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Asymptotic Solutions of the Two-Coulomb-Centre Problem in the Spheroidal Coordinate System

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Abstract

Two-Coulomb-centre quasiradial and quasiangular wavefunctions asymptotic for large distances between the fixed positive charges (nuclei) are derived for the entire space of the negative particle (electron).

1. Introduction

The two-Coulomb-centre problem shares its origin with quantum mechanics, and since then extensive work has been devoted to it. In spite of this, much interest in this problem still exists. The reason is twofold. On one hand, the two-Coulomb-centre system is an important model for the theory of diatomic molecules, much as the hydrogen atom is for the theory of multielectron atoms. On the other hand, this system has many applications, such as in the study of certain scattering problems and the characterization of plasma radiation.

Accurate calculations of the two-Coulomb-centre wavefunctions in the asymptotic region require formidable computational efforts [1]. A number of algorithms are now available which calculate the energy terms and wavefunctions for the Z_1eZ_2 quasi-molecule numerically, within a given accuracy, for both the same [2, 3, 4] and different [5, 6, 7] Coulomb centres.

In spite of the progress achieved in numerical calculations, the asymptotic methods used in different limiting cases play an important role. The reason is that the asymptotic methods yield results in an analytical form, while the usual numerical methods require formidable computational efforts, and the asymptotic methods provide results useful in the appropriate regions to check and replace the difficult numerical methods.

The two-Coulomb-centre problem also was investigated in the relativistic case [8], study of exchange interactions in molecular ion dimers [9], at small intercenter distances in two-dimensional [10] and arbitrary dimensional [11] cases.

The energy terms for the Z_1eZ_2 quasi-molecule can be expanded for large distances R between the Coulomb centres by the sum of asymptotic expressions of two types. Energy requires the so-called long-distance interaction terms (proportional to different powers of $1/R$), which describe the interaction of charge $Z_1(Z_2)$ with the multipole moments of the hydrogen-like ion and exponentially small terms that describe the exchange interaction between nucleus and the hydrogen-like ion. Despite smallness, the exponential terms are of significance when two energy terms of the system $Z_1\mathrm{e}Z_2$ pseudo-cross each other at finite R, or when symmetric and antisymmetric terms converge as $R \to \infty$. An asymptotic expression for the exchange interaction is more difficult to obtain than is the long-distance one, because perturbation theory is not valid for the calculation of exchange interactions [12].

2. Basic equations

The motion of the electron in the field of two fixed nuclei with charges Z_1 and Z_2 is described by the following Schrödinger equation:

$$\left(-\frac{1}{2}\Delta - \frac{Z_1}{r_1} - \frac{Z_2}{r_2}\right)\Phi(\vec{r},R) = E(R)\Phi(\vec{r},R) \tag{1}$$

where r_1 and r_2 are the distances from the electron to nuclei 1 and 2, $E(R)$ is the electron energy and R is the distance between the nuclei. The Schrödinger equation (1) is separable in the prolate spheroidal coordinates:

$$\begin{aligned} &\xi = \frac{r_1+r_2}{R}, \quad &&\eta = \frac{r_1-r_2}{R}, \quad &&\varphi = \arctan\left(\frac{y}{x}\right), \\ &\xi \in [1;\infty], &&\eta \in [-1;1], &&\varphi \in [0;2\pi]. \end{aligned} \tag{2}$$

If we replace the wave function $\Phi(\vec{r},R)$ by the product function

$$\Phi(\vec{r},R) = X(\xi,R)Y(\eta,R)\frac{e^{\pm im\varphi}}{\sqrt{2\pi}} \tag{3}$$

we obtain the quasiradial and quasiangular equations $X(\xi,R)$ and $Y(\eta,R)$

$$\frac{d}{d\xi}\left(\xi^2-1\right)\frac{dX}{d\xi} + \left[\lambda_\xi + \frac{ER^2}{2}\left(\xi^2-1\right) + \left(Z_1+Z_2\right)R\xi - \frac{m^2}{\xi^2-1}\right]X = 0, \tag{4}$$

$$\frac{d}{d\eta}\left(1-\eta^2\right)\frac{dY}{d\eta} + \left[-\lambda_\eta + \frac{ER^2}{2}\left(1-\eta^2\right) - \left(Z_1-Z_2\right)R\eta - \frac{m^2}{1-\eta^2}\right]Y = 0. \tag{5}$$

