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PARTIAL EXPANSION OF THE TWO-CENTER COULOMB GREEN'S FUNCTION

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A general procedure for correct two-centre Coulomb Green's function is given. It is motivated by the incorrect formula of Liu. We start with partial expansion of Green's function in terms of spheroidal functions. Various expansions of regular and irregular radial Coulomb spheroidal functions are also presented. The paper also contains two-centre Green's function for continuous spectrum. This article may be considered as a basis for the three-centre Coulomb problem, which we aim to study in future.

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1 Introduction

The analysis of two-centre Green's function is an important problem because it is of central importance for quantum calculations in molecular and atomic processes and scattering theory of nonrelativistic electron from polar molecules and ions. Some results may appear to be useful also for QQq baryons and QQg mesons.

Let Z_1 and Z_2 be the charges of two nuclei 1 and 2, r_1 and r_2 the distances between the electron (or charged particle with charge q) and the nuclei 1 and 2, respectively, and R is the separation between the centres 1 and 2. The Hamiltonian of two Coulomb centres (the so-called Z_1eZ_2 problem [1]) is

$$H = -\frac{1}{2}\Delta - \frac{Z_1}{r_1} - \frac{Z_2}{r_2}. \tag{1}$$

The need of Green's function appears always when we use the perturbation theory. The zero order approximation is the solution to Schrödinger's equation $H\Psi(\mathbf{r};R) = E(R)\Psi(\mathbf{r};R)$. For the first-order approximation we have an inhomogeneous equation. This equation can be solved by Green's function $G_E(\mathbf{r};\mathbf{r}'|R)$ of the two-centre Coulomb problem. Two-centre Green's function has the same effect in the electron structure theory, and in the theory of molecular spectra as has Coulomb Green's function in atomic theory. However, two-centre Green's function is not so well mathematically investigated as Coulomb Green's function for one particle is.

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So far we do not have closed form of two-centre Green's function, which should be analogous to the Hostler and Pratt relation [2] of the one particle Coulomb Green's function [1]. The reason is simple. There are no adequate simple integral representations of the Coulomb spheroidal functions (CSF). Well-known Laplace method gives usually handy solutions of differential equations in the form of integral representations (e.g. for the hypergeometric and confluent hypergeometric functions, respectively). In the case of CSF, there are modifications of this techniques [3,6], which enable to construct only integral equations and relations.

It should be mentioned that in most applications we are not so much interested in the compact formula for two-centre Green's function, as we are in the expansion $G_E(\mathbf{r};\mathbf{r}'|R)$ in terms of complete system of functions with defined angular quantum numbers (”partial expansion”). First such expansion of two-centre Green's function was given by Laurenzi [7], specially for the H_2^+ ion. In this the case angular functions are identical with the spheroidal functions of free motion in spheroidal coordinates.

In general nonsymmetrical case $(Z_1 \neq Z_2)$, the first partial expansion for $E > 0$ was obtained by Liu [8] who, however, obtained incorrect expression for the radial part of two-centre Green's function $G_E(\mathbf{r};\mathbf{r}'|R)$.

Another class that represents two centre Green's function is presented by the Sturm expansion. This approach was analyzed in detail in [9]. We refer to papers [10, 11] where for Green's function of molecular hydrogen the approximate formulae are obtained within the framework of methods of quantum defect and model potential.

The calculation of the radial Coulomb spheroidal functions (RCSF) represents serious mathematical problem. We have two solutions of the Coulomb wave equation, the regular and the irregular one. If $c^2 = ER^2/2$ and $E > 0$ (continuous spectrum) then we have RCSF of c-type (RCSFc) and for $p^2 = -ER^2/2, \quad E < 0$ (discrete spectrum) we have RCSF of p-type (RCSFp). Recently, a great advance was achieved in the study and calculations of regular and irregular RCSFc's. This was stimulated, in principle, by quantum scattering problems of two-centres [1,8,12–15].

An exhausting analysis of many properties of RCSF and expansions of these functions in a series of special functions was done by Leaver [15]. From recently published papers we should mention especially papers [8, 16] which are devoted to the study of different algorithms for the computer calculations of regular and irregular RCSFs.

However, unsufficient study of RCSF does not allow for more effective aplication of two-centre Green's function to solve current problems of atom and molecular physics. Two-centre Green's function can be used not only in the framework of the perturbation theory of many photon processes for diatomic molecules [10, 11], but we employ this method for the asymptotically exact solution of many-centre Coulomb problems [17]. Our next paper will be devoted to the study of the three-centre Coulomb problem. This problem can be considered as the next step to the solution of defined quantum mechanical problems of four particles. We can apply the obtained results of the solution of similar problems in the atomic collision theory, particularly in the theory of one- and two-electron processes with redistribution in adiabatic slow collisions of multiply charged ions with diatomic molecules or with their positive ions. Our increased interest in atomic processes with redistribution is caused by their great role in the present research of controlled thermonuclear fusion.

This paper can be considered as an introductory part of series of works in which we will devote ourselves to the analysis of asymptotic methods in the three-centre Coulomb problem of discrete or continuous spectrum. Derived semiclassical representation of radial Coulomb Green's function for a pair of two equal charged centres is a subject of further research.

Section 1 presents the structure of the partial expansion of Green's function for the ZeZ problem. Then we further develop the methods described in [15, 18, 19] in Sections 2 and 3. We construct two types of expansion of regular and irregular RCSFp's in series of the ordinary Coulomb functions and in series of the confluent hypergeometric functions. We study the convergence of these expansions. We consider this as a formal basis for the numerical procedure of the solution of the three-term recurrence relation. We obtain asymptotic formulae for acceptable values of the shift parameter ν in power R as $R \to 0$ up to $O(R^3)$ order and in powers $1/R$ as $R \to \infty$ up to $O(1/R^3)$ order, respectively.

In Section 4, a detailed analysis of expansion of regular and irregular RCSFp is given in series of the confluent hypergeometric functions. In Section 5 we deal with two-centre Coulomb Green's function for continuous spectrum.

2 Partial expansion of Green's function in terms of spheroidal function

Green's function of electron in the field of two equivalent Coulomb centres is a solution of Schrödinger's equation

$$\left[-\frac{1}{2}\Delta_{\mathbf{r}} - \frac{Z}{r_1} - \frac{Z}{r_2} - E\right] G_E\left(\mathbf{r}, \mathbf{r}'; R\right) = \delta\left(\mathbf{r} - \mathbf{r}'\right), \tag{2}$$

where $\delta\left(\mathbf{r} - \mathbf{r}'\right)$ denotes the Dirac function and R is the distance between the two centres with the charges Z.

The specificity of force field for the two-centre system ZeZ can be expressed using the prolate spheroidal coordinate system (ξ, η, φ) which is defined in terms of the rectangular coordinate system by

$$\begin{aligned} x &= \tfrac{1}{2}R\sqrt{(1-\eta^2)(\xi^2-1)}\cos\varphi, \\ y &= \tfrac{1}{2}R\sqrt{(1-\eta^2)(\xi^2-1)}\sin\varphi, \\ z &= \tfrac{1}{2}R\eta\xi, \end{aligned}$$

or in terms of the spherical coordinate system by

$$\begin{aligned} \xi &= (r_1 + r_2)/R, \quad && 1 \le \xi < \infty, \\ \eta &= (r_1 - r_2)/R, \quad && -1 \le \eta \le 1, \\ \varphi &= \arctan\left(y/x\right), \quad && 0 \le \varphi < 2\pi. \end{aligned}$$

The wave equation (2) now becomes

$$\begin{aligned} &\{\frac{\partial}{\partial\xi}(\xi^2-1)\frac{\partial}{\partial\xi} + \frac{\partial}{\partial\eta}(1-\eta^2)\frac{\partial}{\partial\eta} + \frac{\xi^2-\eta^2}{(\xi^2-1)(1-\eta^2)}\frac{\partial^2}{\partial\varphi^2} + \frac{ER^2}{2}(\xi^2-\eta^2) + a\xi\}\times \\ &\times G_E\left(\xi, \eta, \varphi; \xi', \eta', \varphi'; R\right) = -\frac{4}{R}\delta(\xi-\xi')\delta(\eta-\eta')\delta(\varphi-\varphi'), \end{aligned} \tag{3}$$

where $a = 2ZR$. Since the angular quantum number ℓ is not a good quantum number in non-central field, we search a solution of Eq. (3) in the form of expansion over the complete system of orthonormal oblate angular spheroidal functions $\bar{S}_{m\ell}(p,\eta)$ [1,7-10]:

$$G_E\left(\xi,\eta,\varphi;\xi',\eta',\varphi'\,|R\right) = \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell} G_{m\ell}\left(\xi,\xi';E\right)\bar{S}_{m\ell}\left(p,\eta\right)\bar{S}^{*}_{m\ell}\left(p,\eta'\right)\frac{e^{im\left(\varphi-\varphi'\right)}}{2\pi}, \quad (4)$$

where $p = \frac{1}{2}R(-2E)^{1/2}$. Angular spheroidal functions $\bar{S}_{m\ell}(p,\eta)$ can be taken from [20]. However, it is preferable to choose the following representation for $\bar{S}_{m\ell}(p,\eta)$ [1]:

$$\bar{S}_{m\ell}(p,\eta) = N_{m\ell}(p)\sum_{r=0,1}^{\infty}{}' d_r^{m\ell}(p)P_{m+r}^{m}(\eta),$$

$$N_{m\ell}(p) = \left[\sum_{r=0,1}^{\infty}{}' \left(d_r^{m\ell}(p)\right)^2\frac{2(2m+r)!}{r!(2m+2r+1)}\right]^{-1/2}, \quad (5)$$

where $P_{m+r}^{m}(\eta)$ are the associated Legendre functions. The prime indicates that summation is taken only over the even values r if $q = \ell - |m|$ is even and over the odd values of r if $q = \ell - |m|$ is odd. The determination of the coefficients $d_r^{m\ell}(p)$ suffices for the determination of angular spheroidal functions. These coefficients are tabulated in [20].

