Boundary solutions of the two-electron Schrödinger equation at two-particle coalescences of the atomic systems

E. Z. Liverts
Racah Institute of Physics, The Hebrew University, Jerusalem 91904, Israel

M. Ya. Amusia
Racah Institute of Physics, The Hebrew University, Jerusalem 91904, Israel
and A. F. Ioffe Physical-Technical Institute, St. Petersburg, 194021, Russia

R. Krivec
Department of Theoretical Physics, J. Stefan Institute, P.O. Box 3000, 1001 Ljubljana, Slovenia

V. B. Mandelzweig
Racah Institute of Physics, The Hebrew University, Jerusalem 91904, Israel
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The limit relations for the partial derivatives of the two-electron atomic wave functions at the two-particle coalescence lines have been obtained numerically using accurate correlation function hyperspherical harmonic method wave functions. The asymptotic solutions of the proper two-electron Schrödinger equation have been derived for both electron-nucleus and electron-electron coalescence. It is shown that the solutions for the electron-nucleus coalescence correspond to the ground and singly excited bound states, including triplet ones. The proper solutions at small distances R from the triple coalescence point were presented as the second order expansion on R and $\ln R$. The vanishing of the Fock's logarithmic terms at the electron-nucleus coalescence line was revealed in the frame of this expansion, unlike the case of electron-electron coalescence. On the basis of the obtained boundary solutions the approximate wave function corresponding to both coalescence lines have been proposed in the two-exponential form with no variational parameters.

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I. INTRODUCTION

Two-electron systems present an excellent basis both for testing the new quantum calculational approaches to many-body systems and for studying a number of photoelectron and other atomic processes. This is because such systems are the simplest ones with enough complexity to contain the main features of a many-body theory. This complexity arises from the electron-electron Coulomb potential which depends on the interelectronic distance $r_{12}=|\mathbf{r}_1-\mathbf{r}_2|$. The proper Hamiltonian for infinite nuclear mass and charge Z, in atomic units used throughout the paper, is given by

$$H=-\frac{1}{2}(\nabla_1^2+\nabla_2^2)-\frac{Z}{r_1}-\frac{Z}{r_2}+\frac{1}{r_{12}}. \tag{1}$$

It does not depend on any experimental constants whose values change considerably with improvements in measurement equipment. Therefore, it provides a standard for theoretical calibration.

It has been established [1] that relativistic and quantum-electrodynamic corrections to the energy levels of an atomic or molecular system require highly accurate nonrelativistic wave functions. Rayleigh-Ritz variational calculations provide a wave function with relative error approximately proportional to the square root of the relative error in the energy. Therefore, if the energies are used to estimate the quality of the wave functions, then it is necessary to calculate the nonrelativistic energies to far greater accuracy than would otherwise be needed.

The alternative way for obtaining the very accurate and locally correct wave functions is a direct solution of the three-body Schrödinger equation. The correlation function hyperspherical harmonic method (CFHHM), employed in this paper, realizes successfully this way of solution [2]. Accuracy of the method is comparable to the most sophisticated variational calculations.

For problems in atomic or molecular physics, eigenfunctions of the Hamiltonian (1) exhibit singular behavior at those points in configuration space where two or more charged particles come together and the resulting potential becomes infinite. For systems with zero total orbital momentum (S states) the wave function depends only on three scalar variables r_1, r_2, and r_{12}, i.e., $\Psi\equiv\Psi(r_1,r_2,r_{12})$. At the two-particle coalescences, the derivatives of the wave function Ψ have discontinuities characterized by the famous Kato cusp conditions [3], which have the simplest form for the S state of a two-electron atomic system

$$\left.\frac{\partial\Psi}{\partial r_1}\right|_{r_1=0}=-Z\Psi(0,R,R)\ (r_2=r_{12}=R), \tag{2}$$

$$\left.\frac{\partial\Psi}{\partial r_2}\right|_{r_2=0}=-Z\Psi(R,0,R)\ (r_1=r_{12}=R), \tag{3}$$

$$\left.\frac{\partial\Psi}{\partial r_{12}}\right|_{r_{12}=0} = \frac{1}{2}\Psi(R,R,0)\ (r_1 = r_2 = R). \tag{4}$$

The conditions (2) and (3) pertain to the situation when the coordinates of one of the electrons and the nucleus coincide. These conditions are valid for the electrons, which have the same (triplet states) or the opposite (singlet states) spin directions. The condition (4) deals with coincidence of coordinates of two electrons. It is valid only for the singlet states, while due to the Pauli exclusion principle $\Psi(R,R,0)=0$ for the triplet states. The inclusion of functions with such cusps into trial wave functions has been shown to improve dramatically the rates of convergence of Rayleigh-Ritz variational calculations [4]. The using of the proper correlation function, which obey the Kato conditions (2)–(4), accelerates considerably the convergence of CFHHM [2] approach, as well.

It is known that the cusp conditions (2)–(4) are consequences of the Coulomb singularity in the potential and provide specific relations between the wave function and its first derivative at the points of coalescence. It was shown in Ref. [5] that the coalescence behavior also uniquely determines the third derivative of the spherically averaged wave function in terms of the lower derivatives. The deduced relations are valid for any atom, molecule, or electron gas in any smooth external field.

There are also singularities involving more than two particle, such as the triple-coincidence singularity in the helium atom, when both electrons simultaneously approach the nucleus. A formal expansion in powers of the hyper-radius $r=\sqrt{r_1^2+r_2^2}$ and its logarithm $\ln r$ about this singular point was proposed by Fock [6] for the S-state wave functions of the helium atom. Subsequently, much effort has been devoted to understanding this expansion. The $O(r^0)$, $O(r^1)$, and $O(r^2 \ln r)$ terms in Fock's expansion are easy to obtain analytically. The $O(r^2)$ term in the expansion has been obtained in closed form by Maslen and co-workers, through the extensive use of computer algebra [7,8]. Myers and co-authors [9] have examined their results, and have verified that the inclusion of this term in the expansion yields a continuous "local" energy, whereas the "local" energy is finite but discontinuous at $r=0$ if the term is omitted. Forrey [10] performed variational calculations of the ground-state energy of helium. His basis set included an explicit treatment of the Fock expansion in hyperspherical coordinates and extra products of Laguerre polynomials in perimetric coordinates. This work has demonstrated that the use of Fock basis functions provided a substantial improvement in the convergence rate.

