# Ground-state energy of a two-electron atom as a function of $\lambda=1/Z$: Singular points and asymptotic behavior

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(Received 11 April 1996)

We study the analytical properties of the exact ground-state energy $E(\lambda)$ of a two-electron atomic ion of nuclear charge $Z$ as a function of the parameter $\lambda=1/Z$. We find that $E(\lambda)$ has a second-order pole at the point $\lambda=\infty$ of a $\lambda$ complex plane. The principal part of the Laurent expansion of $E(\lambda)$ about this point can be found analytically: $E(\lambda)=-4-\lambda^2/4+O(1/\lambda^2)$, $\lambda\to\infty$. We find a new singularity of $E(\lambda)$ at the point $\lambda_1\approx 9.41$ of a $\lambda$ complex plane. [S1050-2947(96)10709-5]

PACS number(s): 31.90.+s

## INTRODUCTION

It is known [1] that with the help of the scaling transformation $\mathbf{r}_i\to\mathbf{r}_i/Z$, the nonrelativistic Hamiltonian of a two-electron atomic ion of nuclear charge $Z$ can be written in atomic units as

$$\widetilde{H}=-\frac{1}{2}\nabla_1^2-\frac{1}{2}\nabla_2^2-\frac{1}{r_1}-\frac{1}{r_2}+\frac{\lambda}{r_{12}}, \tag{1}$$

where $\lambda=1/Z$.

Below, we shall consider the lowest eigenvalue of the Hamiltonian $\widetilde{H}$. Considering in (1) the operator of interelectronic interaction as the perturbing operator, one can write for the ground-state eigenvalue $E(\lambda)$ the Rayleigh-Schrödinger perturbation expansion in powers of $\lambda$,

$$E(\lambda)=\sum_{n=0}^{\infty}E_n\lambda^n. \tag{2}$$

This expansion was proven to have a nonzero radius of convergence [2]. The series (2) defines therefore an analytic function $E(\lambda)$ regular inside some circle with the point $\lambda=0$ as center.

The coefficients $E_n$ for the ground state of a two-electron atom were calculated in a number of works [3–5]. In the present work we use the data from Ref. [6] where the first 400 coefficients $E_n$ were computed.

An important characteristic of an analytic function is the location and nature of its singular points. The radius of convergence of the series (2) is determined by the nearest to $\lambda=0$ in the complex $\lambda$ plane singularity of the function $E(\lambda)$. This singular point of $E(\lambda)$ is well studied. It was shown [6] that this singularity of $E(\lambda)$ is on the positive real axis of a $\lambda$ complex plane. In Ref. [6] it was shown also that this singular point is an essential singularity of $E(\lambda)$. Various estimations of the position of this singular point were given [6–8]. In Ref. [9] we estimated the position of this singularity of $E(\lambda)$ as $\lambda_s\approx 1.097\,660\,79$.

If $\lambda$ is outside the circle of convergence of the series (2), one must use some method of analytical continuation of series (2) to obtain the information about $E(\lambda)$. We have proposed such a method in Ref. [10]. We found that $E(\lambda)$ has a singular point $\lambda_\infty$ at the point $\lambda=\infty$ of a $\lambda$ complex plane. We found numerically that in the vicinity of the singular point $\lambda=\infty$ the function $E(\lambda)$ behaves as $\lambda^\alpha$ where the exponent $\alpha\approx 2$. We showed [10] that if $E(\lambda)$ has other singular points besides $\lambda_s,\lambda_\infty$, their coordinates are to satisfy $\mathrm{Re}(\lambda)>\lambda_s$.

In the present paper we show that $\alpha=2$ exactly and therefore $E(\lambda)$ has a second-order pole at the point $\lambda=\infty$ of a $\lambda$ complex plane. We show that one can find an analytical expression describing the behavior of $E(\lambda)$ when $\lambda\to\infty$. We show that $E(\lambda)$ has another singularity at the point $\lambda_1\approx 9.41$ of a $\lambda$ complex plane.

