Wave Functions of Heliumlike Systems in Limiting Regions

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Abstract

We find approximate analytical presentation of the solutions $\Psi(r_1, r_2, r_{12})$ of Schrödinger equation for two-electron system bound by the nucleus, in the space region $r_{1,2} = 0$ and $r_{12} = 0$ that are of great importance for a number of physical processes. The presentation is 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 correct ones obtained earlier by the Correlation Function Hyperspherical Harmonic (CFHH) method for helium atom, light heliumlike ions and for the negative ion of hydrogen $H^-$. The functions are shown to determine a natural basis for the expansion of CFHH functions in the considered space region. We demonstrate, how these approximate functions simplify the calculations of the high energy ionization processes.
I. INTRODUCTION

The ground states of the two-electron systems bound by the nucleus are described by the wave functions, depending on three variables. These can be the distances between the electrons and the nucleus $r_{1,2}$ and the interelectron distance $r_{12}$. Here we shall find analytical expressions, which would approximate the solutions of the Schrödinger equation $\Psi(r_1, r_2, r_{12})$ in the special cases $r_{1,2} = 0$ and $r_{12} = 0$:

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

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

Note that this problem differs strongly 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 being usually 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. Since the averaged value of the Hamiltonian is determined by the distances, which are of the order of the size of the atom, such functions provide very good approximation at these distances. However, as it was emphasized already in [2], they are not necessary as precise in the limiting cases $r_{1,2} = 0$ and $r_{12} = 0$.

The motivation of our study is that in a number of dynamical problems one needs the bound state wave functions in the such region of variables, where one of the distances is much smaller then the other ones. This takes place in those processes on the bound electrons, which are kinematically forbidden for the free ones. For example, the high energy asymptotic of photoionization 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 of the double photoionization, and for the energy distribution of the Compton scattering at sufficiently small energies of the outgoing electrons. Some of the characteristics of the 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 could be derived numerically. This is a rather complex procedure. Therefore here we shall build the 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 of our approach is the value of the wave functions at the coordinate origin

\[
N = \Psi(0, 0, 0) .
\]  

(2)

Our approach was initiated and encouraged by the large role of the proper treatment of the two-particle coalescence point in the earlier calculations. For example, the binding energies can be reproduced usually with a good accuracy by the approximate wave functions, which are certain combinations of exponential and polynomial factors \[1\]. Such presentation is good enough at distances of the order of the atomic size. However, it was understood long ago that the analytical dependence upon \( R \) is not as simple as that, and the logarithmic terms are presented in the expansion of the wave function near the origin \[4\]. Later it was found that, if \( r_{12} \) or \( r_{12} \) turn to zero, the solution of the Schrödinger equation should satisfy the specific Kato conditions \[5\]. Inclusion of the logarithmic terms \[6\], or accounting of the Kato conditions \[7\] or both \[8\] does not influence much the energy value, but improves strongly the convergence of the procedure of \( \Psi(r_1, r_2, r_{12}) \) calculations. This encouraged us to try a rather simple approach.

As it is shown in this paper, the approximate functions for (1) appear to be

\[
F_A(R) = N \exp \left[ - \left( Z - \frac{1}{2} \right) R \right] ; \quad \Phi_A(R) = N \exp(-2ZR) .
\]

(3)

They have to be compared to precise or highly accurate locally correct functions \( F_{LC}(R) \) and \( \Phi_{LC}(R) \). As such, we use the functions obtained by the Correlation Function Hyperspherical Harmonic (CFHH) method \[9\]. These non-variational wave functions of the two-electron system bound by a light nucleus in \( s \)-state have been obtained by direct solution of the three-body Schrödinger equation \[10\], without additional approximations. They require complicated computer codes for being employed.

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 \( R \). The question is, how long this can last, while \( R \) increases. In other words, we must calculate the characteristics of the processes, which are 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 CFHH functions does not exceed several percents at characteristic distances $\frac{1}{(Z-1/2)}$ and $\frac{1}{2Z}$. The same is the accuracy of the photoionization characteristics.

