

WAVE FUNCTIONS OF HELIUM-LIKE SYSTEMS IN LIMITING REGIONS

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We find an approximate analytic forms for the solutions $\Psi(r_1, r_2, r_{12})$ of the Schrödinger equation for a system of two electrons bound to a nucleus in the spatial regions $r_1 = r_2 = 0$ and $r_{12} = 0$ that are of great importance for a number of physical processes. The forms are based on the well-known behavior of $\Psi(r_1, r_2, r_{12})$ near the singular triple coalescence point. The approximate functions are compared to the locally precise ones obtained earlier by the correlation function hyperspherical harmonic (CFHH) method for the helium atom, light helium-like ions, and the negative ion of hydrogen H^- . The functions are shown to determine a natural basis for the expansion of CFHH functions in the considered spatial region. We demonstrate how these approximate functions simplify calculations of high-energy ionization processes.

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1. INTRODUCTION

The ground states of systems comprising two electrons bound by a nucleus are described by radial wave functions that depend on three variables. These can be the distances between the electrons and the nucleus r_1 , r_2 and the interelectron distance r_{12} . Here, we find analytic expressions that approximate the solutions of the Schrödinger equation $\Psi(r_1, r_2, r_{12})$ in the special cases where $r_1 = r_2 = 0$ and $r_{12} = 0$:

$$F(R) \equiv \Psi(0, R, R); \quad \Phi(R) \equiv \Psi(R, R, 0). \quad (1)$$

We consider the ground states of the helium atom and of the light helium-like ions, including the negative ion of hydrogen H^- . In this paper, we treat the ground states only. Therefore, the total spin of the two-electron system is equal to zero.

We note that this problem is essentially different from the traditional problem of approximating the total wave function $\Psi(r_1, r_2, r_{12})$ [1]. There are numerous wave functions of this kind, with the approximate functions usually given by certain combinations of exponentials and polynomials, while a set of fitting parameters is found by minimization of the energy functional. Thus, the quality of such functions is determined by the accuracy of reproducing the binding energy value. Because the averaged value of the Hamiltonian is determined by the distances of the order of the size of the atom, such functions provide very good approximations at these distances. However, as was already emphasized in [2], they are not necessarily as precise in the limit cases $r_1 = r_2 = 0$ and $r_{12} = 0$.

The motivation for our study is that in a number of dynamical problems, one needs the bound state wave functions in regions of these variables where one of the distances is much smaller than the others. This is the case with those processes involving bound elec-

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trons that are kinematically forbidden for free electrons. For example, the high-energy asymptotic form of the photoionization cross section is expressed in terms of the two-electron function $\Psi(0, R, R)$, where r_1 or r_2 is zero [1]. The same is correct for the nonrelativistic high-energy asymptotic form of double photoionization and for the energy distribution of Compton scattering at sufficiently small energies of the outgoing electrons. Some of the characteristics of double photoionization are expressed in terms of the two-electron function with zero interelectron distance $\Psi(R, R, 0)$ [3]. The straightforward way to obtain the functions $F(R)$ and $\Phi(R)$ is to calculate them from $\Psi(r_1, r_2, r_{12})$ that is derived numerically. This is a rather complicated procedure.

Of course, one can use numerous accurate approximations of the functions $\Psi(r_1, r_2, r_{12})$ by superpositions of analytic functions depending on a large number of variational parameters (see [1] and more recent papers [4] and [5]). However, it would be useful to also have simple (although less precise) wave functions with a small number of parameters explicitly depending on the physical characteristics of the system. This is increasingly true because, as discussed in [6] and [3], there is no common view yet on the relative role of the possible mechanisms of ionization processes. It would therefore be reasonable to have tools not only for accurate computations but also for rapid and explicit estimations.