We would like to emphasize that the calculation of the accurate wave function at the coalescence lines is a very difficult problem just because of their cusp nature. On the other hand, a number of atomic physics problems could be solved by using the functions appearing on the right-hand side (RHS) of Eqs. (2)–(4). The processes of photoionization in the helium atom and heliumlike ions [11] could serve as an example.

It is well known (see, e.g., Refs. [7–9]), that using Hamiltonian (1) we can present the Schrödinger equation for S states of two-electron atoms and ions in the form

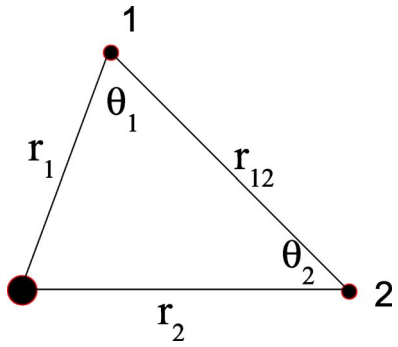

FIG. 1. (Color online) Interparticle coordinates and associated angles for the two-electron atom/ions.

$$-\frac{1}{2}\left[\frac{\partial^2\Psi}{\partial r_1^2}+\frac{\partial^2\Psi}{\partial r_2^2}+2\frac{\partial^2\Psi}{\partial r_{12}^2}+\frac{2}{r_1}\frac{\partial\Psi}{\partial r_1}+\frac{2}{r_2}\frac{\partial\Psi}{\partial r_2}+\frac{4}{r_{12}}\frac{\partial\Psi}{\partial r_{12}}\right.$$
$$\left.+\left(\frac{r_1^2-r_2^2+r_{12}^2}{r_1 r_{12}}\right)\frac{\partial^2\Psi}{\partial r_1\partial r_{12}}+\left(\frac{r_2^2-r_1^2+r_{12}^2}{r_2 r_{12}}\right)\frac{\partial^2\Psi}{\partial r_2\partial r_{12}}\right]$$
$$=\left(\frac{Z}{r_1}+\frac{Z}{r_2}-\frac{1}{r_{12}}+E\right)\Psi. \tag{5}$$

In this paper we provide the accurate analytic solutions of the Schrödinger equation (5) at the coalescence lines for both small and very large R. The Kato cusp conditions (2)–(4) are employed to solve the problem.

Our derivations are based on some limit relations, which have been obtained by numerical calculations of the partial derivatives of Ψ and of the ordinary derivatives of the two-electron wave function taken at the coalescence points. We realize, that numerical proofs of the limit relations at $R\to\infty$ cannot be considered as a rigorous proof of these relations. However, we do believe that high accuracy of numerical calculations, as well as the perfect coincidence of our numerical results for $R\to 0$ with analytical ones, confirms the correctness of our results for $R\to\infty$ too.

II. ELECTRON-NUCLEUS COALESCENCE

To investigate the case of coalescence of one electron and the nucleus in two-electron atoms and ions, one should find the limit as, e.g., r_2 approaches zero for both sides of Eq. (5). It is easier to perform this mathematical operation with the help of following relations:

$$\frac{r_1^2-r_2^2+r_{12}^2}{2r_1 r_{12}}=\cos\theta_1,\ \frac{r_2^2-r_1^2+r_{12}^2}{2r_2 r_{12}}=\cos\theta_2, \tag{6}$$

where θ_1 is the angle between the vectors $\mathbf{r}_1$ and $\mathbf{r}_{12}$, and θ_2 is the angle between $\mathbf{r}_2$ and $\mathbf{r}_{12}$ (see Fig. 1). It is clear that

$$\lim_{r_2\to 0}\theta_1 = 0,\ \lim_{r_2\to 0}\theta_2 = \pi/2. \tag{7}$$

Then, using Eqs. (6) and (7), we can rewrite Eq. (5), taking the limit as r_2 approaches zero:

$$-\frac{1}{2}\left[\frac{\partial^2\Psi}{\partial r_1^2}+\frac{\partial^2\Psi}{\partial r_2^2}+2\left(\frac{\partial^2\Psi}{\partial r_{12}^2}+\frac{\partial^2\Psi}{\partial r_1\partial r_{12}}\right)\right]\Bigg|_{r_2=0}$$
$$-\frac{1}{R}\left(\frac{\partial\Psi}{\partial r_1}+2\frac{\partial\Psi}{\partial r_{12}}\right)\Bigg|_{r_2=0}=\frac{1}{r_2}\left(\frac{\partial\Psi}{\partial r_2}+Z\Psi\right)\Bigg|_{r_2=0}$$
$$+\left(\frac{Z-1}{R}+E\right)\Psi(R,0,R). \tag{8}$$

Here we took into consideration that $r_1=r_{12}=R$ as r_2 approaches zero. Inserting the Kato condition (3) into the RHS of Eq. (8), and assuming that the terms of Eq. (8) must be finite in the whole 3D space, we obtain

$$\left[\frac{\partial^2\Psi}{\partial r_1^2}+\frac{\partial^2\Psi}{\partial r_2^2}+2\left(\frac{\partial^2\Psi}{\partial r_{12}^2}+\frac{\partial^2\Psi}{\partial r_1\partial r_{12}}\right)\right]\Bigg|_{r_2=0}$$
$$+\frac{2}{R}\left(\frac{\partial\Psi}{\partial r_1}+2\frac{\partial\Psi}{\partial r_{12}}\right)\Bigg|_{r_2=0}=2\left(\frac{1-Z}{R}-E\right)\Psi(R,0,R). \tag{9}$$

We could certainly obtain the same equation if we took the limit as r_1 approaches zero ($r_2=r_{12}=R$).

