n coefficients. For this purpose, we use the generalized binomial theorem and write

$$\left(1-\frac{z}{z_0}\right)^{\alpha} = \sum_{n=0}^{\infty}\frac{\Gamma(\alpha+1)}{\Gamma(n+1)\Gamma(\alpha-n+1)}\frac{(-1)^n}{z_0^n}z^n. \quad (5)$$

Considering only the first term in Eq. (4), substituting Eq. (5) into Eq. (4), and then comparing terms of the same powers of z with Eq. (3), we get for large n

$$K_n \simeq c_1\frac{\Gamma(\alpha_1+1)}{\Gamma(n+1)\Gamma(\alpha_1-n+1)}\frac{(-1)^n}{z_0^n}. \quad (6)$$

The values of z_0 and α_1 can be found as follows. Taking the ratio of two successive coefficients K_n, we obtain from Eq. (6)

$$\frac{K_{n-1}}{K_n} \simeq z_0\frac{n}{n-\alpha_1-1}. \quad (7)$$

Taking the limit of this ratio to infinity, we obtain an estimate of z_0. Inserting this estimate of z_0 back into Eq. (7), we get the following estimate for α_1:

$$\alpha_1 \simeq n\left(1-\frac{z_0K_n}{K_{n-1}}\right) - 1. \quad (8)$$

Let us now describe how Eq. (4) can be used for very accurate determination of z_0 and the coefficients c_i if the values of the coefficients α_i are known. Taking j terms in Eq. (4), using Eq. (5), and comparing again terms with the same powers of z in Eqs. (3) and (4), we obtain

$$K_n = \sum_{i=1}^{j} x_n^{(i)}, \quad (9)$$

where

$$x_n^{(i)} = c_i\frac{\Gamma(\alpha_i+1)}{\Gamma(n+1)\Gamma(\alpha_i-n+1)}\frac{(-1)^n}{z_0^n}. \quad (10)$$

Considering Eq. (10) for successive n and taking the ratio of such equations, we express $x_{n-k}^{(i)}$ through $x_n^{(i)}$ as

$$\frac{x_{n-k}^{(i)}}{x_n^{(i)}} = \frac{n(n-1)\cdots(n-k+1)}{(n-\alpha_i-1)(n-\alpha_i-2)\cdots(n-\alpha_i-k)}z_0^k. \quad (11)$$

Inserting this into Eq. (9), we get a system of $j+1$ equations:

$$K_{n_0-k} = \sum_{i=1}^{j} x_{n_0}^{(i)}\frac{n_0(n_0-1)\cdots(n_0-k+1)}{(n_0-\alpha_i-1)(n_0-\alpha_i-2)\cdots(n_0-\alpha_i-k)}z_0^k, \quad (12)$$

for k going from 0 to j. We first solve j linear equations for $x_{n_0}^{(i)}$ using the MAPLE procedure and then insert them into the last nonlinear equation for z_0. This equation is solved by the Newton-Raphson method. The coefficients c_i are then determined from Eq. (10) for $n = n_0$.

We can try to determine even the coefficients d_i by fitting the low-order K_n coefficients to

$$K_n = \sum_{i=1}^{j} x_n^{(i)} + y_n, \quad (13)$$

where

$$\sum_{n=0}^{j} d_n\left(1-\frac{z}{z_0}\right)^n = \sum_{n=0}^{j} y_n z^n. \quad (14)$$

Since K_n and $x_n^{(i)}$ are known we can determine from the last two equations the d_n coefficients. In this way we obtain an estimate of d_0 (i.e., the value of the energy at the singularity) at the border of the convergence of the series (3).

