$\mathcal{MMG}$

Mathematical Modelling and Geometry

Quasiclassical Two-Coulomb-Centre Wave Functions in the Spheroidal Coordinate System

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Abstract. The consistent scheme for obtaining WKB expansions for solutions of the quasiangular equation in quantum mechanical problem of two Coulomb centers $Z_1 e Z_2$ is elaborated. It is shown that in each order of $1/R$ the corrections to the wave function can be expressed by a finite number of the discrete spectrum Coulomb wave functions with modified charge. The simple analytical expressions for the first and second corrections to the wave functions are obtained.

Keywords: quasiclassical approximation, WKB method, two Coulomb centers, asymptotic solutions

PACS numbers: 31.15.xg, 31.15.xp

1. Introduction

Research of an electron motion in the field of two Coulomb centers (so-called $Z_1 e Z_2$ problem) began with the paper of Pauli [1]. Since then, this problem has attracted a lot of interest mostly in connection with the problems of atomic and molecular physics (status of the problem and references on the subject up to 1976 can be found in [2]).

The intensive studies of the problem of two Coulomb centers $Z_1 e Z_2$ during the last thirty years were stimulated not only by the availability of powerful computers and successes achieved with asymptotic methods in solving ordinary differential equations, but also by the requirements of mesomolecular physics [3, 4] and the theory of ion-atom collisions [5]. New results were obtained for both the problem of the hydrogen molecular ion H_2^+ [6] and the problem of two centers with strongly differing charges [7, 8, 9, 10].

A number of algorithms are now available which calculate the energy terms and wave functions for the $Z_1 e Z_2$ quasi-molecule numerically, within a given accuracy, for both the same [11, 12, 13] and different [14, 15, 16] Coulomb centres.

Despite the significant progress made in the numerical solution of the $Z_1 e Z_2$ problem, approximate methods of quantum mechanics are still useful, and often they are the only possible usable methods. This belongs also to the comparison equation method which was developed in the second half of the 1960s [17, 18, 19]. This method generates both the eigenfunctions and the eigenvalues of the quasiradial and quasiangular equations in the asymptotic region for large R. (The results obtained before 1976 are collected, for instance, in the book of Komarov et al [2].)

To solve many problems arising in physics of slow atomic collisions, e.g. for calculation of the matrix element of exchange interaction $\Delta(R)$ of a hydrogen atom (or H-like ion) with a nucleus, it is necessary to know not only two-centre Coulomb spheroidal wave functions but two-centre Coulomb spheroidal quasiradial and quasiangular wave functions too. Thus, for the resonant case ZeZ the exchange matrix element above was determined formerly [20, 21] under the condition requiring that when an electron approaches one of the nuclei the two-centre spheroidal wave function of the electron tends to the one-centre parabolic wave function. The correct result for $\Delta(R)$ can be actually obtained only (it is shown in [22]) when wave functions of zero approximation are considered in the spheroidal system of coordinates. The fact is that the exchange matrix element $\Delta(R)$ is defined by the asymptotic region of electron coordinates where one-centre parabolic and spheroidal wave functions of a hydrogen atom differ essentially from each other. To be more specific, at large distances from the nucleus the set of several Coulomb parabolic wave functions makes a contribution to the asymptotic behaviour of the Coulomb spheroidal wave function. This circumstance makes difficulties for application of the comparison equation method [22] to determination of the mentioned asymptotic behaviour.

The two-Coulomb-centre problem was also investigated in the relativistic case

[23, 24], study of exchange interactions in molecular ion dimers [25], at small intercentre distances in the two-dimensional [26] and arbitrary dimensional [27, 28] cases.

In spite of this, much interest in this problem still exists. The reason is twofold. On the 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.

As a suitable method for calculating the wave functions and all other quantities required in the problem of the interaction of two heavy ions, we propose to employ the quasiclassical approach. This approach allows us to obtain analytic solutions, but it is limited by asymptotically large internuclear distances R. These distances should be so large that the quantum penetrability of the potential barrier separating atomic particles is much smaller than unity. A great number of problems can be pointed out [29, 30, 31], whose solution depends on that region of internuclear distance. We stress, however, that analytic expressions derived for the asymptotic behavior of various splittings and shifts of the potential curves can sometimes be used in the region of internuclear distances that are smaller than those given by the formal criteria of applicability of the asymptotic expansions. Qualitatively, this can be explained by the fact that asymptotic solutions of the two-center problem retain the basic analytic properties of the exact solution [2] rather well, even the first term of the wave function expansion in powers of R^{-1}, up to sufficiently small R, and, thus, reproducing the results of variational calculations [31]. These properties are also conserved for other quantities computed with these functions.