It is seen that the left-hand side (LHS) of Eq. (9) presents a sum of the form $\Sigma_{klm}c_{klm}(R)\Lambda_{lm}^{(k)}(R)$, where for the partial derivatives of Ψ taken at the electron-nucleus coalescence line, we have

$$\Lambda_{l,m}^{(k)}(R)=\lim_{r_2\to 0}\frac{\partial^k\Psi(r_1,r_2,r_{12})}{\partial r_l\partial r_m}\quad (k=1,2;l,m=0,1,2,12). \tag{10}$$

Here $\partial r_0=1$. Then, in the case of the first partial derivatives we have $k=1$, whereas one of the numbers l,m is equal to zero.

Let us now denote the two-electron wave S-function at the electron-nucleus coalescence line as

$$\Psi(R,0,R)\equiv F(R). \tag{11}$$

So, if we could express all of the functions $\Lambda_{l,m}^{(k)}(R)$ through the functions $F(R)$, $F'(R)$, and $F''(R)$, with factors being depending on R, then we obtain an ordinary differential equation of the second order for the function $F(R)$. The prime denotes differentiation, as usual.

Solution of this differential equation under the proper boundary conditions could give us the desired function $F(R)$. We do not yet know how to do this in general form. However, as a first but important step we propose here a method for solving Eq. (9) in the boundary regions, i.e., at very large R and at small R. One should notice that the numerical calculation of $F(R)$ in these regions is particularly difficult.

The direct correlation function hyperspherical harmonic method allows us to calculate numerically the two-electron wave function $\Psi(r_1,r_2,r_{12})$, as well as its special case $F(R)$, with very large accuracy. By using the CFHHM numerical calculations we obtained the following limit relations between the functions mentioned above for the asymptotic region of very large R:

$$\lim_{R\to\infty}\left\{\frac{\Lambda_{1,0}^{(1)}(R)}{F'(R)}\right\}=1, \tag{12}$$

$$\lim_{R\to\infty}\left\{\frac{\Lambda_{1,1}^{(2)}(R)}{F''(R)}\right\}=1, \tag{13}$$

$$\lim_{R\to\infty}\left\{\frac{\Lambda_{2,2}^{(2)}(R)}{F(R)}\right\}=Z^2, \tag{14}$$

$$\lim_{R\to\infty}\left\{\frac{\Lambda_{1,12}^{(2)}(R)}{F(R)}\right\}=0, \tag{15}$$

$$\lim_{R\to\infty}\left\{\frac{\Lambda_{12,12}^{(2)}(R)}{F(R)}\right\}=0, \tag{16}$$

$$\lim_{R\to\infty}\left\{\frac{\Lambda_{12,0}^{(1)}(R)}{F(R)}\right\}=0. \tag{17}$$

The calculations show that these relationships are valid at least to four significant digits. We cannot achieve higher accuracy due to the fact that the inaccuracies of the wave functions and especially of their derivatives go up with R. Note that the asymptotic relations (12)–(17) are valid for the ground states of the two-electron atoms and ions, as well as for its *excited* states, including *triplet* states.

Relations (15)–(17) show that we can neglect the partial derivatives with respect to r_{12}. Moreover, the calculations of the accurate CFHHM wave functions show that the ratio of $F'(R)/F(R)$ achieves a finite value as R approaches infinity. In the next sections we will obtain this ratio as a finite function of Z and E. This property together with the limit relation (12) allows us to neglect the terms proportional to $1/R$ on both sides of Eq. (9). And finally, using the relations (13) and (14), Eq. (9) is transformed into the following simple differential equation:

$$\frac{d^2F_{\rm as}(R)}{dR^2}+(2E+Z^2)F_{\rm as}(R)=0. \tag{18}$$

As is well known, the solution, which is convergent at $R\to\infty$, has the form

$$F_{\rm as}(R)=C_1\exp(-R\sqrt{-2E-Z^2}). \tag{19}$$

The function $F_{\rm as}(R)$ is the asymptotic representation (for very large R) of the accurate two-electron wave function in the situation when one of the electrons "seats" on the nucleus, while the other electron is far away. Equation (12) shows that this function depends on two parameters, the nuclear charge Z and the total energy E of the two-electron atomic system. C_1 is an arbitrary constant. We used only the accurate wave functions of the discrete spectrum ($E<0$) to obtain the relations (12)–(17). The condition of exponent in Eq. (19) to be real leads to the inequality

$$-2E>Z^2 \tag{20}$$

at least for the S states of the helium atom or heliumlike ions with the nuclear charge Z.

TABLE I. Energy levels (in a.u.) of n^kS states for the helium atom and heliumlike ions of $Li^+(Z=3)$ and $B^{3+}(Z=5)$.

n \	He: $k=1$	$k=3$	Li^+: $k=1$	$k=3$	B^{3+}: $k=1$	$k=3$
1	−2.903724		−7.278876		−22.02788	
2	−2.145970	−2.175225	−5.040179	−5.110019	−14.57652	−14.73188
3	−2.061221	−2.068696	−4.733102	−4.751430	−13.41017	−13.45127
4	−2.033566	−2.036524	−4.629208	−4.636571	−13.00797	−13.02461
5	−2.021225	−2.022633	−4.581895	−4.585572	−12.82326	−12.83163
6	−2.014537	−2.015122	−4.556331	−4.558559	−12.72341	−12.72824
7	−2.010629	−2.010870	−4.541111	−4.542445	−12.66341	−12.66654

We have calculated the CFHHM energy levels of the Helium atom and the ions of Li^+ and B^{3+} for both the singlet and triplet S states with $n \leqslant 7$. These data, presented in Table I, confirm the validity of the inequality (20).

It is known [12,13] that helium spectrum can be divided into three distinct parts: (i) the ground and singly excited bound states, (ii) doubly excited bound states, (iii) the continuum states. The energy of singly excited states converge to the value of $E_{fs1}=-Z^2/2$. The energy of doubly excited states, being revealed by experimentalists (see, e.g., a number of references in Ref. [13]), converge to the final state energies, which are higher than E_{fs1}. Therefore, those states are embedded into the continuum spectrum.

