ON THE ASYMPTOTIC SOLUTIONS OF THE TWO COULOMB CENTERS PROBLEM AT SMALL INTERCENTER SEPARATION[1]

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The expansions of a Green's function for the two Coulomb center potential in Coulomb spheroidal functions are built, and the expansion in associated Legendre polynomials for angular Coulomb spheroidal functions is used. In the limit of small intercenter distances, the analytic expressions for coefficients of these expansions are obtained. The solutions of a degenerate hypergeometric equation are used as a basis function system while expanding regular and irregular Coulomb spheroidal functions into series.

1. Introduction

The two Coulomb centers problem of the electron motion in the field of two fixed charges Z_1 and Z_2 located at the distance R from each other, can be used as a helpful model in the study of many molecular processes [1]. In this connection, rather useful for applications becomes the Green's function of the following Schrodinger equation:

$$\left[\hat{H}(\vec{r}) - E(R)\right]\Psi(\vec{r};R) \equiv$$

$$\equiv \left[-\frac{1}{2}\Delta - Z_1/r_1 - Z_2/r_2 - E(R)\right]\Psi(\vec{r};R) = 0, \quad (1)$$

where r_1, r_2 are the distances from the electron to centers 1 and 2, vector $\vec{r}$ denotes the electron position and $E(R)$ - its energy; $\hbar = m = e = 1$.

Equation (1) can be considered as the zero approximation in perturbation theory for a molecular system. Solutions of the inhomogeneous equation arising in the first order of such a theory can be obtained while using the Green's function of the two Coulomb center problem. In the theory of electronic structure and spectra of molecular systems, this function plays the same fundamental role as the one Coulomb center Green's function in the theory of atomic structure.

The most conventional methods of two center Green's functions construction are based mostly on expanding these functions into Fourier series over full basis sets of functions, arising at the separation of variables in the Schrodinger equation (1) in prolate spheroidal coordinates [1]. However, the convenient expansions of the two center Green's function over partial waves have been constructed only in the separate case of molecular hydrogen ion H_2^+ [3], when the angular functions of the problem coincide with the angular functions of free motion (i.e., spheroidal harmonics, [4]).

In more general case of the two-center problem with different charges of nuclei, the same approach demands the angular functions of the problem to be expand in spheroidal harmonics with a subsequent inversion of obtained infinite matrices. The expansions of such a type, leading to cumbersome expressions, are used for studying the scattering by a finite dipole [5].

At the same time, the separation of variables makes interesting the possibility of the two center Green's function expansion directly in the solutions of ordinary differential equations, which are gained on the separation of variables in (1) in the prolate spheroidal coordinates [1].

Here, the expansions of the Green's function of (1) in angular Coulomb spheroidal functions (CSFs) are built. While regular and irregular radial CSFs being expanded into series (Section 3), the solutions Φ and Ψ of a degenerate hypergeometric equation [15], providing the required asymptotic behaviour of the CSFs at small intercenter distances ($R \to 0$), are used as basis functions. These expansions are shown (Section 4) to satisfy the "correspondence principle" stating that all the formulae, obtained for the two-center problem in the spheroidal coordinates, should change in the limit of the united atom (i.e., at $R \to 0$) into the known one-center (spherical) analogues.

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2. Initial Position

The Green's function $G_E\left(\vec{r},\vec{r}';R\right)$ of the Z_1eZ_2 problem is defined by the spectral expansion

$$G_E\left(\vec{r},\vec{r}';R\right)=\sum_j \frac{\Psi_j^*\left(\vec{r};R\right)\Psi_j\left(\vec{r}';R\right)}{E_j(R)-E}, \tag{2}$$

where symbol $\sum_j$ denotes the summarizing over discrete and integration over continuum spectra of the operator $\hat{H}$ in the prolate spheroidal coordinates

$$\xi=(r_1+r_2)/R, \quad 1\le\xi<\infty,$$

$$\eta=(r_1-r_2)/R, \quad -1\le\eta\le 1,$$

$$\varphi=\arctan(y/x), \quad 0\le\varphi<2\pi. \tag{3}$$

The eigenfunctions Ψ_j of three operators, which are commute in pairs – Hamiltonian of the two-center problem, projection of angular momentum $\hat{L}_z$ to the axis $\vec{z}$ (directed from center 1 towards center 2), and separation constant Λ can be represented as the product [1]

$$\Psi_j\left(\vec{r};R\right)\equiv\Psi_{kqm}(\xi,\eta,\varphi;R)=N_{kqm}(p,\alpha,\beta)\times$$

$$\times\Pi_{mk}(p,\alpha;\xi)\,\Xi_{mq}(p,\beta;\eta)\,\frac{e^{im\varphi}}{\sqrt{2\pi}}. \tag{4}$$

The radial CSF $\Pi_{mk}(p,\alpha;\xi)$ and angular CSF $\Xi_{mq}(p,\beta;\eta)$ are the solutions of the system of ordinary differential equations

$$\left\{\frac{d}{d\xi}\left[(\xi^2-1)\frac{d}{d\xi}\right]+\left[-\lambda_{mk}^{(\xi)}-p^2(\xi^2-1)+\right.\right.$$

$$\left.\left.+\,2p\alpha\xi-\frac{m^2}{\xi^2-1}\right]\right\}\Pi_{mk}(p,\alpha;\xi)=0, \tag{5}$$

$$\left\{\frac{d}{d\eta}\left[(1-\eta^2)\frac{d}{d\eta}\right]+\left[\lambda_{mq}^{(\eta)}-p^2(1-\eta^2)+\right.\right.$$

$$\left.\left.+\,2p\beta\eta-\frac{m^2}{1-\eta^2}\right]\right\}\Xi_{mq}(p,\beta;\eta)=0 \tag{6}$$