## THEORY

We recall briefly some results which we shall need below. In Ref. [10] we have shown that the function $E(\lambda)$ can be represented as

$$E(\lambda)\left(1-\frac{\lambda}{\lambda_s}\right)^2=\int_0^\infty tq(t)\exp\left\{-\frac{t\lambda_s}{\lambda_s-\lambda}\right\}dt, \tag{3}$$

where $\lambda_s\approx 1.097\,660\,79$—the nearest to $\lambda=0$ in the complex $\lambda$ plane singularity of $E(\lambda)$. Expanding both sides of Eq. (3) in powers of $\lambda$, one can obtain from (3) the following formula for $q(t)$ [10]:

$$q(t)=\sum_{n=0}^{\infty}\frac{E_n\lambda_s^n}{(n+1)}L_n^{(1)}(t), \tag{4}$$

where $E_n$ are the coefficients of the perturbation expansion (2), $L_n^{(1)}(t)$—the Laguerre polynomials [11]. Using the known properties of the Laguerre polynomials one can derive from (4) the following formula for the coefficients $E_n$ [10]:

$$E_n=\int_0^\infty tq(t)e^{-t}L_n^{(1)}(t)dt. \tag{5}$$

By means of formula (4) the function $q(t)$ can be computed numerically. It is represented in Fig. 1. Our numerical investigation of the function $q(t)$ carried out in Ref. [10] indicates that for large-$t$ values, $q(t)$ behaves as $t^\alpha$, where the exponent $\alpha\approx 2$. We are going to prove that $\alpha=2$ exactly.

Consider the system described by the Hamiltonian (1). Let us suppose that the parameter $\lambda$ in (1) assumes very large

 

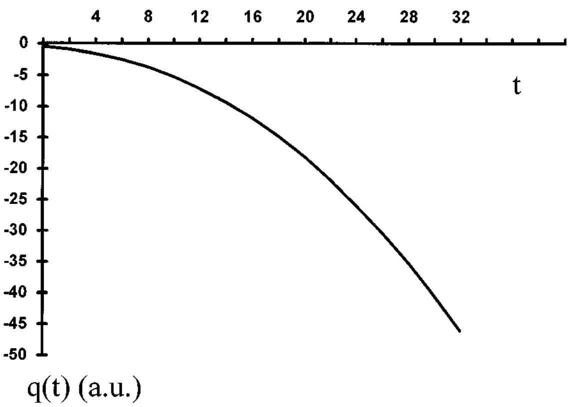


FIG. 1. Plot of the function $q(t)$.

negative values $\lambda \to -\infty$. This limiting case corresponds to the situation when one has two strongly attracting electrons in the field of the nucleus of unit charge. This physical situation can be considered in the framework of a perturbation theory. Introducing the coordinates

$$\vec{R}=\frac{\vec{r}_1+\vec{r}_2}{2}, \quad \vec{\rho}=\vec{r}_1-\vec{r}_2, \tag{6}$$

one can rewrite the Hamiltonian (1) in the following way [12]:

$$\hat{H}=-\frac{\Delta_{\vec{R}}}{4}-\Delta_{\vec{\rho}}-\frac{1}{\left|\vec{R}-\frac{\vec{\rho}}{2}\right|}-\frac{1}{\left|\vec{R}+\frac{\vec{\rho}}{2}\right|}+\frac{\lambda}{\rho}=\hat{H}_0+\hat{V}, \tag{7}$$

where

$$\hat{H}_0=-\frac{\Delta_{\vec{R}}}{4}-\Delta_{\vec{\rho}}-\frac{2}{R}+\frac{\lambda}{\rho}, \tag{8}$$

$$\hat{V}=\frac{2}{R}-\frac{1}{\left|\vec{R}-\frac{\vec{\rho}}{2}\right|}-\frac{1}{\left|\vec{R}+\frac{\vec{\rho}}{2}\right|}. \tag{9}$$