Here λ_ξ and λ_η are the separation constants on R, and m is the modulus of the magnetic quantum number. The two one-dimensional equations (4) and (5) are equivalent to the original Schrödinger equation provided the separation constants are equal:

$$\lambda_\xi = \lambda_\eta. \tag{6}$$

Let us use the new functions

$$U(\xi) = (\xi^2 - 1)^{\frac{1}{2}} X(\xi, R), \qquad V(\eta) = (1 - \eta^2)^{\frac{1}{2}} Y(\eta, R)$$

and introduce new variables

$$\rho_1 = \gamma R(\xi - 1), \quad \rho_1 \in [0, \infty]; \quad \rho_2 = \gamma R(1 + \eta), \quad \rho_2 \in [0, 2\gamma R]$$

where $\gamma = (-2E)^{1/2}$. In the terms of new variables we can rewrite equations (4) and (5) in the following form:

$$\begin{aligned} U''(\rho_1) + \Bigg[-\frac{1}{4} + \left(\frac{Z_1 + Z_2 + \lambda_\xi/R}{2\gamma} - \frac{1 - m^2}{4\gamma R} \right) \frac{1}{\rho_1} + \frac{1 - m^2}{4\rho_1^2} \\ + \left(\frac{Z_1 + Z_2 - \lambda_\xi/R}{4\gamma^2 R} + \frac{1 - m^2}{8\gamma^2 R^2} \right) \frac{1}{1 + \rho_1/2\gamma R} \\ + \frac{1 - m^2}{16\gamma^2 R^2} \frac{1}{(1 + \rho_1/2\gamma R)^2} \Bigg] U(\rho_1) = 0, \end{aligned} \tag{7}$$

$$\begin{aligned} V''(\rho_2) + \Bigg[-\frac{1}{4} + \left(\frac{Z_1 - Z_2 - \lambda_\eta R}{2\gamma} + \frac{1 - m^2}{4\gamma R} \right) \frac{1}{\rho_2} + \frac{1 - m^2}{4\rho_2^2} \\ - \left(\frac{Z_1 - Z_2 + \lambda_\xi/R}{4\gamma^2 R} - \frac{1 - m^2}{8\gamma^2 R^2} \right) \frac{1}{1 - \rho_2/2\gamma R} \\ + \frac{1 - m^2}{16\gamma^2 R^2} \frac{1}{(1 - \rho_2/2\gamma R)^2} \Bigg] V(\rho_2) = 0. \end{aligned} \tag{8}$$

When R is much larger than the size of electron shells centred on the left-hand nucleus ($R \gg r_n < 2n^2/Z_1$, where n is the principal quantum number), the ratios ρ_1/R and ρ_2/R are small quantities in intra-atomic space ($\rho_1, \rho_2 < r_n$). This fact allow us to use the perturbation theory to equations (7) and (8) in intra-atomic space to find the separation constants $\lambda_\xi, \lambda_\eta$ and energetic parameter γ.

3. Perturbation theory

Let us assume that when R tends to infinity, λ has the same order as R. Then in a zero-order approximation (i.e. at $R = \infty$) the equation (7) takes the following form:

$$u''^{(0)}(\rho_1) + \left[-\frac{1}{4} + \frac{\varkappa_1}{\rho_1} + \frac{1 - m^2}{4\rho_1^2} \right] u^{(0)}(\rho_1) = 0 \tag{9}$$

where

$$\varkappa_1 = \frac{Z_1 + Z_2 + \lambda^{(0)}/R}{2\gamma}.$$

The solution of (9) satisfying the boundary condition when $\rho_1 \to 0$ is

$$u^{(0)}(\rho_1) = N_1^{(0)} \exp(-\rho_1/2) \, \rho_1^{(m+1)/2} F\left(\frac{m+1}{2} - \varkappa_1, m + 1, \rho_1 \right) \tag{10}$$

where $N_1^{(0)}$ is the normalization constant, which is determined from the condition