with the boundary conditions

$$\lim_{\xi\to 1}\left(\xi^2-1\right)^{-m/2}\Pi_{mk}(p,\alpha;\xi)=1,$$

$$\lim_{\xi\to\infty}\Pi_{mk}(p,\alpha;\xi)=0, \tag{7}$$

$$\lim_{\eta\to+1-0}\left(1-\eta^2\right)^{-m/2}\Xi_{mq}(p,\beta;\eta)=1, \tag{8}$$

where $\lambda_{mk}^{(\xi)}$ and $\lambda_{mq}^{(\eta)}$ are the separation constants, and the standard designation has been used:

$$\alpha=(Z_2+Z_1)(-2E)^{-1/2},$$

$$\beta=(Z_2-Z_1)(-2E)^{-1/2},$$

$$p=\frac{1}{2}R(-2E)^{1/2}. \tag{9}$$

The index $j=\{kqm\}$ designates the set of quantum numbers, where k and q coincide with the numbers of nodes of the corresponding CSF by the variables ξ and η and azimuthal quantum number $m=0,\pm1,\pm2...$. Further we shall use the set of quantum numbers $\{n\ell m\}$: $n=k+q+m+1$, $\ell=q+m$, which coincides in the limit of united atom with the spherical quantum numbers. Normalization factor $N_j=N_{kqm}(p,a,b)$ is defined by the following condition:

$$\int\Psi_{k'q'm'}^*(\xi,\eta,\varphi;R)\,\Psi_{kqm}(\xi,\eta,\varphi;R)\,d\tau=\delta_{kk'}\delta_{qq'}\delta_{mm'},$$

$$d\tau=\frac{R^3}{8}\left(\xi^2-\eta^2\right)d\xi d\eta d\varphi. \tag{10}$$

The pair of one-dimensional boundary-value problems (5) – (8) for the radial and angular CSF is equivalent to the initial problem (1) under the condition

$$\lambda_{mk}^{(\xi)}(p,\alpha)=\lambda_{mq}^{(\eta)}(p,\beta)=\lambda_{kqm}. \tag{11}$$

Using (11) as the relation between p and E (for the fixed parameters α and β and the fixed quantum numbers m,k,q) and taking into consideration (9), one can derive the discrete energy spectrum of the two Coulomb center problem Z_1eZ_2: $E_j(R)=E_{kqm}(R,Z_1,Z_2)$.

3. Green's Function Expansion in Coulomb Spheroidal Functions

It is well known that the Green's function for (1) is defined by the inhomogeneous equation

$$\left[-\frac{1}{2}\Delta-Z_1/r_1-Z_2/r_2-E(R)\right]G_E\left(\vec{r},\vec{r}';R\right)=$$

$$=\delta\left(\vec{r}-\vec{r}'\right), \tag{12}$$

where $\delta\left(\vec{r}-\vec{r}'\right)$ is the three-dimensional Dirac delta-function. Instead of performing the complicated summation in (2), we use the standard algorithm [9] of Green's function construction of second-order differential equations. Using this way, the important analytic representations for the Green's function of Coulomb [2] and other one center model potentials [10] have been obtained.

Since the azimuthal quantum number ℓ is not a good quantum number in the non-central field, the solution of the non-uniform equation (12) is sought in the form of an expansion in a complete orthonormalized system of prolate angular Coulomb spheroidal functions $\bar{\Xi}_{m\ell}(p,\eta)$ [1]:

$$G_E(\xi,\eta,\varphi;\xi',\eta',\varphi'|R) =$$

$$= \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell} G_{m\ell}(\xi,\xi';E)\,\bar{\Xi}_{m\ell}(p,\eta)\,\bar{\Xi}^{*}_{m\ell}(p,\eta')\times$$

$$\times\frac{e^{im(\varphi-\varphi')}}{2\pi}, \qquad (13)$$

$$\bar{\Xi}_{m\ell}(p,\eta) = N_{m\ell}(p)^{-1}\sum_{r=0}^{\infty} d_r^{m\ell}(p) P^m_{m+r}(\eta),$$

$$N_{m\ell}(p) = \left[\sum_{r=0}^{\infty}\left(d_r^{m\ell}(p)\right)^2 \frac{2(2m+r)!}{m!(2m+2r+1)}\right]^{1/2}. \qquad (14)$$

Here, $P^m_{m+r}(\eta)$ are the associated Legendre polynomials, $d_r^{m\ell}(p)$ coefficients to be found. By substituting expansion (13) into (12), having been written in the prolate spheroidal coordinates (3), and separating the angular variables η and φ, we obtain a differential equation for the radial part of the Green's function $G_{m\ell}(\xi,\xi';E)$:

$$\left\{\frac{d}{d\xi}\left[(\xi^2-1)\frac{d}{d\xi}\right]+\right.$$

$$\left.+\left[-\lambda_{m\ell}-p^2(\xi^2-1)+2p\alpha\xi-\frac{m^2}{\xi^2-1}\right]\right\}\times$$

$$\times G_{m\ell}(\xi,\xi';E) = -\frac{4}{R}\delta(\xi-\xi'), \qquad (15)$$

where $\lambda_{m\ell}$ denote the eigenvalues of the angular problems, corresponding to the oblate CSF $\bar{\Xi}_{m\ell}(p,\beta;\eta)$ [1]. Thus, the function $G_{m\ell}(\xi,\xi';E)$ is the Green's function under one-dimensional radial motion and is conventionally expressed by two linearly independent solutions $\Pi^{(1)}_{m\ell}(p,\xi)\equiv\Pi^{(1)}_{m\ell}(p,\alpha,\lambda_{m\ell};\xi)$ and $\Pi^{(2)}_{m\ell}(p,\xi)\equiv\Pi^{(2)}_{m\ell}(p,\alpha,\lambda_{m\ell};\xi)$ of the uniform equation (5).