Substitution of (4) into Eq. (3) followed by separation of angular parts yields the differential equation for radial Green's function $G_{m\ell}(\xi,\xi';E)$:

$$\left\{\frac{d}{d\xi}\left[(\xi^2-1)\frac{d}{d\xi}\right] + \left[-\lambda - p^2(\xi^2-1) + 2p\alpha\xi - \frac{m^2}{\xi^2-1}\right]\right\}\times$$
$$\times G_{m\ell}(\xi,\xi';E) = -\frac{4}{R}\delta(\xi-\xi'), \quad 1 \le \xi < \infty. \quad (6)$$

Here, $\alpha = 2Z(-2E)^{-1/2}$ is the effective principal quantum number. Equation (6) has solution for those values of the separation constant λ which are equal to eigenvalues $\lambda_{m\ell}(p)$ of the Sturm-Liouville problem

$$\left\{\frac{d}{d\eta}\left[(1-\eta^2)\frac{d}{d\eta}\right] + \left[\lambda_{m\ell} - p^2(1-\eta^2) - \frac{m^2}{1-\eta^2}\right]\right\}S_{m\ell}(p,\eta) = 0,$$
$$|S_{m\ell}(p,\pm 1)| < \infty, \quad -1 \le \eta \le 1. \quad (7)$$

Equation (7) determines oblate angular function $S_{m\ell}(p,\eta)$ of the p-type [1]. Now, one-dimensional Green's function $G_{m\ell}(\xi,\xi';E)$ can be constructed by standard methods. We assume that $\Pi^{(1)}_{m\ell}(p,\xi)$ and $\Pi^{(2)}_{m\ell}(p,\xi)$ are the independent solutions of

$$\left\{\frac{d}{d\xi}\left[(\xi^2-1)\frac{d}{d\xi}\right] + \left[-\lambda_{m\ell} - p^2(\xi^2-1) + 2p\alpha\xi - \frac{m^2}{\xi^2-1}\right]\right\}\Pi_{m\ell}(p,\xi) = 0. \quad (8)$$

The solution $\Pi^{(1)}_{m\ell}(p,\xi)$ is regular as $\xi \to 1$ and diverges as $\xi \to \infty$ and the solution $\Pi^{(2)}_{m\ell}(p,\xi)$ diverges as $\xi \to 1$ and is regular as $\xi \to \infty$. Then radial Green's function

$$G_{m\ell}(\xi,\xi';E) = -\frac{4Z}{\alpha p}\frac{\Pi^{(1)}_{m\ell}(p,\xi_<)\Pi^{(2)}_{m\ell}(p,\xi_>)}{(\xi^2-1)W\left[\Pi^{(1)}_{m\ell}(p,\xi),\Pi^{(2)}_{m\ell}(p,\xi)\right]}, \tag{9}$$

where $\xi_< = \min(\xi,\xi')$, $\xi_> = \max(\xi,\xi')$, and $W\left[\Pi^{(1)}_{m\ell}(p,\xi),\Pi^{(2)}_{m\ell}(p,\xi)\right]$ is the Wronskian of the solutions $\Pi^{(1)}_{m\ell}(p,\xi)$ and $\Pi^{(2)}_{m\ell}(p,\xi)$.

3 Expansion of regular and irregular radial Coulomb spheroidal functions of p-type (RCSFp) over the ordinary Coulomb radial wave functions

Let us look at the radial equation (8) in detail. We introduce the new variable

$$x = p(\xi+1), \quad 2p \le x < \infty \tag{10}$$

and the new function

$$\widetilde{\Pi}_{m\ell}(x) = \left(\frac{\xi+1}{\xi-1}\right)^{m/2}\Pi_{m\ell}(p,\xi). \tag{11}$$

Then equation (8) transforms to

$$\begin{aligned}&\left[\frac{d}{dx}\left(x^2\frac{d}{dx}\right) - x^2 + 2\alpha x - \nu\left(\nu+1\right)\right]\widetilde{\Pi}_{m\ell}\left(x\right) + \frac{p}{x-2p}\times\\ &\times\left[2(m+1)x\frac{d}{dx} + \left(\frac{\nu\left(\nu+1\right)-\lambda_{m\ell}}{p}+2\alpha\right)x - 2\nu\left(\nu+1\right)\right]\widetilde{\Pi}_{m\ell}\left(x\right) \equiv\\ &\equiv T_\nu\widetilde{\Pi}_{m\ell}\left(x\right) + pQ_\nu\widetilde{\Pi}_{m\ell}\left(x\right) = 0.\end{aligned} \tag{12}$$

The splitting of the total operator into two parts has the advantage that the differential operator $T_\nu(x)$ coincides with the radial Schrödinger operator in spherical coordinates for the Coulomb field of the united atom with charge $2Z$ and angular momentum ν. Two linearly independent solutions of the equation $T_\nu R(x) = 0$ are expressed by means of the regular $\widetilde{\Phi}(a,b;x)$ and the irregular $\Psi(a,b;x)$ confluent hypergeometric functions

$$R^{(1)}_\nu(x) \equiv R^{(1)}_{\alpha\nu}(x) = x^\nu e^{-x}\widetilde{\Phi}(-\alpha+\nu+1, 2\nu+2; 2x), \tag{13}$$

$$R^{(2)}_\nu(x) \equiv R^{(2)}_{\alpha\nu}(x) = x^\nu e^{-x}\Psi(-\alpha+\nu+1, 2\nu+2; 2x). \tag{14}$$

The functions $\widetilde{\Phi}(a,b;x)$ and $\Psi(a,b;x)$ are defined by the integral representations

$$\widetilde{\Phi}(a,b;x) = \frac{e^{i\pi a}}{\Gamma(a)}\int_0^1 e^{xt}t^{a-1}\left(1-t\right)^{b-a-1}dt, \quad \left(\mathrm{Re}b > \mathrm{Re}a > 0\right), \tag{15}$$

$$\Psi(a,b;x) = \frac{1}{\Gamma(a)} \int\limits_0^\infty e^{-xt} t^{a-1} \left(1+t\right)^{b-a-1} dt, \quad \left(\mathrm{Re}a > 0, \mathrm{Re}x > 0\right). \tag{16}$$

The regular confluent hypergeometric function $\widetilde{\Phi}(a,b;x)$ differs from the usual normalization [21] of the Kummer series by the factor $e^{i\pi a}\Gamma(b-a)/\Gamma(b)$:

$$\widetilde{\Phi}(a,b;x) = e^{i\pi a}\frac{\Gamma(b-a)}{\Gamma(b)}\Phi(a,b;x) = e^{i\pi a}\frac{\Gamma(b-a)}{\Gamma(b)}\sum_{n=0}^{\infty}\frac{(a)_n x^n}{(b)_n n!}, \tag{17}$$

where $(a)_n$ and $(b)_n$, denote the Pochhammer symbols. The Wronskian of $\widetilde{\Phi}(a,b;x)$ and $\Psi(a,b;x)$ is given by

$$W[\widetilde{\Phi}(a,b;x), \Psi(a,b;x)] = -e^{i\pi a}\frac{\Gamma(b-a)}{\Gamma(a)} x^{-b} e^{x}. \tag{18}$$

The function $\widetilde{\Phi}(a,b;x)$ has an attractive property. Normalized $\widetilde{\Phi}(a,b;x)$ obeys the same differential and recurrence relations as does $\Psi(a,b;x)$ (see (72)–(74)).

In analogy with two independent solutions (13) and (14) of the radial equation $T_\nu R(x) = 0$, we now introduce two independent solutions $\widetilde{\Pi}^{(1)}_{m\ell}(x)$ and $\widetilde{\Pi}^{(2)}_{m\ell}(x)$ of Eq. (2) which are determined by their asymptotic expressions for large value of x,

$$\widetilde{\Pi}^{(1)}_{m\ell}(x) \underset{x\to\infty}{\longrightarrow} (2x)^{-a-1} e^{x}, \quad \widetilde{\Pi}^{(2)}_{m\ell}(x) \underset{x\to\infty}{\longrightarrow} (2x)^{a-1} e^{-x}. \tag{19}$$

Evidently, Eq. (12) gives $T_\ell R(x) = 0$ as $p \to 0$. It is clear that $\widetilde{\Pi}^{(1)}_{m\ell}(x)$ and $\widetilde{\Pi}^{(2)}_{m\ell}(x)$ must reduce for $p = 0$ to regular and irregular functions $R^{(1)}_\ell$ and $R^{(2)}_\ell$, respectively. This suggests to expand the functions $\widetilde{\Pi}^{(1)}_{m\ell}(x)$ and $\widetilde{\Pi}^{(2)}_{m\ell}(x)$ in the form

$$\widetilde{\Pi}^{(1)}_{m\ell}(x) \equiv \widetilde{\Pi}^{(1)}_{m\ell}(\alpha, \lambda_{m\ell}, p; x) = \sum_{s=-\infty}^{\infty} h_s\left(p\,|\alpha, \lambda_{m\ell}, \nu\right) R^{(1)}_{s+\nu}(x), \tag{20}$$

$$\widetilde{\Pi}^{(2)}_{m\ell}(x) \equiv \widetilde{\Pi}^{(2)}_{m\ell}(\alpha, \lambda_{m\ell}, p; x) = \sum_{s=-\infty}^{\infty} h_s\left(p\,|\alpha, \lambda_{m\ell}, \nu\right) R^{(2)}_{s+\nu}(x). \tag{21}$$

The parameter ν is not integer and it must be chosen to satisfy the convergence of the series (20) and (21) for $2p < x < \infty$.