It is easy to conclude that Eq. (20) corresponds to the final state energy $(-Z^2/2)$, and that the limit relations (12)–(17) describe the ground and *singly* excited bound states. So, if the electrons are far away from each other $(R\to\infty)$, then the simplest model one may think of is the model of two independent electrons. The inner electron is bound in a state with principal quantum number N and energy $E_N=-Z^2/(2N^2)$, the outer electron is in a hydrogenlike orbital with energy $E_n=-(Z-1)^2/(2n^2)$ and $n \geqslant N$ assuming a screening of the nuclear charge. The total energy is simply the sum of the one-particle energies. The case of R approaching infinity corresponds to the conditions of $n\to\infty$, $E_n\to 0$, and $E_{\text{total}}=E_{N=1}\equiv E_{fs1}$. So, these arguments give additional evidence to the validity of the limit relations (12)–(17) and, consequently, the asymptotic solution (19) for the ground and singly excited bound states.

We have obtained some limit relations for the functions (10) and (11) in the vicinity of the triple collision point $R=0$ as well. The proper numerical calculations yield for the singlet states

$$\lim_{R\to 0}\left\{\frac{\Lambda^{(1)}_{1,0}(R)}{F(R)}\right\}=-Z, \tag{21}$$

$$\lim_{R\to 0}\left\{\frac{\Lambda^{(1)}_{12,0}(R)}{F(R)}\right\}=\frac{1}{2}, \tag{22}$$

$$\lim_{R\to 0}\left\{\frac{\Lambda^{(2)}_{1,12}(R)}{F(R)}\right\}=-\frac{1}{2}Z. \tag{23}$$

Note that Eq. (21) contains the singlet function $F(R)$, whereas the corresponding Eq. (12) includes the first derivative $F'(R)$. The results for the triplet states are

$$\lim_{R\to 0}\left\{\frac{R^2\Lambda^{(2)}_{1,1}(R)}{F(R)}\right\}=\lim_{R\to 0}\left\{\frac{R\Lambda^{(1)}_{1,0}(R)}{F(R)}\right\}=2, \tag{24}$$

$$\lim_{R\to 0}\left\{\frac{R^2\Lambda^{(2)}_{2,2}(R)}{F(R)}\right\}=-2, \tag{25}$$

$$\lim_{R\to 0}\left\{\frac{R\Lambda^{(2)}_{1,12}(R)}{F(R)}\right\}=\frac{1}{2}, \tag{26}$$

$$\lim_{R\to 0}\left\{\frac{\Lambda^{(1)}_{12,0}(R)}{F(R)}\right\}=\frac{1}{4}. \tag{27}$$

As is known, the two-electron wave functions of the singlet states at the triple coincidence point are nonzero. Therefore, Eqs. (21) and (22) allows to avoid the divergence at $R=0$ for terms proportional to R^{-1} in Eq. (9). The triplet states, which are proportional to R^2 in the vicinity of the triple collision point, don't have to obey such a requirement.

We were able to obtain only the simplest limit relations as R approaches zero. We hope these relations could be good for searching the general solution of Eq. (9). However, to derive the solution for small R we propose another way, which is more precise as well as more reliable. As was mentioned earlier, in Refs. [7,8] analytic expansions of the three-body atomic wave functions were presented. The expansions were derived for the exact solutions of the Schrödinger equation (5) up to the terms of the order r^2 (including $r^2\ln r$). We used some of those results (see Ref. [8], pp. 2796–2797) to obtain the analytical representation of the two-electron wave functions at the two-particle coalescence lines in the vicinity of the triple coincidence point. The same results, but for the singlet states only, could be derived by using Ref. [9]. However, one should be very careful, because in the last reference we found at least three misprints, which could have influence on the final results. The first misprint is a missing factor 2 in the expression for $Y_{2,0}$ [below Eq. (14) [9]]. The second one is the incorrect expression $r_{12}\sin\alpha\cos\theta$ on the RHS of the expression for $Y_{2,1}$ [below Eq. (14) [9]]. The third misprint is the missing function $\cos^{-1}$ before $(\mathbf{r}_1\cdot\mathbf{r}_2/r_1r_2)$ in the RHS of Eq. 11 [9].

So, using the results of Refs. [8,9] and taking the limit as $r_2\to 0$, we obtain for the singlet states

$$F(R) \simeq 1 - R\left(Z - \frac{1}{2}\right) + \frac{R^2}{12}[4Z^2 - 2Z(3 - \ln 2) + 1 - 2E]. \tag{28}$$

The similar result for the triplet states has the form

$$F(R) \simeq R^2\left\{1 - R\left(\frac{2}{3}Z - \frac{1}{4}\right) + \frac{R^2}{10}\left[\frac{5}{3}Z^2 - Z\left(2 - \frac{5}{6}\ln 2\right) + \frac{1}{4} - E\right]\right\}. \tag{29}$$

For simplicity, the wave functions (28) and (29) are normalized by condition $F(0)=1$ for the singlet states, and $[F(R)/R^2]_{R=0}=1$ for the triplet states.

We would like to pay particular attention to the absence of the Fock's logarithmic term in both expressions. This term disappears at the electron-nucleus coalescence line, because of the vanishing Fock's angular coefficient ψ_{21} in the limit as r_2 approaches zero (whereas $r_1 \to r_{12}$) for the singlet states.