Here, we build approximate wave functions $F_A(R)$ and $\Phi_A(R)$ based on the known behavior of the exact wave function only near the triple coalescence point $R = 0$. The only free parameter in our approach is the value of the wave function at the coordinate origin,

$$N = \Psi(0, 0, 0). \quad (2)$$

Our approach was initiated and motivated by the important role played by the proper treatment of the two-particle coalescence point in earlier calculations. For example, the binding energies can usually be reproduced with a good accuracy by approximate wave functions that are certain combinations of exponential and polynomial factors [1]. Approximate wave functions based on exponential and polynomial factors are adequate representations at distances of the order of typical atomic dimensions. However, it was understood long ago that the analytic dependence on R is more complex and that the dependence is logarithmic in the vicinity of the origin [7]. Later, it was found that as r_1 , r_2 or r_{12} tend to zero, the solution of the Schrödinger equation satisfies specific Kato conditions [8]. Inclusion of the logarithmic terms [9] or accounting for the Kato conditions [10] (or both [11]) does not influence

the energy value much, but strongly improves the convergence of the $\Psi(r_1, r_2, r_{12})$ calculations. This encouraged us to try a rather simple approach.

As is shown in this paper, the approximate functions for (1) are given by

$$\begin{aligned} F_A(R) &= N \exp \left[- \left(Z - \frac{1}{2} \right) R \right], \\ \Phi_A(R) &= N \exp(-2ZR). \end{aligned} \quad (3)$$

They have to be compared with precise or highly accurate locally correct functions $F_{LC}(R)$ and $\Phi_{LC}(R)$. For the latter, we use the functions obtained by the correlation function hyperspherical harmonic (CFHH) method [12]. These nonvariational wave functions of the two-electron system in the s -state bound to a light nucleus have been obtained by direct solution of the three-body Schrödinger equation [13], without additional approximations. They require complicated computer codes for solution.

The way we construct the approximate wave functions insures that they reproduce the CFHH functions $F_{LC}(R)$ and $\Phi_{LC}(R)$ with good accuracy at sufficiently small values of R . The question is how long can this last as R increases? In other words, we must calculate the characteristics of the processes determined by $F(R)$ and $\Phi(R)$ at R being of the order of the size of the atom, and compare the results obtained with (3) and with the CFHH functions.

The answer is that the relative discrepancy between functions (3) and the CFHH functions does not exceed several percent at characteristic distances $1/(Z - 1/2)$ and $1/2Z$. The same is the accuracy of experimental detection of the photoionization characteristics.

Of course, this accuracy would not have been sufficient for the calculation of static atomic characteristics, e.g., of energy levels. However, there was qualitative controversy in theoretical results on the double photoionization energy distribution until recently [6], with quantitative results differing by orders of magnitude. Thus, it would be unjustified to aim for too high accuracy in any case. On the other hand, good accuracy of functions (2) prompts a basis for expansion of the CFHH functions. Because functions (3) have the radial dependence of the $1s$ -functions in the Coulomb fields with the respective charges $(Z - 1/2)$ and $2Z$, we can represent the numerical CFHH functions as linear combinations of the functions of this field with the dominant contribution coming from the $1s$ -terms.

We build our approximate wave functions and discuss their relation to other approaches in Sec. 2. We analyze the expansion of the CFHH functions at two-

particle coalescence points in series of the single-particle eigenfunctions of Coulomb fields in Sec. 3. We consider the applications in Sec. 4, and summarize in Sec. 5. The atomic system of units is used throughout this paper.

2. WAVE FUNCTIONS

It is known that at small distances $r_{1,2} \ll Z^{-1}$, the solution of the Schrödinger equation can be written as [14, 15]

$$\begin{aligned} \Psi(r_1, r_2, r_{12}) &= \\ &= N \left[1 - Z(r_1 + r_2) + \frac{1}{2}r_{12} + O(r^2, r^2 \ln r) \right], \end{aligned} \quad (4)$$

with $r = \sqrt{r_1^2 + r_2^2}$. The explicit form of the quadratic terms was found in [14]. Equation (4) is consistent with the more general Kato conditions [8]

$$\begin{aligned} \left. \frac{\partial \Psi(r_1, r_2, r_{12})}{\partial r_1} \right|_{r_1=0} &= -Z\Psi(0, r_2, r_2), \\ \left. \frac{\partial \Psi(r_1, r_2, r_{12})}{\partial r_2} \right|_{r_2=0} &= -Z\Psi(r_1, 0, r_1), \\ \left. \frac{\partial \Psi(r_1, r_2, r_{12})}{\partial r_{12}} \right|_{r_{12}=0} &= \frac{1}{2} \Psi(r_1, r_1, 0), \end{aligned} \quad (5)$$

