



Asymptotics of the two-centre wave function in the spheroidal and spherical bases

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Abstract

The first two terms of the asymptotics (for large internuclear distances R) of the spheroidal wave function of the two-Coulomb-center problem are calculated both in the internuclear region and in the vicinity of each of centers. In the spherical basis, the general formula is obtained for the expansion of a two-center wave function of the left center in two-center spheroidal wave functions. Using this formula, the asymptotics of the two-center wave function in a spherical basis is calculated, which in boundary cases is compared with the results of other authors. The combined use of the approach developed in this paper and the Holstein-Herring method made it possible for the first time to calculate the term proportional to R^{-2} of the asymptotic expansion of the quasimolecule energy in spherical quantum numbers.

1 Introduction

The problem of the motion of a charged particle (electron, muon) in the field of two fixed positive (fixed) Coulomb centers Z_1 and Z_2 located at a distance R from each other (the so-called Z_1eZ_2 problem) is an important model in study of many elementary collision processes of multy-electron atoms and ions: excitation, charge exchange, ionization. In the theory of the structure and spectra of molecules, it plays the same fundamental role as the hydrogen atom problem in the theory of atom. However, unlike the latter, the two-Coulomb-center problem has no solutions in a closed analytical form for arbitrary values of Z_1 , Z_2 , R and quantum numbers. Its exact solution is possible to be obtained by means of only numerical methods. Nevertheless, it is analytically possible to obtain results in the limiting cases of large and small internuclear distances. Historical reviews and an extensive list of bibliographic references to works devoted to the study of the discrete and continuous spectra of the system Z_1eZ_2 and the asymptotic properties of two-center Coulomb spheroidal functions for large and small R are given in the monograph [1] and recent publications [2, 3, 4, 5, 6].

Despite the visibility of the relative simplicity and completeness of the Z_1eZ_2 system research, works devoted to identifying some of the previously unnoticed features of the Z_1eZ_2 problem and to improving the methods for its solving (see,

for example, [2, 3, 4, 5, 6, 7, 8, 9]) continue to appear. In connection with the development of quantum information systems [10, 11, 12] and frequency-time standards of the new generation [13, 14], in recent years, highly excited (Rydberg) states of Z_1eZ_2 system are of particular interest whose study require application of methods developed specifically for problems with a randomly degenerate energy spectrum of unperturbed system [3, 9, 15]. Results of such studies are also of general theoretical interest (important from a general theoretical point of view), since On many grounds, highly excited states of the Z_1eZ_2 system are an intermediate link between states of the continuous spectrum and the ground or low-lying excited states of the two-Coulomb-center problem.

When solving many problems arising in the physics of slow atomic collisions, for example, in order to calculate the two-electron exchange interaction of an excited hydrogen atom with the ion [16], to determine the shape of the nodal surfaces of two-center systems [17], etc., it is necessary to know the two-Coulomb-center spheroidal radial and angular wave functions not only in the main region of the spatial distribution of the electron density but also in the vicinity of the second Coulomb center, where they are strongly perturbed by this center. Until now, the asymptotic behavior of such wave functions was constructed only in the zeroth approximation in $1/R$ [17] and there was no method to consistently find higher approximations.

Additionally, it is worth to note here that the spheroidal basis is only suitable for the wave functions of the problem of two purely Coulomb centers. In interactions with the participation of many-electron atoms/ions, the wave functions are constructed in the spherical quantum numbers. If in the left center region and internuclear region, the asymptotic behavior of such wave functions was repeatedly constructed, for example, using the Holstein-Herring method [18, 19, 20], in the region of the right center, only Chibisov's result [18, 21] exists, where the wave function was calculated only in zero order of R^{-1} using the matching method in the case of the pure Coulomb center Z_2 , and the Green function method in the case of the non-Coulomb center.

2 Basic equations

The motion of an electron in the field of two positive charges Z_1 and Z_2 , fixed at a distance R from each other is described by the following Schrödinger equation ($\hbar = e = m_e = 1$):

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

where r_1 and r_2 are the distances from the electron to the corresponding charges, $E(R)$ is the energy of an electron. The Schrödinger equation (1) permits complete separation of variables in the prolate spheroidal coordinates

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

where x, y, z are the Cartesian coordinates of an electron (the z axis coincides with the internuclear axis). Replacing the wave function $\Psi(\vec{r}, R)$ by the product function

$$\Psi(\vec{r}, R) = \frac{U(\xi, R) V(\eta, R) e^{im\varphi}}{\sqrt{\xi^2 - 1} \sqrt{1 - \eta^2} \sqrt{2\pi}} = \frac{\psi(\xi, \eta, R) e^{\pm im\varphi}}{\sqrt{(\xi^2 - 1)(1 - \eta^2)} \sqrt{2\pi}} \quad (3)$$

and using new variables

$$\mu = \frac{R}{2}(\xi - 1), \quad \mu \in [0, \infty), \quad \nu = \frac{R}{2}(1 + \eta), \quad \nu \in [0, R], \quad (4)$$

we obtain the system of ordinary differential equations for the radial $U(\mu)$ and angular $V(\nu)$ Coulomb spheroidal functions:

$$U'' - \left[\gamma^2 - \frac{Z_1 + Z_2 + \lambda_1/R}{\mu} - \frac{Z_1 + Z_2 - \lambda_1/R}{R + \mu} + \frac{R^2(m^2 - 1)}{4\mu^2(R + \mu)^2} \right] U = 0, \quad (5)$$

$$V'' - \left[\gamma^2 - \frac{Z_1 - Z_2 - \lambda_2/R}{\nu} + \frac{Z_1 - Z_2 + \lambda_2/R}{R - \nu} + \frac{R^2(m^2 - 1)}{4\nu^2(R - \nu)^2} \right] V = 0, \quad (6)$$

where $\gamma = (-2E)^{1/2}$, m is the modulus of the magnetic quantum number, λ_1 and λ_2 are the separation constants depending on R . From a physical point of view, (5) and (6) are one-dimensional Schrödinger equations for two Coulomb and one centrifugal potentials.

Suppose that $U(\mu)$ and $V(\nu)$ satisfy the following boundary conditions:

$$U(0) = 0, \quad U(\mu) \xrightarrow{\mu \rightarrow \infty} 0, \quad V(0) = V(R) = 0. \quad (1)$$

The pair of the one-dimensional boundary value problems for the radial $U(\mu)$ and angular $V(\nu)$ Coulomb spheroidal functions is equivalent to the original problem (1) provided that the separation constants are equal: $\lambda_1 = \lambda_2$.

As it is known (see, for instance, [1, 2, 5, 17, 21, 22] and references therein), the form of the two-center wave function, or rather of its quasi-angular part, depends on the region of space in which the electron is located. In this paper, we denote the wave functions in the region of the left center, the internuclear region and the region of the right center (traditionally also called the alien center/core) by superscripts *I*, *II* and *III*, respectively (see Fig. 1). Below, we will construct the asymptotic expansions (in the large parameter R) for solving the Z_1eZ_2 problem in these three regions of the electron's motion and match them in the overlapping regions.

3 Asymptotics of the two-center wave function. Spheroidal basis

3.1 The region of the left center. When R is much larger than the size of electron shells centered on the left core, the ratios μ/R and ν/R are small values in the intraatomic region (here $r_1 \ll R$). This fact allows us to use the perturbation

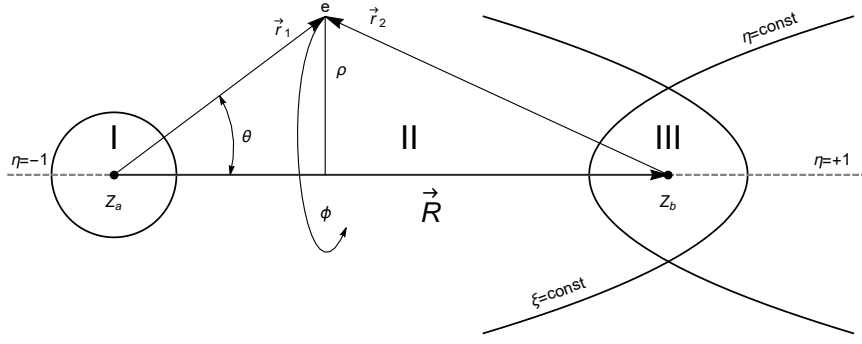


Figure 1: The separation of the space of electronic coordinates into the regions

theory for the equations (5) and (6) in the intraatomic region to find both the separation constant $\lambda_{1,2}$ and the asymptotics of the radial $U(\mu)$ and angular $V(\nu)$ wave functions.

Applying the standard instruments of the Rayleigh–Schrödinger perturbation theory leads to infinite sums of complicated form. In connection with this, perturbation theory schemes that allow finding analytic expressions were proposed in several papers [22, 23, 24]. One of these schemes was developed in [22]. Using it in the case of large internuclear distances R , we have obtained asymptotic expressions for the two-Coulomb-center quasiradial and quasiangular functions $U(\mu)$ and $V(\nu)$ up to terms of the third order in $1/R$ included [5]. In this paper, we restrict ourselves to the terms ~ 1 and $\sim 1/R$. In this approximation, the two-center wave function Ψ^I in the vicinity of the left center has the form (3), where [5, 25]

$$\psi^I(\mu, \nu, R) = C(R)U^I(\mu)V^I(\nu), \quad (2)$$

$$U^I(\mu) = f_{n_1}(\mu), \quad V^I(\nu) = f_{n_2}(\nu), \quad (3)$$

$$f_{n_i}(x) = \left[\frac{(n_i + |m|)!}{n_i!(|m|!)^2(2n_i + |m| + 1)} \right]^{1/2} e^{-\alpha_i \gamma x} (2\gamma x)^{\frac{|m|+1}{2}} F(-n_i, |m| + 1, 2\alpha_i \gamma x). \quad (4)$$

Here the parabolic quantum numbers n_1 and n_2 are related by the relation $n_1 + n_2 + |m| + 1 = n$, where n is the principal quantum number, $F(\alpha, \beta, z)$ is the confluent hypergeometric function, and the normalization coefficient is

$$C = \frac{4\sqrt{\gamma}}{R} \left[\frac{\alpha_1}{2n_1 + |m| + 1} + \frac{\alpha_2}{2n_2 + |m| + 1} \right]^{-1/2}, \quad (5)$$

where

$$\alpha_1 = \left[1 - \frac{Z_1 + Z_2 - \lambda/R}{\gamma^2 R} - \frac{3(1 - m^2)}{4\gamma^2 R^2} \right]^{1/2},$$

$$\alpha_2 = \left[1 + \frac{Z_1 - Z_2 + \lambda/R}{\gamma^2 R} - \frac{3(1 - m^2)}{4\gamma^2 R^2} \right]^{1/2}. \quad (6)$$