Of course, such accuracy would not have been sufficient for the calculation of the static atomic characteristics, e.g. of the energy levels values. However, e.g. there was qualitative controversy in theoretical results on the double photoionization energy distribution until recent time [11], with quantitative results differing by orders of magnitude. Thus it would be unjustified to run for too high accuracy in any case. On the other hand, good accuracy of the functions (2) prompts a basis for expansion of the CFHH functions. Since the functions (3) have the radial dependence of the $1s$-functions in the Coulomb fields with charges $(Z - \frac{1}{2})$ and $2Z$, respectively, one can present the numerical CFHH functions as linear combinations of the functions of this field with the dominative contribution coming from $1s$ terms.

We build our approximate wave functions and discuss their relation to other approaches in Sec.2. We analyze expansion of 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. Atomic system of units is used through the paper.

II. WAVE FUNCTIONS

It is known that at small distances $r_{1,2} \ll Z^{-1}$ the solution of the Schrödinger equation can be presented as [12, 13]

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

(4)

with $r = \sqrt{r_1^2 + r_2^2}$. The explicit form of the quadratic terms was found in [12]. Eq.(4) is consistent with more general Kato conditions [3],

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

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

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

(5)

which are fulfilled for the CFHH functions. Using Eq.(4) we find that at $r_{1,2} \ll Z^{-1}$

$$
F(R) = N \left[ 1 - \left( Z - \frac{1}{2} \right) R + \ldots \right]; \quad \Phi(R) = N \left( 1 - 2ZR + \ldots \right),
$$

(6)
with the dots denoting the higher terms. This provides
\[
\lim_{R \to 0} \frac{1}{F(R)} \frac{dF(R)}{dR} = -Z + \frac{1}{2}, \tag{7}
\]
and
\[
\lim_{R \to 0} \frac{1}{\Phi(R)} \frac{d\Phi(R)}{dR} = -2Z. \tag{8}
\]

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 (3) correspond to a very simple physical pictures. Note that (3) look like the 1s functions in the Coulomb fields with charges \((Z - 1/2)\) and \(2Z\), respectively, that serve in fact as a sort of adjustable parameters. It’s \( R \) dependence is one of 1s electron, while the small probability of the three-particle coalescence is contained in the factor \( N \) determined by Eq.(2). We calculate the latter by using the CFHH functions.

To characterize the quality of our approximate functions, we introduce the
\[
y_1(R) = \log_{10} \left| \frac{F_A(R) - F_{CFHH}(R)}{F_{CFHH}(R)} \right|; \quad y_2(R) = \log_{10} \left| \frac{\Phi_A(R) - \Phi_{CFHH}(R)}{\Phi_{CFHH}(R)} \right| \tag{9}
\]
with the lower indices CFHH denotes the wave functions obtained in [10].

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

One can see that the discrepancy with CFHH functions becomes much greater at \( R \) becoming of the order of the size of the atom, comparing to that at smaller \( R \). However, the precision is still good enough for obtaining results with the accuracy of several percents.
The values of \( N \), the latter being defined by Eq.(2) are presented in Table 1. At large \( Z \) the single-particle hydrogenlike model is expected to become increasingly true, since the interaction between the electrons is \( Z \) times weaker than their interaction with the nucleus. Hence, in the limit \( Z \gg 1 \)

\[
N = N_c = \frac{Z^3}{\pi}.
\]

(10)

The results presented in Table 1 illustrate this tendency. As expected, deviations from the limiting law (10) are of the order \( Z^{-1} \). The actual results are smaller than predicted by (10) since the latter 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 build in order to calculate the ground state energy values [1], thus approximating the solutions of the Schrödinger equation at \( r_{1,2} \) of the order \( Z^{-1} \) (in the case of \( H^- \) they had to reproduce also the very existence of the bound state). Technically, they turn to the single-exponential forms at \( r_1 = r_2 = R \) and do not depend on \( r_{12} \). These functions can be compared to our functions \( \Phi(R) \) defined by Eq.(3). But they do not approximate the locally correct CFHH functions \( \Phi_A(R) \), and, following [2], are not supposed to. We illustrate this statement by presenting in Fig.2 the CFHH function \( \Phi(R) \), our function (3) and the screened Coulomb wave function \( \Phi_s(R) = a^{3/2} \exp(-2aR) \) with \( a = 27/16 \) for helium [1].