The paper is organized as follows. In Section 2, we describe the statement of the problem. In Section 3, using the perturbation theory, we obtain the asymptotic behavior of the wave function of the electron moving near one Coulomb center and perturbed by another. In Section 4, we find the quasiclassical two-Coulomb-centre wave function.

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:

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

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:

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

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

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

we obtain the quasiradial and quasiangular equations for the functions $X(\xi, R)$ 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 depending 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:

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

To find the asymptotic solutions of equations (4) and (5) the following new functions are usually introduced:

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

and new variables

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

These new functions satisfy the following boundary conditions:

$$U(1) = 0, \quad U(\xi) \xrightarrow[\xi \to 0]{} 0, \quad V(\pm 1) = 0.$$

In terms of new variables and new functions we can rewrite equations (4) and (5) in the following form:

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

$$V''\left(\nu\right) - \left[\gamma^2 - \frac{Z_1 - Z_2 - \lambda_\eta/R}{\nu} + \frac{Z_1 - Z_2 + \lambda_\eta/R}{R - \nu} + \frac{R^2(m^2 - 1)}{4\nu^2(R - \nu)^2}\right]V\left(\nu\right) = 0 \tag{8}$$

where $\gamma = (-2E)^{1/2}$.

When R is much larger than the size of electron shells centered on the left-hand nucleus, the ratios μ/R and ν/R are small quantities in intra-atomic space. This fact allow us to use the perturbation theory to equations (7) and (8) in intra-atomic space to find the separation constants $\lambda_\xi, \lambda_\eta$.

3. Perturbation theory and the asymptotic behavior of two-Coulomb-centre quasiradial and quasiangular wave fuctions

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 $R = \infty$) equation (7) takes the following form:

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

where

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

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

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

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

$$\int\limits_0^\infty |u^{(0)}(\mu)|^2 d\mu = 1 \quad \Rightarrow \quad N_1^{(0)} = \left[\frac{(n_1+m)!}{n_1!\,(m!)^2\,(2n_1+m+1)}\right]^{1/2}$$

and $F(\alpha, \beta, x)$ is the confluent hypergeometric function. For the solution (10) to satisfy the boundary condition at infinity, the parameter $(m+1)/2 - \varkappa_1/2\gamma$ 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

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

To find the solution at large but finite values of the parameter R, following [32] 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 wave function $U(\mu)$ to the unperturbed wave functions $u_{n_1}^{(0)}(\mu)$ series:

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

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

$$\left(\lambda - \lambda_{n_1'}^{(0)} - \frac{1-m^2}{2}\right)\langle n_1'|\mu^{-1}|n_1'\rangle c_{n_1'}$$
$$= \sum_{k=0}^\infty \frac{(-1)^{k+1}}{R^k}\left[Z_1 + Z_2 - \lambda/R + (k+3)\frac{1-m^2}{4R}\right]\sum_{n_1''}\langle n_1'|\mu^k|n_1''\rangle c_{n_1''} \tag{11}$$

where $\langle n'_1 | \, \mu^{-1} \, | n'_1 \rangle$ are the matrix elements of the operator μ^k defined by means of the unperturbed functions $u_{n_1}^{(0)}(\mu)$. Here the matrix elements of the operator $1/\mu$ 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,

$$\lambda = \lambda^{(0)} + \lambda^{(1)} + \lambda^{(2)} + ... \qquad c_{n'_1} = c_{n'_1}^{(0)} + c_{n'_1}^{(1)} + c_{n'_1}^{(2)} + ...$$

where $\lambda^{(k)}$ 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 $c_{n'_1}^{(0)} = 0$ for $n'_1 \neq n_1$. To find the first-order approximation, we substitute $\lambda = \lambda_{n_1}^{(0)} + \lambda_{n_1}^{(1)}$ and $c_{n'_1} = c_{n'_1}^{(0)} + c_{n'_1}^{(1)}$ into equation (11) and we keep only the terms of order one. The obtained equation with $n'_1 = n_1$ gives

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

Equation (11) with $n'_1 \neq n_1$ for the coefficients $c_{n'_1}^{(1)}$ gives us

$$c_{n'_1}^{(1)} = \frac{1}{2R(n_1 - n'_1)} \left[2n_1 + m + 1 - 2(Z_1 + Z_2)/\gamma \right] \frac{\langle n'_1 | \mu^0 | n_1 \rangle}{\langle n'_1 | \mu^{-1} | n'_1 \rangle}.$$

All other coefficients and separation constants can be found in the same way. Matrix elements are calculated in a standard way (see Appendix 6)

In the quasiangular case the situation is similar to the quasiradial one – all of the formulae will work if we use the variable ν, 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 ν is R. If R is large, we can extend the upper limit of the variable ν to infinity. The replacement of 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

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

where

$$\lambda_{\xi,\eta}^{(0)} = \gamma(2n_{1,2} + m + 1) - (Z_1 \pm Z_2),$$

$$\lambda_{\xi,\eta}^{(1)} = \frac{1}{2} \left[(2n_{1,2} + m + 1)(2n_{1,2} + m + 1 - 2(Z_1 \pm Z_2)/\gamma) + 1 - m^2 \right],$$

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

where n_1, n_2 and m are parabolic quantum numbers.