The energy parameter $\gamma = \sqrt{-2E}$ and the separation constant λ are equal

$$\gamma = \gamma_0 + \frac{\gamma_1}{R} + \frac{\gamma_2}{R^2}, \quad \lambda = \lambda_0 R + \lambda_1, \quad (7)$$

respectively, where

$$\gamma_0 = \frac{Z_1}{n}, \quad \gamma_1 = \frac{nZ_2}{Z_1}, \quad \gamma_2 = -\frac{n^2 Z_2}{2Z_1^3} [3(n_1 - n_2)Z_1 + nZ_2], \quad (8)$$

$$\lambda_0 = \frac{Z_1}{n}(n_1 - n_2) - Z_2, \quad \lambda_1 = -2n_1 n_2 - (|m| + 1)(n - 1). \quad (9)$$

Taking into account (7)-(9) expressions (5) and (6) are of the corresponding form

$$C = \frac{2\sqrt{2Z_1(2n_1 + |m| + 1)(2n_2 + |m| + 1)}}{nR} \left\{ 1 - \frac{n[(n_1 - n_2)Z_1 - 2nZ_2]}{2Z_1^2 R} \right\}, \quad (10)$$

$$\begin{aligned} \alpha_1 &= 1 - \frac{n[(n_1 - n_2 - n)Z_1 - 2nZ_2]}{2Z_1^2 R}, \quad \alpha_2 = 1 + \frac{n[(n_1 - n_2 + n)Z_1 - 2nZ_2]}{2Z_1^2 R} \\ &+ \frac{1}{8Z_1^4 R^2} [3(m^2 - 1)Z_1^4 - 4n^2 Z_1^2 ((|m| + 1)(n - 1) + 2n_1 n_2) \\ &- 8n^3 Z_2 ((n + n_1 - n_2)Z_1 - 2nZ_2) + n^2 ((n + n_1 - n_2)Z_1 - 2nZ_2)^2]. \end{aligned} \quad (11)$$

Note that the expansions of α_2 , γ and λ in R^{-1} are given here with more precision than the formula (2) requires. This is necessary to obtain a two-center wave function in *II* and *III* regions (see the following subsections below).

3.2 The internuclear region. As noted in [5], when the electron goes away from the left center, the quasi-radial wave function $U^I(\mu)$ contained in (2) retains its form, and formulas (3), (4), and the quasi-angular wave function $V^I(\nu)$ becomes inapplicable. Therefore, in the internuclear region ($r_{1,2} \sim R$), the quasi-angular equation (6) must be solved anew, using non-perturbative methods. For this, we can use the semiclassical WKB method developed in our work [5], which has a wide range of applicability. However, for our purposes that do not require high accuracy, it is more expedient to use the asymptotic Holstein-Herring method [26] (in the literature also called the Landau-Herring method or the corrective function method). This approach to the two-Coulomb-center problem was already used in [25], however, when receiving higher corrections to the solution of the quasi-angle equation, the error was made. Referring for details to the paper [25], we write out here only the corrected final result for the function $V(\nu)$ in the internuclear region:

$$\begin{aligned} V^{II}(\nu) &= V^{I(\text{as})}(\nu) \left(1 - \frac{\nu}{R} \right)^{\frac{Z_1 - Z_2 + \lambda/R}{2\alpha_2 \gamma}} \exp \left(\frac{Z_1 - Z_2 + \lambda/R}{2\alpha_2 \gamma R} \nu \right) \\ &\times \left\{ 1 + \frac{1}{4\gamma_0 R} \left[(k_2^2 - k_2 + m^2 - 1) \frac{\nu}{R - \nu} - (k_2^2 + 3m^2 - 3) \frac{\nu^2}{2R(R - \nu)} \right. \right. \\ &\left. \left. + ((2n_2 + |m| + 1)k_2 + m^2 - 1) \ln \left(1 - \frac{\nu}{R} \right) \right] + O(R^{-2}) \right\}, \end{aligned} \quad (12)$$

where $k_2 = (Z_1 - Z_2 + \lambda_0)/\gamma_0$, $V^{I(\text{as})}(\nu)$ is the asymptotic expansion of quasi-angular wave function $V^I(\nu)$ in ν^{-1} to within terms $O(\nu^{-2})$. Here the function $V^{II}(\nu)$ satisfies the boundary condition

$$V^{II}(\nu) \underset{\nu \sim \sqrt{R}}{=} V^{I(\text{as})}(\nu) [1 + O(R^{-2})]. \quad (13)$$

Note that if in the formula (12) instead of $V^{I(\text{as})}(\nu)$ use the exact expression of $V^I(\nu)$ from (3), then this formula will define the two-center quasi-radial wave function $V(\nu)$, valid in both regions I , II and satisfying the boundary condition

$$V^{II}(\nu) \xrightarrow{\nu \rightarrow 0} V^I(\nu) [1 + O(R^{-2})]. \quad (14)$$