$$\int_0^\infty |u^{(0)}(\rho_1)|^2 d\rho_1 = 1 \quad \Rightarrow \quad N_1^{(0)} = \left[\frac{(n_1+m)!}{n_1!\,(m!)^2\,(2n_1+m+1)}\right]^{1/2}$$

and $F(\alpha, \beta\, x)$ is the confluent hypergeometric function. For the solution (10) to satisfy the boundary condition at infinity, the parameter $(m+1)/2 - \varkappa_1$ should be equal to zero or a negative integer $(m+1)/2 - \varkappa_1 = -n_1, (n_1 = 0, 1, 2, ...)$. Hence for the separation constant $\lambda^{(0)}(R)$ we obtain

$$\lambda_{n_1}^{(0)}(R) = R[\gamma(2n_1+m+1) - (Z_1+Z_2)].$$

To find the solution at large but finite values of the parameter R, we shall use the perturbation theory. In equation (7), we shall consider the energy as a parameter with a certain given value and the separation constant λ as an eigenvalue of the corresponding operator. Then the computation of the corrections to the eigenvalue and eigenfunction acquires a standard character. We expand the desired wavefunction $U(\rho_1)$ to the unperturbed wavefunctions $u_{n_1}^{(0)}(\rho_1)$ series:

$$U(\rho_1) = \sum_{n_1'} c_{n_1'}(R) u_{n_1'}^{(0)}(\rho_1).$$

Substituting this expansion into (7), multiplying the obtained equality by $u_{n_1}^{(0)*}$ and integrating, we find

$$\left(\lambda - \lambda_{n_1'}^{(0)} - \frac{1-m^2}{2}\right) \langle n_1'|\rho_1^{-1}|n_1'\rangle\, c_{n_1'}$$
$$= \sum_{k=0}^{\infty} \frac{(-1)^{k+1}}{(2\gamma R)^k} \left[\frac{Z_1+Z_2-\lambda/R}{2\gamma} + (k+3)\,\frac{1-m^2}{8\gamma R}\right] \sum_{n_1''} \langle n_1'|\rho_1^k|n_1''\rangle c_{n_1''}. \quad (11)$$

Here the matrix elements of the operator $1/\rho_1$ are diagonal. Relation (11) allows us to calculate any order of corrections to the eigenvalue and eigenfunction.

Let us express the separation constant and expansion coefficient in the following forms

$$\lambda = \lambda^{(0)} + \lambda^{(1)} + \lambda^{(2)} + ... \qquad c_{n_1'} = c_{n_1'}^{(0)} + c_{n_1'}^{(1)} + c_{n_1'}^{(2)} + ...$$

Here $\lambda^{(k)}$ and $c_{n_1'}^{(k)}$ are the values of the R^{-k+1} and R^{-k} orders respectively.

To determine the corrections to the nth eigenvalue and eigenfunction, we put $c_{n_1}^{(0)} = 1$ and $c_{n_1'}^{(0)} = 0$. To find the first-order approximation, we substitute $\lambda = \lambda^{(0)} + \lambda^{(1)}$ and $c_{n_1'} = c_{n_1'}^{(0)} + c_{n_1'}^{(1)}$ into equation (11) and we kept only the terms of order one. The obtained equation with $n_1' = n_1$ gives

$$\lambda_{n_1}^{(1)} = \frac{1}{2}\left[(2n_1+m+1)(2n_1+m+1 - \frac{2(Z_1+Z_2)}{\gamma}) + 1 - m^2\right].$$

Equation (11) with $n_1' \neq n_1$ for the coefficients $c^{(1)}_{n_1'}$ gives us

$$c^{(1)}_{n_1'} = \frac{1}{4\gamma R(n_1 - n_1')} \left[2n_1 + m + 1 - \frac{2(Z_1 + Z_2)}{\gamma}\right] \frac{\langle n_1'|\rho_1^0|n_1\rangle}{\langle n_1'|\rho_1^{-1}|n_1'\rangle}.$$