At first glance, it is natural to assume that all of the Fock's logarithmic terms are canceled at the electron-nucleus coalescence line. However, such an assumption proved to be incorrect. We verified the angular coefficients ψ_{31}, ψ_{41} and ψ_{42}, corresponding to the logarithmic terms in the Fock's expansion up to the terms of order $r^4, r^4 \ln^2 r$ (singlet states). The exact expressions for these quantities could be found, e.g., in Ref. [7]. All of these three angular coefficients proved to be nonzero. So, we conclude that the first logarithmic term $\psi_{21} r^2 \ln r$ of the Fock's expansion is the only one to vanish at the electron-nucleus coalescence line, at least for the singlet states. Equation (29) shows additionally that for the triplet states all of the logarithmic terms, up to the fourth order in r, are canceled in the limit as $r_2 \to 0$ (or $r_1 \to 0$). Accordingly, the values of the first and second derivatives $F'(0), F''(0)$ for the singlet states and $[F(R)/R^2]'_{R=0}$, $[F(R)/R^2]''_{R=0}$ for the triplet states are finite. We verified the validity of the expansions (28) and (29) by direct calculation of these derivatives in the limit as $R \to 0$, using the accurate Ψ functions. The results coincided with the calculations performed according to the analytical formulas (28) and (29) within the accuracy of five significant digits.

Note that double-limit relations (21)–(27), as well as similar ones from the next section (electron-electron sticking) for $R \to 0$ could be obtained analytically by using expansions of Ref. [8]. We do not know the adequate analytical way to obtain the limit relations at $R \to \infty$. However, all of the limit relations presented here were derived and checked numerically with inaccuracy, which was not higher than 0.01%. We believe that high accuracy of numerical calculations and the perfect accuracy of our numerical results for $R \to 0$, speaks in favor of correctness of our results for $R \to \infty$.

III. ELECTRON-ELECTRON COALESCENCE

For the case of forming the two-electron coalescence or the coincidence of the coordinates of the both electrons, one should take the limit as $r_{12} \to 0$ on both sides of the Eq. (5). In this case we have (see Fig. 1):

$$\lim_{r_{12}\to 0} \theta_1 = \lim_{r_{12}\to 0} \theta_2 = \pi/2. \tag{30}$$

Then, in the limit as $r_{12} \to 0$ both terms with the mixed partial derivatives vanish in Eq. (5), and we can write

$$-\frac{1}{2}\left(2\frac{\partial^2\Psi}{\partial r_1^2} + 2\frac{\partial^2\Psi}{\partial r_{12}^2}\right)\Bigg|_{r_{12}=0} - \frac{2}{R}\frac{\partial\Psi}{\partial r_1}\Bigg|_{r_{12}=0} = \frac{2}{r_{12}}\left(\frac{\partial\Psi}{\partial r_{12}} - \frac{1}{2}\Psi\right)\Bigg|_{r_{12}=0} + \left(\frac{2Z}{R} + E\right)\Psi(R,R,0). \tag{31}$$

When deriving Eq. (31), we took into account that $r_1 = r_2 = R$ as r_{12} approaches zero. Then, using the Kato condition (4) in the RHS of Eq. (31), we obtain

$$\left(\frac{\partial^2\Psi}{\partial r_1^2} + \frac{\partial^2\Psi}{\partial r_{12}^2}\right)\Bigg|_{r_{12}=0} + \frac{2}{R}\frac{\partial\Psi}{\partial r_1}\Bigg|_{r_{12}=0} = -\left(\frac{2Z}{R} + E\right)\Psi(R,R,0). \tag{32}$$

From the CFHHM numerical calculations, we obtain the following relation:

$$\lim_{r_{12}\to 0} \frac{\partial\Psi(r_1,r_2,r_{12})}{\partial r_1} = \frac{1}{2}\frac{d\Phi(R)}{dR}, \tag{33}$$

where

$$\Phi(R) = \Psi(R,R,0). \tag{34}$$

The relation (33) is not a double-limit relation like all the other similar relations presented in the Sec. II. It is the only relation of such form obtained. It is valid for all $0 \leqslant R \leqslant \infty$ and $Z \geqslant 1$. The excited states are included as well. Using Eq. (33), we can rewrite Eq. (32) in the form

$$\left(\frac{\partial^2\Psi}{\partial r_1^2} + \frac{\partial^2\Psi}{\partial r_{12}^2}\right)\Bigg|_{r_{12}=0} = g(R), \tag{35}$$

where

$$g(R) = -\frac{1}{R}\frac{d\Phi(R)}{dR} - \left(\frac{2Z}{R} + E\right)\Phi(R). \tag{36}$$

Calculation of the ordinary first derivative $d\Phi/dR$ is considerably more precise than the calculation of the partial derivatives of the second order. The proper calculation of the function $g(R)$ and its comparison with the ordinary second derivative $d^2\Phi/dR^2$ yields, in the limit of R approaching infinity:

$$\lim_{R\to\infty}\left\{\frac{\Phi''(R)}{g(R)}\right\} = 4. \tag{37}$$

Then, using the limit relation (37), we can rewrite Eq. (36) in the limit of very large R:

$$\frac{1}{4}\frac{d^2\Phi_{as}}{dR^2} + E\Phi_{as} = 0. \tag{38}$$

As before, we neglected the terms proportional to R^{-1} in Eq. (36). The proper solution of the differential equation (38) has the form

$$\Phi_{as}(R) = \bar{C}_1 \exp(-2R\sqrt{-E}), \tag{39}$$

where $\bar{C}_1$ is an arbitrary constant. The function $\Phi_{as}(R)$ is the asymptotic representation of the accurate two-electron atomic wave function for the case of two electrons being at the same point but far away from the nucleus. Unlike F_{as}, Eq. (39) shows that Φ_{as} depends on only one parameter, energy E. As far as we consider the discrete spectrum, then $E<0$ and consequently the exponent on the RHS of Eq. (39) is negative.

Moreover, we obtained the following relation in the limit as $R\to 0$:

$$\lim_{r_1=r_2=R\to 0} \lim_{r_{12}\to 0} \frac{\partial\Psi(r_1,r_2,r_{12})}{\partial r_1} = -Z \lim_{R\to 0} \Phi(R). \tag{40}$$

It enables one to avoid the divergence at $R=0$ for the terms that are proportional to R^{-1} in the general Eq. (32) for the case, when two electrons are at the same point.