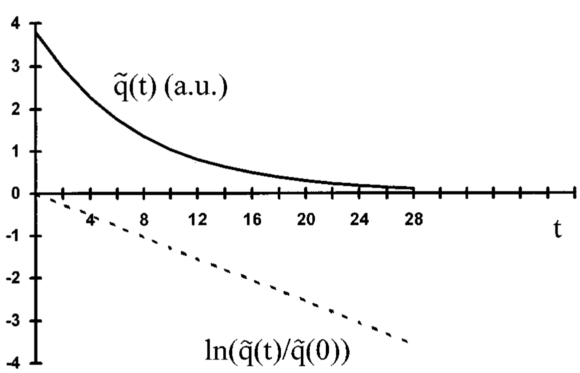


FIG. 2. Plots of the functions $\tilde{q}(t)$ (solid line) and $\ln[\tilde{q}(t)/\tilde{q}(0)]$ (dashed line).

When $\lambda \to -\infty$, one can treat operator $\hat{V}$ as the perturbing operator. The Hamiltonian $\hat{H}_0$ is a sum of two hydrogenlike Hamiltonians. The lowest eigenvalue of $\hat{H}_0$ is $E^0(\lambda) = -\lambda^2/4-4$. One can easily calculate the first-order correction to this eigenvalue. We shall not need its exact value below. We shall use only the fact that, as elementary calculation shows, the order of magnitude of the first-order correction to $E^0(\lambda)$ is $O(\lambda^{-2})$ when $\lambda \to -\infty$. We have thus the following perturbation expansion for $E(\lambda)$ when $\lambda \to -\infty$:

$$E(\lambda)=-\frac{\lambda^2}{4}-4+O\left(\frac{1}{\lambda^2}\right), \quad \lambda \to -\infty. \tag{10}$$

Let us suppose that the perturbation expansion (10) converges for sufficiently large $\lambda$. Then Eq. (10) will imply that the function $E(\lambda)$ has a second-order pole at the point $\lambda=\infty$. Our numerical study of the function $q(t)$ confirms this hypothesis.

One can see from Eq. (3) that in order to reproduce the asymptotic behavior (10), the function $q(t)$ from (3) should have the following large-$t$ asymptotic behavior:

$$q(t) \sim -\frac{\lambda_s^2 t^2}{24}+\frac{\lambda_s^2 t}{4}-4-\frac{\lambda_s^2}{4}, \quad t \to \infty. \tag{11}$$

This formula reproduces correctly the asymptotic behavior of the function $q(t)$. Let us represent the function $q(t)$ as

$$q(t)=-\frac{\lambda_s^2 t^2}{24}+\frac{\lambda_s^2 t}{4}-4-\frac{\lambda_s^2}{4}+\tilde{q}(t). \tag{12}$$

One can easily calculate the function $\tilde{q}(t)$ numerically. It is represented in Fig. 2 (solid curve). One can see, that for the large-$t$ values $\tilde{q}(t)$ tends to zero. The numerical analysis of $\tilde{q}(t)$ indicates that for the large-$t$ values it decays exponentially as $e^{-ct}$ where $c \approx 0.132$. We note also that $\tilde{q}(t)$ does not deviate appreciably from the exponential function for all values of the variable $t$. In Fig. 2 we present the plot of $\ln[\tilde{q}(t)/\tilde{q}(0)]$ (dashed curve). One can see that the plot of $\ln[\tilde{q}(t)/\tilde{q}(0)]$ as a function of $t$ yields nearly a straight line.

Exponential decay of $\tilde{q}(t)$ implies that the perturbation expansion (10) converges for sufficiently large $|\lambda|$. Indeed, for the exponentially decaying $\tilde{q}(t)$ the integral

$$\int_0^\infty t\tilde{q}(t)\exp\left\{-\frac{t\lambda_s}{\lambda_s-\lambda}\right\}dt \tag{13}$$

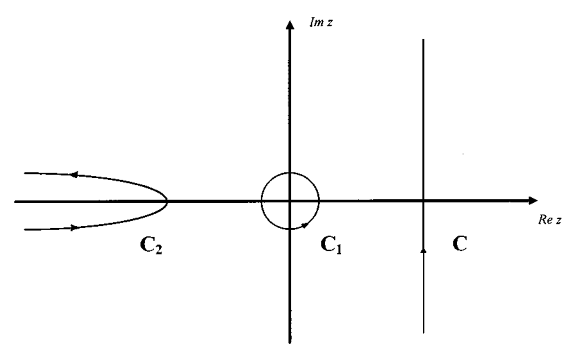


FIG. 3. Contour of integration in formula (14).