3.3 The region of the right center. When approaching the right center, $U^I(mu)$ retains its behavior, and the quasi-angle wave function obtained in the internuclear domain (12) becomes singular, because $\nu \rightarrow R$. The solution of the quasi-angle equation (6) that is regular at $\nu = R$ can be obtained using the technique applied by Gershtein and Krivchenkov [17] in calculating the zeroth term of the asymptotic behavior in $1/R$ of quasi-angular wave function in the vicinity of right center. As a result, we get

$$V^{III}(\nu) = C_{III} e^{-\tilde{\alpha}_2 \gamma \tilde{\nu}} (2\gamma \tilde{\nu})^{\frac{|m|+1}{2}} F(-\tilde{n}_2, |m| + 1, 2\tilde{\alpha}_2 \gamma \tilde{\nu}), \quad (15)$$

where

$$\tilde{\nu} = R - \nu, \quad \tilde{n}_2 = n_2 + n \left(\frac{Z_2}{Z_1} - 1 \right) - \frac{Z_2(Z_2 - Z_1)}{\gamma_0^3 R}, \quad \tilde{\alpha}_2 = 1 + \frac{Z_2 - Z_1 + \lambda_0}{2\gamma_0^2 R}. \quad (16)$$

In zeroth order in $1/R$, expression (15) coincides with the result of Gershtein and Krivchenkov [17] up to the factor C_{III} , which is not defined in [17]. The normalization constant C_{III} can be found by matching the asymptotics of the functions V^{III} and V^{II} at a sufficient distance from the right center, i.e. in the region $\tilde{\nu} \sim \sqrt{R}$:

$$C_{III} = \frac{\Gamma(-\tilde{n}_2) (2\tilde{\alpha}_2 \gamma R)^{\tilde{n}_2 + |m| + 1} (-2\alpha_2 \gamma R)^{n_2}}{\sqrt{n_2! (|m|!)^2 (n_2 + |m|)! (2n_2 + |m| + 1)}} \times \exp \left[-\alpha_2 \gamma R + \frac{Z_1 - Z_2 + \lambda/R}{2\alpha_2 \gamma} - \frac{n_2(n_2 + |m|)}{2\gamma_0 R} \right]. \quad (17)$$

Summarizing up the results obtained in this section, we can assert that we managed to construct normalized two-center wave functions on a spheroidal basis, which in each of the three regions I , II , III have the following form:

$$\Psi_{n_1 n_2 m}^{I, II, III} = C(R) \frac{R^2}{4} \frac{U^I(\mu) V^{I, II, III}(\nu) e^{im\varphi}}{\sqrt{\mu(R + \mu)\nu(R - \nu)} \sqrt{2\pi}}. \quad (18)$$

Here, in the notation of two-center spheroidal wave functions, we used more convenient parabolic quantum numbers $\{n_1, n_2, m\}$, through which the spheroidal quantum numbers $\{n, q, m\}$ can always be expressed [1, 17].

4 Transition from spheroidal to spherical basis

Let us begin by considering a simpler problem — the quantum mechanical problem of the hydrogen atom, for which the Schrödinger equation is separable in spherical, parabolic, and spheroidal coordinates [27, 28, 29]. The transition between spherical and parabolic bases in the wave function of this problem is carried out using the well-known exact formulas [27, 29]. So, for example, the Coulomb spherical wave function ψ_{nlm}^{sph} can be represent through Coulomb parabolic functions $\psi_{n_1 n_2 m}^{par}$ using expressions [27, 29]

$$\psi_{nlm}^{sph} = (-1)^{l+\frac{m-|m|}{2}} \sum_{n_2=0}^{n-|m|-1} (-1)^{n_2} C_{\frac{n-1}{2}, \frac{n-1}{2}-n_2; \frac{n-1}{2}, |m|+n_2-\frac{n-1}{2}}^{l, |m|} \psi_{n_1 n_2 m}^{par}, \quad (19)$$

where $C_{j_1 m_1 j_2 m_2}^{j m}$ are the Clebsch-Gordan coefficients.

Also, the spheroidal basis can be expanded in the parabolic one:

$$\psi_{nqm}^{sphr} = \sum_{n_2=0}^{n-|m|-1} U_{nqm}^{n_2} \psi_{n_1 n_2 m}^{par}. \quad (20)$$

In the papers [28, 29], three-term recurrence relations were constructed for the coefficients $U_{nqm}^{n_2}$. If we restrict ourselves to the first two terms in the expansions of $U_{nqm}^{n_2}$ in R^{-1} , then we get

$$\begin{aligned} \psi_{nqm}^{sphr} = & \psi_{n_1 n_2 m}^{par} + \frac{\sqrt{n_1(n_1+|m|)(n_2+1)(n_2+|m|+1)}}{2\gamma_0 R} \psi_{n_1-1, n_2+1, m}^{par} \\ & - \frac{\sqrt{n_2(n_2+|m|)(n_1+1)(n_1+|m|+1)}}{2\gamma_0 R} \psi_{n_1+1, n_2-1, m}^{par} + O(R^{-2}). \end{aligned} \quad (21)$$

Obviously, there is the expansion inverse to (20) – the expansion of the parabolic basis in the spheroidal one, and, taking into account (19), the expansion of the spherical basis in the spheroidal one

$$\psi_{nlm}^{sph} = \sum_{n_2=0}^{n-|m|-1} \bar{U}_{n_1 n_2 m}^l \psi_{nqm}^{sphr}. \quad (22)$$

The coefficients $\bar{U}_{n_1 n_2 m}^l$ of the expansion (22) also satisfy certain three-term recurrent relations and can be calculated either approximately or numerically. Below we obtain them in the form of expansions in R^{-1} to within terms $O(R^{-2})$.

