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Quasiclassical approach to the two-Coulomb-centre problem

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Abstract

The asymptotic expressions for the two-Coulomb-centre quasiradial and quasiangular wave functions are obtained for large internuclear distances R by means of the modified perturbation theory. It is shown that in each order of $1/R$ the corrections to the wave functions can be expressed by a finite number of Coulomb wave functions with the modified charge. Simple analytical expressions for the first, second, and third corrections are derived.

The recurrent scheme of finding the quasiclassical solutions of the one-dimensional equation at separation of the Schrödinger equation in the prolate spheroidal coordinates has been elaborated. In the framework of this scheme quasiclassical two-Coulomb-centre wave functions for large distances between the fixed positive charges (nuclei) have been constructed for the entire space of the negative particle (electron). Our method provides simple uniform estimates for eigenfunctions at arbitrary internuclear distances R including the $R \gg 1$. In contrast to perturbation theory, the interaction need not be very small in quasiclassical approximation, and its applicability domain is hence wider that permits analyzing qualitative laws for the behavior and properties of quantum mechanical systems.

1 Introduction

The quantum-mechanical problem of the motion of an electron in a field of two Coulomb centres with charges Z_1 and Z_2 placed at a distance R from each other (the so-called Z_1eZ_2 problem) has been thoroughly studied in the framework of the Schrödinger equation since the late 1920s. The status of the problem and references on the subject up to 1976 can be found in [1]. The intensive studies of this problem during the last forty years were stimulated not only by the availability of powerful computers and the successes achieved with asymptotic methods in solving ordinary

differential equations, but also by the requirements of mesomolecular physics [2, 3] and the theory of ion-atom collisions [4]. New results were obtained for both the problem of the hydrogen molecular ion H_2^+ (see, for instance, [5, 6] and references therein) and the problem of two centres with strongly differing charges [7, 8, 9, ?]. This problem for the Dirac equation was considered within asymptotic methods in [11, 12]. At the same time, in a series of papers the Z_1eZ_2 problem was studied at small R in spaces of both reduced [13] and arbitrary dimensions [14, 15].

As a suitable method for calculating the wave functions and all other quantities required in the two-Coulomb-centre problem we propose to employ the quasiclassical approach. This approach allows us to obtain analytic solutions, but it is limited to asymptotically large internuclear distances R. These distances should be sufficiently such large that the quantum penetrability of the potential barrier separating the atomic particles is much smaller than unity. A great number of problems can be pointed out [16, 17, 18], whose solution depends on this region of internuclear distances.

The paper is organized as follows. In Section 2 , we give the basic equations of the Z_1eZ_2 problem in the spheroidal system of coordinates. In Section 3 , we obtain the asymptotic expansions (at large R) of the two-Coulomb-centre quasiradial and quasiangular wave functions up to terms of the third order of $1/R$ by means of the modified perturbation theory. In Section 4, the consistent scheme for obtaining WKB expansions for solutions of the quasiangular equation in the Z_1eZ_2 problem is elaborated.

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:

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

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:

$$\xi = (r_1 + r_2)/R, \quad \eta = (r_1 - r_2)/R, \quad \phi = \arctan(y/x), \tag{2}$$

$$\xi \in [1; \infty), \qquad \eta \in [-1; 1], \qquad \phi \in [0; 2\pi),$$

where x, y, z are the Cartesian coordinates of electron (z-axis aligned with the internuclear axis). If we replace the wave function $\Phi(\vec{r}, R)$ by the product function

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

and use new variables

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

we obtain the quasiradial and quasiangular equations for functions $U(\xi, R)$ and $V(\eta, R)$

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

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

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

These new functions satisfy the following boundary conditions:

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

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 (5) and (6) are equivalent to the original Schrödinger equation provided the separation constants are equal:

$$\lambda_\xi = \lambda_\eta. \quad (7)$$

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 (5) and (6) in intra-atomic space to find the separation constants $\lambda_\xi, \lambda_\eta$.

3 Perturbation theory and the asymptotic behaviour of the quasiradial and quasiangular wave functions

In this section we give the basic formulae for asymptotic behavior of two-Coulomb-centre quasiradial and quasiangular wave functions in the vicinity of left-hand nucleus [21] which will be employed for sewing with quasiclassical solutions of $Z_1 e Z_2$ problem obtained in the below-barrier region (see Section 4).