which are satisfied for the CFHH functions. Using Eq. (4), we find that at $r_1, r_2 \ll Z^{-1}$,

$$\begin{aligned} F(R) &= N \left[1 - \left(Z - \frac{1}{2} \right) R + \dots \right], \\ \Phi(R) &= N (1 - 2ZR + \dots), \end{aligned} \quad (6)$$

with the dots denoting higher-order terms. Therefore,

$$\lim_{R \rightarrow 0} \frac{1}{F(R)} \frac{dF(R)}{dR} = -Z + \frac{1}{2} \quad (7)$$

and

$$\lim_{R \rightarrow 0} \frac{1}{\Phi(R)} \frac{d\Phi(R)}{dR} = -2Z. \quad (8)$$

We require Eqs. (7) and (8) to be satisfied by our approximate functions $F_A(R)$ and $\Phi_A(R)$ for all R . This leads to Eq. (3).

The functions in (3) correspond to a very simple physical picture. We note that Eqs. (3) look like the $1s$ -functions in the Coulomb fields with the charges $Z - 1/2$ and $2Z$, which serve in fact as a sort of adjustable parameters. The R -dependence is the one of

the $1s$ -electron, while the small probability of the three-particle coalescence is contained in the factor N determined by Eq. (2). We calculate it using the CFHH functions.

To characterize the quality of our approximate functions, we introduce

$$\begin{aligned} y_1(R) &= \lg \left| \frac{F_A(R) - F_{CFHH}(R)}{F_{CFHH}(R)} \right|, \\ y_2(R) &= \lg \left| \frac{\Phi_A(R) - \Phi_{CFHH}(R)}{\Phi_{CFHH}(R)} \right|, \end{aligned} \quad (9)$$

where the subscript CFHH denotes the wave functions obtained in [13].

The accuracy of functions (3) increases rapidly with increasing the nuclear charge Z . However, even for the negative ion H^- ($Z = 1$), the accuracy is rather high. At characteristic values $R \sim (Z - 1/2)^{-1}$ and $R \sim (2Z)^{-1}$, the error of the function Φ_A for H^- is about 6%, but only about 1% for the function F_A . The errors increase at larger values of R . They exceed 10% at the distances at which the wave functions are already very small. The functions $y_i(R)$ defined by Eqs. (9), which describe the R -dependence of the errors, are presented in Fig. 1. We show the results for helium ($Z = 2$) because most of the studies of two-electron systems are carried out for this case. We also give results for $Z = 4$ to illustrate the Z -dependence. The curve for H^- ($Z = 1$) is also presented, because this case is most difficult for investigations. The dip in the graph in Fig. 1a is a result of the logarithmic scale, because the logarithm of the absolute value of the difference of the two functions tends to $-\infty$ at the points where the difference changes sign. The overall accuracy of the solution can therefore be inferred only at the values of R not too close to the dip.

One can see that as R approaches the order of the size of the atom, the discrepancy with the CFHH functions becomes much greater than that at smaller R . However, the precision is still good enough for obtaining results with the accuracy of several percent.

The values of N defined by Eq. (2) are presented in Table 1. At large Z , the single-particle hydrogen-like model is expected to become increasingly true, because the interaction between the electrons is Z times weaker than their interaction with the nucleus. Hence, in the limit $Z \gg 1$,

$$N = N_c = \frac{Z^3}{\pi}. \quad (10)$$

The results in Table 1 illustrate this tendency. As expected, deviations from the limit law (10) are of the