To get an estimate of the energy inside the radius of convergence we sum the first n_0 available terms of the series (3):

$$E(Z) = Z^2\sum_{n=0}^{n_0} K_n Z^{-n}. \quad (15)$$

This estimate can be improved by replacing the unknown coefficients K_n, for n from n_0+1 to infinity, by their large

TABLE I. The position of the singularity z_0 for the ground-state energy of two-electron atoms determined from the series (3) by the method described in Sec. II. n_0 is equal to 19. j denotes the number of terms taken in Eq. (9). The value of z_0 taken in additional calculations is that obtained for $j = 5$.

j	$z_0^{(j)}$	$z_0^{(j)} - z_0^{(j-1)}$
1	1.098 900 6	
2	1.106 872 1	0.007 971
3	1.108 237 6	0.001 365
4	1.108 482 7	0.000 245
5	1.108 549 6	0.000 066
6	1.108 375 9	−0.000 173

TABLE II. The coefficients c_i defined by Eqs. (4), (17), and (18) for the ground-state energy of two-electron atoms obtained by the method described in Sec. II. j is the number of terms taken in Eq. (9).

j	$c_1^{(j)}$	$c_2^{(j)}$	$c_3^{(j)}$	$c_4^{(j)}$	$c_5^{(j)}$
1	−0.194 633				
2	−0.248 210	−0.164 504			
3	−0.262 686	−0.249 831	−0.109 421		
4	−0.266 019	−0.277 330	−0.174 897	−0.041 795	
5	−0.267 086	−0.288 189	−0.210 594	−0.083 429	−0.014 379

TABLE III. Estimates of the energy in atomic units of the $1\,^1S$ state of two-electron atoms from the perturbation series. The relative errors in parentheses are with respect to the variational values $E(Z=1) = -0.527751016544377$ and $E(Z=2) = -2.9037243770341195$ given in [11].

Z	$E(Z)$, Eq. (15)	$E(Z)$, Eq. (16)
1	$-0.527\,709\,300\,401\,615$ $(0.79\ 10^{-4})$	$-0.527\,751\,008\,531\,809\,318$ $(0.15\ 10^{-7})$
2	$-2.903\,724\,376\,985\,056\,696$ $(0.16\ 10^{-10})$	$-2.903\,724\,377\,034\,051\,942$ $(0.23\ 10^{-13})$

order values (9),

$$E(Z) = Z^2\left(\sum_{n=0}^{n_0} K_n Z^{-n} + \sum_{n=n_0+1}^{\infty}\sum_{i=1}^{j} x_n^{(i)} Z^{-n}\right). \tag{16}$$

III. RESULTS AND DISCUSSION

For the ground state we plotted the ratios of K_{n-1}/K_n for n from 13 to 19 with respect to $1/n$ and we observed the straight line. Thus, we made a Thiele extrapolation of these ratios with respect to $1/n$. We obtained $z_0 = 1.108354$. Further we extrapolated Eq. (8) from the same interval. We arrived at the value $\alpha_1 = 1.515$. This suggests that the exact value is

$$\alpha_1 = 3/2. \tag{17}$$

For $i > 1$ the simplest possibility is to take

$$\alpha_i = \alpha_{i-1} + 1. \tag{18}$$

This choice is justified *a posteriori*. If α_i are not correct, then the procedure described in the previous section for determination of z_0 and c_i does not work. The results given in Tables I and II show that the stabilization is actually very good, up to $j = 5$. Therefore, we believe that our choice of α_i is correct.

The radius of convergence $z_0 = 1.1085$ found here differs from that found in [7] ($z_0 = 1.09766$). Also, the nature of the singularity found there is of a much more complicated type than that found here. The reason for the discrepancy lies in the fact that in [7] the numerical analysis was performed on the coefficients K_n from the interval $n = 25$ to $n = 401$, while here we used the interval from $n = 13$ to $n = 19$. One has to keep in mind that high coefficients of the convergent series are very difficult to determine. Certainly, the coefficients from the interval $n = 13$ to $n = 19$ are much more accurate than the coefficients from the interval $n = 25$ to $n = 401$. Consequently, any analysis made on low coefficients is much more reliable than that made on high coefficients. Further, the leading large-order behavior of the coefficients K_n is determined by Eq. (6) for $\alpha_1 = 3/2$. That means that one needs just the two parameters z_0 and c_1 to fix it precisely. On the other hand Eq. (84) of [7] contains as many as four parameters.