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 equations (5), (6) take the following form:

$$u''^{(0)}(\mu) - \left[\gamma^2 - \frac{\varkappa_1}{\mu} + \frac{m^2-1}{4\mu^2}\right] u^{(0)}(\mu) = 0, \quad (8)$$

$$v''^{(0)}(\nu) - \left[\gamma^2 - \frac{\varkappa_2}{\nu} + \frac{m^2-1}{4\nu^2}\right] v^{(0)}(\nu) = 0, \quad (9)$$

where

$$\varkappa_i = Z_1 \pm Z_2 \pm \lambda^{(0)}/R.$$

Hereinafter, $i = 1$ and the upper sign correspond to the quasiradial case, $i = 2$ and the lower sign – to the quasiangular one.

The solutions of (8) and (9) satisfying the boundary conditions when $\mu, \nu \to 0$ are

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

$$v^{(0)}(\nu) = N_2^{(0)} \exp(-\gamma\nu)(2\gamma\nu)^{(m+1)/2} F\left(\frac{m+1}{2} - \frac{\varkappa_2}{2\gamma}, m+1, 2\gamma\nu\right), \tag{11}$$

where $N_{1,2}^{(0)}$ are the normalization constants, which are determined from the conditions

$$\int_0^\infty |u^{(0)}(\mu)|^2 d\mu = 1, \quad \int_0^\infty |v^{(0)}(\nu)|^2 d\nu = 1 \Rightarrow N_{1,2}^{(0)} = \left[\frac{(n_{1,2}+m)!}{n_{1,2}!\,(m!)^2\,(2n_{1,2}+m+1)}\right]^{1/2}$$

and $F(\alpha, \beta, z)$ is the confluent hypergeometric function. In order for the solutions (10) and (11) to satisfy the boundary conditions at infinity, the parameter $(m+1)/2 - \varkappa_{1,2}/2\gamma$ should be equal to zero or a negative integer, $(m+1)/2 - \varkappa_{1,2}/2\gamma = -n_{1,2}$, $(n_{1,2} = 0, 1, 2, \dots)$. Hence for the separation constants $\lambda_{n_{1,2}}^{(0)}(R)$ we obtain

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

where the upper sign corresponds to the quasiradial case and the lower sign - to the quasiangular case.

To find the solution at large but finite values of the parameter R, following [21] we shall use the perturbation theory. In equations (5), (6), 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 functions $U(\mu)$ and $V(\nu)$ to the unperturbed wave functions $u_{n_1}^{(0)}(\mu)$ and $v_{n_2}^{(0)}(\nu)$ series:

$$U(\mu) = \sum_{n_1'} c_{n_1'}(R) u_{n_1'}^{(0)}(\mu), \qquad V(\nu) = \sum_{n_2'} c_{n_2'}(R) v_{n_2'}^{(0)}(\nu).$$

Substituting expansion for $U(\mu)$ into (5) and expansion for $V(\nu)$ into (6), multiplying the obtained quasiradial equality by $u_{n_1}^{(0)*}$ and quasiangular equality by $v_{n_2}^{(0)*}$ and integrating we find

$$\left(\lambda_i - \lambda_{n_i'}^{(0)} - \frac{1-m^2}{2}\right) \langle n_i' | \rho_i^{-1} | n_i' \rangle\, c_{n_i'}$$
$$= \frac{1}{2\gamma} \sum_{k=0}^{\infty} \frac{(-1)^{i\,k+1}}{(2\gamma R)^k} \left[Z_1 \pm Z_2 \mp \lambda/R \pm (k+3)\frac{1-m^2}{4R}\right] \sum_{n_i''} \langle n_i' | \rho_i^k | n_i'' \rangle\, c_{n_i''} \tag{12}$$