The recurrence relations for the basis functions $R^{(1)}_{s+\nu}(x)$ and $R^{(2)}_{s+\nu}(x)$ can be derived by successive elementary formulae relating the adjacent confluent hypergeometric functions or by the well developed technique of integral representations of the confluent hypergeometric functions. The second possibility is more constructive. From definitions (13) and (14) and the integral representations (15) and (16) it follows that $R^{(1)}_{s+\nu}(x)$ and $R^{(2)}_{s+\nu}(x)$ obey the same recurrence relation ($R_{s+\nu}(x) = R^{(1)}_{s+\nu}(x)$ or $R_{s+\nu}(x) = R^{(2)}_{s+\nu}(x)$)

$$A_s R_{\nu+s-1}(x) + \left(B_s - \frac{1}{x}\right) R_{s+\nu}(x) + C_s R_{s+\nu+1}(x) = 0 \tag{22}$$

and satisfy the same differential relation

$$\frac{dR_{\nu+s}(x)}{dx} = K_s R_{\nu+s-1}(x) + M_s R_{\nu+s+1}(x), \tag{23}$$

where the coefficients A_s, B_s, C_s, K_s and M_s do not depend on x and they are defined as

$$A_s = -\frac{s+\nu+\alpha}{2(s+\nu)(2s+2\nu+1)}, \quad B_s = \frac{\alpha}{(s+\nu)(s+\nu+1)},$$

$$C_s = \frac{2(s+\nu-\alpha+1)}{(s+\nu+1)(2s+2\nu+1)},$$

$$K_s = -\frac{s+\nu+\alpha}{2(2s+2\nu+1)}, \quad M_s = -\frac{2(s+\nu-\alpha+1)}{2s+2\nu+1}. \tag{24}$$

The substitution of Eq. (20) or (21) in Eq. (12) with subsequent use of the differential equation $T_{\nu+s}R_{\nu+s}(x) = 0$ and of the recurrence formulae (22) and (23) yields the recurrence relation for $h_s(\nu)$

$$\alpha_s h_{s+1}(\nu) + \beta_s h_s(\nu) + \gamma_s h_{s-1}(\nu) = 0, \tag{25}$$

where

$$\alpha_s = \frac{(s+\nu+1-m)(s+\nu+\alpha+1)}{2s+2\nu+3}p, \quad \beta_s = (s+\nu)(s+\nu+1) - \lambda_{m\ell},$$

$$\gamma_s = -\frac{4(s+\nu-\alpha)(s+\nu+m)}{2s+2\nu-1}p.$$

The recurrence formula (25) constitutes a system of linear homogeneous difference equations. The coefficients $h_s(\nu)$ given by Eq. (25) are determined up to arbitrary multiplier which can be fixed to be consistent with the asymptotic behavior of the functions $\widetilde{\Pi}^{(1)}_{m\ell}(x)$ and $\widetilde{\Pi}^{(2)}_{m\ell}(x)$ at infinity by conditions

$$\sum_{s=-\infty}^{\infty} h_s(\nu) \frac{\Gamma(s+\nu+\alpha+1)}{\Gamma(s+\nu-\alpha+1)} \frac{e^{i\pi(s+\nu-\alpha+1)}}{2^{s+\nu}} = 1 \tag{26}$$

for $\widetilde{\Pi}^{(1)}_{m\ell}(x)$ and

$$\sum_{s=-\infty}^{\infty} \frac{h_s(\nu)}{2^{s+\nu}} = 1 \tag{27}$$

for the function $\widetilde{\Pi}^{(2)}_{m\ell}(x)$. In order to evaluate the Wronskian of $\widetilde{\Pi}^{(1)}_{m\ell}(x)$ and $\widetilde{\Pi}^{(2)}_{m\ell}(x)$, we consider the asymptotic form of these functions and their derivatives as $\xi \to \infty$. Then

$$2p(\xi^2-1)W\left[\widetilde{\Pi}^{(1)}_{m\ell}(x), \widetilde{\Pi}^{(2)}_{m\ell}(x)\right] = -1. \tag{28}$$

Using formulae (9)–(11) and (20)–(28), it is possible to find radial Green's function

$$G_{m\ell}(\xi,\xi';E)=\frac{8Z}{\alpha}\left(\frac{(\xi-1)(\xi'-1)}{(\xi+1)(\xi'+1)}\right)^{m/2}\widetilde{\Pi}^{(1)}_{m\ell}\left(p(\xi_<+1)\right)\widetilde{\Pi}^{(2)}_{m\ell}\left(p(\xi_>+1)\right), \qquad (29)$$

where $\xi_<$ ($\xi_>$) is the smaller (larger) one of ξ and ξ', and

$$\widetilde{\Pi}^{(1)}_{m\ell}(p(\xi+1))=\exp[-p(\xi+1)]\times$$
$$\times\sum_{s=-\infty}^{\infty}h_s(\nu)[p(\xi+1)]^{\nu+s}\widetilde{\Phi}(-\alpha+\nu+s+1,2\nu+2s+2;2p(\xi+1)), \qquad (30)$$
$$\widetilde{\Pi}^{(2)}_{m\ell}(p(\xi+1))=\exp[-p(\xi+1)]\times$$
$$\times\sum_{s=-\infty}^{\infty}h_s(\nu)[p(\xi+1)]^{\nu+s}\Psi(-\alpha+\nu+s+1,2\nu+2s+2;2p(\xi+1)). \qquad (31)$$

General application of series (30) and (31) depends on the rapidity of convergence which is, in principle, determined by the behaviour of the coefficients $h_s(\nu)$ for $s\to\pm\infty$. The three-term recurrence relation (TRR) for the coefficients $h_s(\nu)$ (25) considered as a second order linear homogeneous difference equation posseses two independent solution sequences $\{h^-_s\}\equiv\{h^-_s:s=...,-2,-1,0,1,2,...\}$ and $\{h^+_s\}\equiv\{h^+_s:s=...,-2,-1,0,1,2,...\}$. These solutions have two different asymptotic behaviors for large $|s|$.

It follows that $\lim\limits_{s\to\pm\infty}(h^-_s/h^+_s)=0$ from the analysis of TRR (25). In this case (see, e.g., [19]) we say that $\{h^-_s\}$ represents minimal solution of (25) as $s\to\pm\infty$. Arbitrary non-minimal solution $\{h^+_s\}$ of TRR, linearly independent of $\{h^-_s\}$, is called a dominant solution as $s\to\pm\infty$. To obtain the convergency of the expansions (30) and (31), we must choose the minimal solution of TRR as $s\to\infty$ and as $s\to-\infty$. It follows from the following consideration that the dominant solution $\{h^+_s\}$ does not fulfill this requirements because h^+_s/h^+_{s-1} (h^+_s/h^+_{s+1}) becomes unbound as $s\to+\infty$ ($s\to-\infty$).

The TRR (25) contains a free parameter ν. This means that ν in expansion (30) and (31) is not arbitrary and must be chosen in analogy with determination of the eigenvalues of separation constant in the theory of the spheroidal and Coulomb spheroidal functions [1]. The procedure of finding necessary values ν can be simplified due to the close relation between three-term recurrence relations and the infinite continued fractions.

The recurrence relation (25) can be written in the form

$$\frac{h_s(\nu)}{h_{s-1}(\nu)}=-\frac{\gamma_s}{\beta_s+\alpha_s h_{s+1}(\nu)/h_s(\nu)},\quad (s\ge+1),$$
$$\frac{h_s(\nu)}{h_{s+1}(\nu)}=-\frac{\alpha_s}{\beta_s+\gamma_s h_{s-1}(\nu)/h_s(\nu)},\quad (s\ge-1). \qquad (32)$$

The successive application of (32) enables us to express these relations in the form of infinite continued fractions

$$\frac{h_s(\nu)}{h_{s-1}(\nu)}=\frac{-\gamma_s}{\beta_s-}\frac{\alpha_s\gamma_{s+1}}{\beta_{s+1}-}\frac{\alpha_{s+1}\gamma_{s+2}}{\beta_{s+2}-}... \qquad (33)$$

for positive $s = +1, +2, +3, ...$ and

$$\frac{h_s(\nu)}{h_{s+1}(\nu)} = \frac{-\alpha_s}{\beta_s -} \frac{\alpha_{s-1}\gamma_s}{\beta_{s-1} -} \frac{\alpha_{s-2}\gamma_{s-1}}{\beta_{s-2} -} ... \tag{34}$$

for negative $s = -1, -2, -3, ...$

But this process is effective only if

$$\lim_{s\to+\infty} \frac{h_{s+1}(\nu)}{h_s(\nu)} = 0, \quad \lim_{s\to-\infty} \frac{h_{s-1}(\nu)}{h_s(\nu)} = 0. \tag{35}$$

Clearly, in general case (for arbitrary ν) possible solutions of Eq. (25) form the dominant sequence $\{h_s^+(\nu)\}$ as $s \to \pm\infty$, and thus the ratios of subsequent coefficients in expansions (30) and (31) grow for large $|s|$ as

$$\lim_{s\to+\infty} \frac{h_{s+1}^+(\nu)}{h_s^+(\nu)} \sim -\frac{2s}{p}, \quad \lim_{s\to-\infty} \frac{h_{s-1}^+(\nu)}{h_s^+(\nu)} \sim -\frac{s}{2p}. \tag{36}$$

This means that the series (30), (31) and their corresponding continued fractions (33), (34) diverge for the coefficients h_s^+ which form dominant sequence $\{h_s^+\}$ as $s \to \pm\infty$. Necessary minimal solution of the difference equation (25) which fulfil the asymptotic conditions (35) exists only for a specific value $\nu_{m\ell} \equiv \nu_{m\ell}(p, \alpha, \lambda_{m\ell})$ of the parameter ν. Then we can infer that the series (30) and (31), which represent the solution of Eq. (12), converge. In such a way we deduce the equation for the acceptable value $\nu_{m\ell}$. Such $\nu_{m\ell}$ and relations (33) and (34) give the minimal solutions of Eq. (25) via the infinite continued fractions.

The recurrence equation (25) at $s = 0$ requires

$$\beta_0 = -\alpha_0 \frac{h_1}{h_0} - \gamma_0 \frac{h_{-1}}{h_0}. \tag{37}$$

Substituting the right-hand sides of (33) and (34) into (37) we obtain the characteristic equation as a sum of two infinite continued fractions for acceptable value of ν:

$$\beta_0 = \frac{\alpha_{-1}\gamma_0}{\beta_{-1} -} \frac{\alpha_{-2}\gamma_{-1}}{\beta_{-2} -} \frac{\alpha_{-3}\gamma_{-2}}{\beta_{-3} -} ... + \frac{\alpha_0\gamma_1}{\beta_1 -} \frac{\alpha_1\gamma_2}{\beta_2 -} \frac{\alpha_2\gamma_3}{\beta_3 -} ... \quad . \tag{38}$$

We have minimal solutions of Eq. (25) which converge as $s \to \pm\infty$ only for roots $\nu_{m\ell}$ of Eq. (38).

To verify the correctness of this proposition, we must study the behavior of h_s^-/h_{s-1}^- and h_s^-/h_{s+1}^- for large positive and negative s, respectively. Immediately from (32) we find that

$$\lim_{s\to+\infty} \frac{h_s^-}{h_{s-1}^-} = \frac{2p}{s} \left[1 - \frac{1}{s}\left(\nu + \alpha - m + \frac{1}{2}\right) + O\left(\frac{1}{s^2}\right)\right], \tag{39}$$

$$\lim_{s\to-\infty} \frac{h_s^-}{h_{s+1}^-} = -\frac{p}{2s} \left[1 - \frac{1}{s}\left(\nu - \alpha + m + \frac{1}{2}\right) + O\left(\frac{1}{s^2}\right)\right]. \tag{40}$$

On the other hand the sufficient conditions of the convergence of the infinite continued fraction (34), (35) and (38) require

$$\left|\frac{\alpha_{s-1}\gamma_s}{\beta_{s-1}\beta_s}\right| < \frac{1}{4}, \quad \left|\frac{\alpha_{-s}\gamma_{-s+1}}{\beta_{-s}\beta_{-s+1}}\right| < \frac{1}{4} \tag{41}$$

for sufficiently large positive s.

