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THE WKB METHOD FOR THE QUANTUM MECHANICAL TWO-COULOMB-CENTER PROBLEM

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Using a modified perturbation theory, we obtain asymptotic expressions for the two-center quasiradial and quasiangular wave functions for large internuclear distances R. We show that in each order of $1/R$, corrections to the wave functions are expressed in terms of a finite number of Coulomb functions with a modified charge. We derive simple analytic expressions for the first, second, and third corrections. We develop a consistent scheme for obtaining WKB expansions for solutions of the quasiangular equation in the quantum mechanical two-Coulomb-center problem. In the framework of this scheme, we construct semiclassical two-center wave functions for large distances between fixed positively charged particles (nuclei) for the entire space of motion of a negatively charged particle (electron). The method ensures simple uniform estimates for eigenfunctions at arbitrary large internuclear distances R, including $R \gg 1$. In contrast to perturbation theory, the semiclassical approximation is not related to the smallness of the interaction and hence has a wider applicability domain, which permits investigating qualitative laws for the behavior and properties of quantum mechanical systems.

Keywords: semiclassical approximation, WKB method, two Coulomb centers, asymptotic solution

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1. Introduction

The quantum mechanical problem of the motion of an electron in the field of two Coulomb centers with charges Z_1 and Z_2 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]. 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, e.g., [5]–[7] and the references therein) and the problem of two centers with strongly differing charges [8]–[11]. This problem for the Dirac equation was considered

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with asymptotic methods in [12], [13]. At the same time, in a series of papers, the Z_1eZ_2 problem was studied at small R in spaces of both reduced [14] and arbitrary dimensions [15], [16].

To solve many problems arising in the physics of slow atomic collisions, for example, to calculate the matrix element of the exchange interaction $\Delta(R)$ of a hydrogen atom (or hydrogen-like ion) with a nucleus, we must know the two-Coulomb-center spheroidal quasiradial and quasiangular wave functions. In the resonant case ZeZ, the abovementioned exchange matrix element was previously determined [17], [18] based on the requirement that close to a nucleus, the two-center spheroidal wave function of the electron passes into the one-center parabolic wave function. In fact, the correct result for $\Delta(R)$ can be obtained only if the wave functions of the zeroth approximation are considered in a spheroidal coordinate system (this was shown in [19]). The point is that the exchange matrix element $\Delta(R)$ is defined by the asymptotic region of electron coordinates where the one-center parabolic and spheroidal wave functions of a hydrogen atom differ essentially from each other. More precisely, at large distances from the nucleus, a whole set of Coulomb parabolic wave functions contributes to the asymptotic behavior of the Coulomb spheroidal wave function. This makes it difficult to apply the comparison equation method [1], [8], [9], [11] to determine the mentioned asymptotic behavior (see, e.g., [19]).

As a suitable method for calculating the wave functions and all other needed quantities in the two-Coulomb-center problem, we propose using the semiclassical approach. This approach allows obtaining analytic solutions, but it is limited to asymptotically large internuclear distances R. These distances must be sufficiently large that the quantum penetrability of the potential barrier separating the atomic particles is much smaller than unity. A great number of problems whose solution depends on this region of internuclear distances can be indicated [20]–[22].

This paper is structured as follows. In Sec. 2, we give the basic equations of the Z_1eZ_2 problem in the spheroidal coordinate system. In Sec. 3, we use a modified perturbation theory to obtain the asymptotic expansions (at large R) of the two-Coulomb-center quasiradial and quasiangular wave functions up to terms of the third order in $1/R$. In Sec. 4, we develop a consistent scheme for obtaining WKB expansions for solutions of the quasiangular equation for the Z_1eZ_2 problem in the under-barrier region.

2. Basic equations

The motion of an electron in the field of two fixed nuclei with the charges Z_1 and Z_2 is described by the Schrödinger equation ($\hbar = e = m_e = 1$)

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

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

$$\begin{gathered} \xi = \frac{r_1 + r_2}{R}, \qquad \eta = \frac{r_1 - r_2}{R}, \qquad \phi = \arctan\frac{y}{x}, \\ \xi \in [1; \infty), \qquad \eta \in [-1; 1], \qquad \phi \in [0; 2\pi), \end{gathered} \tag{2}$$

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

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

and use the new variables

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

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

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

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

where $\gamma = (-2E)^{1/2}$. These new functions satisfy the boundary conditions

$$U(1) = 0, \qquad U(\xi) \xrightarrow[\xi \to \infty]{} 0, \qquad V(\pm 1) = 0. \tag{7}$$

In (5) and (6), λ_1 and λ_2 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 if the separation constants are equal:

$$\lambda_1 = \lambda_2. \tag{8}$$

If R is much larger than the size of the electron shells centered on the left-hand nucleus, the ratios μ/R and ν/R are small quantities in the intra-atomic space. This allows using the perturbation theory for Eqs. (5) and (6) in this region and finding both the separation constants $\lambda_{1,2}$ and the asymptotic behavior of the quasiradial and quasiangular wave functions $U(\mu)$ and $V(\nu)$.