The approximate solution of the Eq. (32) at small R may now be obtained by neglecting the terms that are not proportional to R^{-1} in that equation. Also using Eq. (33), we have the equation

$$\frac{d\Phi_2}{dR} + 2Z\Phi_2 = 0, \tag{41}$$

with the the solution

$$\Phi_2(R) = \bar{C}_2 \exp(-2ZR). \tag{42}$$

We can again use the approach developed in the works [8,9] at $r_{12}\to 0$ ($r_1=r_2=R$). However, one should not forget that the expressions presented in these papers are valid only for $r_2<r_1$. In Ref. [10] the angular coefficients $\psi_{00},\psi_{10},\psi_{21},\psi_{20}$ of the Fock expansion are expressed through Pluvinage coordinates ζ and η [14], which are more symmetric and are valid for arbitrary r_1 and r_2. Taking into account that the scaling transformation $\mathbf{r}\to\mathbf{r}/Z$ was applied to the Hamiltonian in Ref. [14], we obtained under the simplifying normalizing condition of $\Phi(0)=1$:

$$\Phi(R) \simeq 1 - 2ZR + R^2\left[\frac{2Z}{3}\left(\frac{2}{\pi}-1\right)\ln R - \frac{E}{3} + \frac{5}{3}Z^2 + \delta_z\right] \tag{43}$$

with

$$\delta_z = \frac{2Z}{3}\left(\frac{1}{\pi}-1\right)\ln 2 + \frac{1}{6} + \frac{Z}{3} + 2a_{2,1}. \tag{44}$$

Here $a_{2,1}$ is an unknown coefficient of the homogeneous solution, which cannot be deduced from the local behavior of the Schrödinger equation near the nucleus [8–10]. It is a very difficult problem to calculate exactly $a_{2,1}$, because of the presence of the logarithmic term on the RHS of Eq. (43). However, we have evaluated δ_z (and consequently $a_{2,1}$) using the accurate CFHHM wave functions. This yielded the following approximate dependence:

$$\delta_z \simeq \frac{1}{2} - \frac{3}{10}Z. \tag{45}$$

This linear part of the Z dependence is the most accurate one for $2\leqslant Z\leqslant 5$. We found that the term $-E/3$ in Eq. (43) expresses correctly the dependence of $\Phi(R)$ on the state of excitation, while the term $(5/3)Z^2$ represents accurately the nonlinear dependence of $\Phi(R)$ upon the nuclear charge Z. Note that using the proper formulas from Refs. [8,9] yields the erroneous term Z^2 instead of the correct result $(5/3)Z^2$ in the expression (43). As we can see, the Fock's logarithmic term is preserved at the electron-electron coalescence line, unlike the case of the electron-nucleus line. Hence, the second derivative $\Phi''(R)$ has a logarithmic singularity at the origin. It is seen that solutions (42) and (43) coincide in the first order approximation at small R.

IV. RESULTS AND DISCUSSIONS

In Secs. II and III we have obtained analytical representations of the accurate two-electron wave functions at the boundary regions of both two-particle coalescence lines. We found that the behavior of these boundary solutions both at small and at large distances R has an exponential character. These properties enable us to propose a simple approximate representation for the ground state wave functions in the two-exponential form. The main idea is that the first exponential represents the behavior at small R and the second exponential represents the behavior at very large R. So, let us consider the following function:

$$f(R) = C\{\exp(-\lambda R) + \gamma\exp(-\beta R)\}, \tag{46}$$

with

$$\lambda = \alpha(1+\gamma) - \gamma\beta. \tag{47}$$

Here C, α, β, and γ are arbitrary parameters. This two-exponential function possesses an important peculiarity:

$$\frac{f'(0)}{f(0)} = -\alpha, \tag{48}$$

that is the ratio of the first derivative to the function itself at the origin ($R=0$) depends upon only one parameter α. Let the second exponential in the RHS of Eq. (46) present the behavior of the wave functions in question at very large R. Then according to the results of the previous sections [see Eqs. (19) and (28)], we can put $\beta_s=\sqrt{-2E-Z^2}$ and $\alpha_s=Z-1/2$ for the electron-nucleus coalescence line of the singlet states. Considering C as the normalization constant, we have only one unknown parameter γ. It can be obtained using the second derivative of the wave function $F(R)$ at the origin. Then the double differentiation of the general function (46) yields, in the limit of R approaching zero

TABLE II. The parameters λ, β, and γ for the approximate wave functions at the electron-nucleus coalescence line. The lower index s signifies that the parameter presents a singlet state.

Z	2	3	4	5
λ_s	1.58574	2.75657	3.93411	5.11350
β_s	1.34441	2.35793	3.36320	4.36599
γ_s	0.551062	1.80594	3.17337	4.57790

$$h \equiv \frac{f''(0)}{f(0)} = \frac{[\alpha(1+\gamma) - \gamma\beta]^2 + \gamma\beta^2}{1+\gamma}. \tag{49}$$

On the other hand, we have from Eq. (28):

$$h_s = \frac{1}{6}[4Z^2 - 2Z(3 - \ln 2) + 1 - 2E]. \tag{50}$$

Equation (49) is a quadratic with respect to parameter γ. It has two roots: $\gamma_1 = -1$ and $\gamma_2 = (h-\alpha^2)/(\alpha-\beta)^2$. While the root γ_1 yields a trivial solution $f(R)=0$, we retain only the solution $\gamma = \gamma_2$. Using Eq. (50) and taking into consideration the values of parameters α_s and β_s mentioned above, we obtain

$$\gamma_s = \frac{4(Z \ln 2 - E - Z^2) - 1}{3(1 - 2Z + 2\sqrt{-2E - Z^2})^2}. \tag{51}$$

The exponent λ of the first exponential plays an important part in constructing the approximate function (46). Note that it does not represent the behavior of this function at the origin. Both exponentials give contributions to the correct behavior of the function (46) in this boundary region according to Eqs. (48) and (49). However, the inequality $\lambda > \beta$ must be valid if we want the exponent β to present the approximate function (46) at very large R. So, using Eq. (51) and the proper expressions for parameters α_s and β_s we have for the ground state

$$\lambda_s = \frac{2 - 4E + 8Z^2 - 4Z[3(1+\beta_s) - \ln 2] + 6\beta_s}{6[2(Z-\beta_s) - 1]}. \tag{52}$$

In Table II we present the numerical values of the exponents λ_s and β_s as well as the factor γ_s for the helium atom and several heliumlike ions. As one can see from Table II, the parameter λ_s is greater than β_s for all Z presented.