From the asymptotic expansion of (25) as $s \to \pm\infty$ we obtain

$$\lim_{s\to+\infty}\left|\frac{\alpha_{s-1}\gamma_s}{\beta_{s-1}\beta_s}\right| = \left(\frac{p}{s}\right)^2\left[1 - \frac{2\nu}{s} + O\left(\frac{1}{s^2}\right)\right], \tag{42}$$

$$\lim_{s\to+\infty}\left|\frac{\alpha_{-s}\gamma_{-s+1}}{\beta_{-s}\beta_{-s+1}}\right| = \left(\frac{p}{s}\right)^2\left[1 - \frac{2(\nu+1)}{s} + O\left(\frac{1}{s^2}\right)\right]. \tag{43}$$

Thus, for $p > 1$ and $|s| > 2p$, the conditions (41) are satisfied. It is important to keep in mind this estimate and to choose the minimal number of terms in continued fraction (38) that will be needed for the computation of $\nu_{m\ell}(p)$ with required accuracy.

The algorithms of numerical solution of Eq. (38) are chosen differently. Their detailed description is given in [8,15,19] and we will not discuss this problem here. We only note that for all used algorithms it is necessary to accept accurate starting estimate for the acceptable values. This starting estimate can be obtained by the asymptotic expansion of $\nu_{m\ell}(p)$ for large p ($p \gg 1$) or small p ($p \ll 1$).

In the case when $m = O(1)$, $\ell = O(1)$, $\alpha = O(1)$ and $p \to 0$, the asymptotic expression for $\nu_{m\ell}(p)$ in the united-atom approximation ($R \ll 1$) is obtained by the method proposed in [18]. The result is

$$\nu_{m\ell}(p) = \ell + [\nu]_2 p^2 + [\nu]_4 p^4 + ..., \tag{44}$$

where

$$[\nu]_2 = -\frac{2\alpha^2[\ell(\ell+1) - 3m^2]}{(2\ell+1)\ell(\ell+1)(2\ell-1)(2\ell+3)}, \quad [\nu]_4 = \alpha^2\left(\nu^{(0)}_{m\ell} + \alpha^2\nu^{(2)}_{m\ell}\right),$$

$$\nu^{(0)}_{m\ell} = \frac{12[\ell^2(\ell+1)^2 - m^2(18\ell^2+18\ell-5) + 25m^4]}{\ell(\ell+1)(2\ell+1)(2\ell+5)(2\ell-3)(2\ell-1)^2(2\ell+3)^2},$$

$$\nu^{(2)}_{m\ell} = \frac{6[2\ell(\ell+1) - 3m^2]A_{m\ell} - 2\ell^3(\ell+1)^3[40\ell(\ell+1)(6\ell^2+6\ell-11)+3]}{(2\ell-3)(2\ell+5)[\ell(\ell+1)(2\ell+1)(2\ell-1)(2\ell+3)]^3},$$

$$A_{m\ell} = \{7\ell(\ell+1)[40\ell(\ell+1)(2\ell^2+2\ell-3)+9]+45\}m^2.$$

It follows from the formula (44), that $\nu_{m\ell}(0) = [\nu]_0 = \ell$, i.e. acceptable value in the united-atom approximation is equal to orbital angular momentum.

The solutions $\nu_{m\ell}(p)$ to Eq. (38) are not ambiguous. They are actually periodic with the period 1. If $\nu_{m\ell}(p)$ is the solution (38) (for fixed m, ℓ, α, and p), then $\nu_{m\ell}(p) \pm n$ are solutions of Eq. (38) for arbitrary integer n. Roots of Eq. (38) that are integer or half-integer, and they are spurious. As $p \to 0$, these roots do not acquire the values of angular orbital momentum ℓ. The mechanism of the appearance of spurious roots is described in detail in papers [15, 18].

To select the acceptable value $\nu = \nu_{m\ell}(p)$ for fixed quantum numbers m, ℓ, α and for given p from the set of roots of Eq. (38), we start with the solution of Eq. (38) for $p \ll 1$. We take the asymptotic value given by (44) as an initial value of $\nu_{m\ell}(p)$. Then we increase p using arbitrary step size Δp and we find the solution of Eq. (38). By continuation of this method we can evaluate $\nu_{m\ell}(p)$ for given p.

In Table 1 we see the values of $\nu_{m\ell}$ obtained by the asymptotic formula (44), as compared to the numerical solutions of Eq. (38) found by the minimization of continued fractions. This method was proposed and performed in a calculation corresponding to continued fractions in the theory of the polyspheroidal periodic functions [22].

For smaller parameter $p = (-2E)^{1/2}R/2$ and larger orbital angular momentum we obtain better agreement between the asymptotic expansion (44) and the numerical solution of Eq. (38) (see Table 1). For example, values $\nu_{00}(\alpha, R)$ determined by (44) with an accuracy up to $O(R^6)$ agree with the corresponding values that are obtained with relative accuracy $\epsilon = 10^{-12}$ numerically for $R = 0.025$ with the accuracy of nine digits, for $R = 0.25$ with the accuracy of five digits. The agreement mentioned for the both values shows that it is not necessary to compute $\nu_{m\ell}(\alpha, R)$ numerically for small R. The first three terms of expansion (44) give the correct value of $\nu_{m\ell}(\alpha, R)$ with three per cent accuracy. Such high accuracy selection of the initial approximation of $\nu_{m\ell}(\alpha, R)$ provides the stability of iterative process [22] with the step size of $\Delta R \leq 0.1Z$ over $0 \leq R \leq 6$ and avoids spurious solutions of Eq. (38).

After the calculation of acceptable values of $\nu_{m\ell}(\alpha, R)$, the coefficients of expansion $h_s^-(\nu_{m\ell})$ for $s = \pm 1, \pm 2, ...$ are defined by formulae (33) and (34) in terms of the largest coefficient h_0 (for given m and ℓ). Then the value h_0 is calculated from the relation (26) in case of RCSFp $\tilde{\Pi}^{(1)}_{m\ell}(p, \xi)$ and from relation (27) for RCSFp $\tilde{\Pi}^{(2)}_{m\ell}(p, \xi)$.

Finally, the convergence of the series (20) and (21) is defined by the asymptotic behavior of ratios $h_s^- R_{\nu+s}(x)/h_{s-1}^- R_{\nu+s}(x)$ for large positive s, and of $h_s^- R_{\nu+s}(x)/h_{s+1}^- R_{\nu+s+1}(x)$ for large negative s. Here, $R_{\nu+s}(x) = R^{(1)}_{\nu+s}(x)$ or $R_{\nu+s}(x) = R^{(2)}_{\nu+s}(x)$. One of the important properties of basis functions $R_{\nu+s}(x)$ is that apart from the differential equation $T_{\nu+s}R_{\nu+s}(x) = 0$, these functions fulfill the linear recurrence difference equation of the second order (22). Then, owing to the terminology used in this paper, the sequence of the functions $R^{(1)}_{\nu+s}(x)$, $s = 0, 1, 2...$ generates minimal solution, but $R^{(2)}_{\nu+s}(x)$, $(s = 0, 1, 2...)$ is a dominant solution of Eq. (22) as $s \to +\infty$. For $s^2 \gg 2\alpha p$ we have from (22)

$$\lim_{s\to+\infty} \frac{R^{(1)}_{\nu+s}(x)}{R^{(1)}_{\nu+s-1}(x)} = -\frac{x}{4s}\left[1 + \frac{1}{s}\left(\alpha - \nu - \frac{1}{2}\right) + O\left(\frac{1}{s^2}\right)\right], \quad (s \gg x),$$

$$\lim_{s\to+\infty} \frac{R^{(2)}_{\nu+s}(x)}{R^{(2)}_{\nu+s-1}(x)} = \frac{s}{x}\left[1 + \frac{1}{s}\left(\alpha + \nu - \frac{1}{2}\right) + O\left(\frac{1}{s^2}\right)\right], \quad (s \gg x). \tag{45}$$

Tab. 1. Acceptable values $\nu_{m\ell}(\alpha, R)$ as $R \to 0$ for $Z_1 = Z_2 = Z = 1$ system

	$\alpha = \sqrt{2}; E = -1$		$\alpha = \sqrt{2}; E = -1$	
R	$\nu_{00}^{a)}$	$\nu_{00}^{b)}$	$\nu_{01}^{a)}$	$\nu_{01}^{b)}$
0.025	0.000416661	0.000416661	0.999917	0.999917
0.05	0.00166658	0.00166657	0.999667	0.999667
0.10	0.00666567	0.00666519	0.998665	0.998665
0.20	0.0266743	0.0266430	0.994641	0.994641
0.30	0.0602401	0.05988	0.987868	0.987872
0.40	0.108375	0.106287	0.978242	0.978261
0.50	0.174353	0.165741	0.965602	0.965677
0.60	0.269069	0.23808	0.949715	0.949948

a) Acceptable values obtained by the numerical solution of Eq. (38)
b) Acceptable values that are obtained by the asymptotic formula (44).

According to (22), we find

$$\lim_{s\to+\infty} \frac{R_{\nu+s+1}(x)}{R_{\nu+s-1}(x)} = \frac{1}{4} \quad (1 \ll s \ll x).$$

Combination of (39) and (45) yields

$$\lim_{s\to+\infty} \frac{h_s^- R_{\nu+s}^{(1)}(x)}{h_{s-1}^- R_{\nu+s-1}^{(1)}(x)} = -\frac{px}{2s^2}\left[1 - \frac{2\nu+1-m}{s} + O\left(\frac{1}{s^2}\right)\right],$$

$$\lim_{s\to+\infty} \frac{h_s^- R_{\nu+s}^{(2)}(x)}{h_{s-1}^- R_{\nu+s-1}^{(2)}(x)} = \frac{2p}{x}\left[1 + \frac{m-1}{s} + O\left(\frac{1}{s^2}\right)\right]. \tag{46}$$

The ratio test of the series (30) with positive s shows that this part is absolutely convergent for an arbitrary finite p and $x = p(\xi+1)$. For positive s, part of the expansion (31) converges for all $\xi > 1$, but diverges for $\xi = 1$.