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

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

where

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

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

We note that the right-hand side state is given by the above formulae if Z_1 is replaced by Z_2 and vice versa, 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 $n_1' + n_2' + m + 1 = n'$.

So within the perturbation theory we have found the asymptotic (for large R) solutions of equations (7) and (8). Normalizing the total wave function $\psi(\mu, \nu, \varphi)$ to unity we obtain the wave function of the electron moving near the first nucleus and perturbed by the second one up to R^{-2}:

$$\psi = C\left[f_{n_1}^{(0)}(\mu) + \sum_{p=1}^{2}\sum_{k=-p}^{p} c_{n_1+k}^{(p)} f_{n_1+k}^{(0)}(\mu)\right]\left[f_{n_2}^{(0)}(\nu) + \sum_{p=1}^{2}\sum_{k=-p}^{p} c_{n_2+k}^{(p)} f_{n_2+k}^{(0)}(\nu)\right] \tag{16}$$

where

$$f_l^{(0)}(x) = \left(\frac{(l+m)!}{l!(m!)^2(2l+m+1)}\right)^{1/2}(2\gamma x)^{(m+1)/2} e^{-\gamma x} F(-l,\, m+1,\, 2\gamma x),$$

Here $n = n_1 + n_2 + m + 1$ and for $p = 1, 2$ we found all of the $c_{n_{1,2}+k}^{(p)}$ coefficients (for details see [32]). For normalization constant C see Appendix 7.

The obtained function (16) describes the electron behaviour in the main region of distribution of the electron density. Our next issue is to determine the two-centre quasi-angular wave function $V(\nu)$ in the inter-nuclear region when an electron is located far from both Coulomb centres.

4. WKB solutions of the quasiangular equation in the inter-centre region

Although the perturbation theory allows solving principal problems connected with expansions of eigenvalues $\lambda_{\xi,\eta}(R)$ and eigenfunctions $U(\mu)$ and $V(\nu)$ in powers of $1/R$, determination of next terms of these expansions meets quickly increasing numerical obstacles. Solutions of equations (7), (8) at large R can be represented

in a quite simple and compact form using the WKB method (or quasiclassical approximation) which was elaborated and became famous as one of the most effective approximate methods for solving quantum mechanical problems (see, for instance, [33], [34], [35], [36]). The WKB method allows one to obtain simple uniform estimates for eigenfunctions at arbitrary internuclear distances R including $R >> 1$. Another preference of the quasiclassical asymptotic expansions is their simplicity. Moreover, in contrast with perturbation theory, the interaction does not need to be very small in the quasiclassical approximation, and its applicability domain is hence wider, which permits analyzing qualitative laws for the behavior and properties of quantum mechanical systems.

Below we construct quasiclassical solutions of the quasiangular equation in the classically forbidden region.

Let us rewrite the quasiangular equation (8) in the form of the one-dimensional Schrödinger equation:

$$V'' - \frac{q^2}{\hbar^2} V = 0 \qquad (17)$$

where $q = \sqrt{2(U_{eff} - E)}$, and the function

$$U_{eff}(\nu) = -\frac{\tilde{Z}_1}{\nu} - \frac{\tilde{Z}_2}{R - \nu} + \frac{\hbar^2 (m^2 - 1)}{8\nu^2 (1 - \nu/R)^2}, \qquad \tilde{Z}_{1,2} = \left[\pm(Z_1 - Z_2) - \lambda/R\right]/2$$

plays a role of the effective potential energy (see fig. 1).
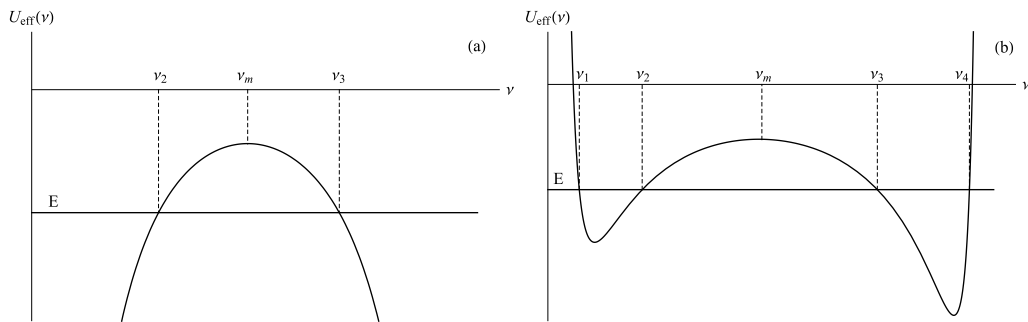