All other coefficients and separation constants we can find in the same way. Matrix elements are calculated in standard way. Here we give the values of some of them:

$$\langle n_1|\rho_1^{-1}|n_1\rangle = \frac{1}{2n_1 + m + 1} \qquad \langle n_1|\rho_1^0|n_1\rangle = 1$$

$$\langle n_1|\rho_1^1|n_1\rangle = \frac{6n_1(n_1 + m + 1) + (m + 1)(m + 2)}{2n_1 + m + 1}$$

$$\langle n_1 - 1|\rho_1^0|n_1\rangle = \langle n_1 - 1|\rho_1^0|n_1\rangle = -\left(\frac{n_1(n_1 + m)}{(2n_1 + m + 1)(2n_1 + m - 1)}\right)^{1/2}$$

$$\langle n_1 + 1|\rho_1^0|n_1\rangle = \langle n_1 + 1|\rho_1^0|n_1\rangle = -\left(\frac{(n_1 + 1)(n_1 + m + 1)}{(2n_1 + m + 1)(2n_1 + m + 3)}\right)^{1/2}$$

$$\langle n_1 - 1|\rho_1^1|n_1\rangle = \langle n_1 - 1|\rho_1^0|n_1\rangle = -2\left(\frac{n_1(n_1 + m)(2n_1 + m)^2}{(2n_1 + m + 1)(2n_1 + m - 1)}\right)^{1/2}$$

$$\langle n_1 + 1|\rho_1^1|n_1\rangle = \langle n_1 + 1|\rho_1^0|n_1\rangle = -2\left(\frac{(n_1 + 1)(n_1 + m + 1)(2n_1 + m + 2)^2}{(2n_1 + m + 1)(2n_1 + m + 3)}\right)^{1/2}$$

In the quasiangular case the situation is similar to quasiradial one – all of the formulae will work if we change the sign of R and Z_2 and also replace the parabolic quantum number n_1 by n_2. Note that the upper limit of the variable ρ_2 is $2\gamma R$, but if R is large, the $2\gamma R$ is also large, and we can extend the upper limit of the variable ρ_2 to infinity. The replacement of $2\gamma R$ by infinity corresponds to the calculations of the integrals with the accuracy of the exponentially small terms when determining the matrix elements.

After calculations we get the separation constants in the form

$$\lambda_{\xi,\eta} = \pm\lambda^{(0)}_{\xi,\eta} R + \lambda^{(1)}_{\xi,\eta} \pm \frac{\lambda^{(2)}_{\xi,\eta}}{R} + \ldots \tag{12}$$

where

$$\lambda^{(0)}_{\xi,\eta} = \gamma(2n_{1,2} + m + 1) - (Z_1 \pm Z_2)$$
$$\lambda^{(1)}_{\xi,\eta} = \frac{1}{2}\left[(2n_{1,2} + m + 1)(2n_{1,2} + m + 1 - 2(Z_1 \pm Z_2)/\gamma) + 1 - m^2\right]$$
$$\lambda^{(2)}_{\xi,\eta} = \frac{1}{8\gamma}\left\{\left(2n_{1,2} + m + 1 - \frac{2(Z_1 \pm Z_2)}{\gamma}\right)\left[(2n_{1,2} + m + 1)\frac{2(Z_1 \pm Z_2)}{\gamma}\right.\right.$$
$$\left.\left. -8n_{1,2}\left(n_{1,2} + m + 1\right) - (m + 1)(m + 3)\right] - (2n_{1,2} + m + 1)\left(1 - m^2\right)\right\} \tag{13}$$

where n_1, n_2 and m are parabolic quantum numbers.

The parameter γ can be determined from the (6). Taking into consideration that $n_1 + n_2 + m + 1 = n$ we get

$$\gamma = \gamma_0 + \frac{\gamma_1}{R} + \frac{\gamma_2}{R^2} + \ldots \tag{14}$$

where

$$\gamma_0 = \frac{Z_1}{n}, \qquad \gamma_1 = \frac{nZ_2}{Z_1},$$
$$\gamma_2 = -\frac{n^2 Z_2}{2Z_1^3}\left[3(n_1 - n_2)Z_1 + nZ_2\right]. \tag{15}$$

As we mentioned above, $E = -\gamma^2/2$, so energy E and (14) give the well known [1] multipole expansion for the energy of hydrogen-like ion eZ_1 being perturbed by the remote nucleus Z_2.