is a regular function of λ at the point $\lambda=\infty$ and can be expanded into a convergent series in powers of $1/\lambda$ for sufficiently large λ. Therefore the function $E(\lambda)$ given by formula (3) has a second-order pole at the point $\lambda=\infty$. The leading terms of the Laurent expansion of $E(\lambda)$ about this point are given by formula (10).

The behavior of the function $q(t)$ can be understood with the help of the following arguments. Using the inverse Laplace transform formula, one obtains from (3)

$$tq(t)=\frac{1}{2\pi i}\int_C \frac{E(z)}{z^2}\,e^{zt}dz, \tag{14}$$

where $z=\lambda_s/(\lambda_s-\lambda)$ and the contour of integration $C$ is chosen so that all singular points of $E(z)$ are situated on the left of $C$. As we have mentioned above, all singular points of $E(z)$ are located in the left-half plane of a $z$ complex plane. Therefore, we can choose for the contour $C$ in (14) any straight line $\mathrm{Re}(z)=a>0$. The function $E(\lambda)$ considered as a function of a variable $z$ has a second-order pole at the point $z=0$. Using formula (10) one can obtain the first few terms of a Laurent expansion of $E(z)$ about the point $z=0$:

$$E(z)=-\frac{\lambda_s^2}{4z^2}+\frac{\lambda_s^2}{2z}-4-\frac{\lambda_s^2}{4}+O(z^2). \tag{15}$$

The integral along the contour $C$ in formula (14) can be represented as a sum of two integrals, the integral taken around the circle $C_1$ and the integral taken along the contour $C_2$, as shown in Fig. 3.

$$q(t)=\frac{1}{2\pi i t}\left(\int_{C_1}\frac{E(z)}{z^2}\,e^{zt}dz+\int_{C_2}\frac{E(z)}{z^2}\,e^{zt}dz\right). \tag{16}$$

Using the expansion (15) one can see that the integral around the circle $C_1$ gives for $q(t)$ a second-order polynomial coinciding with the right-hand side of Eq. (11),

$$\frac{1}{2\pi i t}\int_{C_1}\frac{E(z)}{z^2}\,e^{zt}dz=-\frac{\lambda_s^2 t^2}{24}+\frac{\lambda_s^2 t}{4}-4-\frac{\lambda_s^2}{4}. \tag{17}$$

The function $\tilde{q}(t)$ defined by Eq. (12) can be therefore expressed as

$$\tilde{q}(t)=\frac{1}{2\pi i t}\int_{C_2}\frac{E(z)}{z^2}\,e^{zt}dz. \tag{18}$$

One can move the contour $C_2$ to the left until it meets a singular point of the function $E(z)/z^2$. If we suppose that the nearest to the $z=0$ singular point is on the negative real axis at some point $z=-c$, $c>0$, then it is easy to see that for the large positive $t$ the function $\tilde{q}(t)$ will be exponentially decaying as $e^{-ct}$. We have thus reason to believe that $E(z)$ has a singular point at $z_1=-c$, where $c\approx 0.132$. Coming back to the variable λ we obtain the position of the singular point $\lambda_1$ in a λ complex plane:

$$\lambda_1=\lambda_s\left(1+\frac{1}{c}\right)\approx 9.41. \tag{19}$$

TABLE I. Function $\tilde{q}(t)$ and approximation (24).

| $t$ | $\tilde{q}(t)$ | $\tilde{q}(t)_{\mathrm{app}}$ |
|---|---|---|
| 0 | 3.801 22 | 3.801 22 |
| 1 | 3.362 08 | 3.362 08 |
| 2 | 2.959 07 | 2.959 07 |
| 3 | 2.599 02 | 2.600 42 |
| 4 | 2.280 10 | 2.283 55 |
| 5 | 1.999 09 | 2.004 39 |
| 6 | 1.752 40 | 1.758 83 |
| 7 | 1.536 45 | 1.543 03 |
| 8 | 1.347 78 | 1.353 50 |
| 9 | 1.183 18 | 1.187 10 |
| 10 | 1.039 66 | 1.041 05 |
| 11 | 0.914 52 | 0.912 89 |
| 12 | 0.805 33 | 0.800 46 |