The solution $\Pi^{(1)}_{m\ell}(p,\xi)$ is regular at $\xi\to 1$ and divergent at infinity, and $\Pi^{(2)}_{m\ell}(p,\xi)$ is, contrary, divergent at $\xi\to 1$ and regular at infinity. Then, according to the general theory of second-order linear differential equations [9], the radial part of the Green's function $G_{m\ell}(\xi,\xi';E)$ can be given by

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

$$Z = Z_1 + Z_2. \qquad (16)$$

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

Now we consider the radial uniform equation (5) in more detail. We proceed, in this equation, to new independent variables and to new sought functions according to the formulae

$$\tilde{\Pi}^{(\pm)}_{m\ell}(x_\pm) = \left(\frac{\xi\pm 1}{\xi\mp 1}\right)^{m/2}\Pi_{m\ell}(p,\xi), \qquad (17)$$

$$x_\pm = p(\xi\pm 1), \quad (2p\le x_+<\infty, \quad 0\le x_-<\infty).$$

Hereinafter, the upper signs are related to $\tilde{\Pi}^{(+)}_{m\ell}(x_+)$, and the lower ones to $\tilde{\Pi}^{(-)}_{m\ell}(x_-)$. By transformations (17), Eq. (5) is reduced to two separate equations for $\tilde{\Pi}^{(\pm)}_{m\ell}(x_\pm)$:

$$\left[\frac{d}{dx_\pm}\left(x_\pm^2\frac{d}{dx_\pm}\right)-x_\pm^2+2\alpha x_\pm-s(s+1)\right]\tilde{\Pi}^{(\pm)}_{m\ell}(x_\pm)$$

$$+\frac{p}{x_\pm\mp 2p}\left[\pm 2(m+1)x_\pm\frac{d}{dx_\pm}\right.$$

$$\left.+\left(\frac{s(s+1)-\lambda_{m\ell}}{p}\pm 2\alpha\right)x_\pm\mp 2s(s+1)\right]\tilde{\Pi}^{(\pm)}_{m\ell}(x_\pm)$$

$$\equiv T_s(x_\pm)\tilde{\Pi}^{(\pm)}_{m\ell}(x_\pm)+pQ_\pm(x_\pm)\tilde{\Pi}^{(\pm)}_{m\ell}(x_\pm)=0. \qquad (18)$$

The exact sense and aim of the partitioning of differential operators performed here will be understood at further consideration. But the idea can be explained in a couple of words by the following physical speculations. The operator $T_s(x)$ formally coincides with the radial Schrodinger operator in the spherical coordinates for the Coulomb one center potential with the charge $Z = Z_1 + Z_2$ and the orbital momentum s. When p tends to zero, both Eqs. (18) go over into one $T_sR(x) = 0$ $(0\le x<\infty)$, whose two independent solutions are the functions $R_s^{(1)}(x)$ and $R_s^{(2)}(x)$, expressed directly in terms of the regular Φ and irregular Ψ solutions of a degenerate hypergeometric equation [15]:

$$R_s^{(1)}(x) \equiv x^s e^{-x} \Phi(-\alpha + s + 1, 2s + 2, 2x), \tag{19}$$

$$R_s^{(2)}(x) \equiv x^s e^{-x} \Psi(-\alpha + s + 1, 2s + 2, 2x). \tag{20}$$

The above speculations suggest the regular $\widetilde{\Pi}_{m\ell}^{(1,\pm)}(x_\pm)$ and the irregular $\widetilde{\Pi}_{m\ell}^{(2,\pm)}(x_\pm)$ solutions of each of Eqs. (18) to be given as the following infinite sums:

$$\widetilde{\Pi}_{m\ell}^{(1,\pm)}(x_\pm) \equiv \widetilde{\Pi}_{m\ell}^{(1,\pm)}(\alpha, \lambda_{m\ell}, p; x_\pm) =$$

$$= \sum_{s=0}^{\infty} h_s^{(\pm)}(p\,|\alpha, \lambda_{m\ell})\, R_s^{(1)}(x_\pm), \tag{21}$$

$$\widetilde{\Pi}_{m\ell}^{(2,\pm)}(x_\pm) \equiv \widetilde{\Pi}_{m\ell}^{(2,\pm)}(\alpha, \lambda_{m\ell}, p; x_\pm) =$$

$$= \sum_{s=0}^{\infty} \tilde{h}_s^{(\pm)}(p\,|\alpha, \lambda_{m\ell})\, R_s^{(2)}(x_\pm), \tag{22}$$

where the expansion coefficients $h_s^{(\pm)}$ and $\tilde{h}_s^{(\pm)}$ are to be determined. Having substituted these expansions into the corresponding equations (18) and having used the recurrent relations [16] for the basis functions $R_s^{(1)}(x)$ and $R_s^{(2)}(x)$, we obtain two infinite three-term systems of linear equations for the coefficients $h_s^{(\pm)} \equiv h_s^{(\pm)}(p|\alpha, \lambda_{m\ell})$, $\tilde{h}_s^{(\pm)} \equiv \tilde{h}_s^{(\pm)}(p|\alpha, \lambda_{m\ell})$:

$$\pm p\alpha_s h_{s-1}^{(\pm)} + (\beta_s - \lambda_{m\ell}) h_s^{(\pm)} \mp p\gamma_s h_{s+1}^{(\pm)} = 0, \tag{23}$$

$$s = 0, 1, 2..., \quad h_{-1}^{(\pm)} = 0;$$

$$\mp p\tilde{\alpha}_s \tilde{h}_{s-1}^{(\pm)} + (\tilde{\beta}_s - \lambda_{m\ell}) \tilde{h}_s^{(\pm)} \pm p\tilde{\gamma}_s \tilde{h}_{s+1}^{(\pm)} = 0, \tag{24}$$