To appreciate the point made in the previous paragraph, take z_0 and c_i from Tables I and II for $j = 5$; our prediction for K_{20} based on Eq. (9) is then $-0.768616348 \times 10^{-5}$, whereas the actual coefficient K_{20} given in Table III of [7] is $-0.768616263 \times 10^{-5}$, the relative difference being 10^{-7}. The relative error of the asymptotic formula given in [7] for K_{20} is 0.6×10^{-2}. Our prediction for K_{200} is -0.222×10^{-15}, while the value given in [7] is -0.301×10^{-15}.

Further we summed the series (3) by means of Eqs. (15) and (16) and compared the result with a variational calculation [11]. The results are given in Table III and confirm our analysis. Now we turn our attention to the $2\,^3S$ state. Studying the ratios K_{n-1}/K_n and Eq. (8) for n from 9 to 19 we observed that starting with $n = 14$ the values of α_1 oscillate. Therefore we consider only the coefficients up to $n = 13$. We take the same values of α_i as for the ground state. Estimates of z_0 and c_i are given in Tables IV and V. The stabilization is even better than for the ground state, up to $j = 6$. Also, as seen from Table VI, inclusion of the remainder improves the agreement with the variational result even more than for the ground state. We note that contrary to the expectation made in [7] the value of z_0 is *larger* than 1, though for Z equal to 1 the state lies above the ionization threshold (see Table VI), in agreement with the theorem given in [12].

We also tried to determine the coefficients d_n from Eqs. (13) and (14). The results for the singlet and triplet states are given in Tables VII and VIII, respectively. The stabilization is worse than for the c_i coefficients. Nevertheless, the results suggest that the exact value of d_0 is $-1/2$. This means that $z_0 = z_c$. The same conclusion was obtained in [7]. We would like to note that with this identification our choice of α_1 is consistent with the rigorous theorem given in [13] that the energy approaches the value $E(z_c) = -1/2$ linearly.

To better understand what is going on at the singularity, we recall that the eigenvalues are determined variationally as the roots of the characteristic polynomial of the Nth order in E,

$$P_N(E(z), z) = 0. \tag{19}$$

Our choice of α_i implies that the energy can be at the vicinity of the singularity expanded in integer powers of $u = (1 - z/z_0)^{1/2}$. Thus, we make the substitution

$$z = z_0(1 - u^2) \tag{20}$$

TABLE IV. The same as in Table I, but for the $2\,^3S$ state of two-electron atoms. n_0 is equal to 13. The value of z_0 taken in additional calculations is that obtained for $j = 6$.

j	$z_0^{(j)}$	$z_0^{(j)} - z_0^{(j-1)}$
1	1.009 616 7	
2	1.027 127 3	0.017 510
3	1.032 620 4	0.005 493
4	1.035 207 8	0.002 587
5	1.036 486 9	0.001 279
6	1.036 737 7	0.000 250
7	1.035 981 8	−0.000 755

TABLE V. The same as in Table II, but for the $2\,^3S$ state of two-electron atoms.

j	$c_1^{(j)}$	$c_2^{(j)}$	$c_3^{(j)}$	$c_4^{(j)}$	$c_5^{(j)}$	$c_6^{(j)}$
1	−0.234 356					
2	−0.340 525	−0.199 347				
3	−0.395 411	−0.391 928	−0.136 894			
4	−0.429 077	−0.550 596	−0.333 952	−0.060 020		
5	−0.448 341	−0.656 284	−0.501 178	−0.143 542	−0.010 598	
6	−0.452 350	−0.679 623	−0.541 524	−0.167 070	−0.014 865	−0.000 163

and expand the energy in the series

$$E(z) = \sum_{n=0}^{\infty} b_n u^n. \tag{21}$$

Comparing this expansion with that in Eq. (4) with α_i given by Eqs. (17) and (18) we see that $b_0 = d_0, b_1 = 0, b_2 = d_1, b_3 = c_1$, and so on. By inserting the last two equations into Eq. (19) and comparing the terms of the same powers of u we obtain successively

$$P_N(E = b_0, u^2 = 0) = 0, \tag{22}$$

$$\frac{\partial P_N}{\partial E} b_1 = 0, \tag{23}$$

$$\frac{\partial P_N}{\partial E} b_2 + \frac{\partial^2 P_N}{\partial E^2} b_1^2 + \frac{\partial P_N}{\partial u^2} = 0, \tag{24}$$