Here $\langle n_i | \rho_i^k | n_i' \rangle$ are the matrix elements of the operators $\rho_1^k = (2\gamma\mu)^k$ and $\rho_2^k = (2\gamma\nu)^k$ defined by means of the unperturbed functions $u_{n_1}^{(0)}(\mu)$ and $v_{n_2}^{(0)}(\nu)$, respectively. Relation (12) 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,

$$\lambda = \lambda^{(0)} + \lambda^{(1)} + \lambda^{(2)} + \lambda^{(3)} + \ldots \qquad c_{n'_{1,2}} = c^{(0)}_{n'_{1,2}} + c^{(1)}_{n'_{1,2}} + c^{(2)}_{n'_{1,2}} + c^{(3)}_{n'_{1,2}} + \ldots$$

where $\lambda^{(k)}$ and $c^{(k)}_{n'_{1,2}}$ 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 $c^{(0)}_{n_{1,2}} = 1$ and $c^{(0)}_{n'_{1,2}} = 0$ for $n'_{1,2} \neq n_{1,2}$. To find the first-order approximation, we substitute $\lambda = \lambda^{(0)}_{n_{1,2}} + \lambda^{(1)}_{n_{1,2}}$ and $c_{n'_{1,2}} = c^{(0)}_{n'_{1,2}} + c^{(1)}_{n'_{1,2}}$ into equation (12) and we keep only the terms of order one. The obtained equation with $n'_{1,2} = n_{1,2}$ gives

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

Equation (12) with $n'_{1,2} \neq n_{1,2}$ for the coefficients $c^{(1)}_{n'_{1,2}}$ gives us

$$c^{(1)}_{n'_{1,2}} = \pm\frac{2n_{1,2} + m + 1 - 2(Z_1 \pm Z_2)/\gamma}{2R(n_{1,2} - n'_{1,2})}\frac{\langle n'_{1,2}|\rho^0|n_{1,2}\rangle}{\langle n'_{1,2}|\rho^{-1}|n'_{1,2}\rangle}.$$

The coefficient $c^{(1)}_{n_{1,2}}$ can be determined from the normalization condition for the wave function $u_{n_1} = u^{(0)}_{n_1} + u^{(1)}_{n_1}\left(v_{n_2} = v^{(0)}_{n_2} + v^{(1)}_{n_2}\right)$ keeping only the terms proportional to R^{-1}

$$c^{(1)}_{n_{1,2}} = \pm\frac{2n_{1,2} + m + 1 - 2(Z_1 \pm Z_2)/\gamma}{2R}.$$

The next corrections to the eigenalues and the eigenfunctions can be calculated in the same way. For the second-order corrections we obtain

$$\lambda^{(2)}_{n_{1,2}} = \pm\frac{1}{8R}\left\{A_{1,2}\left[(\Phi_{1,2} - A_{1,2})\Phi_{1,2} - 4T_{1,2} - m^2 - 3\right] - \Phi_{1,2}(1 - m^2)\right\},$$

$$\begin{aligned} c^{(2)}_{n'_{1,2}} = \pm\frac{1}{R(n'_{1,2} - n_{1,2})}\Bigg\{&\left(\lambda^{(1)}_{n_{1,2}} - \frac{1 - m^2}{2}\right)c^{(1)}_{n'_{1,2}} \\ &\mp\frac{1}{\langle n'_{1,2}|\rho^{-1}|n'_{1,2}\rangle}\Bigg[\frac{1}{R}\left(\lambda^{(1)}_{n_{1,2}} - \frac{3(1 - m^2)}{4}\right)\langle n'_{1,2}|n_{1,2}\rangle \\ &+\left(\lambda^{(0)}_{n_{1,2}}/R \mp (Z_1 \pm Z_2)\right)\left(\sum_{n''_{1,2}}\langle n'_{1,2}|n''_{1,2}\rangle c^{(1)}_{n''_{1,2}} \mp \frac{\langle n_{1,2}|\rho|n'_{1,2}\rangle}{R}\right)\Bigg]\Bigg\}, \end{aligned}$$

$$c^{(2)}_{n_{1,2}} = \frac{1}{2R^2}\left\{\frac{m^2 - 1}{2} - A_{1,2}\left[\Phi_{1,2} + 2 + \frac{4n_{1,2}(n_{1,2} + m)}{\Phi_{1,2}}\right] + \frac{A_{1,2}}{4}(T_{1,2} + 4)\right\},$$

where $\Phi_{1,2} = 2n_{1,2} + m + 1$, $A_{1,2} = \Phi_{1,2} - 2(Z_1 \pm Z_2)/\gamma$ and $T_{1,2} = 2n_{1,2}(n_{1,2} + m + 1) + m$.