$$s = 0, 1, 2..., \quad \tilde{h}_{-1}^{(\pm)} = 0.$$

To make the representation shorter, the following notations are introduced:

$$\alpha_s = \frac{2\left(s^2 - \alpha^2\right)(s + m)}{s\,(2s - 1)\,(2s + 1)}, \quad \beta_s = \tilde{\beta}_s = s\,(s + 1),$$

$$\gamma_s = 2\,(s + 1)\,(s + 1 - m)\,; \tag{25}$$

$$\tilde{\alpha}_s = \frac{4(s - \alpha)(s + m)}{2s - 1},$$

$$\tilde{\gamma}_s = \frac{(s + \alpha + 1)(s - m + 1)}{2s + 3}. \tag{26}$$

The recurrent systems (23) ((24)) determine the coefficients $h_s^{(\pm)}$ ($\tilde{h}_s^{(\pm)}$) to within arbitrary factors fixed by the conditions

$$\sum_{s=0}^{\infty} h_s^{(\pm)} \frac{\Gamma(2s + 2)}{2^s \Gamma(s + 1 - \alpha)} = 1, \quad \sum_{s=0}^{\infty} 2^{-s} \tilde{h}_s^{(\pm)} = 1. \tag{27}$$

The obtained recurrent relations (23), (24) do not enable one to get explicit expressions for the coefficients $h_s^{(\pm)}$ and $\tilde{h}_s^{(\pm)}$. However, the procedure of their calculation is considerably simplified due to a close relationship between the three-term recurrent systems and well-elaborated technique of chain (or continuous) fractions. This circumstance essentially simplifies the creation of effective algorithms for calculation of the regular and irregular CSFs $\widetilde{\Pi}_{m\ell}^{(1,\pm)}(x_\pm)$, $\widetilde{\Pi}_{m\ell}^{(2,\pm)}(x_\pm)$. The proposed two types of expansions (21) and (22), not being asymptotic in the full sense, have better convergence at small p.

The presented expansions (21), (22) should be treated as Fourier series in the complete systems of functions $R_s^{(1)}(x_\pm)$ and $R_s^{(2)}(x_\pm)$, respectively. The coefficients $h_s^{(\pm)}$ and $\tilde{h}_s^{(\pm)}$ are the Fourier coefficients of the functions $\widetilde{\Pi}_{m\ell}^{(1,\pm)}(x_\pm)$, $\widetilde{\Pi}_{m\ell}^{(2,\pm)}(x_\pm)$ and the convergence is treated in the sense of the Fourier series uniform convergence.

Now we calculate the value of the Wronskian $W\left[\Pi_{m\ell}^{(1)}(p, \xi), \Pi_{m\ell}^{(2)}(p, \xi)\right]$. Using the known asymptotic expressions for the degenerate hypergeometric functions at high values of the argument [15]

$$\Phi(a, b, x) = \frac{\Gamma(b)}{\Gamma(a)} e^x x^{a-b} \left[1 + O\left(|x|^{-1}\right)\right],$$

$$\Psi(a, b, x) = x^{-a} \left[1 + O\left(|x|^{-1}\right)\right] \tag{28}$$

and taking into account the "normalization" conditions (27) for the coefficients $h_s^{(\pm)}$ and $\tilde{h}_s^{(\pm)}$, one can readily obtain

$$2p(\xi^2 - 1) W\left[\Pi_{m\ell}^{(1)}(p, \xi), \Pi_{m\ell}^{(2)}(p, \xi)\right] = -1. \tag{29}$$

Expression (16) with the account of the Wronskian value from equation (29) can now be given by

$$G_{m\ell}(\xi, \xi'; E) = \frac{8Z}{\alpha} \left(\frac{x_\mp x'_\mp}{x_\pm x'_\pm}\right)^{m/2} \times$$

$$\times \widetilde{\Pi}_{m\ell}^{(1,\pm)}(x_{\pm<})\, \widetilde{\Pi}_{m\ell}^{(2,\pm)}(x_{\pm>}), \tag{30}$$

where the functions $\widetilde{\Pi}_{m\ell}^{(1,\pm)}(x_{\pm<})$ and $\widetilde{\Pi}_{m\ell}^{(2,\pm)}(x_{\pm>})$ are still given by Eqs. (21), (22).

4. Limiting Values and Asymptotic Expansions of the Two-Center Green's Function at Small Intercenter Distances

It seems interesting to consider the limiting expressions from the obtained strict formulae (13), (30) at $R \to 0$ and to compare them to the known results for the one-center Green's function [11]. It follows from (3) that, at $R \to 0$ and finite r, the prolate spheroidal coordinates go over into the spherical ones r, θ, and φ: $\xi \to 2r/R$, $\eta \to \cos\theta$. If, in the equation for the oblate angular Coulomb spheroidal functions $\Xi_{m\ell}(p,\eta)$, the variable substitution $\eta \to \cos\theta$ is performed and the terms, changing into zero at $R \to 0$, are discarded, it goes over into the equation for the associated Legendre polynomials $P_\ell^m(\cos\theta)$. This means that the angular part of the solutions of the Schrodinger equation (1) goes over in this limit into the angular part of the one-center Coulomb problem in the spherical coordinates. Hence, the limiting relations

$$\Xi_{m\ell}(p,\eta)\frac{e^{im\varphi}}{\sqrt{2\pi}} \xrightarrow[R\to 0]{} \sqrt{\frac{(2\ell+1)(\ell-m)!}{4\pi(\ell+m)!}}\times$$
$$\times P_\ell^m(\cos\theta)e^{im\varphi} \equiv Y_{m\ell}(\theta,\varphi),$$
$$\lambda_{m\ell}(p) \xrightarrow[R\to 0]{} \ell(\ell+1) \tag{31}$$

are valid. By substituting this value for $\lambda_{m\ell}$ in (15), carrying out the substitution of variable $\xi \to 2r/R$, and keeping only the terms main in R, we obtain an equation for the radial part of the Green's function for the one center Coulomb potential [11].