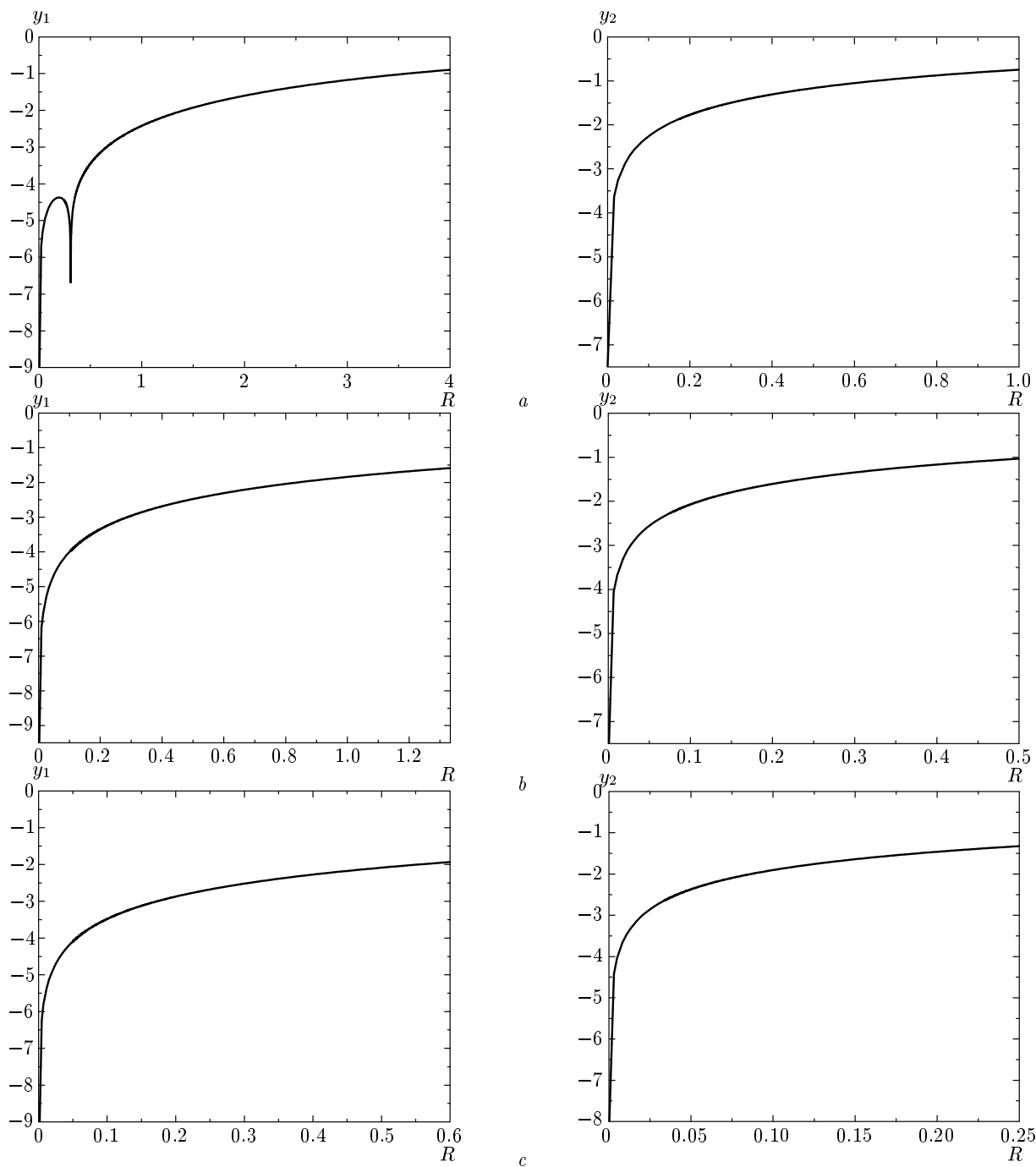


Fig. 1. The functions $y_1(R)$ and $y_2(R)$ defined by Eq. (9), for the negative ion $H^-(Z = 1)$ (a), for atomic helium ($Z = 2$) (b), and for the ion $Be^{++}(Z = 4)$ (c)

order of Z^{-1} . The actual results are smaller than predicted by (10) because Eq. (10) does not include the electron repulsion, which diminishes this value.