As is well known, [1], the spheroidal wave functions of the two-Coulomb-center problem at $R \rightarrow \infty$ are transformed to one-center ones and, accordingly, they can also be represented in both parabolic and spherical bases. Since for calculations of various matrix elements in the physics of slow ion-atomic collisions it is often necessary to know two-center wave functions in the spherical basis, we dwell on them.

Similarly to (22), we write the expansion of the two-center wave function in the spherical basis Φ_{nlm} in the two-center spheroidal wave functions $\Psi_{n_1 n_2 m}$ obtained in the previous section as follows

$$\Phi_{nlm} = \sum_{n_2=0}^{n-|m|-1} V_{n_1 n_2 m}^l \Psi_{n_1 n_2 m}, \quad (23)$$

where $V_{n_1 n_2 m}^l(R)$ are the coefficients to be determined. Although the type of the wave functions Ψ_{nlm} and $\Psi_{n_1 n_2 m}$ depends on the region of determination (*I*, *II*, *III*), the coefficients $V_{n_1 n_2 m}^l(R)$ in the formula (23) always remains constant. We will seek them in the form of expansions in R^{-1} :

$$V_{n_1 n_2 m}^l(R) = V_{n_1 n_2 m}^{l(0)} + \frac{V_{n_1 n_2 m}^{l(1)}}{R} + \frac{V_{n_1 n_2 m}^{l(2)}}{R^2} + \dots, \quad (24)$$

where the expansion coefficients $V_{n_1 n_2 m}^{l(i)}$ ($i = 0, 1, 2, \dots$) do not depend on R .

Let us find the first two terms of the expansion (24), having considered the formula (23) in the left center region (*I* region), where (as it is easy to check with (18))

$$\Psi_{n_1 n_2 m}^I = \psi_{nqm}^{sphr} [1 + O(R^{-2})]. \quad (25)$$

Having substituted (21), (24) and (25) into (23) and retaining the first two terms of the expansion in R^{-1} , we get to within terms $O(R^{-2})$

$$\begin{aligned} \Phi_{nlm}^I = & \sum_{n_2=0}^{n-|m|-1} V_{n_1 n_2 m}^{l(0)} \psi_{n_1 n_2 m}^{par} + R^{-1} \sum_{n_2=0}^{n-|m|-1} \left[V_{n_1 n_2 m}^{l(1)} \psi_{n_1 n_2 m}^{par} \right. \\ & + \frac{\sqrt{n_1(n_1 + |m|)(n_2 + 1)(n_2 + |m| + 1)}}{2\gamma_0} V_{n_1 n_2 m}^{l(0)} \psi_{n_1-1, n_2+1, m}^{par} \\ & \left. - \frac{\sqrt{n_2(n_2 + |m|)(n_1 + 1)(n_1 + |m| + 1)}}{2\gamma_0} V_{n_1 n_2 m}^{l(0)} \psi_{n_1+1, n_2-1, m}^{par} \right]. \quad (26) \end{aligned}$$

As the boundary condition (40) for the wave function Φ_{nlm}^{II} obtained using the Holstein-Herring method shows, in the left center region, the equality similar to (25)

$$\Phi_{nlm}^I = \psi_{nlm}^{sph} [1 + O(R^{-2})] \quad (27)$$

is valid. Having substituted (27) with (19) into the left-hand side of (26) and equated to zero the coefficients of each power of R , we obtain the system of equations for calculating the zeroth and first terms of the expansion (24) which can be solved with taking into account the linear independency of the Coulomb parabolic

functions $\psi_{n_1 n_2 m}^{par}$:

$$V_{n_1 n_2 m}^{l(0)} = (-1)^{l+n_2+\frac{m-|m|}{2}} C_{\frac{n_1-1}{2}, \frac{n_2-1}{2}-n_2; \frac{n_1-1}{2}, |m|+n_2-\frac{n_1-1}{2}}^{l, |m|}; \quad (28)$$

$$\begin{aligned} V_{n_1 n_2 m}^{l(1)} &= (2\gamma_0)^{-1} \left[-\sqrt{(n_1+1)(n_1+|m|+1)n_2(n_2+|m|)} V_{n_1+1, n_2-1, m}^{l(0)} \right. \\ &+ \left. \sqrt{(n_2+1)(n_2+|m|+1)n_1(n_1+|m|)} V_{n_1-1, n_2+1, m}^{l(0)} \right] = \frac{(-1)^{l+n_2+1+\frac{m-|m|}{2}}}{2\gamma_0} \\ &\times \left[\sqrt{(n_1+1)(n_1+|m|+1)n_2(n_2+|m|)} C_{\frac{n_1-1}{2}, \frac{n_2-1}{2}-n_2+1; \frac{n_1-1}{2}, |m|+n_2-1-\frac{n_1-1}{2}}^{l, |m|} \right. \\ &\left. - \sqrt{(n_2+1)(n_2+|m|+1)n_1(n_1+|m|)} C_{\frac{n_1-1}{2}, \frac{n_2-1}{2}-n_2-1; \frac{n_1-1}{2}, |m|+n_2+1-\frac{n_1-1}{2}}^{l, |m|} \right]. \quad (29) \end{aligned}$$