In [14] the function \( F(R) \) for \( H^- \), \( He \) and \( Li^+ \) was approximated by a hydrogenlike function with the effective charge \( Z_{eff} \) treated as a variational parameter. The values of \( Z_{eff} \) for \( Z = 1, 2, 3 \) have been found to be 0.58, 1.53 and 2.52, correspondingly. In [15] the function \( F(R) \) for the ion \( H^- \) have been analyzed at large distances. We do not claim our functions to be true in this \( R \)-region, which is not essential for us since of prime importance is the \( R \) domain within the atomic radius.

### III. Expansion of CFHH Functions in Series of the Coulomb Field Eigenfunctions

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

Introducing the common notation $X(R)$ for the functions $F(R)$ and $\Phi(R)$ we present the normalized functions $X_N(R) = \frac{1}{C_X}X(R)$ with $C_X = \int_0^\infty R^2 X^2(R) dR$. 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 presented as:

$$F_N(R) = \sum a_i f_i(R); \quad \Phi_N(R) = \sum b_i \varphi_i(R),$$

(11)

with $\sum$ denoting the sum over the states of discrete spectrum and integration over continuum

$$a_i = \int_0^\infty R^2 F_N(R) f_i^*(R) dR; \quad b_i = \int_0^\infty R^2 \Phi_N(R) \varphi_i^*(R) dR.$$  

(12)

For $f_i(R)$ and $\varphi_i(R)$ normalized to one, it is

$$\sum a_i^2 = \sum b_i^2 = 1.$$  

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

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

IV. EXAMPLES OF APPLICATION

As we said above, one of the possible application of the functions (3) is the high energy photoionization processes. Let us start with the single photoionization. The high energy nonrelativistic asymptotic for the K-shell ionization cross section can be written as

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

(14)
where \( m \) is electron mass and \( c \) is the speed of light. The properties of the ionized states contained in the factor

\[
C = \int_0^\infty R^2 F(R)\psi_K(R)dR .
\]

(15)

Here \( F(R) \) is determined by Eq.(1), while \( \psi_K(R) \) is the single-particle function of the K-electron in 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 the functions (3) we compare the results for the factor \( C \) calculated by using the CFHH functions and the functions (3). In the latter case we find an analytic expression

\[
C = \frac{2NZ^{3/2}}{\sqrt{\pi}(2Z - 1/2)^3} ,
\]

(16)

providing \( C = 0.102 \) for the case of atomic helium. The numerical calculations with the CFHH functions give \( C = 0.103 \) in this case. Hence, employing the approximate function (3) leads to the error of 1%. Earlier the authors of [16] found that the value of \( C \) obtained by using the Hylleraas-type variational function is well approximated by employing a hydrogenlike function with \( Z_{eff} = Z - 0.53 \).

Now let us turn to the case of the double photoionization. The shape of the spectrum curve of the double photoionization changes with the photon energy growth. The mechanisms which cause these changes are explained in [3]. While the photon energy \( \omega \) is smaller than certain value \( \omega_1 \), the energy distribution approaches its minimum at the central point, with the equal energies of the outgoing electrons, \( \varepsilon_{1,2} \), i.e. \( \varepsilon_1 = \varepsilon_2 \). There is a peak at the central point at \( \omega > \omega_1 \), which splits into two at \( \omega > \omega_2 \). Thus, there is a local minimum at \( \varepsilon_1 = \varepsilon_2 \) at \( \omega > \omega_2 \).