$$\frac{\partial P_N}{\partial E} b_3 + b_1 \left(\frac{\partial^3 P_N}{\partial E^3} b_2 + \frac{\partial^2 P_N}{\partial E \partial u^2} \right) = 0, \tag{25}$$

$$\frac{\partial P_N}{\partial E} b_4 + \frac{1}{2}\frac{\partial^2 P_N}{\partial E^2}\left(b_2^2 + 2b_3 b_1\right) + b_2 \frac{\partial^2 P_N}{\partial E \partial u^2} + \frac{1}{2}\frac{\partial^2 P_N}{\partial (u^2)^2} = 0, \tag{26}$$

$$\frac{\partial P_N}{\partial E} b_5 + b_3 \left(\frac{\partial^2 P_N}{\partial E^2} b_2 + \frac{\partial^2 P_N}{\partial E \partial u^2} \right) + b_1 \left(\frac{\partial^2 P_N}{\partial E^2} b_4 + \frac{\partial^3 P_N}{\partial E^2 \partial u^2} b_2 + \frac{\partial^3 P_N}{\partial E \partial (u^2)^2} \right) = 0, \tag{27}$$

and so on. It is understood that derivatives are evaluated at the point $E = b_0$ and $u = 0$. Equation (22) is just an equation for the particular eigenvalue b_0 for the particular value of the coupling constant z_0. For $b_1 \neq 0$, Eq. (23) is a condition for the particular eigenvalue b_0 to be twofold degenerate [14]. If z_0 is the closest singularity to the origin, then for this value of the coupling constant the ground and first excited state *of the same symmetry* intersect [9,14,15]. Equation (24) is then a quadratic equation for b_1. The two roots correspond to the fact that one can approach the point z_0 either from the ground state or from the first excited state [9]. Equation (24) is then a linear equation for b_2, Eq. (25) is a linear equation for b_3, and so on.

However, one can see that if

$$\left.\frac{\partial P_N(E, u^2)}{\partial E}\right|_{E=b_0, u=0} = 0 \tag{28}$$

and $b_1 = 0$, Eq. (24) implies

$$\left.\frac{\partial P_N(E, u^2)}{\partial u^2}\right|_{E=b_0, u=0} = 0. \tag{29}$$

Equation (25) is then identically zero, but Eqs. (26) and (27) are very hard to fulfill. In fact, there are only two possibilities: Either $b_2 = 0$ or

$$\left.\frac{\partial^2 P_N(E, u^2)}{\partial E^2}\right|_{E=b_0, u=0} = 0; \tag{30}$$

that is, the energy is at least three times degenerate at the singularity. In either case Eqs. (26) and (27) imply

$$\left.\frac{\partial^2 P_N(E, u^2)}{\partial E \partial u^2}\right|_{E=b_0, u=0} = 0 \tag{31}$$

and

$$\left.\frac{\partial^2 P_N(E, u^2)}{\partial (u^2)^2}\right|_{E=b_0, u=0} = 0, \tag{32}$$

respectively. The latter possibility, Eq. (30), is much more natural. It is very unlikely that Eq. (30) is not satisfied, while Eqs. (31) and (32) are. Moreover, the result in Table VII for $b_2 = d_1$ is consistent only with the latter possibility. Further, it is unlikely that equations obtained from Eq. (19) by comparing the higher orders of u will be fulfilled unless

$$\left.\frac{\partial^n P_N(E, u^2)}{\partial E^n}\right|_{E=b_0, u=0} = 0 \tag{33}$$

for all n. This means that the energy is at the point z_0 infinitely degenerate.

TABLE VI. Estimates of the energy in atomic units of the $2\,^3S$ state of two-electron atoms from the perturbation series. The relative error in parentheses is with respect to the variational value $E(Z = 2) = -2.17522937823679130$ given in [11].