For the third-order corrections we obtain

$$\begin{aligned} \lambda^{(3)}_{n_{1,2}} = \frac{1}{4R^2}\Bigg\{&\frac{\Phi_{1,2}A^3_{1,2}}{2} - \frac{A^2_{1,2}}{2}\left[(\Phi_{1,2} - A_{1,2})\Phi_{1,2} - 18T_{1,2} - 5m^2 - 13\right] \\ &+\Phi_{1,2}A_{1,2}\left[(\Phi_{1,2} - A_{1,2})\Phi_{1,2} + 2(3 - m^2)\right] + (1 - m^2)(4T_{1,2} + m^2 + 3)\Bigg\}, \end{aligned}$$

$$c_{n'_{1,2}}^{(3)} = \pm\frac{1}{R(n_{1,2}-n'_{1,2})}\left\{-\lambda_{n_{1,2}}^{(2)}c_{n'_{1,2}}^{(1)} - \left(\lambda_{n_{1,2}}^{(1)} - \frac{1-m^2}{2}\right)c_{n'_{1,2}}^{(2)}\right.$$

$$\pm\frac{1}{\langle n'_{1,2}|\rho^{-1}|n'_{1,2}\rangle}\left[\frac{\lambda_{n_{1,2}}^{(2)}}{R}\langle n_{1,2}|n'_{1,2}\rangle \mp \left(Z_1 \pm Z_2 \mp \lambda_{n_{1,2}}^{(0)}/R\right)\sum_{n''_{1,2}} c_{n''_{1,2}}^{(2)}\langle n''_{1,2}|n'_{1,2}\rangle\right.$$

$$+\left(\frac{\lambda_{n_{1,2}}^{(1)}}{R} - \frac{3(1-m^2)}{4R}\right)\sum_{n''_{1,2}}\langle n'_{1,2}|n''_{1,2}\rangle c_{n''_{1,2}}^{(1)} \mp \frac{\lambda_{n_{1,2}}^{(1)}+m^2-1}{R^2}\langle n_{1,2}|\rho|n'_{1,2}\rangle$$

$$\left.\left.+\frac{Z_1 \pm Z_2 \mp \lambda_{n_{1,2}}^{(0)}/R}{R}\sum_{n''_{1,2}} c_{n''_{1,2}}^{(1)}\langle n''_{1,2}|\rho|n'_{1,2}\rangle \mp \frac{Z_1 \pm Z_2 \mp \lambda_{n_{1,2}}^{(0)}/R}{R^2}\langle n_{1,2}|\rho^2|n'_{1,2}\rangle\right]\right\},$$

$$c_{n_{1,2}}^{(3)} = \pm\frac{m^2-1}{4R^3}\left(\Phi_{1,2} - 4\langle n_{1,2}|\rho|n_{1,2}\rangle\right) \pm \frac{A_{1,2}^2}{4R^3}\left[\Phi_{1,2}(T_{1,2}-1) + 10\langle n_{1,2}|\rho|n_{1,2}\rangle\right]$$

$$\pm\frac{A_{1,2}}{8R^3}\left[(1-m^2)(T_{1,2}+4) + 4(8T_{1,2}+m^2+13)\right] \pm \frac{A_{1,2}^3}{16R^3}(3T_{1,2}+10).$$

Note that in the quasiangular case 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.

In the given above formulae, the transfer from the left-hand side centre Z_1 to the right-hand side one Z_2 is realized by means of the replacements $Z_1 \leftrightarrow Z_2$, $n_i \to n'_i$, $\nu \to R-\nu$, $\phi \to -\phi$. The parabolic quantum numbers n'_1, n'_2 of the right-hand side centre satisfy the condition $n'_1 + n'_2 + m + 1 = n'$.