To verify how good are the approximate functions (46) with the parameters of Table II, we have drawn the curves $y(R) = \log_{10}|[F_s(R) - f_s(R)]/F_s(R)|$ on Fig. 2. $F_s(R)$ and $f_s(R)$ are the accurate and the approximate functions, respectively. One can see from Fig. 2 that the approximate curves are very close to the exact ones at small R. However, even at quite large R the accuracy is not lower than 10%. The total accuracy is increasing with the nuclear charge Z.

The triplet states of the two-electron atomic systems are always excited states. Only the electron-nucleus coalescence line is formed for these states according to the Pauli exclusion principle. It is important that the corresponding wave function at the coalescence line $F_t(R)$ behaves according to Eq. (29) similar to R^2 as R approaches zero. Therefore, the

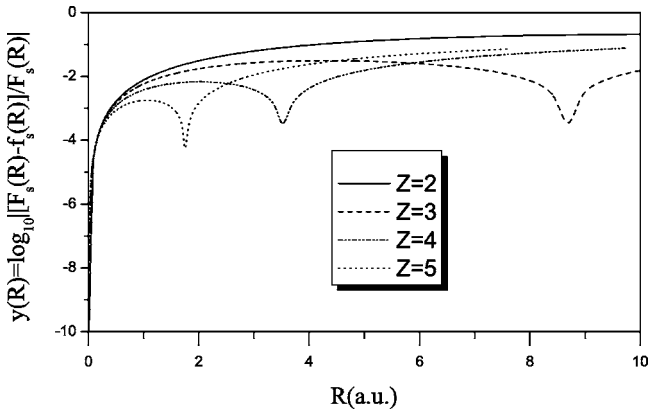

FIG. 2. Deviation of the approximate function $f_s(R)$ from the exact value $F_s(R)$ at the electron-nucleus coalescence line for the ground states of the two-electron atom/ions with the nuclear charge $Z=2,3,4,5$.

function (46) is not suitable in this case. Instead, for the lowest energy triplet state we can propose the simple approximate function of the form

$$f_t(R) = C_t R[\exp(-\lambda_t R) - \exp(-\beta_t R)], \tag{53}$$

where $\beta_t = \sqrt{-2E_t - Z^2}$ has to describe the behavior of $F(R)$ at very large R. It is easy to derive the following property of this function at the origin:

$$\left\{ \frac{d}{dR}\left[\frac{f_t(R)}{R^2}\right]\left[\frac{f_t(R)}{R^2}\right]^{-1} \right\}\Bigg|_{R=0} = -\frac{1}{2}(\lambda_t + \beta_t). \tag{54}$$

On the other hand, according to Eq. (29) the exact representation of $F_t(R)$ yields the value of $(1/4 - 2Z/3)$ for this quantity. So we obtain for the unknown exponent

$$\lambda_t = \frac{4}{3}Z - \frac{1}{2} - \beta_t. \tag{55}$$

It is easy to verify that the inequality $\lambda_t > \beta_t$ is valid for all Z. This condition is necessary to make the behavior of $f_t(R)$ close to the correct one. Figure 3 demonstrates the quite satisfactory behavior of the approximate functions (53), especially for $R < 5$ a.u. We can observe that at small R the accuracy of $f_t(R)$ decreases with increasing Z, whereas at large R it increases with Z. The dips on the graphs of Fig. 2 and 3 are artifacts of the logarithmic scale, since the logarithm of the absolute value of the difference of the two functions goes to $-\infty$ at the points of crossing the functions. The overall accuracy therefore can be inferred only at the values of R not too close to the dip.

The case of the electron-electron coalescence is the most complicated, because of the presence of the logarithmic term in the Eq. (43). However, the general two-exponential form (46) can be applied in this case too, but without the representation (47).

For simplicity, let us put $C = 1/(1+\gamma)$ in Eq. (46). Then we obtain the approximate function $f_e(R)$, which obeys the condition $f_e(0) = 1$, that in turn enables one to compare $f_e(R)$ with the expansion (43) in a simple manner. The exponent β representing the behavior at very large R is

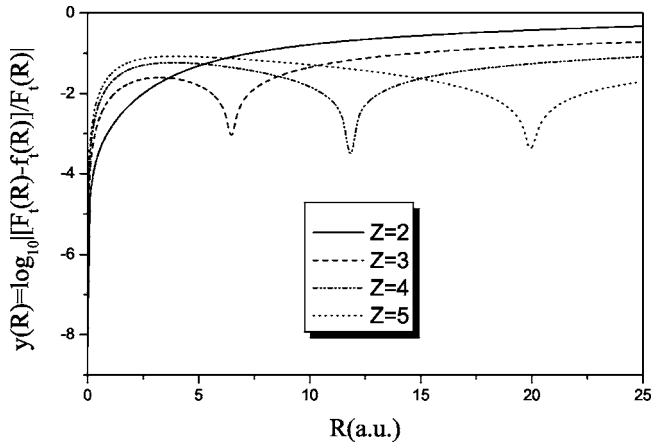

FIG. 3. Deviation of the approximate function $f_t(R)$ from the exact value $F_t(R)$ for the $2S$-triplet states of the two-electron atom and ions with nucleus charges $Z=2,3,4,5$.