Z	$E(Z)$, Eq. (15)	$E(Z)$, Eq. (16)
1		−0.499 991 582 046 787
2	−2.175 229 321 840 030 517 (0.25 10^{-7})	−2.175 229 378 229 568 174 (0.33 10^{-11})

TABLE VII. The coefficients d_i defined by Eqs. (4), (17), and (18) for the ground-state energy of two-electron atoms obtained by the method described in Sec. II. j is the number of terms taken in Eq. (9).

j	$d_0^{(j)}$	$d_1^{(j)}$	$d_2^{(j)}$	$d_3^{(j)}$	$d_4^{(j)}$	$d_5^{(j)}$
1	−0.410 5	−0.394 8				
2	−0.470 7	−0.324 9	0.208 3			
3	−0.524 1	−0.127 5	−0.015 5	0.289 1		
4	−0.489 7	−0.274 6	0.243 5	0.136 1	0.144 7	
5	−0.499 7	−0.221 2	0.132 2	0.288 8	0.107 9	0.055 6

To check this conclusion numerically we need a characteristic polynomial for Eq. (2). To obtain it one has to do the variational calculation in some basis. The most advantageous is the basis built up from the explicitly correlated functions as that used in [7,11]. However, the convergence of the conditions for the singularity, Eqs. (22) and (28), is likely to be slow with increasing N. But then the numerical solution of Eqs. (22) and (28) is rather difficult for large N.

This obstacle can be circumvented by considering an effective characteristic polynomial [10]. This polynomial can be constructed directly from known coefficients K_n without actually doing any variational calculation at all. It is based on the observation that the characteristic polynomial for eigenvalues (19) has the generic form

$$P_N = \sum_{k=0}^{N} E^k \sum_{j=0}^{n-k} f_j^k z^j, \tag{34}$$

where f_j^k are parameters determined by the matrix elements of the Hamilton operator. We can determine them from the perturbation coefficients as follows. Setting $f_0^N = 1$ and inserting expansion (3) into the last equation and expanding it in the series in z up to the $N(N+3)/2 - 1$ order we obtain $N(N+3)/2$ equations (where we consider also the zeroth order) for the same number of unknowns f_j^k. For example, to construct P_4 we need coefficients K_n from 0 to 13, for P_5 we need K_n up to 19, and for P_6 up to 26.

Thus we have enough coefficients to construct P_4 for the triplet state and P_5 for the singlet state. We search for the roots of these polynomials first at the physical values of $Z = 1, 2, \ldots$ and then at the singularity z_0. For the singlet and triplet states we take the values of z_0 given in Tables VII and VIII for $j = 5$ and $j = 6$, respectively. The results are displayed in Tables IX and X. First, it is seen from the tables that for the physical values of Z the effective characteristic polynomial represents an alternative way to improve the perturbation result. Second, if we search for the roots of the characteristic polynomial and its derivatives at the singularity z_0, at least one of the roots is always very close to $b_0 = -1/2$. Thus, Eqs. (22) and (28)–(32) are satisfied within numerical errors. This is an independent check that the value of z_0 is correct and that the conclusion we arrived at, namely that the energy is at the singularity at least three times degenerate, is also correct. For the singlet state the results are less convincing. Therefore, we took another seven coefficients from Table III of [7] and constructed P_6. It is seen from Table X that Eqs. (28)–(32) are for this polynomial well satisfied.

TABLE IX. Roots of the effective characteristic polynomial P_4 for the $2\,^3S$ state of two-electron atoms. The polynomial was obtained from 14 coefficients of the series (3) by the method described in Sec. III.

$4P_4(1/2)$	−2.923 60	−2.373 49	−2.175 229 378 199	119.614
$P_4(z_0)$	−0.622 682	−0.520 806	−0.500 662	30.6371
$\frac{\partial P_4(z_0)}{\partial E}$	−0.585 846	−0.510 286	22.8408	
$\frac{\partial^2 P_4(z_0)}{\partial E^2}$	−0.548 096	15.0445		
$\frac{\partial P_4(z_0)}{\partial z}$	−0.560 437	−0.495 788	6.40283	
$\frac{\partial^2 P_4(z_0)}{\partial E \partial z}$	−0.528 188	4.09259		
$\frac{\partial^2 P_4(z_0)}{\partial z^2}$	−5.73418	−0.518 597		

IV. CONCLUSIONS

In this paper we analyzed the perturbation coefficients for the two lowest energy levels $E(Z)$ of two-electron atoms. The results of this paper clearly show that to get maximum information about the expanded function it is not necessary to know an exceedingly large number of the perturbation coefficients. Rather, it is necessary to know only a moderate number of them, but with great accuracy. We showed that in such a case one can deduce the large-order behavior of the perturbation coefficients. This information can be further used for significant improvement of the perturbation estimate of the exact energy.