Using (14) and (15) we can write the expression for the separation constant in form

$$\lambda_{n_1,n_2,m}(R) = \lambda_0 R + \lambda_1 + \frac{\lambda_2}{R} + \ldots \tag{16}$$

where

$$\begin{aligned}
\lambda_0 &= \frac{Z_1}{n}(n_1 - n_2) - Z_2, \\
\lambda_1 &= -2n_1 n_2 - (m+1)(n-1), \\
\lambda_2 &= \frac{n}{2Z_1^2}\{(n_1 - n_2)[2n_1 n_2 + (m+1)(n-1)]Z_1 \\
&+ n[3(m+1)(n_1 + n_2) + 6n_1 n_2 + (m+1)(m+2)]Z_2\}.
\end{aligned} \tag{17}$$

We note that the right-hand-side state is given by the above formulae if Z_1 is replaced by Z_2, and the parabolic quantum numbers n_1, n_2 are replaced by the right-hand-side parabolic quantum numbers n_1', n_2', that satisfy the condition $n_1' + n_2' + m + 1 = n'$.

4. Asymptotic spheroidal wavefunctions

Now we can determine the eigenfunctions of quasiradial (7) and quasiangular (8) equations in the region $0 \le \rho_1 < 2\gamma R$ and $0 \le \rho_2 < 2\gamma R$, when $R \gg 2n^2/Z_1$.

After some simple transformations, we rewrite (7) and (8) as follows:

$$U'' + \left[-\frac{\alpha_1^2}{4} + \frac{\beta_1}{\rho_1} + \frac{1-m^2}{4\rho_1^2} - \frac{Z_1 + Z_2 - \lambda/R}{4\gamma^2 R}\frac{\rho_1/2\gamma R}{1 + \rho_1/2\gamma R} - \frac{1-m^2}{8\gamma^2 R^2}\frac{\rho_1/\gamma R + 3\rho_1^2/8\gamma^2 R^2}{(1+\rho_1/2\gamma R)^2}\right] U = 0 \tag{18}$$

$$V'' + \left[-\frac{\alpha_2^2}{4} + \frac{\beta_2}{\rho_2} + \frac{1-m^2}{4\rho_2^2} - \frac{Z_1 - Z_2 + \lambda/R}{4\gamma^2 R}\frac{\rho_2/2\gamma R}{1 - \rho_2/2\gamma R} + \frac{1-m^2}{8\gamma^2 R^2}\frac{\rho_2/\gamma R - 3\rho_2^2/8\gamma^2 R^2}{(1-\rho_2/2\gamma R)^2}\right] V = 0 \tag{19}$$

where

$$\alpha_{1,2} = \left[1 \mp \frac{Z_1 \pm Z_2 \mp \lambda/R}{\gamma^2 R} - \frac{3(1-m^2)}{4\gamma^2 R^2}\right]^{1/2} \simeq 1 \mp \frac{A_{1,2}}{2\gamma_0 R} + \frac{B_{1,2}}{8\gamma_0^2 R^2} + \frac{C_{1,2}}{16\gamma_0^3 R^3} + \dots$$

$$\beta_{1,2} = \frac{Z_1 \pm Z_2 \pm \lambda/R}{2\gamma} \mp \frac{1-m^2}{4\gamma R} \simeq \frac{2n_1+m+1}{2} - \frac{A_1(2n_1+m+1)}{4\gamma_0 R} + \dots$$

where

$$A_{1,2} = 2n_{2,1} + m + 1 \pm 2\gamma_1$$
$$B_{1,2} = 4\lambda_1 - 3(1-m^2) - A_{1,2}^2 \pm 8\gamma_1 A_{1,2}$$
$$C_{1,2} = A_{1,2}B_{1,2} + 4\left(2A_{1,2}(2\gamma_0\gamma_2 - 3\gamma_1^2) \mp \gamma_1(4\lambda_1 - 3(1-m^2)) \pm 2\gamma_0\lambda_2\right).$$