Therefore, we have shown that the application of the modified scheme of perturbation theory [21] allows us to obtain simple expansions in powers of $1/R$ of the wave function of a hydrogen-like atom in the field of point charge. Hereby, within terms of order R^{-3} the function ψ of formula (3) is of the form

$$\psi^{pert}(\mu,\nu) = CU^{pert}(\mu)V^{pert}(\nu), \tag{13}$$

where

$$U^{pert} = f_{n_1}^{(0)}(\mu) + \sum_{p=1}^{3}\sum_{k=-p}^{p} c_{n_1+k}^{(p)} f_{n_1+k}^{(0)}(\mu),$$

$$V^{pert} = f_{n_2}^{(0)}(\nu) + \sum_{p=1}^{3}\sum_{k=-p}^{p} c_{n_2+k}^{(p)} f_{n_2+k}^{(0)}(\nu),$$

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

and for $p = 1, 2, 3$ all the $c_{n_i+k}^{(p)}$ coefficients have been derived above.

Let us normalize the total wave function (3), (13) within terms of order R^{-3}. For the normalization constant C we finally obtain

$$C(R) = \sqrt{\frac{2}{\gamma R}} \left\{ \sum_{i=1}^{2} \left[\langle n_i|\rho_i^{-1}|n_i\rangle \left(1 + 2c_{n_i}^{(1)} + |c_{n_i}^{(1)}|^2 + 2c_{n_i}^{(2)} + 2c_{n_i}^{(3)}\right) \right.\right.$$
$$\left. + 2 \sum_{k=-1}^{1} c_{n_i+k}^{(1)} c_{n_i+k}^{(2)} \langle n_i + k|\rho_i^{-1}|n_i + k\rangle \right]$$
$$\left. + \frac{1}{R^2} \sum_{i=1}^{2} \langle n_i|\rho_i^1|n_i\rangle \left(1 - 2c_{n_i}^{(1)}\right) - \frac{\langle n_1|\rho_1^2|n_1\rangle - \langle n_2|\rho_2^2|n_2\rangle}{R^3} \right\}^{-1/2}. \tag{14}$$

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

Solutions of equations (5), (6) at large R can be represented in a quite simple and compact form using the WKB method. This method allows us to obtain simple uniform estimates for eigenfunctions at arbitrarily large internuclear distances R including $R \gg 1$. Other advantage of quasiclassical asymptotic expansions is their simplicity. Below we construct quasiclassical solutions of the quasiangular equation in the classically forbidden region.

Let us rewrite the quasiangular equation (6) in the form of the one-dimensional Schrödinger equation:

$$V'' - \frac{q^2}{\hbar^2} V = 0 \tag{15}$$

where $q = \sqrt{2(U_{eff} - E)}$ and the function U_{eff} plays a role of the effective potential energy in the quasiangular equation:

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

Here the Planck constant $\hbar$ is restored explicitly and the following notation is introduced: ν_i $(i = \overline{1,4})$ are the turning points, ν_m is the point where the effective potential reaches a maximum. Moreover, the quantity q is real and coincides with the quasiangular momentum of a classical particle within imaginary unit i, $q(\nu) > 0$ at $\nu_2 < \nu < \nu_3$.

Let us represent the solution of (15) in the form of the expansion in powers of $\hbar$:

$$V^{quas} = e^{S/\hbar}, \quad S = \sum_{k=-1}^{\infty} \hbar^k S_k \tag{16}$$

Having substituted (16) into (15) and equating to zero the coefficients of each power of $\hbar$, we arrive at the system of differential equations of the 1st order for

the unknown functions $S_k(\nu)$

$$\left(S'_{-1}\right)^2 = q^2; \tag{17}$$

$$2S'_{-1}S'_0 + S''_{-1} = 0; \tag{18}$$

$$2S'_{-1}S'_k + S''_{k-1} + \sum_{j=0}^{k-1} S'_j S'_{k-j-1} = 0, \quad k = 1, 2, \ldots. \tag{19}$$

As a solution of (17) we choose the function

$$S_{-1}(\nu) = -\int_{\nu_2}^{\nu} q(\nu')d\nu' \tag{20}$$

corresponding to exponential damping of V^{quas} in the under-barrier region. The equation for S_0 is solved in the closed species:

$$S_0 = \log(C_0/\sqrt{q}).$$

Finally, solutions of all the next equations of the recurrent system (19) are expressed by means of quadratures

$$S_k = \int \frac{1}{2q}\left(S''_{k-1} + \sum_{j=0}^{k-1} S'_j S'_{k-j-1}\right) d\nu + C_k, \quad C_k = \text{const}, \quad k = 1, 2, \ldots. \tag{21}$$