Figure 1: The "effective potential energy" $U_{eff}(\nu)$: a) when $m = 0, 1$, b) when $m > 1$; ν_i, $i = \overline{1,4}$ are the roots of the equation $q(\nu) = 0$, ν_m is the maximum point.

We seek the solution of (17) in the following form:

$$V = e^{S/\hbar} \sum_{k=0}^{\infty} \hbar^k \varphi^{(k)}. \qquad (18)$$

Having substituted (18) into (17), preliminary renewing the Planck constant $\hbar$, and equating to zero the coefficients of each power of $\hbar$, we arrive at the system of the

first-order differential equations for the unknown functions $S(\nu)$ and $\varphi^{(n)}(\nu)$

$$(S')^2 = q^2; \tag{19}$$

$$2S'\varphi^{(0)'} + S''\varphi^{(0)} = 0; \tag{20}$$

$$2S'\varphi^{(k+1)'} + S''\varphi^{(k+1)} + \varphi^{(k)''} = 0, \quad k = 0, 1, 2, \ldots . \tag{21}$$

According to the general conditions of the quasiclassical approximation applicability [37], the potential barrier should be quite wide ($\nu_2 \ll \nu_3$ where $\nu_{2,3}$ are the internal turning points). This gives us the requirement

$$2\tilde{Z}_2/\gamma^2 R \ll 1 \tag{22}$$

which always can be fulfilled for large R. Then one can sew the WKB solution (18) with the asymptotics found by expanding the perturbated function (16) by powers of ν^{-1}:

$$\Psi(\mu, \nu) \xrightarrow[\nu_2 \ll \nu \ll \nu_3]{} \Psi^{as}(\mu, \nu) \tag{23}$$

In the below-barrier region $\nu_2 < \nu < \nu_3$ as a solution of (19) we choose the decreasing function

$$S(\nu) = -\int_{\nu_2}^{\nu} q(\nu')d\nu' \tag{24}$$

The solutions of the linear equations (20) and (21) corresponding to it are of the form

$$\varphi^{(0)} = \frac{C^{(0)}}{\sqrt{q}},$$

$$\varphi^{(1)} = \frac{1}{\sqrt{q}}\left[\int \frac{\varphi^{(0)''}}{2\sqrt{q}}d\nu + C^{(1)}\right],$$

$$\varphi^{(k)} = \frac{1}{\sqrt{q}}\left[\int \frac{\varphi^{(k-1)''}}{2\sqrt{q}}d\nu + C^{(k)}\right].$$

Calculating the integrals in $\varphi^{(k)}$ and applying the boundary condition (22) we find that $\varphi^{(2)} \sim R^{-3}$. Therefore, restricting ourselves by the terms of order R^{-2} we obtain the quasiclassical wave function in the below-barrier region

$$V = \frac{C'}{\sqrt{q}}\exp\left[-\int_{\nu_2}^{\nu} q d\nu'\right]\left(1 + \frac{\tilde{Z}_2}{4\gamma^3(R-z)^2} - \frac{\tilde{Z}_1}{4\gamma^3 z^2}\right)$$

where

$$C' = C(R)(-1)^{n_2} e^{-\tilde{Z}_1/\gamma} Q_+ Q_- \left[1 + \frac{C_1}{R} + \frac{C_2}{R^2}\right],$$

$$Q_\pm = \left(\frac{\tilde{Z}_1}{\gamma} \pm \frac{\sqrt{m^2-1}}{2} \right)^{\{n_2+1/[1\pm\sqrt{(m-1)/(m+1)}]\}/2},$$

$$C_1 = -\frac{2n_2 + m + 1 - 2(Z_1 - Z_2)/\gamma}{2\gamma},$$

$$C_2 = \frac{1}{16\gamma^4}\left\{ 2\left(46n_2^2 + 46n_2 m + 50n_2 + m(9m+25) + 14\right)\right.$$
$$\left. -(2n_2+m+1)\left[16(Z_1-Z_2)^2 + \gamma^2\left(30n_2^2 + 30n_2 m + 34n_2 + m(2m+17) + 13\right)\right] \right\}$$
$$- \frac{16\tilde{Z}_1^3 \tilde{Z}_2(7\tilde{Z}_1 + 10\tilde{Z}_2) - 8\gamma^2\tilde{Z}_1(m^2-1)(3\tilde{Z}_1^2 + 8\tilde{Z}_1\tilde{Z}_2) + \gamma^4(8\tilde{Z}_1 + 5\tilde{Z}_2)(m^2-1)^2}{16\gamma^5[(m^2-1)\gamma^2 - 4\tilde{Z}_1^2]}.$$