Although here we have restricted ourselves to only the first two terms of the expansion (24), using the method outlined above, we can also find the coefficients for the higher corrections $V_{n_1 n_2 m}^{l(2)}$, $V_{n_1 n_2 m}^{l(3)}$, etc. We also note that, since in the left center region, the two-center wave functions in both bases transform to within terms $O(R^{-2})$ to the one-center ones (see formulas (25)) and (27)), the coefficients $\bar{U}_{n_1 n_2 m}^l$ of the expansion (22) of the Coulomb spherical wave functions in the spheroidal wave functions coincide with the found above $V_{n_1 n_2 m}^l$, i.e. $\bar{U}_{n_1 n_2 m}^l = V_{n_1 n_2 m}^l [1 + O(R^{-2})]$.

Note that in the internuclear region (where $\sqrt{R} \lesssim \nu, \tilde{\nu} \lesssim R, \tilde{\nu} = R - \nu$), and in the region of the right center (where $\nu \sim R, 0 \leq \tilde{\nu} \lesssim \sqrt{R}$) the use of the formula (23) is greatly simplified, because the functions $\Psi_{n_1 n_2 m}^{II}$ depending on the quantum number n_1 have different order with respect to R . Thus, in the internuclear region (in the region of the right center) each subsequent term in the sum (23) is R (R^2) times less than the previous one.

5 Asymptotics of the two-center wave function. Spherical basis

5.1 The region of the left center. In the region I , as the formula (27) shows, the two-center spherical function Φ_{nlm}^I coincides with the Coulomb spherical wave function $\psi_{nlm}^{sph} = R_{nl}(r_1)Y_{lm}(\theta_1, \varphi_1)$ to within terms $O(R^{-2})$. If for specific calculations of matrix elements the wave function Φ_{nlm}^I needs to be known in spheroidal coordinates, to obtain it one can take the Coulomb wave function $\psi_{nlm}^{sph}(r_1, \theta_1, \varphi_1)$ and transmit there from the spherical coordinates of the left center (r_1, θ_1, φ_1) to the spheroidal coordinates (ξ, η, φ) , where $\varphi = \varphi_1$. However, this procedure will lead to complicated dependencies that do not allow for factorization of integration along the variables μ and ν . Thus, it is preferable to use expansion (23), in which, obviously, according to the selection rules, only a few terms of the entire sum will rest.

If we consider the asymptotic region $\nu \sim \sqrt{R}$, when the electron is at a rather large distance from its nucleus, and the influence of a right center is still weak (i.e., on the border between regions I and II), the asymptotics in ν^{-1} of the wave

function Φ_{nlm}^I in the spheroidal coordinates up to a phase factor, which can be omitted here, is of the form:

$$\begin{aligned} \Phi_{nlm}^{I(as)} &= a_1 B_{lm} 2^{|m|} \mu^{\frac{|m|}{2}} \nu^{n-1-\frac{|m|}{2}} e^{-\gamma_0(\mu+\nu)} \left(1 + \frac{l(l+1) - n(n-1)}{2\gamma_0\nu} \right) \\ &\times \left(1 - \frac{|m|\nu}{2R} \right) \left[1 + \frac{(2n - |m| - 2)\mu}{2R} - \frac{l(l+1) - (|m|+1)(n-1)}{|m|+1} \right. \\ &\times \left. \frac{\mu}{\nu} \left(1 - \frac{\nu}{R} \right) + O(R^{-2}) \right] \frac{e^{im\varphi}}{\sqrt{2\pi}}, \end{aligned} \quad (30)$$

where

$$a_1 = \frac{\gamma_0(2\gamma_0)^n}{\sqrt{Z_1(n+l)!(n-l-1)!}}, \quad B_{lm} = \frac{1}{2^{|m|+1/2}|m|!} \left[\frac{(2l+1)(l+|m|)!}{(l-|m|)!} \right]^{1/2} \quad (31)$$

are the asymptotic coefficients of the Coulomb radial wave function $R_{nl}(r_1)$ for large r_1 and the spherical function $Y_{lm}(\theta_1, \varphi_1)$ at small angles θ_1 , respectively:

$$R_{nl}^{as}(r_1) = a_1 r_1^{n-1} e^{-\gamma_0 r_1} \left[1 + \frac{l(l+1) - n(n-1)}{2\gamma_0 r_1} + O(r_1^{-2}) \right], \quad (32)$$

$$Y_{lm}^{as}(\theta_1, \varphi_1) = B_{lm} \sin^{|m|} \theta_1 \left[1 - \frac{(l+|m|+1)(l-|m|)}{4(|m|+1)} \sin^2 \theta_1 + O(\sin^4 \theta_1) \right] \frac{e^{im\varphi_1}}{\sqrt{2\pi}}. \quad (33)$$