If we neglect the last two terms in the square brackets of (18) and (19), we obtain the Whittaker equation. The solution regular at $\rho_{1,2} = 0$ is

$$\rho_{1,2}^{\frac{m+1}{2}} e^{-\frac{\alpha_{1,2}\rho_{1,2}}{2}} F\left(-\sigma_{1,2} + \frac{m+1}{2}, m+1, \alpha_{1,2}\rho_{1,2}\right)$$

where $\sigma_{1,2} = \beta_{1,2}/\alpha_{1,2}$. Let us find the solutions of (18) and (19) as a product

$$U_{n_1}(\rho_1) = M_{n_1}(\rho_1) f_{n_1}(\rho_1), \tag{20}$$
$$V_{n_2}(\rho_2) = M_{n_2}(\rho_2) f_{n_2}(\rho_2). \tag{21}$$

where

$$M_{n_{1,2}}(\rho_{1,2}) = \rho_{1,2}^{\frac{m+1}{2}} e^{-\frac{\alpha_{1,2}\rho_{1,2}}{2}} F\left(-n_{1,2}, m+1, \alpha_{1,2}\rho_{1,2}\right) \tag{22}$$

Substituting (20) and (21) to (18) and (19) for functions $f_{n_{1,2}}(\rho_{1,2})$ we get the equations

$$f''_{n_{1,2}} + \frac{2M'_{n_{1,2}}}{M_{n_{1,2}}} f'_{n_{1,2}} - \left[\frac{Z_1 \pm Z_2 \mp \lambda/R}{4\gamma^2 R} \frac{\rho_{1,2}/2\gamma R}{1 \pm \rho_{1,2}/2\gamma R} - \frac{A_{1,2}a_{1,2}}{8\gamma_0^2 R^2} \frac{1}{\rho_{1,2}} \pm \frac{1-m^2}{8\gamma^2 R^2} \frac{\rho_{1,2}/\gamma R \pm 3\rho_{1,2}^2/8\gamma^2 R^2}{(1 \pm \rho_{1,2}/2\gamma R)^2}\right] f_{n_{1,2}} = 0. \tag{23}$$

Here $a_{1,2} = 6n_{1,2}(n_{1,2}+m+1) + (m+1)(m+2)$.

The fraction $\rho_{1,2}/\gamma R$ appearing in (23) is $O(R^{-1})$ when $\rho_{1,2} < r_n$ and $O(R^0)$ when $\rho_{1,2} \sim R$. This means that to $O(R^{-2})$ equation has different asymptotic forms inside and outside the intra-atomic region. To overcome this difficulty, we consider separately the two regions $0 \le \rho_{1,2} < r_n \approx \sqrt{2\gamma R}$ and $\sqrt{2\gamma R} < \rho_{1,2} < 2\gamma R$.

In the region $0 \le \rho_{1,2} < \sqrt{2\gamma R}$ the ratio of $\rho_{1,2}/\gamma R$ is a small quantity. That's why we can expand the expression in the square brackets of (23) in powers of $\rho_{1,2}/\gamma R$. We will have the equation

$$f''_{n_{1,2}} + \frac{2M'_{n_{1,2}}}{M_{n_{1,2}}} f'_{n_{1,2}} - \left(\frac{A_{1,2}}{8\gamma_0^2 R^2} K_{1,2}(\rho_{1,2}) \pm \frac{1-m^2-\lambda_1}{8\gamma_0^3 R^3}\rho_{1,2}\right) f_{n_{1,2}} = 0 \tag{24}$$

Here

$$K_{1,2}(\rho_{1,2}) = \left(1 - \frac{3\gamma_1}{\gamma_0 R}\right)\rho_{1,2} \mp \frac{\rho_{1,2}^2}{2\gamma_0 R} + \frac{\rho_{1,2}^3}{4\gamma_0^2 R^2} - \frac{a_{1,2}}{\rho_{1,2}}.$$

The solution of (24) is

$$f_{n_{1,2}}(\rho_{1,2}) = \exp\left(\int^{\rho_{1,2}} M_{n_{1,2}}^{-2}(\rho'_{1,2}) \int^{\rho'_{1,2}} P_{1,2}(\rho''_{1,2}) M_{n_{1,2}}^2(\rho''_{1,2}) d\rho''_{1,2} d\rho'_{1,2}\right) \quad (25)$$

where

$$P_{1,2}(\rho''_{1,2}) = \frac{A_{1,2}}{8\gamma_0^2 R^2} G_{1,2}(\rho''_{1,2}) \pm \frac{1 - m^2 - \lambda_1}{8\gamma_0^3 R^3}\rho''_{1,2}.$$