Now we investigate the limiting transitions in the recurrent relations (23), (24) and in expansions (21), (22) for the radial functions $\tilde{\Pi}_{m\ell}^{(i,\pm)}(x_\pm)$, $(i = 1,2)$. In the $R \to 0$ limit, the three-term recurrent relations (23), (24) go over into the following one-term relations:

$$[s(s+1) - \ell(\ell+1)]h_s^{(\pm)} = [s(s+1) - \ell(\ell+1)]\tilde{h}_s^{(\pm)} = 0.$$

Hence, at $R \to 0$ in each sum of (27), only one term with $s = \ell$ differs from zero, therefore

$$h_s^{(\pm)} \xrightarrow[R\to 0]{} \frac{2^s\Gamma(s+1-\alpha)}{\Gamma(2s+2)}\delta_{s\ell}, \quad \tilde{h}_s^{(\pm)} \xrightarrow[R\to 0]{} 2^s\delta_{s\ell}. \tag{32}$$

These formulae along with (19)–(22) and (31) show that, in the $R \to 0$ limit, the regular $\tilde{\Pi}_{m\ell}^{(1,\pm)}(x_\pm)$ and irregular $\tilde{\Pi}_{m\ell}^{(2,\pm)}(x_\pm)$ solutions of equations (18) behave as follows:

$$\tilde{\Pi}_{m\ell}^{(1,\pm)}(p(\xi\pm 1)) \xrightarrow[R\to 0]{} \frac{\Gamma(\ell+1-\alpha)}{\Gamma(2\ell+2)}\times$$
$$\times \exp\left(-\frac{Zr}{\alpha}\right)\left(\frac{2Zr}{\alpha}\right)^\ell\times$$
$$\times\Phi\left(\ell+1-\alpha, 2\ell+2, \frac{2Zr}{\alpha}\right), \tag{33}$$

$$\tilde{\Pi}_{m\ell}^{(2,\pm)}(p(\xi\pm 1)) \xrightarrow[R\to 0]{} \exp\left(-\frac{Zr}{\alpha}\right)\left(\frac{2Zr}{\alpha}\right)^\ell\times$$
$$\times\Psi\left(\ell+1-\alpha, 2\ell+2, \frac{2Zr}{\alpha}\right). \tag{34}$$

Finally, using the obtained formulae (31)–(34), we can easily verify that the Green's function (13), (30) goes over, as expected, into the Green's function of the atomic potential [10, 11] at $R \to 0$:

$$G_E\left(\vec{r},\vec{r}'\right) = \sum_{\ell,m} g_\ell(r,r';E)Y_{m\ell}(\theta,\varphi)Y^*_{m\ell}(\theta',\varphi'),$$

$$g_\ell(r,r';E) = \frac{4Z}{\alpha}\frac{\Gamma(\ell+1-\alpha)}{\Gamma(2\ell+2)}\left(\frac{2Zr_<}{\alpha}\right)^\ell\left(\frac{2Zr_>}{\alpha}\right)^\ell\times$$
$$\times\exp\left[-\frac{Z}{\alpha}(r_< + r_>)\right]\Phi\left(\ell+1-\alpha, 2\ell+2, \frac{2Zr_<}{\alpha}\right)\times$$
$$\times\Psi\left(\ell+1-\alpha, 2\ell+2, \frac{2Zr_>}{\alpha}\right). \tag{35}$$

In many physical problems, whose examples are considered in [1], the asymptotic of the Green's function $G_E\left(\vec{r},\vec{r}';R\right)$ should be known at small values of the intercenter distance. Hence, the necessity of the asymptotic expansions of the $\Xi_{m\ell}(p,\eta)$, $\tilde{\Pi}_{m\ell}^{(1,\pm)}(x_\pm)$, and $\tilde{\Pi}_{m\ell}^{(2,\pm)}(x_\pm)$ functions in a small parameter at the fixed quantum numbers ℓ and m to be constructed arises. We use an asymptotic method, proposed by Abramov and Slavyanov [13], to search for such expansions.

We begin with the prolate angular Coulomb spheroidal function $\Xi_{m\ell}(p,\eta)$. Instead of the expansion (14), we can use an expansion of the form

$$\Xi_{m\ell}(p,\eta) = e^{-p\eta}\sum_{n=m-\ell}^{\infty} d_n^{m\ell}P_{\ell+n}^m(\eta). \tag{36}$$

The expansion coefficients $d_n^{m\ell}$ in (36) fulfill the three-term recurrent relations [1]:

$$d_{n-1}^{m\ell}2p\frac{(\ell+n-m)(\beta+\ell+n)}{2\ell+2n-1}-$$

$$-d_n^{m\ell}[(\ell+n)(\ell+n+1)-\lambda_{m\ell}^{(\eta)}]+$$

$$+d_{n+1}^{m\ell}2p\frac{(\ell+n+n+1)(\beta-\ell-n-1)}{(2\ell+2n+3)}=0. \tag{37}$$

We search for the separation constant $\lambda_{m\ell}^{(\eta)}$ and the expansion coefficients $d_n^{m\ell}$ in the form of asymptotic series in the powers of a small parameter p^2:

$$d_n^{m\ell}=p^{|n|}\sum_{j=0}^{\infty}\left[d_n^{m\ell}\right]_{2j}p^{2j}, \quad d_0=1, \tag{38}$$

$$\lambda_{m\ell}^{(\eta)}=\sum_{j=0}^{\infty}\left[\lambda_{m\ell}^{(\eta)}\right]_{2j}p^{2j}. \tag{39}$$

By substituting these expansions consequently into each equation of system (31), starting from $n=0$, and equating the coefficients at the equal powers of p^2 to zero, we obtain the recurrent relations to determine the expansion coefficients $\left[d_n^{m\ell}\right]_{2j}$ and $\left[\lambda_{m\ell}^{(\eta)}\right]_{2j}$. The chain of equations, corresponding to $n=0$, enables the $[\lambda_{m\ell}^{(\eta)}]_{2j}$ values to be expressed in terms of coefficients $\left[d_{\pm n}^{m\ell}\right]_{2j}$.