Both sequences $\{R_{\nu+s}^{(1)}(x)\}$ and $\{R_{\nu+s}^{(2)}(x)\}$ form the couple of dominant solutions of the difference equation (22) as $s \to -\infty$. From (22) we obtain

$$\lim_{s\to-\infty} \frac{R_{\nu+s}(x)}{R_{\nu+s+1}(x)} = -\frac{4s}{x}\left[1 + \frac{1}{s}\left(\nu - \alpha + \frac{3}{2}\right) + O\left(\frac{1}{s^2}\right)\right], \quad (|s| \gg x). \tag{47}$$

The relations (40) and (47) yield under the condition $s^2 \gg 2\alpha p$

$$\lim_{s\to-\infty} \frac{h_s^- R_{\nu+s}(x)}{h_{s+1}^- R_{\nu+s+1}(x)} = \frac{2p}{x}\left[1 - \frac{m-1}{s} + O\left(\frac{1}{s^2}\right)\right], \tag{48}$$

which implies that the parts of the series (30) and (31) are convergent for all positive ξ, but are divergent at $\xi = 1$ for the negative s.

Therefore the values of functions $\Pi^{(1)}_{m\ell}(p,\xi)$ and $\Pi^{(2)}_{m\ell}(p,\xi)$ can be calculated with necessary accuracy by the summation of the series (30) and (31)

$$\Pi^{(1)}_{m\ell}(p,\xi) = \left(\frac{\xi-1}{\xi+1}\right)^{\frac{m}{2}} \sum_{s=-\infty}^{\infty} h^{-}_{s}(\nu_{m\ell}) R^{(1)}_{s+\nu_{m\ell}}(p(\xi+1)), \tag{49}$$

$$\Pi^{(2)}_{m\ell}(p,\xi) = \left(\frac{\xi-1}{\xi+1}\right)^{\frac{m}{2}} \sum_{s=-\infty}^{\infty} h^{-}_{s}(\nu_{m\ell}) R^{(2)}_{s+\nu_{m\ell}}(p(\xi+1)) \tag{50}$$

for $\xi \in (1,\infty)$. The calculations of the basis functions $R^{(1)}_{s+\nu_{m\ell}}$ and $R^{(2)}_{s+\nu_{m\ell}}$ can be done easily numerically, using an algorithm described in detail in [22, 23].

For large intercentre separations ($p \gg 1$) and for ξ close to 1, the series (49) and (50) converge slowly as follows from estimates (46) and (48) and from numerical calculations [23]. This is related to the character of the asymptotic behavior of the basis functions $R^{(1,2)}_{s+\nu_{m\ell}}(p(\xi+1))$ for large s and $\xi \to 1$. In Sec. 4 we will show other very useful expansions. In spite of not very large p (for example $p < 5$) and not very small value of ξ ($\xi > 1$) the series (49) and (50) are appropriate for numerical calculations.

4 The limit form of two-centre Green's function at small intercentre separation. Special cases of expansion for $\Pi^{(1,2)}_{m\ell}(p,\xi)$

It is interesting to analyze the relations (3) and (29)–(31) in the limit of $R \to 0$ ($p \to 0$), and to compare the results to the familiar ones of Coulomb Green's function [24]. It follows from (11) that for $R \to 0$ and finite r, the prolate spheroidal coordinates reduce to the spherical ones r, θ and φ

$$\xi \to 2r/R, \quad \eta \to \cos\theta. \tag{51}$$

Equation (7) reduces to the equation for the associated Legendre functions $P^m_\ell(\cos\theta)$. Then the angle function for the ZeZ problem coincides with the one-centre Coulomb function, i.e.

$$\lim_{p\to 0} \bar{S}_{m\ell}(p,\eta)\frac{e^{im\varphi}}{\sqrt{2\pi}} = N_{m\ell}P^m_\ell(\cos\theta)\frac{e^{im\varphi}}{\sqrt{2\pi}} \equiv Y_{m\ell}(\theta,\varphi), \quad N_{m\ell} = \sqrt{\frac{(2\ell+1)(\ell-m)!}{2(\ell+m)!}}, \tag{52}$$

$$\lim_{p\to 0} \lambda_{m\ell}(p) = \ell(\ell+1). \tag{53}$$

By inserting this limit value of $\lambda_{m\ell}$ into Eq. (6) and substituting $\xi = 2r/R$, we obtain the equation for radial Coulomb Green's function.

Now, we study the limit transitions for $R \to 0$ in (25) and for radial functions $\Pi^{(1)}_{m\ell}(p(\xi+1))$ and $\Pi^{(2)}_{m\ell}(p(\xi+1))$ in expansions (49), (50). We use the zero term in the expansion (44) for permissible values $\nu_{m\ell}(p)$ and the limit value (53). Then (25) gives

$$[(s+\ell)(s+\ell+1)-\ell(\ell+1)]h_s = 0, \quad s = 0, \pm 1, \pm 2, ... \tag{54}$$

for $R \to 0$. It follows from (54) for $R \to 0$ that in every series (26), (27) and (49), (50) only the terms with $s = 0$ are non-zero. Then the limit values of h_s as $R \to 0$ are given by the relations

$$\lim_{p\to 0} h_s(p) = \frac{2^\ell \Gamma(-\alpha+\ell+1)}{\Gamma(\alpha+\ell+1)} e^{-i\pi(-\alpha+\ell+1)} \delta_{s0} \tag{55}$$

for the expansion (49) of function $\Pi^{(1)}_{m\ell}(p(\xi+1))$ and

$$\lim_{p\to 0} h_s(p) = 2^\ell \delta_{s0} \tag{56}$$

for the expansion (50) of the function $\Pi^{(2)}_{m\ell}(p(\xi+1))$.

These formulae together with Eqs. (49) and (50) as $R \to 0$ show that the radial Coulomb spheroidal functions of p-type $\Pi^{(i)}_{m\ell}(p,\xi) = [(\xi-1)/(\xi+1)]^{m/2} \widetilde{\Pi}^{(i)}_{m\ell}(p(\xi+1))$ have the required behavior for $R \to 0$

$$\lim_{p\to 0} \Pi^{(1)}_{m\ell}(p,\xi) = \frac{\Gamma(-\alpha+\ell+1)}{\Gamma(2\ell+2)} \left(\frac{4Zr}{\alpha}\right)^\ell \times$$
$$\times \exp\left(-\frac{2Zr}{\alpha}\right) \Phi\left(-\alpha+\ell+1, 2\ell+2; \frac{4Zr}{\alpha}\right), \tag{57}$$

$$\lim_{p\to 0} \Pi^{(2)}_{m\ell}(p,\xi) = \left(\frac{4Zr}{\alpha}\right)^\ell \exp\left(-\frac{2Zr}{\alpha}\right) \Psi\left(-\alpha+\ell+1, 2\ell+2; \frac{4Zr}{\alpha}\right). \tag{58}$$

Now, according to Eqs. (52), (57) and (58), we can easily show that for the problem ZeZ (model of hydrogenlike molecular ion) two-centre Coulomb Green's function defined by formulae (3), and (29)–(31) gives radial Green's function for the one-centre Coulomb problem of charge $2Z$ in spherical coordinates as $R \to 0$

$$\lim_{R\to 0} G_E(\mathbf{r};\mathbf{r}'|R) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} g_\ell(r,r';E) Y_{m\ell}(\theta,\varphi) Y^*_{m\ell}(\theta',\varphi') \equiv G^{(k)}_E(\mathbf{r},\mathbf{r}'), \tag{59}$$

where

$$g_\ell(r,r';E) = \frac{8Z}{\alpha} \frac{\Gamma(-\alpha+\ell+1)}{\Gamma(2\ell+2)} \left(\frac{4Zr_<}{\alpha}\right)^\ell \left(\frac{4Zr_>}{\alpha}\right)^\ell exp\left(-\frac{2Z}{\alpha}(r_< + r_>)\right) \times$$
$$\times \Phi\left(-\alpha+\ell+1, 2\ell+2; \frac{4Zr_<}{\alpha}\right) \Psi\left(-\alpha+\ell+1, 2\ell+2; \frac{4Zr_>}{\alpha}\right). \tag{60}$$

So, we have proved that radial Green's functions (3), (29)–(31) comply with the principle of correspondence so that all functions for the two-centre Coulomb problem defined in the spheroidal coordinates must give one-centre Coulomb analogies for $R \to 0$.

Now, we consider some different special cases of the solution of the Eq. (8) that follow from Eqs. (49) and (50) for specific values of α and ν. If $\alpha = 0$ ($Z = 0$) and $\nu = \ell$, then the coefficients $h_s(0, \lambda_{m\ell}, \ell|p) = 0$ for $s \leq m - \ell - 1$ and the sumation in series (49), (50) begins with $m - \ell$. In this case the confluent hypergeometric functions $\Phi(s + \ell + 1, 2s + 2\ell + 2; 2x)$ and $\Psi(s + \ell + 1, 2s + 2\ell + 2; 2x)$ are expressed by known formulae [21] using the modified Bessel functions of the first order $I_{s+\ell+\frac{1}{2}}(x)$ and of the third order $K_{s+\ell+\frac{1}{2}}(x)$ (Macdonald function) respectively. Then after easy transformations we obtain expansion of the radial spheroidal function in cylindrical functions [1, 20]

$$\Pi^{(1)}_{m\ell}(0, \lambda_{m\ell}, p; \xi) = \sqrt{\frac{\pi}{2p(\xi+1)}} \left(\frac{\xi - 1}{\xi + 1}\right)^{\frac{m}{2}} \sum_{s=0}^{\infty} h_s \frac{(-1)^{s+m+1}}{2^{s+m}} I_{s+m+1/2}\left(p(\xi + 1)\right), \quad (61)$$

$$\Pi^{(2)}_{m\ell}(0, \lambda_{m\ell}, p; \xi) = \sqrt{\frac{1}{2\pi p(\xi+1)}} \left(\frac{\xi - 1}{\xi + 1}\right)^{\frac{m}{2}} \sum_{s=0}^{\infty} \frac{h_s}{2^{s+m}} K_{s+m+1/2}\left(p(\xi + 1)\right). \quad (62)$$

The coefficients h_s in these expansions comply with Eq.(25), where α_s, β_s and γ_s have the following form

$$\alpha_s = \frac{(s+1)(s+m+1)}{2s+2m+3} p,$$
$$\beta_s = (s+m)(s+m+1) - \lambda_{m\ell}, \quad \gamma_s = -\frac{4(s+m)(s+2m)p}{2s+2m-1}. \quad (63)$$

For practical purpose, this a is very useful analytical continuation of the functions $\Pi^{(1)}_{m\ell}(0, \lambda_{m\ell}, p; \xi)$ (61) and $\Pi^{(2)}_{m\ell}(0, \lambda_{m\ell}, p; \xi)$ (62) on the axis $[0, +i\infty)$. This continuation with respect to the normalization is identical with the oblate radial spheroidal functions of the first and second order (see [1]).