In the region $\sqrt{2\gamma R} < \rho_{1,2} < 2\gamma R$ our wavefunctions can be constructed using iterative method. For this region we expand the function $f_{n_{1,2}}(\rho_{1,2})$ in equations (23) using the well known [13] expansion for the confluent hypergeometric function:

$$F(-n_{1,2}, m+1, \alpha_{1,2}\rho_{1,2}) = \frac{m!(-\alpha_{1,2}\rho_{1,2})^{n_{1,2}}}{(n_{1,2}+m)!} G(-n_{1,2}, -n_{1,2}-m, -\alpha_{1,2}\rho_{1,2})$$

where

$$G(-\alpha_{1,2}\rho_{1,2}) = 1 - \frac{n_{1,2}(n_{1,2}+m)}{1!(\alpha_{1,2}\rho_{1,2})} + \frac{n_{1,2}(n_{1,2}-1)(n_{1,2}+m)(n_{1,2}+m+1)}{2!(\alpha_{1,2}\rho_{1,2})^2} - \dots$$

Using this expansion we can write

$$\frac{2M'_{n_{1,2}}(\rho_{1,2})}{M_{n_{1,2}}(\rho_{1,2})} = -\alpha_{1,2} + \frac{2n_{1,2}+m+1}{\rho_{1,2}} + \frac{2n_{1,2}(n_{1,2}+m)}{\rho_{1,2}^2} + \dots \quad (26)$$

and the desired functions $f_{n_{1,2}}(\rho_{1,2})$ in the region $\sqrt{2\gamma R} < \rho_{1,2} < 2\gamma R$ satisfying the equations

$$\begin{aligned} f''_{n_{1,2}} &+ \left(-\alpha_{1,2} + \frac{2n_{1,2}+m+1}{\rho_{1,2}} + \frac{2n_{1,2}(n_{1,2}+m)}{\rho_{1,2}^2}\right) f'_{n_{1,2}} \\ &- \left[\frac{Z_1 \pm Z_2 \mp \lambda/R}{4\gamma^2 R} \frac{\rho_{1,2}/2\gamma R}{1 \pm \rho_{1,2}/2\gamma R} - \frac{a_{1,2}A_{1,2}}{8\gamma_0^2 R^2}\frac{1}{\rho_{1,2}}\right. \\ &\left.\pm \frac{1-m^2}{8\gamma^2 R^2} \frac{\rho_{1,2}/\gamma R \pm 3\rho_{1,2}^2/8\gamma^2 R^2}{(1 \pm \rho_{1,2}/2\gamma R)^2}\right] f_{n_{1,2}} = 0. \end{aligned} \quad (27)$$

We seek the solutions of the last equation as a series

$$f_{n_{1,2}}(\rho_{1,2}) = f_{n_{1,2}}^{(0)}(\rho_{1,2}) + f_{n_{1,2}}^{(1)}(\rho_{1,2}) + f_{n_{1,2}}^{(2)}(\rho_{1,2}) + \dots$$

where $f_{n_{1,2}}^{(k)}(\rho_{1,2})$ is of order R^{-k}. Substituting this expansion and expansions (12) and (14) to (27) and keeping only terms, which proportional to R^{-1} we get the equation

$$f_{n_{1,2}}^{(0)\prime}(\rho_{1,2}) + \frac{A_{1,2}}{4\gamma_0 R}\frac{\rho_{1,2}/2\gamma_0 R}{1 \pm \rho_{1,2}/2\gamma_0 R} f_{n_{1,2}}^{(0)}(\rho_{1,2}) = 0,$$

which solution is

$$f^{(0)}_{n_{1,2}}(\rho_{1,2}) = \left[1 \pm \frac{\rho_{1,2}}{2\gamma_0 R}\right]^{A_{1,2}/2} \exp\left(\mp\frac{A_{1,2}\rho_{1,2}}{4\gamma_0 R}\right). \qquad (28)$$