5.2 The internuclear region. Substituting into (23) the two-center wave function $\Psi_{n_1 n_2 m}^{II}$ from (18), we obtain (up to the same phase factor as for Φ_{nlm}^I)

$$\begin{aligned} \Phi_{nlm}^{II} &= a_1 B_{lm} 2^{|m|} \mu^{\frac{|m|}{2}} \nu^{n-1-\frac{|m|}{2}} \exp \left[-\gamma_0(\mu+\nu) - \frac{Z_2\nu}{\gamma_0 R} \right] \left(1 - \frac{\nu}{R} \right)^{\frac{|m|}{2} - \frac{Z_2}{\gamma_0}} \\ &\times \left[1 + \frac{l(l+1) - n(n-1)}{2\gamma_0\nu} \right] \left\{ 1 + \frac{3Z_2(1+|m|-n)\nu}{2\gamma_0^2 R^2} + \frac{Z_2\nu}{\gamma_0^2 R(R-\nu)} \right. \\ &\times \left[\frac{Z_2}{\gamma_0} \left(1 - \frac{\nu}{2R} \right) - \frac{|m|}{2} \right] + \frac{Z_2(Z_2 - Z_1)}{\gamma_0^3 R} \ln \left(1 - \frac{\nu}{R} \right) + \frac{(2n - |m| - 2)\mu}{2R} \\ &\left. - \frac{l(l+1) - (|m|+1)(n-1)\mu}{|m|+1} \left(1 - \frac{\nu}{R} \right) + O(R^{-2}) \right\} \frac{e^{im\varphi}}{\sqrt{2\pi}}. \end{aligned} \quad (34)$$

It is easy to see that as $\nu \ll R$ the wave function Φ_{nlm}^{II} transmits into $\Phi_{nlm}^{I(as)}$ (30).

Transmitting from the spheroidal coordinates $\{xi, \eta, \varphi\}$ to the spherical ones of the left center $\{r_1, \theta_1, \varphi_1\}$ with $\theta_1 \ll 1$ we obtain the asymptotic behavior of the two-center wave function Φ_{nlm}^{II} in the vicinity of the z internuclear axis:

$$\begin{aligned} \Phi_{nlm}^{II(as)} &= R_{nl}^{as}(r_1) Y_{lm}^{as}(\theta_1, \varphi_1) \left(1 - \frac{r_1}{R} \right)^{-Z_2/\gamma_0} \exp \left(-\frac{Z_2 r_1}{\gamma_0 R} \right) \\ &\times \left\{ 1 + \frac{3Z_2(1+|m|-n)r_1}{2\gamma_0^2 R^2} + \frac{Z_2}{\gamma_0^2 R} \left[\frac{Z_2}{\gamma_0} \left(1 - \frac{r_1}{2R} \right) - \frac{|m|}{2} \right] \frac{r_1}{R-r_1} \right. \\ &\left. - \frac{Z_2 r_1^2 \sin^2 \theta_1}{4\gamma_0(R-r_1)^2} + \frac{Z_2(Z_2 - Z_1)}{\gamma_0^3 R} \ln \left(1 - \frac{r_1}{R} \right) + O(R^{-2}) \right\}. \end{aligned} \quad (35)$$

The two-center spherical wave function Φ_{nlm}^{II} can also be calculated by the Holstein-Herring method [26] already used above. However, in order to find it in the internuclear domain, it is needed to know the E_2/R^2 correction term in the energy expansion of the Z_1eZ_2 quasimolecule in R^{-1} :

$$E = E_0 - \frac{Z_2}{R} + \frac{E_2}{R^2} + \frac{E_3}{R^3} + \dots, \quad (36)$$

where $E_0 = -\gamma_0^2/2$ is the energy of a hydrogen-like ion eZ_1 . Although for real atoms, as is known (see for instance [21]), E_2 and E_3 are equal to zero, and $E_4 = -\varepsilon_1 Z_2^2/2$, where ε_1 is the polarizability of the considered state of the unperturbed of the atom eZ_1 , when solving the problem of two purely Coulomb centers, the account of E_2/R^2 is required.

If in the parabolic quantum numbers the value E_2 for the problem Z_1eZ_2 is obtained analytically [1]:

$$E_2 = \frac{3Z_2n(n_1 - n_2)}{2Z_1}, \quad (37)$$

in the spherical basis it is unknown, since the application of the standard Rayleigh-Schrödinger perturbation theory here leads to infinite sums in the equations for determining corrections of the order of R^{-2} and higher. However, this value can be calculated by comparing the two-center wave functions Φ_{nlm}^{II} found independently by the Holstein-Herring method and by "re-quantizing" (23) from the spheroidal basis to the spherical one.

It should be noted that in order to obtain the asymptotics of the Φ_{nlm}^{II} in R^{-1} the Holstein-Herring method was used repeatedly by many authors (see, for example, [18, 19, 20]). However, either the leading term of the asymptotics of the two-center wave function [18] was calculated, or the next correction $\sim 1/R$ was calculated but only for the s -states ($l = m = 0$) of the system Z_1eZ_2 and provided $E_2 = 0$ [19, 20].