Further, we investigated the nature of the singularity. The conclusion drawn from this discussion is the following. The behavior of the energy $E(Z)$ near the singularity is given by Eq. (4) with α_i given by Eqs. (17) and (18). The singularity is a branching point between the two sheets of the Riemann surface. At the same time the degree of degeneracy of the energy is definitely greater than two and most likely infinite. This is different from what was found for the singularities of simpler quantum mechanical systems [9,15]. There, the

TABLE VIII. The same as in Table VII but for the $2\,^3S$ state of two-electron atoms.

j	$d_0^{(j)}$	$d_1^{(j)}$	$d_2^{(j)}$	$d_3^{(j)}$	$d_4^{(j)}$	$d_5^{(j)}$	$d_6^{(j)}$
1	−0.552 4	0.161 7					
2	−0.449 8	−0.086 7	0.451 4				
3	−0.529 8	0.202 7	0.223 7	0.402 5			
4	−0.491 1	0.042 9	0.592 6	0.380 6	0.223 5		
5	−0.502 1	0.103 0	0.529 5	0.658 3	0.290 9	0.055 1	
6	−0.500 9	0.096 9	0.558 2	0.670 4	0.343 7	0.059 8	0.002 2

TABLE X. Roots of the effective characteristic polynomials for the ground state of two-electron atoms. The polynomials P_5 and P_6 were obtained from 19 and 26 coefficients of the series (3), respectively.

$4P_5(1/2)$	$-5.102\,58$	$-2.903\,724\,377\,034\,035$	$-1.267\,53-0.657i$	$-1.26753+0.657i$	5104.36	
$P_5(1)$	$-1.491\,08$	$-0.527\,751\,081\,978\,668$	$-0.511\,932$	$-0.071\,028$	1280.24	
$P_5(z_0)$	$-1.564\,16$	$-0.498\,260$	$-0.497\,298$	$-0.049\,439$	1281.15	
$\frac{\partial P_5(z_0)}{\partial E}$	$-1.270\,67$	$-0.497\,779$	$-0.188\,477$	1024.79		
$\frac{\partial^2 P_5(z_0)}{\partial E^2}$	$-0.974\,182$	$-0.330\,505$	768.433			
$\frac{\partial P_5(z_0)}{\partial z}$	-21.1025	$-0.497\,806$	$-0.217\,767$	5.041 76		
$\frac{\partial^2 P_5(z_0)}{\partial E \partial z}$	-15.5528	$-0.359\,129$	3.329 69			
$\frac{\partial^2 P_5(z_0)}{\partial z^2}$	$-0.429\,434$	$0.229\,047-0.998i$	$0.229\,047+0.998i$			
$4P_6(1/2)$	-16.7773	$-2.994\,90$	$-2.903\,724\,377\,034\,330$	$-2.454\,62$	11.2643	5690.54
$P_6(1)$	$-4.246\,18$	$-0.549\,727$	$-0.528\,385$	$-0.527\,750\,677$	3.029 57	1426.74
$P_6(z_0)$	$-4.264\,44$	$-0.515\,610$	$-0.500\,411$	$-0.497\,377$	3.080 34	1427.65
$\frac{\partial P_6(z_0)}{\partial E}$	$-3.419\,60$	$-0.510\,107$	$-0.498\,826$	2.269 78	1189.62	
$\frac{\partial^2 P_6(z_0)}{\partial E^2}$	$-2.569\,32$	$-0.504\,466$	1.453 88	951.591		
$\frac{\partial P_6(z_0)}{\partial z}$	$-4.989\,058$	$-0.509\,500$	$-0.498\,637$	1.695 91	170.611	
$\frac{\partial^2 P_6(z_0)}{\partial E \partial z}$	$-3.748\,229$	$-0.504\,072$	1.017 83	136.282		
$\frac{\partial^2 P_6(z_0)}{\partial z^2}$	$-1.336\,64-2.065i$	$-1.33664+2.065i$	$-0.503\,725$	2.434 59		

number of branches of the Riemann surface was always equal to the degree of degeneracy of the energy.