The coefficients $\left[d_n^{m\ell}\right]_{2j}$, $j\geq 0$ are determined consequently from the recurrent systems of equations, corresponding to $n=\pm1,2,\ldots$. The first six coefficients of expansion (39) are given by

$$[\lambda_{m\ell}^{(\eta)}]_0=\ell(\ell+1), \tag{40}$$

$$[\lambda_{m\ell}^{(\eta)}]_2=2p^2\frac{(\ell^2+\ell-1+m^2)}{(2\ell-1)(2\ell+3)}+$$

$$+2p^2\frac{\beta^2(\ell^2+\ell-3m^2)}{\ell(\ell+1)(2\ell-1)(2\ell+3)}, \tag{41}$$

$$[\lambda_{m\ell}^{(\eta)}]_4=-2\frac{(\ell^2-m^2)(\beta^2-\ell^2)}{\ell^2(4\ell^2-1)}\left(\frac{(\ell^2-m^2)(\beta^2-\ell^2)}{\ell(4\ell^2-1)}-\right.$$

$$-\frac{[(\ell+1)^2-m^2][\beta^2-(\ell+1)^2]}{(\ell+1)(2\ell+1)(2\ell+3)}-$$

$$\left.-\frac{[(\ell-1)^2-m^2][\beta^2-(\ell-1)^2]}{(2\ell-1)^2(2\ell-3)}\right)-$$

$$-2\frac{[(\ell+1)^2-m^2][\beta^2-(\ell+1)^2]}{(\ell+1)^2\,(4(\ell+1)^2-1)}\times$$

$$\times\left(-\frac{[(\ell+1)^2-m^2][\beta^2-(\ell+1)^2]}{(\ell+1)\,(4(\ell+1)^2-1)}+\right.$$

$$+\frac{(\ell^2-m^2)(\beta^2-\ell^2)}{\ell(4\ell^2-1)}+$$

$$\left.+\frac{[(\ell+2)^2-m^2][\beta^2-(\ell+2)^2]}{(2\ell+3)^2(2\ell+5)}\right). \tag{42}$$

For the sake of space saving, the coefficient $[\lambda_{m\ell}^{(\eta)}]_6$ given in Appendix 1.

Unfortunately the numerical data for Coulomb spheroidal functions are represented not so widely as for spheroidal functions (see, for example, [4]). Therefore, we have compared calculations by our asymptotic formula (39) with numerical data from [12] for bound states of Z_1eZ_2 systems. Thus, the value of p is taken relevant to the energy of a bound state. Some results are presented in Tables 1 and 2. Expansion (39) for the separation constant $\lambda_{m\ell}^{(\eta)}$ as a function of p is valid in a broad range of parameters. The results are better for larger m and ℓ.

Now we proceed to consider the asymptotic behaviour of the regular and irregular radial CSFs $\tilde{\Pi}_{m\ell}^{(1,\pm)}(x_\pm)$, $\tilde{\Pi}_{m\ell}^{(2,\pm)}(x_\pm)$ at small values of the p parameter. For this purpose we can make use of their expansions (21) and (22) in the solutions of the degenerate hypergeometric equation.

Similarly to Eq. (38), the coefficients of expansions (21), (22) can be sought in the form of power series:

$$h_s^{(\pm)}=p^{|s|}\sum_{j=0}^{\infty}\left[h_s^{(\pm)}\right]_{2j}p^{2j},$$

$$\tilde{h}_s^{(\pm)}=p^{|s|}\sum_{j=0}^{\infty}\left[\tilde{h}_s^{(\pm)}\right]_{2j}p^{2j}. \tag{43}$$

Table 1. Separation constant for the ground state $1s\sigma$, $Z_1=1$, $Z_2=2$

R	p	$\lambda_{00}^{(\eta)}$ Our results	$\lambda_{00}^{(\eta)}$ [12]
0.2	0.290953	0.049553	0.049553
0.4	0.554405	0.175242	0.175244
0.6	0.794506	0.347491	0.347538
0.8	1.01837	0.546972	0.547375
1.0	1.23153	0.760295	0.762415
1.2	1.43806	0.976566	0.984442

Table 2. Separation constant for the state $2p\sigma$, $Z_1=1$, $Z_2=2$

R	p	$\lambda_{00}^{(\eta)}$ Our results	$\lambda_{00}^{(\eta)}$ [12]
0.2	0.150799	2.01311	2.01311
0.4	0.306268	2.05382	2.05382
0.6	0.469837	2.12594	2.12594
0.8	0.64160	2.23417	2.23415
1.0	0.818029	2.38169	2.38156
1.2	0.994205	2.56837	2.56895

The coefficients of these series are found consequently from the recurrent equations (23), (24) after substitution of expansions (39) for the eigenvalues $\lambda^{(\eta)}_{m\ell}$ of the Sturm-Liouville problem, which determines the prolate angular Coulomb spheroidal functions $\bar{\Xi}_{m\ell}(p,\eta)$. The explicit expressions for $\left[h_s^{(\pm)}\right]_{2j}$, $\left[\tilde{h}_s^{(\pm)}\right]_{2j}$ are rather cumbersome and will be represented in another publication.