In the present paper, the first two terms of the asymptotics of Φ_{nlm}^{II} for large R for any states are found by the Holstein-Herring method taking into account the value of E_2/R^2 in the expansion (36) of the energy of the Z_1eZ_2 quasimolecule. Omitting the mathematical calculations, we present only the final result of the calculation of the two-center spherical wave function:

$$\begin{aligned} \Phi_{nlm}^{II} = & R_{nl}^{as}(r_1)Y_{lm}(\theta_1, \varphi_1) \left[\frac{r_1 + r_2 - R \cos \theta_1}{R(1 - \cos \theta_1)} \right]^{Z_2/\gamma_0} \exp \left(-\frac{Z_2 r_1}{\gamma_0 R} \right) \left\{ 1 + \frac{E_2 r_1}{\gamma_0 R^2} \right. \\ & + \frac{Z_2}{\gamma_0^2 R} \left[\frac{R - r_2 - r_1 \cos \theta_1}{r_1 \sin \theta_1} \frac{1}{Y_{lm}} \frac{\partial Y_{lm}}{\partial \theta_1} - (n-1) \ln \frac{R + r_2 - r_1 \cos \theta_1}{2R} \right. \\ & - \ln \frac{R + r_2 + r_1}{2R} - \ln \frac{R + r_2 - r_1}{2R} + \frac{Z_2}{\gamma_0} \left(\frac{r_1}{2R} - \ln \frac{R + r_2 + r_1}{R + r_2 - r_1} \right. \\ & \left. \left. + \frac{R}{R + r_2 - r_1} - \frac{R}{R + r_2 + r_1} \right) \right] + O(R^{-2}) \left. \right\}, \quad (38) \end{aligned}$$

satisfying the boundary condition

$$\Phi_{nlm}^{II} \Big|_{r_1 \sim \sqrt{R}} = R_{nl}^{as}(r_1)Y_{lm}(\theta_1, \varphi_1) [1 + O(R^{-2})]. \quad (39)$$

Note that similarly to the quasi-angular wave function $V^{II}(\nu)$, if in (38) instead of the asymptotics of the radial wave function $R_{nl}^{as}(r_1)$ one uses the exact expression $R_{nl}(r_1)$ [27], then the formula (38) will define the two-center spherical wave function Φ_{nlm} in both domains I and II , and the boundary condition (39) transforms into the following relation:

$$\Phi_{nlm}^{II} \xrightarrow{r_1 \rightarrow 0} \Phi_{nlm}^I [1 + O(R^{-2})] = \varphi_{nlm}^{sph} [1 + O(R^{-2})], \quad (40)$$

and thus leads to the formula (27).

When expanding (38) in the vicinity of the internuclear axis ($\theta_1 \ll 1$), it transmits to (35) if E_2 is substituted by the expression (37) with $n_1 = 0$, $n_2 = n - |m| - 1$. Thus, in the spherical basis, there occurs the energy levels degeneration of multiplicity $n - |m|$, i.e. instead of $n - |m|$ levels (corresponding to $n_1 = 0, 1, \dots, n - |m| - 1$) in parabolic quantum numbers we have only one energy level in the spherical one. Additionally, in both bases, the degeneracy by the sign of the magnetic quantum number m is present.

5.3 The region of the right center. In this region, the formula (23) leads to the following expression for the spherical wave function (up to the same phase factor as for Φ_{nlm}^I and Φ_{nlm}^{II})

$$\begin{aligned} \Phi_{nlm}^{III} &= \tilde{C}_{III} \frac{(2\gamma\mu)^{\frac{|m|+1}{2}}}{\sqrt{\mu(R+\mu)}} e^{-\alpha_1\gamma\mu} \frac{(2\gamma\tilde{\nu})^{\frac{|m|+1}{2}}}{\sqrt{\tilde{\nu}(R-\tilde{\nu})}} e^{-\tilde{\alpha}_2\gamma\tilde{\nu}} F(-\tilde{n}_2, |m| + 1, 2\tilde{\alpha}_2\gamma\tilde{\nu}) \\ &\times [1 + O(R^{-2})], \end{aligned} \quad (41)$$

$$\begin{aligned} \tilde{C}_{III} &= (-1)^{n-|m|-1} \sqrt{\frac{(2l+1)(l+|m|)!(n-1)!(n-|m|-1)!}{(|m|!)^2(|m|+1)(l-|m|)!(n+l)!(n-l-1)!}} \\ &\times \left[1 + \frac{l(l+1) - (|m|+1)(n-1)}{2\gamma_0 R} \right] \frac{R^2}{4} C(R) C_{III}(R), \end{aligned} \quad (42)$$

where all constants of γ , C , C_{III} , α_1 , $\tilde{\alpha}_2$, \tilde{n}_2 are determined above and taken here with $n_1 = 0$, $n_2 = n - |m| - 1$.

It is easy to show that in the parabolic coordinates, the leading term of the expansion (41) coincides with Chibisov's result [18, 21].

Summary

In this paper, we have elaborated the recurrent scheme of constructing asymptotic expansions of two-center wave functions in an arbitrary order of R^{-1} in the entire space of electron's distribution. Using this scheme we have obtained first two term of the asymptotics of two-center wave functions in not only "natural" spheroidal basis but also in the spherical basis of the left centre. Having these wave functions and inter-electron interaction operator constructed in our previous papers [30, 31, 32, 33, 34] we are able to calculate the two-electron exchange interaction of an excited hydrogen atom with the ion taking into account the retardation and spin effects that will be an aim of our further works.

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