It would be desirable to extend the analysis made here to many-body perturbation theory.

ACKNOWLEDGMENTS

The financial support of MSMT Grant No. 0021620835 is gratefully acknowledged.

[1] P. J. Mohr, Phys. Rev. A **32**, 1949 (1985); see also P. J. Mohr and J. Sapirstein, *ibid.* **62**, 052501 (2000); I. Lindgren *et al.*, *ibid.* **51**, 1167 (1995); S. A. Blundell *et al.*, *ibid.* **48**, 2615 (1993); T. Kagawa and U. I. Safronova, Phys. Scr. **45**, 569 (1992); L. N. Ivanov, E. P. Ivanovna, and U. I. Safronova, J. Quant. Spectrosc. Radiat. Transfer **15**, 553 (1975); S. P. Goldman and G. W. F. Drake, J. Phys. B **16**, L183 (1983).

[2] E. P. Ivanova and U. I. Safronova, J. Phys. B **8**, 1591 (1975).

[3] U. I. Safronova and A. M. Urnov, J. Phys. B **12**, 3171 (1979); **13**, 869 (1980).

[4] Z.-C. Yan, M. Tambasco, and G. W. F. Drake, Phys. Rev. A **57**, 1652 (1998); D. K. Watson and S. V. ONeil, *ibid.* **12**, 729 (1975); K. Aashamar, G. Lyslo, and J. Midtal, J. Chem. Phys. **52**, 3324 (1970); F. C. Sanders and R. E. Knight, Phys. Rev. A **27**, 1279 (1983).

[5] A. I. Mikhailov *et al.*, Phys. Rev. A **69**, 032703 (2004).

[6] A. Derevianko *et al.*, Phys. Rev. A **58**, 4453 (1998).

[7] J. D. Baker, D. E. Freund, R. N. Hill, and J. D. Morgan III, Phys. Rev. A **41**, 1247 (1990).

[8] P. Serra, S. Kais, and N. Moiseyev, Phys. Rev. A **64**, 062502 (2001).

[9] J. Zamastil and F. Vinette, J. Phys. A **38**, 4009 (2005); see also L. Skála, J. Čížek, and J. Zamastil, *ibid.* **32**, L123 (1999); F. M. Fernández, G. A. Arteca, and E. A. Castro, J. Math. Phys. **28**, 323 (1987).

[10] J.Čížek, E. J. Weniger, P. Bracken, and V. Špirko, Phys. Rev. E **53**, 2925 (1996).

[11] G. W. F. Drake, ed., *Atomic, Molecular and Optical Physics Handbook* (American Institute of Physics, Woodbury, NY, 1996).

[12] M. Hoffman-Ostenhof and T. Hoffman-Ostenhof, J. Phys. A **17**, 3321 (1984).

[13] M. Hoffman-Ostenhof, T. Hoffman-Ostenhof, and B. Simon, J. Phys. A **16**, 1125 (1983).

[14] C. M. Bender and S. A. Orszag, *Advanced Mathematical Methods for Scientists and Engineers* (McGraw-Hill, New York, 1978). See also B. Simon, Ann. Phys. (NY) **58**, 76 (1970); B. Simon, in *Cargese Lectures in Physics 1970*, Vol. 5, edited by D. Bessis (Gordon and Breach, New York, 1972), p. 383.

[15] C. M. Bender and T. T. Wu, Phys. Rev. **184**, 1231 (1969); see also G. Alvarez and H. J. Silverstone, Phys. Rev. A **50**, 4679 (1994); P. E. Shanley, Phys. Lett. A **117**, 161 (1986).