Of course, there are numerous simple approximate wave functions of the type

$$\Psi_A(r_1, r_2, r_{12}) = c (\exp(-ar_1 - br_2) + \exp(-ar_2 - br_1)),$$

which are built in order to calculate the ground-state energy values [1] and approximate the solutions of the Schrödinger equation at r_1 and r_2 of the order of Z^{-1} (in the case of H^- , they must also reproduce the very

Table 1. The value $F(0) = \Phi(0) = N$ for several values of Z . The ratio $\tilde{r} = N/N_c$ with N_c defined by Eq. (10) illustrates the convergence to the high- Z limit

Z	1	2	3	4	5	6
N	0.071	1.37	5.77	15.2	31.6	56.8
$\tilde{r} = \frac{N}{N_c}$	0.22	0.61	0.67	0.74	0.79	0.83

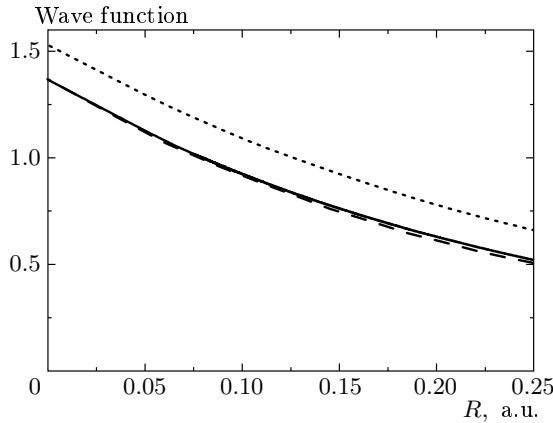


Fig. 2. The exact and approximate helium wave functions at the electron–electron coalescence line. Exact curve (solid line), $N \exp(-4R)$ (dashed line), $(\alpha^3/\pi) \exp(-2\alpha R)$, $\alpha = 27/16$ (dotted line)

existence of the bound state). Technically, they turn to the single-exponential forms at $r_1 = r_2 = R$ and are independent of r_{12} . These functions can be compared with our functions $\Phi(R)$ defined by Eq. (3). But they do not approximate the locally correct CFHH functions $\Phi_A(R)$, and, as argued in [2], are not supposed to. In Fig. 2, we illustrate this statement by presenting the CFHH function $\Phi(R)$, our function (3), and the screened Coulomb wave function

$$\Phi_s(R) = \frac{\alpha^3}{\pi} e^{-2\alpha R}$$

with $\alpha = 27/16$ for helium [1].

In Ref. [16], the function $F(R)$ for H^- , He, and Li^+ was approximated by a hydrogen-like function with the effective charge Z_{eff} treated as a variational parameter. The respective values of Z_{eff} for $Z = 1, 2, 3$ have been found to be 0.58, 1.53 and 2.52. In Ref. [17], the function $F(R)$ for the ion H^- was analyzed at large distances. We do not claim our functions to be ac-

curate in this R -region, which is not essential because the R -domain within the atomic radius is of primary importance.

3. EXPANSION OF THE CFHH FUNCTIONS IN SERIES IN THE COULOMB FIELD EIGENFUNCTIONS

The R -dependence of the approximate wave functions $F_A(R)$ and $\Phi_A(R)$ in (3) is the same as that of $1s$ -functions in the Coulomb fields of the nuclei with the respective charges $Z_1 = Z - 1/2$ and $Z_2 = 2Z$. The high precision of these functions suggests that the eigenfunctions of the Schrödinger equations in these fields form convenient series for expansion of the CFHH functions $F(R)$ and $\Phi(R)$.