Let us go on to the determination of conditions under which the functions $\Pi^{(1)}_{m\ell}(p, \xi)$ and $\Pi^{(2)}_{m\ell}(p, \xi)$ defined by (26), (27), (49) and (50) are transformed to physical solutions that represent the radial part $\bar{\Pi}_{mk}(p, \xi)$ of radial wave functions of the two-centre problem ZeZ. Here, k is number of zeros of the function $\bar{\Pi}_{mk}(p, \xi)$ located in interval $\xi \in (1, \infty)$. Assume Green's function $G_E(\mathbf{r}; \mathbf{r}'|R)$ as a function of energy E has poles at points $E = E_j(R)$ that correspond to the discrete energy spectrum of the problem ZeZ: $E_j(R) = E_{N\ell m}(R)$, $\quad j = (N\ell m)$, $\quad N = k + \ell + 1$, $\quad N = 1, 2, 3, \ldots$. According to radial Green's function which is expressed by (9) these poles are zeros of the Wronskian $W\left[\Pi^{(1)}_{m\ell}(p, \xi), \Pi^{(2)}_{m\ell}(p, \xi)\right]$ and $E_{N\ell m}(R)$ satisfies the condition

$$-\alpha_{N\ell m} + \nu_{m\ell}(E_{N\ell m}) + 1 = -k, \quad k = 0, 1, 2, ..., \quad (64)$$

where $\alpha_{N\ell m} = 2Z/\sqrt{-2E_{N\ell m}(R)}$. Residues of $G_{m\ell}(\xi, \xi'; E)$ at poles $E_{N\ell m}(R)$ represent the product of normalized radial parts of eigenfunctions for the ZeZ problem [24]:

$$\bar{\Pi}_{mk}(p, \xi)\bar{\Pi}_{mk}(p, \xi') = \lim_{E \to E_{N\ell m}} [(E_{N\ell m} - E) G_{m\ell}(\xi, \xi'; E)]. \quad (65)$$

We may easily determine this limit for $G_{m\ell}(\xi, \xi'; E)$ expressed by Eqs. (29)–(31) when we take into account the normalization conditions (26) and (27). The calculations show that for the energy $E_{N\ell m}(R)$, which is the eigenvalue of the problem ZeZ, the functions $\Pi^{(1)}_{m\ell}(p,\xi)$ and $\Pi^{(2)}_{m\ell}(p,\xi)$ are linearly dependent and that they are identical to the radial part $\bar{\Pi}_{m\ell}(p,\xi)$ of the two-centre problem [1].

5 Expansions of an regular and irregular radial Coulomb spheroidal functions of p-type in series of confluent hypergeometric functions

We transform the differential equation (8) for the radial Coulomb spheroidal function of p-type by taking out the appropriate behavior of eigenfunctions at the singular points of the differential equation, namely $\xi = -1$, $\xi = 1$, and $\xi = \infty$. We find that near $\xi = -1$ it is $(\xi + 1)^{m/2}$, near the $\xi = 1$ it is $(\xi - 1)^{m/2}$, and at the infinity point it is either $\exp(-p(1+\xi))$ or $\exp(p(1+\xi))$. We therefore introduce new function $V(z) \equiv V_{m\ell}(z)$ by

$$\Pi_{m\ell}(p,\xi) = \left(\xi^2 - 1\right)^{m/2} e^{-p(\xi+1)} V_{m\ell}(z), \quad z = 2x = 2p(\xi + 1). \tag{66}$$

We readily find that $V(z)$ satisfies the differential equation

$$z(z - z_0)V''(z) + \left(D_1 + zD_2 - z^2\right) V'(z) + (D_3 + zD_4)V(z) = 0, \tag{67}$$

where

$$V'(z) \equiv \frac{dV(z)}{dz}, \quad z_0 = 4p, \quad D_1 = -z_0(m+1), \quad D_2 = 2(m+1) + z_0,$$
$$D_3 = m(m+1) - \lambda_{m\ell} - 2p\sigma, \quad D_4 = \sigma = \alpha - (m+1). \tag{68}$$

We will find the regular solution $V^{(1)}(z)$ and irregular solution $V^{(2)}(z)$ to Eq. (67) in the form of series of confluent hypergeometric functions Φ and Ψ, specified by

$$V^{(1)}(z) \equiv V^{(1)}_{m\ell}(\alpha, \lambda_{m\ell}, p; x) = \sum_{s=-\infty}^{\infty} g_s(\alpha, \lambda_{m\ell}, \nu|p)\widetilde{\Phi}(-\alpha + m + 1, s + \nu; 2x), \tag{69}$$

$$V^{(2)}(z) \equiv V^{(2)}_{m\ell}(\alpha, \lambda_{m\ell}, p; x) = \sum_{s=-\infty}^{\infty} g_s(\alpha, \lambda_{m\ell}, \nu|p)\Psi(-\alpha + m + 1, s + \nu; 2x), \tag{70}$$

where ν is not an integer. We use the same notation as in part 2, i.e. $\widetilde{\Phi}$ and Ψ denote the regular and the irregular confluent hypergeometric functions, respectively. We introduce short notation

$$\widetilde{\Phi}_s(z) \equiv \widetilde{\Phi}(-\alpha + m + 1, s + \nu; 2x), \quad \Psi_s(z) \equiv \Psi(-\alpha + m + 1, s + \nu; 2x).$$

Let $\Re_s(z)$ denote an arbitrary function of $\widetilde{\Phi}_s(z)$ or $\Psi_s(z)$. The functions $\widetilde{\Phi}_s(z)$ and $\Psi_s(z)$ represent linearly independent solutions of confluent hypergeometric equation

$$z\frac{d^2\Re_s(z)}{dz^2} + (s + \nu - z)\frac{d\Re_s(z)}{dz} + \sigma\Re_s(z) = 0 \tag{71}$$

and therefore $\Re_s(z)$ satisfies three-term recurrence differential relations

$$z\Re_{s+1}(z) - (s+\nu-1+z)\Re_s(z) + (s+\nu-1+\sigma)\Re_{s-1}(z) = 0 \tag{72}$$

and obeys the following differential relations

$$\frac{d\Re_s(z)}{dz} = \Re_s(z) - \Re_{s+1}(z), \tag{73}$$

$$z\frac{d\Re_s(z)}{dz} = (1-s-\nu)\Re_s(z) + (s+\nu-1+\sigma)\Re_{s-1}(z). \tag{74}$$

The Wronskian of $\widetilde{\Phi}_s(z)$ and $\Psi_s(z)$ is given by (18).

Substituting (69) or (70) into (67) and using Eq. (71) and formulas (72)–(74), we obtain the three-term recurrence system

$$\rho_s g_{s+1}(\nu) + \kappa_s g_s(\nu) + \delta_s g_{s-1}(\nu) = 0 \tag{75}$$

with recurrence coefficients

$$\rho_s = -(s+\nu+\sigma)[s+\nu+1-2(m+1)], \quad \delta_s = 4p(m-s-\nu+2),$$

$$\kappa_s = (s+\nu)[s+\nu+4p-1-2(m+1)] + 2p[\sigma-2(m+1)] + (m+1)(m+2) - \lambda_{m\ell}. \tag{76}$$

The structure of the recurrence relation (75) shows that in a general case (for arbitrary ν) the solutions of Eq. (67) given by (69) and (70) are divergent for all finite values of argument. As in part 3, the coefficients expansion g_s and acceptable values $\nu_{m\ell}(p)$ at which the series (69) and (70) converge can be obtained by solving equation (75) using the method of continued fractions. To separate a minimal convergent solution to the equation (75) for $s \to \pm\infty$, it is necessary to set asymptotic conditions:

$$\lim_{s\to+\infty} \frac{g_{s+1}(\nu)}{g_s(\nu)} = 0, \quad \lim_{s\to-\infty} \frac{g_{s-1}(\nu)}{g_s(\nu)} = 0. \tag{77}$$

As well as in the section 3, we obtain for acceptable values $\nu_{m\ell}(p)$ transcendental equation as a sum of two infinite continued fractions

$$\kappa_0 = \frac{\rho_{-1}\delta_0}{\kappa_{-1}-}\,\frac{\rho_{-2}\delta_{-1}}{\kappa_{-2}-}\,\frac{\rho_{-3}\delta_{-2}}{\kappa_{-3}-}\ldots + \frac{\rho_0\delta_1}{\kappa_1-}\,\frac{\rho_1\delta_2}{\kappa_2-}\,\frac{\rho_2\delta_3}{\kappa_3-}\ldots \quad . \tag{78}$$

Required values $\nu_{m\ell}(p)$ satisfying equation (78), can be calculated (as in the section 3) by minimizing continued fractions of (78) using numerical calculations [22]. We take the required zeroth approximation for $\nu_{m\ell}(p)$ at $p \gg 1$ in the form of asymptotic expansion as $p \to \infty$

$$\bar{\nu}_{m\ell}(p) = \frac{(3+3m+2\mu-\sigma)}{2} + \frac{1}{4p}\left(-1-m-2\mu(1+m+\mu) + \frac{(-1+m+2\mu-\sigma)}{8}\times\right.$$

$$\left.\times\left[-1+3m^2-4\mu(\mu+1)+\sigma(4+\sigma)+2m(1-2\mu+2\sigma)\right]\right) + O\left(p^{-2}\right), \tag{79}$$

where σ is determined by Eq. (68) and $\mu = (\ell - m)/2$ for even $(\ell - m)$ and $\mu = (\ell - m - 1)/2$ for odd $(\ell - m)$. To distinguish requested values that correspond to the expansion (69) and (70) from the values for the expansions (49) and (50), we use bar over $\nu_{m\ell}$.