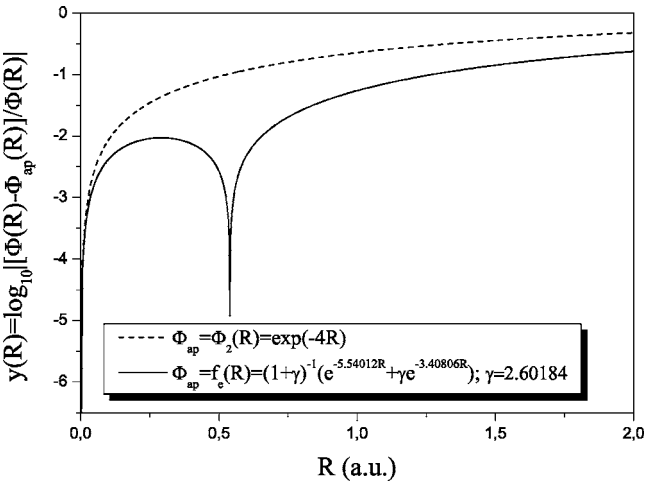

FIG. 4. Deviation of the approximate functions $f_e(R)$ and $\Phi_2(R)$ from the exact wave function $\Phi(R)$ at the electron-electron coalescence line for the helium atom.

equal to $\beta_e=2\sqrt{-E}$ and has to obey the inequality $\lambda_e>\beta_e$, according to the asymptotic representation (39). So, we have two unknown parameters λ_e and γ_e. The factor γ_e has to be positive, because the ground state wave function is nodeless. Then, for the first derivative $f_e'(R)$ at the origin we have $f_e'(0)=-(\lambda_e+\beta_e\lambda_e)/(1+\gamma_e)$. Comparing this formula with Eq. (43), we obtain the first constraint

$$\lambda_e = 2Z + \gamma_e(2Z - \beta_e). \tag{56}$$

It is easy to verify that the inequality $2Z>\beta_e$ is valid for all $Z\geqslant 1$. Therefore, for the parameters λ_e and γ_e obeying the constraint (56), the condition $\lambda_e>\beta_e$ will be valid for any positive γ_e. To obtain the second constraint for the parameters λ_e and γ_e, one can use for example an integral property of the exact wave function $\Phi(R)$ such as the normalization integral $S=\int_0^\infty \Phi^2(R)R^2dR$ with $\Phi(0)=1$. It is easy to calculate S using the accurate CFHHM wave functions available. Replacing $\Phi(R)$ by $f_e(R)$ in the integrand, and executing a simple integration, we obtain the second constraint in the form

$$\frac{1}{(2\lambda_e)^3} + \frac{2\gamma_e}{(\lambda_e+\beta_e)^3} + \frac{\gamma_e^2}{(2\beta_e)^3} = \frac{S}{2}(1+\gamma_e)^2. \tag{57}$$

The simplest way of solving the set of the equations (56) and (57) is using the well-known program MATHEMATICA [15]. The equations have a number of roots (including complex ones). However, only one root turned out to be real and positive, and therefore it could be applicable to γ_e. The corresponding solutions along with the other accompanying quantities E, S, and β_e are presented in Table III. It is seen from Table III that the approximate function parameters fulfill all the conditions mentioned above.

The degree of coincidence for the accurate and approximate helium wave functions at the electron-electron coalescence line is presented in Fig. 4. The solid line describes the deviation curve for the two-exponential approximate function $f_e(R)$ of the helium atom. For comparison, we have also drawn the corresponding one-exponential function (42), presented by the dotted line. The graphs are limited by the value of $R=2$ a.u., because of the very fast decay of the two-electron atomic wave functions at the electron-electron coalescence line. For example, if $\Phi(0)=1$, then $\Phi(2)\simeq 0.0006$ (for $Z=2$). For comparison, we can point out that the corresponding value of the wave function at the electron-nucleus coalescence line $F_s(2)\approx 100\Phi(2)$. The graphs on Fig. 4 demonstrate that the two-exponential function is considerably more accurate than the one-exponential one $\Phi_2(R)$. All of the approximate functions presented in this section could be employed for the evaluation of different atomic phenomena, and processes of the atomic photoionization in particular.

V. CONCLUSION

We have considered and analyzed some particular solutions of the Schrödinger equation for the two-electron atom

TABLE III. Parameters β_e, λ_e, and γ_e of the approximate wave functions at the electron-electron coalescence line. The accompanying values of the total energy E and the integrals S are presented as well.

Z	$-E$	S	β_e	λ_e	γ_e
2	2.9037244	0.00452855	3.40806	5.54012	2.60184
3	7.2799134	0.00127463	5.39626	8.32976	3.8589
4	13.655566	0.000524535	7.39069	11.1232	5.12583
5	22.030917	0.000264651	9.38742	13.9178	6.39552

or ion (with the nucleus charge Z and the total energy E) using the accurate CFHHM wave functions. We have obtained mathematical relations between the partial derivatives taken at the two-particle coalescence lines and the ordinary derivatives of the wave function taken at the same coalescence lines. The relations were found for the limit cases of very large and small distances R between one of the electrons and the other electron close to the nucleus (electron-nucleus coalescence) or between the two electrons close together and the nucleus (electron-electron coalescence). We have obtained the only relation valid for all $R \geqslant 0$ and $Z \geqslant 1$. It connects the first partial derivative on r_1 (or r_2) and the first ordinary derivative of wave function at the electron-electron coalescence line.

We have examined both singlet and triplet S states, and obtained the asymptotic solutions (for very large R) with the exponents $(-R\sqrt{-2E-Z^2})$ or $(-2R\sqrt{-E})$ for the electron-nucleus or electron-electron coalescence, respectively. These results turned out to be valid for the ground and singly excited bound states. We have derived the second-order expansions in R and $\ln R$ in the vicinity of the triple coalescence point for small R. We have found that the Fock's logarithmic terms vanished at the electron-nucleus coalescence line, unlike the case of the electron-electron coalescence, but only in the framework of the second-order expansion.

We have proposed simple two-exponential approximations for the two-electron atomic wave functions at the coalescence points. The approximations are valid for the lowest energy (nodeless) states. It was demonstrated that all of the approximate functions have quite satisfactory accuracy and could be employed at least for the initial qualitative evaluation of a number of phenomena in the atomic physics.

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