Concluding, it is also worth to notice that an approach to solving the perturbation-theory nonlinear equations, related to the Timan–Schwarz method application, has been also discussed in the literature (See e. g. [6, 7]). These approaches are formally equivalent, but the Green's function method possesses an advantage, being known in various fields of physics and universal in applications.

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APPENDIX 1

Expression for $[\lambda^{(\eta)}_{m\ell}]_6$

$$A_1 = \frac{(\ell^2-m^2)[m^2-(1-\ell)^2](5\ell-2)}{\ell^3(1-2\ell)^4(2\ell-3)(2\ell+1)}, \quad A_2 = -\frac{[m^2-(1+\ell)^2][m^2-(2+\ell)^2](7+5\ell)}{(1+\ell)^3(1+2\ell)(3+2\ell)^4(5+2\ell)},$$

$$B_1 = A_1\left[\ell^2(\ell-1)^2-[1+2\ell(\ell-1)]\beta^2+\beta^4\right], \quad B_2 = A_2\left[(1+\ell)^2(2+\ell)^2-[5+2\ell(3+\ell)]\beta^2+\beta^4\right],$$

$$[\lambda^{(\eta)}_{\ell m}]_6 = (B_1+B_2)[\lambda^{(\eta)}_{\ell m}]_2 + \frac{(\beta^2-\ell^2)(\ell^2-m^2)(2\ell-3)}{2\ell^3(1+2\ell)[3+4\ell(\ell-2)]}\left(([\lambda]_2)^2-2\ell[\lambda]_4\right) - \frac{[\beta^2-(1+\ell)^2][(1+\ell)^2-m^2]}{2(1+2\ell)(3+2\ell)(1+\ell)^3}\left(([\lambda]_2)^2+2(1+\ell)[\lambda]_4\right)+$$

$$+A_2\frac{2[(1+\ell)^2-\beta^2][\beta^2-(2+\ell)^2]^2[m^2-(2+\ell)^2]}{(3+2\ell)(5+2\ell)(7+5\ell)} + A_2\frac{2(1+\ell)[m^2-(3+\ell)^2][(1+\ell)^2-\beta^2][(2+\ell)^2-\beta^2][(3+\ell)^2-\beta^2]}{3(2+\ell)(7+2\ell)(5+2\ell)(7+5\ell)}-$$

$$-A_1\frac{2[\beta^2-(1-\ell)^2][\beta^2-\ell^2]}{3(\ell-1)(2\ell-5)(2\ell-1)(5\ell-2)}\left(5+\beta^2[-5+\ell(15(1-\ell)+4\ell^2)]+\right.$$

$$\left.+m^2[-5+\beta^2(5-4\ell)+\ell(15(1-\ell)+4\ell^2)]+\ell[-29+62\ell+\ell^2(-58+25\ell-4\ell^2)]\right).$$

APPENDIX 2

Here,we give the coefficients of expansion (38) for the angular Coulomb spheroidal function (36):

$$C_n = \frac{\ell+n+\beta}{2\ell+2n-1}, \quad D_n = \frac{\ell+n+m+1}{2\ell+2n+3},$$

$$\left[d_1^{m\ell}\right]_0 = \frac{(1+\ell-m)}{1+\ell}C_1, \quad \left[d_{-1}^{m\ell}\right]_0 = \frac{(\ell-\beta)}{\ell}D_{-1},$$

$$\left[d_2^{m\ell}\right]_0 = \frac{(1+\ell-m)(2+\ell-m)}{(1+\ell)(3+2\ell)}C_1C_2, \quad \left[d_{-2}^{m\ell}\right]_0 = \frac{(\ell-1-\beta)(\ell-\beta)}{\ell(2\ell-1)}B_{-2}D_{-1},$$

$$\left[d_1^{m\ell}\right]_2 = \frac{(1+\ell-m)C_1[-2(2+\ell-m)(2+\ell-\beta)C_2D_1+[\lambda^{(\eta)}_{m\ell}]_2(3+2\ell)]}{2(1+\ell)^2(3+2\ell)},$$

$$\left[d_{-1}^{m\ell}\right]_2 = \frac{(\ell-\beta)D_{-1}[-2(-1+\ell-m)(-1+\ell-\beta)C_{-1}D_{-2}+[\lambda^{(\eta)}_{m\ell}]_2(1-2\ell)]}{2\ell^2(2\ell-1)},$$

$$\left[d_3^{m\ell}\right]_0 = \frac{(3+\ell-m)}{3(2+\ell)}C_3\left[d_2^{m\ell}\right]_0, \quad \left[d_{-3}^{m\ell}\right]_0 = \frac{(-2+\ell-\beta)}{3(\ell-1)}D_{-3}\left[d_{-2}^{m\ell}\right]_0,$$

$$\left[d_4^{m\ell}\right]_0 = \frac{(4+\ell-m)}{2(5+2\ell)}C_4\left[d_3^{m\ell}\right]_0, \quad \left[d_{-4}^{m\ell}\right]_0 = \frac{(-3+\ell-\beta)}{2(2\ell-3)}D_{-4}\left[d_{-3}^{m\ell}\right]_0,$$

$$\left[d_3^{m\ell}\right]_2 = \frac{2(3+\ell-m)C_3\left[d_2^{m\ell}\right]_2 - 2(4+\ell-\beta)D_3\left[d_4^{m\ell}\right]_0 + \left[d_3^{m\ell}\right]_0[\lambda_{m\ell}^{(\eta)}]_2}{6(2+\ell)},$$

$$\left[d_{-3}^{m\ell}\right]_2 = \frac{2(3-\ell+m)C_{-3}\left[d_{-4}^{m\ell}\right]_0 + 2(-2+\ell-\beta)D_{-3}\left[d_{-2}^{m\ell}\right]_2 - \left[d_{-3}^{m\ell}\right]_0[\lambda_{m\ell}^{(\eta)}]_2}{6(\ell-1)},$$