If $E(z)$ has another singular point $z_2$ in the left half plane of a complex $z$ plane, its coordinates are to satisfy: $\mathrm{Re}(z_2)<\mathrm{Re}(z_1)$. In the λ complex plane this inequality can be written as

$$\frac{\mathrm{Re}(\lambda_2)-\lambda_s}{|\lambda_2-\lambda_s|^2}>\frac{1}{\lambda_1-\lambda_s}\approx 0.12. \tag{20}$$

Thus if, besides $\lambda_s$ and $\lambda_1$, $E(\lambda)$ has another singular point $\lambda_2$, its coordinates in the λ complex plane must satisfy inequality (20).

We turn now to more detailed study of the properties of the function $\tilde{q}(t)$. It was shown in Ref. [6] that the large-order coefficients of the perturbation expansion (2) have the following large-$n$ asymptotic behavior:

$$E_n\sim n^{\beta}e^{-\alpha n^{1/2}}, \tag{21}$$

where $\beta\approx -1.94$ and $\alpha\approx 0.272$.

While calculating the coefficients $E_n$ with $n>2$ one can substitute in (5) the function $\tilde{q}(t)$ instead of $q(t)$. [Since $\tilde{q}(t)$ and $q(t)$ differ by the second-order polynomial, both methods of calculation give identical results due to the orthogonality properties of the Laguerre polynomials.] As we have seen the function $\tilde{q}(t)$ is nearly an exponential function $e^{-ct}$. However, $\tilde{q}(t)$ cannot be an exponential function exactly. If $\tilde{q}(t)$ were an exponential function, $E(\lambda)$ calculated accord-

TABLE II. Coefficients $E_n$, with exact and approximate values.

| $n$ | $E_n^{\mathrm{exact}}$ | $E_n^{\mathrm{app}}$ |
|---|---|---|
| 0 | −1 | −0.999 177 |
| 1 | 0.625 | 0.623 261 |
| 2 | −0.157 666 | −0.157 332 |
| 3 | 0.008 699 | 0.009 766 |
| 4 | −0.000 889 | −0.000 536 |
| 5 | −0.001 036 | −0.001 142 |
| 6 | −0.000 613 | −0.000 804 |
| 7 | −0.000 372 | −0.000 522 |

ing to (3) would be a rational function of λ and the large-order coefficients $E(n)$ would decay exponentially as $e^{-bn}$ with some $b>0$.

One can show that in order to reproduce the $n^{\beta}e^{-\alpha n^{1/2}}$ behavior of $E_n$, the function $\tilde{q}(t)$ must have a singular point on the negative-$t$ axis. Indeed, for large $n$ the Laguerre polynomials oscillate rapidly [13]:

$$L_n^{(1)}(t)\sim\frac{1}{\sqrt{\pi}}e^{t/2}t^{-3/4}n^{1/4}\cos\left[2\sqrt{nt}-\frac{3\pi}{4}\right]+O(n^{-1/4}). \tag{22}$$

Using the standard methods of asymptotic evaluation of integrals of rapidly oscillating functions [14], one can show that if $\tilde{q}(t)$ has a branch point or logarithmic singularity on the negative real axis, the integral (5) will have the asymptotic of type (21). One can verify it directly. For example, if $\tilde{q}(t)=(1+at)^{\gamma}$, $a>0$, direct calculation of the integral (5) gives

$$\int_0^{\infty}t\tilde{q}(t)e^{-t}L_n^{(1)}(t)dt=(n+1)a^{\gamma}\frac{\Gamma(n-\gamma)}{\Gamma(-\gamma)}\times U\left(n-\gamma,-\gamma-1,\frac{1}{a}\right), \tag{23}$$

where $U(b,c,z)$—a confluent hypergeometric function [11]. Using the known properties of $U(b,c,z)$, one can show that for $n\to\infty$, the expression on the right-hand side of (23) behaves as $n^{-\gamma/2-5/4}\exp[-2(n/a)^{1/2}]$, giving the asymptotic (21) with an appropriate choice of the parameters $a,\gamma$ in formula (23).