With the common notation $X(R)$ for the functions $F(R)$ and $\Phi(R)$, we introduce the normalized functions

$$X_N(R) = \frac{1}{C_X^{1/2}} X(R),$$

where

$$C_X = \int_0^\infty R^2 X^2(R) dR.$$

Thus,

$$\int_0^\infty R^2 X_N^2(R) dR = 1.$$

In the expansions over the complete sets of some eigenfunctions, $X_N(R)$ can be represented as

$$F_N(R) = \sum_i a_i f_i(R), \quad \Phi_N(R) = \sum_i b_i \varphi_i(R), \quad (11)$$

where \sum_i denotes summation over the discrete-spectrum states and integration over the continuum, and

$$\begin{aligned} a_i &= \int_0^\infty R^2 F_N(R) f_i^*(R) dR, \\ b_i &= \int_0^\infty R^2 \Phi_N(R) \varphi_i^*(R) dR. \end{aligned} \quad (12)$$

For $f_i(R)$ and $\varphi_i(R)$ normalized to unity, we have

$$\sum_i a_i^2 = \sum_i b_i^2 = 1. \quad (13)$$

Choosing the solutions of the Schrödinger equations in the Coulomb fields with the charges $Z_1 = Z - 1/2$ and $Z_2 = 2Z$ as the respective functions $f_i(R)$ and $\varphi_i(R)$,

Table 2. The coefficients of the two lowest terms in expansions (11) of the CFHH functions in terms of the Coulomb functions. The coefficients of the next terms are limited by the conditions $|a_i| < \tilde{a}$, $|b_i| < \tilde{b}$, while the values of $\tilde{a} = (1 - a_{1s}^2 - a_{2s}^2)^{1/2}$ and $\tilde{b} = (1 - b_{1s}^2 - b_{2s}^2)^{1/2}$ are presented in the two bottom lines

Z	1	2	3	4
a_{1s}	0.98482	0.99970	0.99991	0.99996
b_{1s}	0.99067	0.99807	0.99918	0.99955
a_{2s}	-0.144	-0.020	-0.010	-0.007
b_{2s}	-0.108	-0.046	-0.030	-0.022
\tilde{a}	0.097	0.015	0.008	0.005
\tilde{b}	0.082	0.041	0.028	0.021

we find the values a_{1s} and b_{1s} given in Table 2. For atomic helium, $a_{1s} = 0.9997$ and $b_{1s} = 0.998$. High accuracy of functions (3) corresponds to domination of the terms a_{1s}^2 and b_{1s}^2 in sums (13).

The precision of calculations can be improved by adding the contributions of the higher states in accordance with Eq. (12). Of course, only the s -states are involved in our case. For example, $a_{2s} = -0.02$ and $b_{2s} = -0.05$ in the case of atomic helium. The results for other values of Z are given in Table 2. This procedure allows achieving any desired accuracy, controlled by Eq. (13).

4. EXAMPLES OF APPLICATION

As mentioned above, one of the possible applications of functions (3) is given by high-energy photoionization processes. We start with single photoionization. The high-energy nonrelativistic asymptotic form of the K -shell ionization cross section can be written as [1]

$$\sigma = \frac{2^{11/2} \pi e^2 Z^2 C^2}{3mc\omega^{7/2}}, \tag{14}$$

where m is the electron mass and c is the speed of light. The properties of the ionized states are contained in the factor

$$C = \int_0^\infty R^2 F(R) \psi_K(R) dR, \tag{15}$$

where $F(R)$ is determined by Eq. (1) and $\psi_K(R)$ is the single-particle function of the K -electron in the residual ion. In our case, $\psi_K(R)$ is just the $1s$ -function of the Coulomb field with the charge Z .

In the single-particle approximation, C is simply the value of the single-particle wave function at the coordinate origin. To illustrate the quality of functions (3), we compare the results for the factor C calculated using the CFHH functions and functions (3). In the latter case, we find the analytic expression

$$C = \frac{2NZ^{3/2}}{\sqrt{\pi}(2Z - 1/2)^3}, \tag{16}$$

yielding $C = 0.102$ for atomic helium. Numerical calculations with the CFHH functions give $C = 0.103$ in this case. Hence, using approximate function (3) leads to an error of 1%. Earlier, the authors of [18] found that the value of C obtained by using the Hylleraas-type variational function is well approximated by using a hydrogen-like function with $Z_{eff} = Z - 0.53$.