$$\left[d_2^{m\ell}\right]_2 = \frac{2(2+\ell-m)C_2\left[d_1^{m\ell}\right]_2 - 2(3+\ell-\beta)D_2\left[d_3^{m\ell}\right]_0 + \left[d_2^{m\ell}\right]_0[\lambda_{m\ell}^{(\eta)}]_2}{2(3+2\ell)},$$

$$\left[d_{-2}^{m\ell}\right]_2 = \frac{2(2-\ell+m)C_{-2}\left[d_{-3}^{m\ell}\right]_0 + 2(-1+\ell-\beta)D_{-2}\left[d_{-1}^{m\ell}\right]_2 - \left[d_{-2}^{m\ell}\right]_0[\lambda_{m\ell}^{(\eta)}]_2}{2(2\ell-1)},$$

$$\left[d_1^{m\ell}\right]_4 = \frac{(1+\ell)\left[-2(2+\ell-\beta)D_1\left[d_2^{m\ell}\right]_2 + \left[d_1^{m\ell}\right]_2[\lambda_{m\ell}^{(\eta)}]_2\right] + (1+\ell-m)C_1[\lambda_{m\ell}^{(\eta)}]_4}{2(1+\ell)^2},$$

$$\left[d_{-1}^{m\ell}\right]_4 = \frac{-2\ell(-1+\ell-m)C_{-1}\left[d_{-2}^{m\ell}\right]_2 + \ell\left[d_{-1}^{m\ell}\right]_2[\lambda_{m\ell}^{(\eta)}]_2 + (\ell-\beta)D_{-1}[\lambda_{m\ell}^{(\eta)}]_4}{2\ell^2}.$$

1. *Komarov I.V., Ponomarev L.I., Slavyanov S.Yu.* Spheroidal and Coulomb Spheroidal Functions.– M.: Nauka, 1976.
2. *Hostler L., Pratt R.K.* // Phys. Rev. Lett.–1963. – **10**. – N 11. – P. 469; *Hostler L.*//J. Math. Phys.– 1964. – **5**, N 5. – P. 591.
3. *Laurenzi B.J.*//J. Chem. Phys. – 1971. – **55**, N 6. – P. 2681.
4. *Flammer C.* Spheroidal Wave Functions.– Stanford, California, 1957.
5. *Shimizu M.*//J. Phys. Soc. Jap.– 1963. – **18**. – P. 811.
6. *Gontier Y., Trahin M.*//Phys. Rev. Mod.A. – 1971. – **4**. – P. 1896.
7. *Vetchinkin S.V.* Theoretical Problems of Chemical Physics.– M.: Nauka, 1982.
8. *Grozdanov T.P., Janev R.K., Lazur V.Yu.* // Phys. Rev. A. – 1985. – **32**. – N 6. – P. 3425; *Lazur V.Yu., Mashyka Yu. Yu., Janev R. K., Grozdanov T.P.* // Teor. Mat. Fiz. – 1991. – **87**, N 1. – P. 97.
9. *Morse P.M., Feshbach H.* Methods of Theoretical Physics. – Vol.1.– New York: McGrawHill, 1953.
10. *Bakhrakh V.L., Vetchinkin S.I.* // Teor. Mat. Fiz. – 1971. – **6**, N 3. – P. 392.
11. *Khristenko S.V.*//Ibid. – 1975. – **22**, N 1. – P. 31.
12. *Ponomarev L.I., Puzynina T.P.* Quantum Mechanical, Two Coulomb Center Problem III. Tables of Terms. – Dubna, 1967.– (Preprint P4-3175).
13. *Abramov D.I., Slavyanov S.Yu.* // J.Phys. B. – 1978. – **11**. – P. 2229.
14. *Khristenko S.V., Maslov A.I., Shevelko V.P.* Molecules and Their Spectroscopic Properties.– Berlin: Springer, 1998.
15. *Bateman H. Erdelyi A.* Higher Transcendental Functions. – Vol. 1.– New York: McGrawHill, 1953.
16. *Lazur V.Yu., Khoma M.V., Karbovanets M.I.*// Ukr.Fiz.Zhurn. – 2001. – **47**. – N 11. P. 1213.

ПРО АСИМПТОТИЧНІ РОЗВ'ЯЗКИ ЗАДАЧІ ДВОХ КУЛОНІВСЬКИХ ЦЕНТРІВ НА МАЛИХ МІЖЦЕНТРОВИХ ВІДСТАНЯХ

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Р е з ю м е

Побудовано розклади двоцентрової функції Гріна за кулонівськими сфероїдальними функціями. Для розкладів кутових кулонівських сфероїдальних функцій використано приєднані поліноми Лежандра. В границі малих міжцентрових відстаней отримано аналітичні вирази для коефіцієнтів цих розкладів. Як базисні системи при розкладанні регулярних та нерегулярних кулонівських сфероїдальних функцій в ряди використано розв'язки виродженого гіпергеометричного рівняння.

ОБ АСИМПТОТИЧЕСКИХ РЕШЕНИЯХ ЗАДАЧИ ДВУХ КУЛОНОВСКИХ ЦЕНТРОВ НА МАЛЫХ МЕЖЦЕНТРОВЫХ РАССТОЯНИЯХ

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Р е з ю м е

Построены разложения двухцентровой функции Грина по кулоновским сфероидальным функциям. Для разложений угловых кулоновских сфероидальных функций использованы присоединенные полиномы Лежандра. Для малых межцентровых расстояний получены аналитические выражения для коэффициентов этих разложений. В качестве базисных систем при разложении регулярных и нерегулярных кулоновских сфероидальных функций в ряды использованы решения вырожденного гипергеометрического уравнения.