5. Conclusions

In this paper we have developed the consistent scheme for obtaining WKB expansions for solutions of the quasiangular equation in quantum mechanical problem of two Coulomb centers $Z_1 e Z_2$. It is shown that in each order of $1/R$ the corrections to the wave function can be expressed by a finite number of the discrete spectrum Coulomb wave functions with modified charge. The simple analytical expressions for the first and second corrections to the wave functions are obtained. These expressions will be used in our further investigations when calculating the asymptotic behavior of the matrix element of the one-electron exchange interaction potential determining the process of one-electron charge transfer between the hydrogen atom and multiply charged ion.

6. Appendix A. The matrix elements

Here we give the values of the matrix elements for $k = -1, 0, 1, 2$, $\rho_1 = 2\gamma\mu$

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

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

$$\langle n_1 | \rho_1^2 | n_1 \rangle = \frac{1}{2n_1 + m + 1}\left[(m+1)(m+2)(m+3) + 12n_1(m+2)(m+3)\right.$$
$$\left. + 30n_1(n_1-1)(m+3) + 20n_1(n_1-1)(n_2-2)\right]$$

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

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

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

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

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

$$\langle n_1 + 2|\rho_1^1|n_1\rangle = \langle n_1 + 2|\rho_1^1|n_1\rangle = \left(\frac{(n_1+1)(n_1+2)(n_1+m+1)(n_1+m+2)}{(2n_1+m+1)(2n_1+m+5)}\right)^{1/2}$$

It should be noted that in [32] there is a mistake in the formula for the matrix element $\langle n_1 + 1|\rho_1^1|n_1\rangle$.

7. Appendix B. The normalization constant

The normalization constant for the perturbated wave function (16) has the form

$$C(R) = \sqrt{\frac{2\gamma^{3/2}}{\pi W^+}}\left\{1 - \frac{1}{\gamma R}\left[\frac{4n(n_1-n_2)}{W^+} + \frac{2Z_1}{\gamma}\frac{W^-}{W^+} + \frac{2Z_2}{\gamma}\right]\right.$$
$$\left. + \frac{1}{\gamma^2 R^2}\left[D_0 + \frac{Z_1}{\gamma}D_1 + \frac{Z_2}{\gamma}D_2 + D_3\right]\right\}.$$

Here

$$A_i = 6n_i(n_i+m+1) + (m+1)(m+2), \quad B_i = 2n_i+m+1, \quad C_i = n_i(n_i+m+1),$$

$$K = 6n_1n_2 + (m+1)(3n-2m-1), \qquad W^+ = \frac{A_1}{B_1} + \frac{A_2}{B_2}, \qquad W^- = \frac{A_1}{B_1} - \frac{A_2}{B_2},$$

$$D_0 = \frac{m^2-1}{16}\left(1 - \frac{1}{K}\right) - \frac{nG_0}{8W^+} + \frac{3n^2(n_1-n_2)^2}{2(W^+)^2},$$

$$D_1 = \frac{1}{2W^+}\left[3n(n_1-n_2)W^- + \frac{G_1}{4} + 25(C_1+C_2) - \frac{1}{8}\left(\frac{1}{B_1^2} + \frac{1}{B_2^2}\right)\right],$$

$$D_2 = \frac{n_1-n_2}{4K}\left(37B_1B_2 - \frac{(1-m^2)^2}{B_1B_2}\right),$$

$$D_3 = \frac{3Z_1^2}{8\gamma^2}\left[\left(\frac{W^-}{W+}\right)^2 - 2\right] + \frac{3Z_1Z_2}{4\gamma^2}\frac{W^-}{W^+} - \frac{3Z_2^2}{8\gamma^2},$$

$$G_0 = 9n(m+1) + 18(n_1^2 - n_1n_2 + n_2^2) + (m+2)(5m+31),$$

$$G_1 = 36n(m+1) + 36(n_1^2 + n_2^2) - 2m^2 + 64m + 118.$$

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