We now turn to the case of double photoionization. The shape of the spectrum curve of double photoionization changes as the photon energy increases. The mechanisms that cause these changes are explained in [3]. While the photon energy ω is smaller than a certain value ω_1 , the energy distribution approaches its minimum at the central point, with the equal energies of the outgoing electrons, i.e., $\varepsilon_1 = \varepsilon_2$. There is a peak at the central point for $\omega > \omega_1$, which splits into two for $\omega > \omega_2$. Thus, there is a local minimum at $\varepsilon_1 = \varepsilon_2$ for $\omega > \omega_2$.

The values of ω_1 and ω_2 were obtained in [19] using the CFHH functions. We do not repeat the derivation of the corresponding equations here. Instead, we explain their origin and formulate them in order to illustrate how functions (3) allow obtaining approximate solutions.

The values of ω_1 and ω_2 can be given as solutions of the following equation, which involves the functions $F(R)$ and $\Phi(R)$ [19]:

$$\lambda\mu = \omega^{9/2} A(\omega), \tag{17}$$

where λ is a numerical coefficient,

$$\mu = \int_0^\infty dr |F(r)|^2, \tag{18}$$

and the function A depends on ω in a more complicated way,

$$A(\omega) = \int_{-1}^{+1} dt t^2 (1 - 2t^2) D(\omega^2 t^2), \tag{19}$$

with

$$D(q^2) = \left| \int_0^\infty \frac{\sin(qr)}{qr} \Phi(r) r^2 dr \right|^2. \tag{20}$$

Table 3. The values of ω_1 and ω_2 (Sec. 4) in keV for the ground states of the lightest helium-like systems, calculated using the CFHH functions [13] and functions (3)

Z	1	2	3	4
ω_1 , this work	0.67	2.11	3.92	6.14
ω_1 , [13]	0.55	1.93	3.70	5.89
ω_2 , this work	4.86	9.71	14.5	19.3
ω_2 , [13]	3.97	8.89	13.7	18.5

Using the exact CFHH functions requires tedious computations. However, approximate wave functions (3) allow obtaining analytic expressions for both left-hand side and right-hand side of Eq. (17). Setting $F(r) = F_A(r)$ and $\Phi(r) = \Phi_A(r)$, we obtain

$$\mu = \frac{1}{2Z - 1}$$

and

$$A(\omega) = \frac{1}{\omega^6} \times \left(\frac{6a^6 + 13a^4 + 2a^2 + 3}{6a^2(a^2 + 1)^3} + \frac{1 - 2a^2}{2a^3} \operatorname{arctg} \frac{1}{a} \right) \quad (21)$$

with $a = 2Z/\omega$.

The values of ω_1 and ω_2 obtained by using the CFHH functions and functions (3) are presented in Table 3. It can be seen that the discrepancy between the two sets of results decreases rapidly with increasing Z . Being 22 % for H^- and 9 % for He, it becomes 4 % for $Z = 4$.

5. SUMMARY

We have built very simple analytical approximations (3) for the wave functions $F(R)$ and $\Phi(R)$ describing ground states of two-electron systems bound by the Coulomb field of a nucleus in the spatial regions $r_1 = r_2 = 0$ and $r_{12} = 0$. The presentation is based on the behavior of the exact solution of the Schrödinger equation near the three-particle coalescence singularity. Comparing our functions (3) with the locally correct CFHH functions for the ion H^- , atomic helium, and light helium-like ions (relativistic corrections, which are of the order of $(Z/137)^2$, are not included), we found good agreement in a large interval of the values of R . As is evident, the precision of the approximate functions increases with increasing the nuclear charge Z .

We have shown that the solutions of the single-particle Schrödinger equations in Coulomb fields with charges $Z_1 = Z - 1/2$ and $Z_2 = 2Z$ provide natural bases for the expansion of the functions $F(R)$ and $\Phi(R)$ with dominant $1s$ -terms. The tendency for their domination increases with Z . The approach is more precise for $F(R)$ than for $\Phi(R)$.

Examples presented in Sec. 4 show that even for the lightest helium-like systems, such as H^- and He, wave functions (3) can be used for estimations of the physical parameters at least.

The high precision of such a simple approximation that properly treats singularities in the wave function is in agreement with the conventional belief that singularities determine important physical characteristics such as high-energy photoionization cross sections.

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