The asymptotic expansion (79) was obtained in [23] by the method which was published in [1]. Therefore we do not show the details of derivation here. The calculations performed in [23] showed that values $\bar{\nu}_{m\ell}$ obtained by Eq. (79) agree with values that obtained for relative error $\varepsilon = 10^{-12}$ by computer for the case $m, \ell \leq 5, \quad R \sim 5 \div 10$ with an accuracy of up to 2%, and for $m, \ell \leq 5, \quad R \sim 12 \div 20$ with an accuracy of up to 1%. The agreement of these values does not depend only on R, but also on Z, E, and p.

It follows from the structure analysis of Eqs. (76) and (78) that the equation $\kappa_0 = 0$ is a limited form of the transcendent equation (78) as $p \to 0$. Further, in the united atom approximation ($R \to 0$), the permissible value $\bar{\nu}_{m\ell}(p)$ must attain the value equal to the maximal root of the equation $\kappa_0 \left(\bar{\nu}_{m\ell}(0)\right) = 0$. So, the zeroth term of the asymptotic expansion of $\bar{\nu}_{m\ell}(p)$ is $\bar{\nu}_{m\ell}(0) = m + \ell + 2$. This value $\bar{\nu}_{m\ell}$ is convenient for finding permissible value for small p and for control calculations.

The convergence of the continued fractions (78) (at least for $|s| > 4p$)has been proved in Eq. (23). Therefore we will prove convergence of the expansions (69) and (70). Again, we denote the coefficients that correspondent to the minimal convergent solution of the difference equation (75) for $s \to \pm\infty$ by g_s^-, $s = ..., -2, -1, 0, +1, +2, ...\}$.

At first, we establish the limit values of ratios g_s^-/g_{s-1}^- as $s \to +\infty$ and g_s^-/g_{s+1}^- as $s \to -\infty$. The relation (75) yields

$$\lim_{s\to+\infty} \frac{g_s^-}{g_{s-1}^-} = \frac{4p}{s}\left[1 + \frac{m+1-\nu}{s} + O\left(s^{-2}\right)\right], \tag{80}$$

$$\lim_{s\to-\infty} \frac{g_s^-}{g_{s+1}^-} = 1 + \frac{1+\alpha-m}{s} + O\left(s^{-2}\right). \tag{81}$$

Using the terminology of the previous part, $\widetilde{\Phi}_s(z)$ is the minimal solution and $\Psi_s(z)$ is the dominant solution to (72) for $s \to \infty$. It follows immediately from (72)

$$\lim_{s\to+\infty} \frac{\widetilde{\Phi}_s(z)}{\widetilde{\Phi}_{s-1}(z)} = 1 + \frac{\alpha-m-1}{s} + O\left(s^{-2}\right), \tag{82}$$

$$\lim_{s\to+\infty} \frac{\Psi_s(z)}{\Psi_{s-1}(z)} = \frac{s}{2x}\left[1 + \frac{2x}{s}(\nu-2) + O\left(s^{-2}\right)\right], \tag{83}$$

for large positive s.

Now, we suppose that both solutions of Eq. (72) $\widetilde{\Phi}_s(z)$ and $\Psi_s(z)$ are dominant for $s \to -\infty$. We obtain using (72)

$$\lim_{s\to-\infty} \frac{\Re_s(z)}{\Re_{s+1}(z)} = 1 + \frac{m+1-\alpha}{s} + O\left(s^{-2}\right). \tag{84}$$

This result together with the asymptotic relation (81) gives

$$\lim_{s\to-\infty} \frac{g_s^-\Re_s(z)}{g_{s+1}^-\Re_{s+1}(z)} = 1 + \frac{2}{s} + O\left(s^{-2}\right). \tag{85}$$

Therefore, the ratio test implies that the negative parts of the series (69) and (70) converge for any $z = 2x = 2p(\xi+1)$. Further it follows from Eqs. (80) and (82) imply that

$$\lim_{s\to+\infty} \frac{g_s^- \widetilde{\Phi}_s(z)}{g_{s-1}^- \widetilde{\Phi}_{s-1}(z)} = \frac{4p}{s}\left(1+\frac{\alpha-\nu}{s}+O\left(s^{-2}\right)\right), \tag{86}$$

so that the series (69) is uniformly convergent (for arbitrary p, α and ν) with regard to (85), and not only for $\xi \in [1,\infty)$, but for whole numeric axis.

Finally, combination of (80) and (83) gives

$$\lim_{s\to+\infty} \frac{g_s^- \Psi_s(z)}{g_{s-1}^- \Psi_{s-1}(z)} = \frac{2p}{x}\left(1+\frac{m+1-\nu+2x(\nu-2)}{s}+O\left(s^{-2}\right)\right). \tag{87}$$

If $|x| > 2p$ ($|\xi+1| > 2$), then the series (70) converges as it follows from asymptotic (85).

Evidently, the rapidity of the convergence of both series (49) and (50) for large ξ exceeds substantially the rapidity of the convergence of the series (69) and (70). In spite of this, it is convenient to use partial sums of the series (69) and (70) to calculate radial Coulomb spheroidal functions $\Pi_{m\ell}^{(1,2)}(p,\xi)$ of p-type with given accuracy

$$\Pi_{m\ell}^{(1)}(p,\xi) = (\xi^2-1)^{m/2} e^{-p(\xi+1)} \sum_{s=-\infty}^{\infty} g_s^-(\bar\nu_{m\ell}) \widetilde{\Phi}(-\alpha+m+1, s+\bar\nu_{m\ell}; 2p(\xi+1)), \tag{88}$$

$$\Pi_{m\ell}^{(2)}(p,\xi) = (\xi^2-1)^{m/2} e^{-p(\xi+1)} \sum_{s=-\infty}^{\infty} g_s^-(\bar\nu_{m\ell}) \Psi(-\alpha+m+1, s+\bar\nu_{m\ell}; 2p(\xi+1)). \tag{89}$$

Numerical experiments show that to obtain, for example, $\Pi_{m\ell}^{(1)}(p,\xi)$ at $\xi = 1$, $p \le 5$ with relative accuracy 10^{-18} we need large number of terms ($|s| > 100$) in the expansion (88) [23].

Therefore, it is more convenient to use the combination of the series (49) and (50) and (88) and (89) for practical numerical calculations. The values of the regular radial Coulomb functions and of irregular radial Coulomb functions of p-type are calculated in inverse order (from ∞ to 1) by using the expansions (49) and (50), and by initial values that are given at a distant point where asymptotic expression (19) holds.

Since the expansions (88) and (89) converge slowly, we use $\Pi_{m\ell}^{(1)}(p,\xi)$ and $\Pi_{m\ell}^{(2)}(p,\xi)$ in ordinary direction (from 1 to ∞) only in the neighborhood of the point $\xi = 1$ for evaluation. Starting at $\xi = 1$, we continue to the point ξ_0 ($\xi_0 > 1$) where we can determine the values of regular and irregular functions, using expressions (49) and (50) with necessary accuracy. Of course, the regular and the irregular solutions of (49) and (50) and 88) and (89) have to match at $\xi = \xi_0$ because the "normalization" of the coefficient is not determined by expressions (26) and (27).

This method of obtaining solutions $\Pi_{m\ell}^{(1)}(p,\xi)$ and $\Pi_{m\ell}^{(2)}(p,\xi)$ is analogous to the algorithm which is explained in [15] and used in [8] for the calculation of regular and irregular radial Coulomb spheroidal functions of the c-type in the theory of scattering by two Coulomb centres [1, 12, 25].

6 Two-centre Green's function of continuous spectrum

For positive energy ($E > 0$) an expansion of Green's function $G_{E>0}(\mathbf{r};\mathbf{r}'|R)$ is constructed by the normalized prolate angular spheroidal functions $\bar{S}_{m\ell}(c,\eta)$ [1]. But the radial part of Green's function $G_{m\ell}(\xi,\xi';E>0)$ satisfies an equation which differs from Eq. (6) by replacing $p \to -ic$ and $\alpha \to -i\alpha^*$. Then we can express the radial part of Green's function by the regular $\Pi^{reg}_{m\ell}(c,\xi)$ and the irregular $\Pi^{irreg}_{m\ell}(c,\xi)$ solutions of homogeneous equation, i.e.

$$G_{m\ell}(\xi,\xi';E>0) = \frac{4Z}{c\alpha^*}\frac{\Pi^{reg}_{m\ell}(c,\xi_<)\left[\Pi^{reg}_{m\ell}(c,\xi_>) + i\Pi^{irreg}_{m\ell}(c,\xi_>)\right]}{(\xi^2-1)W\{\Pi^{reg}_{m\ell}(c,\xi),\left[\Pi^{reg}_{m\ell}(c,\xi) + i\Pi^{irreg}_{m\ell}(c,\xi)\right]\}}, \qquad (90)$$

where $\alpha^* = -ZR/c, c = kR/2$ and $E = k^2/2$.

For practical calculations we use representations $\Pi^{reg}_{m\ell}(c,\xi)$ and $\Pi^{irreg}_{m\ell}(c,\xi)$ as linear combinations of the Coulomb functions $F_{\nu+s}(\alpha^*,x)$ and $G_{\nu+s}(\alpha^*,x)$ [15]:

$$\Pi^{reg}_{m\ell}(c,\xi) = \frac{1}{2}\left(\frac{\xi-1}{\xi+1}\right)^{\frac{m}{2}}\left[\Pi^{(+)}_{m\ell}(x) + \Pi^{(-)}_{m\ell}(x)\right], \qquad (91)$$

$$\Pi^{irreg}_{m\ell}(c,\xi) = \frac{1}{2i}\left(\frac{\xi-1}{\xi+1}\right)^{\frac{m}{2}}\left[\Pi^{(+}_{m\ell})(x) - \Pi^{(-)}_{m\ell}(x)\right], \qquad (92)$$

$$\Pi^{(\pm)}_{m\ell}(x) = \sum_{s=-\infty}^{\infty}\bar{h}_s(\alpha^*,\lambda_{m\ell}(c),\nu|c)R^{(\pm)}_{\nu+s}(x), \qquad (93)$$

$$R^{(\pm)}_{\nu+s}(x) = x^{-1}[G_{\nu+s}(\alpha^*,x) \pm iF_{\nu+s}(\alpha^*,x)], \quad x = c(\xi+1), \qquad (94)$$

where $x = c(\xi+1)$. Here, the plus (minus) sign corresponds to $R^{(+)}_{\nu+s}(x)$ ($R^{(-)}_{\nu+s}(x)$); $\lambda_{m\ell}(c)$ are eigenvalues of the angular equation of prolate spheroidal functions $S_{m\ell}(c,\eta)$ [1].