The values of \( \omega_{1,2} \) were obtained in [17] by using the CFHH functions. We shall not repeat derivation of the corresponding equations here. We rather explain their origin and put them down, in order to illustrate, how the functions (3) enable to obtain approximate solutions.

The values of \( \omega_{1,2} \) can be presented as solutions of the following equation, which involves the functions \( F(R) \) and \( \Phi(R) \) [17]:

\[
\lambda\mu = \omega^{9/2}A(\omega) ,
\]

(17)
with $\lambda$ being a certain numerical coefficient, and

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

while the function $A$ depends on $\omega$ in a more complicated way:

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

with

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

Employing the exact CFHH functions requires tedious computations. However, using the approximate wave functions (3) one can obtain analytical expressions for both left-hand side and right-hand side of Eq.(17). Putting $F(r) = F_A(r)$ and $\Phi(r) = \Phi_A(r)$ we obtain $\mu = \frac{1}{2Z-1}$, while

$$A(\omega) = \frac{1}{\omega^6} \left( \frac{6\alpha^6 + 13\alpha^4 + 2\alpha^2 + 3}{6\alpha^2(\alpha^2 + 1)^3} + \frac{1 - 2\alpha^2}{2\alpha^3} \arctan \frac{1}{\alpha} \right) \quad (21)$$

with $a = 2Z/\omega$.

The values of $\omega_{1,2}$ obtained by using the CFHH functions and the functions (3) are presented in Table 3. One can see that the discrepancy between two sets of results drops rapidly with $Z$ growth. Being 22% for $H^-$ and 9% for helium, it becomes 4% for $Z = 4$.

V. SUMMARY

We build very simple analytical presentations (3), for the wave functions $F(R)$ and $\Phi(R)$ describing ground states of two-electron systems bound by the Coulomb field of the nucleus in the space regions $r_{1,2} = 0$ 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) to the locally correct CFHH functions for the ion $H^-$, atomic helium and light heliumlike ions (relativistic corrections, which are of the order $(Z/137)^2$ are not included), we found good agreement in a large interval of the values of the $R$. As is evident the precision of the approximate functions increases with the nuclear charge $Z$ growth.
We show that the solutions of the single-particle Schrödinger equations in the Coulomb fields with the charges $Z_1 = Z - 1/2$ and $Z_2 = 2Z$ provide natural basis for expansion of the functions $F(R)$ and $\Phi(R)$ with the domination of 1s terms. The latter tendency increases with $Z$. The approach is more precise for the function $F(R)$, then for $\Phi(R)$.

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

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

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TABLE I: 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|
| $\tilde{r}$ | 0.22 | 0.61| 0.67| 0.74| 0.79| 0.83|

TABLE II: The coefficients of the two lowest terms of 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 |

TABLE III: The values of $\omega_1$ and $\omega_2$ (Sect.4) in keV for the ground states of the lightest heliumlike systems, calculated by using the CFHH functions [10] and the functions (3).

| $Z$ | 1   | 2   | 3   | 4   |
|-----|-----|-----|-----|-----|
| $\omega_1$ – this work | 0.67 | 2.11 | 3.92 | 6.14 |
| $\omega_1$ – [10] | 0.55 | 1.93 | 3.70 | 5.89 |
| $\omega_2$ – this work | 4.86 | 9.71 | 14.5 | 19.3 |
| $\omega_2$ – [10] | 3.97 | 8.89 | 13.7 | 18.5 |
FIG. 1: The functions $y_1(R)$ and $y_2(R)$ defined by Eq. (9), for the negative ion $\text{H}^{-}(Z = 1)$ — Fig.1a, for atomic helium ($Z = 2$) — Fig.1b, and for the ion $\text{Be}^{++}(Z = 4)$ — Fig.1c.
FIG. 2: The exact and the approximate helium wave functions at the electron-electron coalescence line.