The equations for $f^{(1)}_{n_{1,2}}(\rho_{1,2})$ and $f^{(2)}_{n_{1,2}}(\rho_{1,2})$ we can obtain keeping the terms which are proportional to R^{-2} and R^{-3}. All of these equations will be linear nonhomogeneous differential equations of the first order. After integrating them, we have

$$f_{n_{1,2}}(\rho_{1,2}) = f^{(0)}_{n_{1,2}}(\rho_{1,2}) \left[1 + \frac{S_{1,2}(\rho_{1,2})}{2\gamma_0 R} + \frac{T_{1,2}(\rho_{1,2})}{4\gamma_0^2 R^2}\right] \qquad (29)$$

where

$$S_{1,2}(\rho_{1,2}) = \frac{B_{1,2}}{4}\frac{\rho_{1,2}}{2\gamma_0 R} - 2\gamma_1(n \pm \gamma_1)\ln\chi_{1,2} \mp [n_{2,1}(n_{2,1}+m) - \gamma_1(1 \mp \gamma_1)]\frac{1}{\chi_{1,2}},$$

$$T_{1,2}(\rho_{1,2}) = \frac{B_{1,2}^2}{32}\frac{\rho_{1,2}^2}{4\gamma_0^2 R^2} \pm \frac{C_{1,2}}{4}\frac{\rho_{1,2}}{2\gamma_0 R} + 2\gamma_1^2(n \pm \gamma_1)^2 \ln^2\chi_{1,2}$$
$$\pm 2\gamma_1(n \pm \gamma_1)(n_{2,1}(n_{2,1}+m) \mp \gamma_1(1 \pm \gamma_1))\frac{\ln\chi_{1,2}}{\chi_{1,2}}$$
$$\pm \gamma_1(n \pm \gamma_1)\left[6(\gamma_1 \pm (n_1 - n_2)) - \frac{B_{1,2}}{2}\frac{\rho_{1,2}}{2\gamma_0 R}\right]\ln\chi_{1,2} + \frac{P_{1,2}}{\chi_{1,2}} + \frac{Q_{1,2}}{\chi_{1,2}^2},$$
$$\chi_{1,2} = 1 \pm \frac{\rho_{1,2}}{2\gamma_0 R},$$

$$P_{1,2} = [n_{2,1}(n_{2,1}+m) \mp \gamma_1(1 \pm \gamma_1)]\left(\frac{B_{1,2}}{4} + 2n_{1,2} + m + 1\right)$$
$$\pm 2\gamma_1(n \pm \gamma_1)(2n_{1,2} + m \pm 2\gamma_1) - 2A_{1,2}(\gamma_1^2 - \gamma_0\gamma_2) \pm \gamma_1\left(n^2 - (n_1 - n_2)^2\right),$$

$$Q_{1,2} = \frac{1}{2}[(n_{2,1}(n_{2,1}+m) \mp \gamma_1(1 \pm \gamma_1))((n_{2,1}-1)(n_{2,1}+m-1) \mp \gamma_1(3 \pm \gamma_1))$$
$$-2A_{1,2}\gamma_1^2 \pm \gamma_1(1 - m^2)].$$

In the quasiangular case these formulae are invalid for $\rho_2 \approx 2\gamma_0 R$ (in close vicinity to nucleus Z_2), where $1/(1 - \rho_2/2\gamma_0 R)$ is not a quantity of the order of unity but is greater, although it should be noted that the width of this "prohibited" region is small in comparison with the whole region $[0; 2\gamma R]$, and, besides, the wavefunctions corresponding to the left-hand-side state are extremely small there.

5. Conclusions

The quasiradial and quasiangular wavefunctions are derived for the electron moving in the field of two Coulomb centres with arbitrary charges, Z_1 and Z_2, when the distance between the centres is large.

The two-Coulomb-centre wavefunctions of the symmetric quasi-molecule $Z_1 e Z_2$ are either the sum or the difference of the wavefunctions centred on the left- and right-hand nuclei. The non-symmetric ($Z_1 \neq Z_2$) but resonance case ($Z_1/n = Z_2/n'$) needs special consideration.

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