The Coulomb functions $F_{\nu+s}(\alpha^*,x)$ and $G_{\nu+s}(\alpha^*,x)$ are the same ones as in [15,26]. Integral representation of these functions

$$G_{\nu+s}(\alpha^*,x) \pm iF_{\nu+s}(\alpha^*,x) = \frac{e^{\pi\alpha^*/2}e^{\pm ix}(2x)^{-\nu-s}}{[\Gamma(\nu+s+1+i\alpha^*)\Gamma(\nu+s+1-i\alpha^*)]^{1/2}}\times$$

$$\times\int_0^\infty e^{-t}t^{\nu+s\pm i\alpha^*}(t\mp 2ix)^{\nu+s\mp i\alpha^*}dt, \qquad (95)$$

is similar to (15) and (16).

Another important formula is given using the complex confluent hypergeometric function of the second kind $\Psi(\alpha,\gamma;z)$:

$$2^{-1}R^{(\pm)}_{\nu+s}(x) = (2x)^{-1}[G_{\nu+s}(\alpha^*,x) \pm iF_{\nu+s}(\alpha^*,x)] = (-1)^s e^{\mp i\pi(\nu+1/2)}\times$$

$$\times e^{\pi\alpha^*/2}\left[\frac{\Gamma(\nu+s+1\pm i\alpha^*)}{\Gamma(\nu+s+1\mp i\alpha^*)}\right]^{1/2}(2x)^{\nu+s}e^{\pm ix}\Psi(\nu+s+1\pm i\alpha^*,2\nu+2s+2;\mp 2ix). \qquad (96)$$

The Wronskian is

$$W\left[F_{\nu+s}(\alpha^*,x),G_{\nu+s}(\alpha^*,x)\right]=-1, \tag{97}$$

and the asymptotic formula of $G_{\nu+s}(\alpha^*,x)\pm iF_{\nu+s}(\alpha^*,x)$ (as $x\to\infty$) is defined as

$$G_{\nu+s}(\alpha^*,x)\pm iF_{\nu+s}(\alpha^*,x)\underset{x\to\infty}{\longrightarrow} exp\left[\pm i\left(x-\alpha^*\ln 2x-(s+\nu)\frac{\pi}{2}+\sigma_{\nu+s}\right)\right], \tag{98}$$

with the Coulomb phase

$$\sigma_{\nu+s}=-\frac{i}{2}\ln\left[\frac{\Gamma(s+\nu+1+i\alpha^*)}{\Gamma(s+\nu+1-i\alpha^*)}\right]. \tag{99}$$

Taking into account Eq. (12) for the radial Coulomb spheroidal functions of p-type and replacing $p\to -ic$, $\alpha\to -i\alpha^*$, we obtain

$$\begin{aligned}&\left[\frac{d}{dx}\left(x^2\frac{d}{dx}\right)-x^2+2\alpha^*x-\nu(\nu+1)\right]\Pi^{(\pm)}_{m\ell}(x)+\frac{c}{x-2c}\times\\&\times\left[2(m+1)x\frac{d}{dx}+\left(\frac{\nu(\nu+1)-\lambda_{m\ell}(c)}{c}-2\alpha^*\right)x-2\nu(\nu+1)\right]\Pi^{(\pm)}_{m\ell}(x)=0,\end{aligned} \tag{100}$$

where $x=c(\xi+1)$, $2c\le x<\infty$. As in the case for the radial Coulomb spheroidal function of the p-type $\widetilde{\Pi}^{(1,2)}_{m\ell}(x)$ by the substitution of the expansion (93) into Eq. (100) and the recurrence formula for the Coulomb functions $F_{\nu+s}(\alpha^*,x)$ and $G_{\nu+s}(\alpha^*,x)$, we obtain the recurrence relations for $\bar h_s(\nu)\equiv\bar h_s(\alpha^*,\lambda_{m\ell}(c),\nu|c)$

$$\bar\alpha_s\bar h_{s+1}(\nu)+\bar\beta_s\bar h_s(\nu)+\bar\gamma_s\bar h_{s-1}(\nu)=0, \tag{101}$$

with

$$\begin{aligned}&\bar\alpha_s=-\frac{2c(s+\nu+1)(s+\nu+1-m)}{2s+2\nu+3}S_{s+1},\quad \bar\gamma_s=-\frac{2c(s+\nu)(s+\nu+m)}{2s+2\nu-1}S_s,\\&\bar\beta_s=(s+\nu)(s+\nu+1)(1+2cQ_s)-2c\alpha^*-\lambda_{m\ell}(c),\\&S_s=\frac{\left((s+\nu)^2+(\alpha^*)^2\right)^{1/2}}{(s+\nu)},\quad Q_s=\frac{\alpha^*}{(s+\nu)(s+\nu+1)}.\end{aligned} \tag{102}$$

After replacing $\alpha_s\to\bar\alpha_s$, $\beta_s\to\bar\beta_s$ and $\gamma\to\bar\gamma_s$ in the characteristic equation (38), we obtain acceptable values of $\nu_{m\ell}(c)$ for system (101).

The convergence of the series (93) and of the corresponding continued fraction has been proved for $x>2c$ in papers [5, 19]. The algorithm of the calculation of $\nu_{m\ell}(c)$, $\Pi^{reg}_{m\ell}(c,\xi)$ and $\Pi^{irreg}_{m\ell}(c,\xi)$ and its numerical results are given in [8]. The calculation of the Coulomb functions $F_{\nu+s}(\alpha^*,x)$ and $G_{\nu+s}(\alpha^*,x)$ was realized in [8, 15]. For fixed c and large x equation (100) takes the form

$$\left[\frac{d}{dx}x^2\frac{d}{dx}+x^2-2\alpha^*x-2\alpha^*c-\lambda_{m\ell}(c)+O\left(x^{-1}\right)\right]\Pi^{(\pm)}_{m\ell}(x)=0. \tag{103}$$

Then we can write two linearly independent solutions to Eq. (100), as the linear combination of the two Coulomb functions $F_{\nu_0}(\alpha^*, x)$ and $G_{\nu_0}(\alpha^*, x)$ of ν_0th order:

$$\lim_{x\to\infty} \Pi^{(\pm)}_{m\ell}(x) = \frac{G_{\nu_0}(\alpha^*, x) \pm iF_{\nu_0}(\alpha^*, x)}{x}\left(1 + O(x^{-3})\right), \tag{104}$$

$$\nu_0 = -\frac{1}{2} \pm \frac{1}{2}\sqrt{1 + 8\alpha^* c + 4\lambda_{m\ell}(c)}. \tag{105}$$

The asymptotics of the solutions as $s \to \infty$ have the form

$$\lim_{x\to\infty} \Pi^{(\pm)}_{m\ell}(x) = 2(2x)^{-(1\pm i\alpha^*)} e^{\pm ix} \left(1 + O(1/x)\right). \tag{106}$$

If we use the series (93) and the asymptotic representation (98) for the Coulomb functions $F_{\nu+s}(\alpha^*, x)$ and $G_{\nu+s}(\alpha^*, x)$, we gain more accurate information about behavior of functions $\Pi^{(\pm)}_{m\ell}(x)$ as $x \to \infty$. In the first approximation we obtain

$$\Pi^{(\pm)}_{m\ell}(x) = \frac{\exp\left[\pm i(x - \alpha^* \ln(2x) - \Phi_\pm)\right]}{x} + O(x^{-2}). \tag{107}$$

The phase $\Phi_\pm \equiv \Phi_\pm(c, \alpha^*, \lambda_{m\ell}(c))$ is a real function of parameters c, α^*, $\lambda_{m\ell}(c)$:

$$\Phi_\pm = \pm i \ln \left(\sum_{s=-\infty}^{\infty} \bar{h}_s \exp\{\mp i \left[(s + \nu)\pi/2 - \sigma_{s+\nu}\right]\} \right). \tag{108}$$

We must know this function for calculations of the cross-section on two Coulomb centres [1, 12, 13, 15].

Using the asymptotic formula (104), (91) and (92), we obtain the Wronskian of functions $\Pi^{reg}_{m\ell}(c, \xi)$ and $\Pi^{reg}_{m\ell}(c, \xi) + i\Pi^{irreg}_{m\ell}(c, \xi)$

$$W\left[\Pi^{reg}_{m\ell}(c, \xi), \left(\Pi^{reg}_{m\ell}(c, \xi) + i\Pi^{irreg}_{m\ell}(c, \xi)\right)\right] = \frac{i}{c(\xi^2 - 1)}. \tag{109}$$

Using this value of the Wronskian, we can write radial part of Green's function in its final form:

$$G_{m\ell}(\xi, \xi'; E > 0) = 2ik\Pi^{reg}_{m\ell}(c, \xi_<)\left[\Pi^{reg}_{m\ell}(c, \xi_>) + i\Pi^{irreg}_{m\ell}(c, \xi_>)\right]. \tag{110}$$

The problems that are connected to different expansions of the regular and/or irregular radial Coulomb functions of the c-type by series of different basis functions are analyzed in detail in papers [8,12,15]. In particular, in [15], the expansions of $\Pi^{reg}_{m\ell}(c, \xi)$ and $\Pi^{irreg}_{m\ell}(c, \xi)$ are obtained similarly to expansion (88) and (89). The formal transition $p \to -ic$, $\alpha \to -i\alpha^*$ in (66)–(78) leads to expansions in series of the complex functions with complex coefficients, which are rather complicated object for direct calculations. For these and other reasons, we use expansion [15] of the Jaffe's type [27] for the calculations of the regular radial Coulomb functions and the irregular Coulomb functions of c-type at small values of the argument. Thus the regular solution

$\Pi_{m\ell}^{reg}(c,\xi)$ is calculated from 1 to ∞ by (91) and (93). But $\Pi_{m\ell}^{irreg}(c,\xi)$ is calculated from ∞ to 1, starting from (91) and (93). Such a combined way of numerical calculations has used in [8].

In conclusion we compare the results obtained for radial Green's functions $G_{m\ell}(\xi,\xi'; E>0)$ in this article with the correspondent formulae of the paper [8]. So, formula (42) in [8] contains an error: we should read $4/R$ instead of $R/4$. The same formula does not contain the factor $(\xi^2-1)^{-1}$, what follows from the general expression for Green's function for arbitrary linear differential equation of the second order [28]. In addition, the Wronskian does not agree with the normalization of the regular and irregular radial Coulomb functions of the c-type, which was used in [8]. Apparently, the specified errors resulted in an incorrect final expression (44) of [8], which determines the radial part of two-centre Green's functions.

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