The numerical investigation of the function $\tilde{q}(t)$ shows that it can be approximated by the following formula:

$$\tilde{q}(t)_{\mathrm{app}}=\tilde{q}(0)(1+at)^{\epsilon}e^{-ct}, \tag{24}$$

where $c=0.132\,175$, $\epsilon=0.008\,958\,14$, and $a=1.860\,37$. From Table I one can see that the approximation $\tilde{q}(t)_{\mathrm{app}}$ is accurate to better than 1 part in 100 for $t\in[0,12)$. We note also that function (24) gives a reasonable approximation to the low-order coefficients $E_n$. In Table II we present the first few exact $E_n$ (the data from Ref. [6]) and $E_n$ calculated according to (5) with $q(t)$ given by (12) and (24). We observe a good agreement for the coefficients $E_0,E_1,E_2$. To achieve better agreement for $E_n$ with $n>2$, one should use more exact approximation to $\tilde{q}(t)$. We did not succeed in constructing such an approximation due to the following problem of a numerical character. While calculating $\tilde{q}(t)$ according to (12) one obtains $\tilde{q}(t)$ with some error due to the error in $\lambda_s$. This numerical error in $\tilde{q}(t)$ grows with $t$. There is another source of the numerical inaccuracy. While calculating $q(t)$ according to (4) the round-off errors and errors in $E_n$ and $\lambda_s$ lead to the error in $q(t)$. The function $\tilde{q}(t)$ is therefore known with some inaccuracy. We estimate that $\tilde{q}(t)$ is accurate to four decimal places for $t<15$. This circumstance did not allow us to increase the accuracy of our approximation for $\tilde{q}(t)$.

We would like to make one observation from (24). The parameter $\epsilon$ in formula (24) is very small. One should note that this circumstance does not depend on the particular type of approximation used in (24). As we have seen, the function $\tilde{q}(t)$ is nearly an exponential function. On the other hand, to reproduce correctly the asymptotic (21), $\tilde{q}(t)$ must have a singular point on the negative real axis. Both these requirements lead to the presence of a small parameter in any formula approximating the function $\tilde{q}(t)$.

An interesting question is what can play the role of a small parameter in the problem considered. The smallness of the deviation of $\tilde{q}(t)$ from the exponential function signifies that there may exist some kind of perturbation expansion in powers of a small parameter in the Coulomb three-body problem.

## REMARKS AND PROSPECTS

We summarize the analytic properties of $E(\lambda)$ as follows. The function $E(\lambda)$ has a second-order pole at the point $\lambda=\infty$. It can be represented as

$$E(\lambda)=-4-\frac{\lambda^2}{4}+\tilde{E}(\lambda), \tag{25}$$

where the function $\tilde{E}(\lambda)$ is regular at the point $\lambda=\infty$ and $\tilde{E}(\lambda)=O(1/\lambda^2)$ in the vicinity of this point. The function $\tilde{E}(\lambda)$ has an essential singularity at the point $\lambda_s\approx1.097\,660\,79$, and another singular point at $\lambda_1\approx9.41$. If $E(\lambda)$ has any other singular points, their coordinates must satisfy inequality (20).

Our results indicate that some small parameter may be present in the theory of a two-electron atom. Whether one can construct the perturbation expansion using the fact of the presence of this small parameter is an open question. In the case of a positive answer to this question one might hope to calculate analytically the numerical constants introduced so far $(\lambda_s,c)$. We believe this question deserves further consideration.

## ACKNOWLEDGMENTS

The author is grateful to Dr. S. N. Gordienko for useful discussions. Financial support by the Russian Foundation of Fundamental Research (Project Code No. 93-02-14284) is acknowledged.

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