For further consideration it is convenient to introduce two ranges of ν variation: $0 \leqslant \nu \ll \nu_m$ and $\nu_2 \ll \nu \ll \nu_3$. In the first range the formulae received in section are valid, and we employed the quasiclassical approach to find the quasiangular function $V(\nu)$ determining the behaviour of an electron in the under-barrier region $\nu_2 < \nu < \nu_3$. It should be noted that where these ranges overlap, the results obtained by the perturbation theory and by the quasiclassical approximation coincide. This allows us to find the integration constants C_k by means of matching the quasiclassical solution V^{quas} with asymptotic expansion of V^{pert} (14) in powers of $1/\nu$:

$$V^{quas}(\nu) \xrightarrow[\nu_2 \ll \nu \ll \nu_m]{} V^{as}(\nu) \tag{22}$$

For satisfaction of (22), it is necessary that the internuclear distance be much larger than that at which the potential barrier in the quasiangular equation disappears, i.e.

$$R \gg R_0 = \left[2(\tilde{Z}_1 + \tilde{Z}_2) + \sqrt{4\tilde{Z}_1^2 + \gamma^2(1-m^2)} + \sqrt{4\tilde{Z}_2^2 + \gamma^2(1-m^2)}\right]/2\gamma^2. \tag{23}$$

Therefore, the solution of the quasiangular equation (15) in the quasiclassical approximation, which satisfies the boundary condition (22), is of the form (hereinafter $\hbar = 1$)

$$V^{quas} = \frac{C_0}{\sqrt{q}} \exp\left[-\int_{\nu_2}^{\nu} q d\nu' + S_1 + S_2\right] \tag{24}$$

where the quasiclassical corrections S_1 and S_2 are determined by the formulae

$$S_1 = -\frac{\tilde{Z}_1}{4\gamma^3\nu^2}\left(1+\frac{17\tilde{Z}_1}{6\gamma^2\nu}\right)+\frac{\tilde{Z}_2}{4\gamma^3(R-\nu)^2}\left(1+\frac{17\tilde{Z}_2}{6\gamma^2(R-\nu)}\right)$$
$$+\frac{m^2-1}{16\gamma^3}\left(\frac{1}{\nu^3}+\frac{1}{\nu^2 R}-\frac{1}{R(R-\nu)^2}-\frac{1}{(R-\nu)^3}\right)+\frac{\tilde{Z}_1\tilde{Z}_2}{2\gamma^5 R^3}\log\frac{\nu}{R-\nu}$$
$$+\frac{\tilde{Z}_1\tilde{Z}_2}{4\gamma^5 R}\left(\frac{3}{(R-\nu)^2}-\frac{3}{\nu^2}+\frac{1}{R}\left[\frac{1}{R-\nu}-\frac{1}{\nu}\right]\right)+C_1, \tag{25}$$

$$S_2 = \frac{\tilde{Z}_1}{4\gamma^4\nu^3}+\frac{\tilde{Z}_2}{4\gamma^4(R-\nu)^3}+C_2, \tag{26}$$

and expressions for the integration constants C_0, C_1, and C_2 are too cumbersome and not given here.

Thus, the obtained formula (24) determines the quasiclassical asimptotic behaviour of solutions of the quasiangular equation (15) when $\hbar \to 0$ and is valid in the under-barrier region $\nu_2 < \nu < \nu_3$.

The final expression for two-Coulomb-centre wave function Ψ of Z_1eZ_2 system has the form (3) where

$$\psi(\mu,\nu) = C(R)\, U^{pert}(\mu)\, V^{quas}(\nu), \tag{27}$$

and the normalization constant $C(R)$ is still given by formula (14).

Conclusion

The asymptotic formulae for the two-Coulomb-centre quasiradial and quasiangular wave functions are obtained for large internuclear distances R by means of the modified perturbation theory. Simple analytical expressions for the first, second, and third corrections to quasiradial and quasiangular functions, which are necessary for statement of boundary conditions in adiabatic representation of the three-body problem [1], are derived.

In the framework of the quasiclassical approach the analytical expression for solutions of the quasiangular equation (6) in the region of under-barrier electron motion was obtained.

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