3. Perturbation theory and the asymptotic behavior of two-Coulomb-center quasiradial and quasiangular wave functions

In a theoretical description of the behavior of hydrogen-like atoms in the field of a point charge, we first need to construct the perturbation theory for large internuclear distances R. Although this problem has been investigated for many years, the existing methods are unable to find a simple series for the 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 [23]–[25]. One of these schemes was developed in [25]. Using it in the case of large internuclear distances R, we obtain asymptotic expressions for the two-Coulomb-center quasiradial and quasiangular functions $U(\mu)$ and $V(\nu)$ up to terms of the third order in $1/R$.

The formal scheme for our further calculations consists of the following steps. We represent the original differential operator L in Eqs. (5) and (6) as a sum $L = L_0 + L_1/R$. The limit differential operator L_0 is obtained from the original operator L as $R \to \infty$. We then expand the functions $U(\mu)$ and $V(\nu)$ in the basis functions $u^{(0)}_{n_1}(\mu)$ and $v^{(0)}_{n_2}(\nu)$, which are defined as solutions of the equations $L^{(\mu)}_0 u^{(0)}_{n_1}(\mu) = 0$ and $L^{(\nu)}_0 v^{(0)}_{n_2}(\nu) = 0$ and can be expressed in terms of known special functions.

We consider the limit case $R \to \infty$. In this case, λ has the same order as R. In the zeroth-order approximation (i.e., at $R = \infty$), Eqs. (5) and (6) then become

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

$$\frac{d^2 v^{(0)}(\nu)}{d\nu^2} - \left[\gamma^2 - \frac{\varkappa_2}{\nu} + \frac{m^2 - 1}{4\nu^2}\right] v^{(0)}(\nu) = 0, \tag{10}$$

where

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

Here and hereafter, $i = 1$, and the upper sign correspond to quasiradial case (5), and $i = 2$ and the lower sign correspond to quasiangular case (6).

The solutions of Eqs. (9) and (10) satisfying boundary conditions (7) as $\mu, \nu \to 0$ are

$$u^{(0)}(\mu) = N_1^{(0)} e^{-\gamma\mu} \, (2\gamma\mu)^{(m+1)/2} \, F\left(\frac{m+1}{2} - \frac{\varkappa_1}{2\gamma}, \, m+1, \, 2\gamma\mu\right), \tag{11}$$

$$v^{(0)}(\nu) = N_2^{(0)} e^{-\gamma\nu} \, (2\gamma\nu)^{(m+1)/2} \, F\left(\frac{m+1}{2} - \frac{\varkappa_2}{2\gamma}, \, m+1, \, 2\gamma\nu\right), \tag{12}$$

where $N_i^{(0)}$ are the normalization factors defined by the conditions

$$\int_0^\infty |u^{(0)}(\mu)|^2 \, d\mu = 1, \qquad \int_0^\infty |v^{(0)}(\nu)|^2 \, d\nu = 1,$$

and $F(\alpha, \beta, z)$ is the confluent hypergeometric function. For solutions (11) and (12) to satisfy the boundary conditions at infinity, the parameter $(m+1)/2 - \varkappa_i/2\gamma$ must be equal to zero or a negative integer,

$$\frac{m+1}{2} - \frac{\varkappa_i}{2\gamma} = -n_i, \quad n_i = 0, 1, 2, \ldots.$$

The numbers n_1, n_2, and m are parabolic quantum numbers. Hence, for the separation constants $\lambda_{n_i}^{(0)}(R)$, we obtain

$$\lambda_{n_i}^{(0)}(R) = \pm R[\gamma(2n_i + m + 1) - (Z_1 \pm Z_2)]. \tag{13}$$

To find the solution at large but finite values of the parameter R, we use the perturbation theory following [25]. In Eqs. (5) and (6), we regard the energy as a parameter and the separation constant λ_i as an eigenvalue of the corresponding operator. Corrections to the eigenvalues and eigenfunctions are then computed standardly.

We expand the sought wave functions $U(\mu)$ and $V(\nu)$ in the system of unperturbed wave functions $u_{n_1}^{(0)}(\mu)$ and $v_{n_2}^{(0)}(\nu)$:

$$U(\mu) = \sum_{n_1'} c_{n_1'}(R) u_{n_1'}^{(0)}(\mu), \qquad V(\nu) = \sum_{n_2'} c_{n_2'}(R) v_{n_2'}^{(0)}(\nu). \tag{14}$$

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

$$\begin{aligned}\left(\lambda_i - \lambda_{n_i'}^{(0)} - \frac{1-m^2}{2}\right) \langle n_i' | \rho_i^{-1} | n_i' \rangle \, c_{n_i'} = \\ = \frac{1}{2\gamma} \sum_{k=0}^{\infty} \frac{(-1)^{ik+1}}{(2\gamma R)^k} \left[Z_1 \pm Z_2 \mp \frac{\lambda}{R} \pm (k+3) \frac{1-m^2}{4R}\right] \sum_{n_i''} \langle n_i' | \rho_i^k | n_i'' \rangle \, c_{n_i''}.\end{aligned} \tag{15}$$

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 $\rho_2^k = (2\gamma\nu)^k$ on the respective unperturbed functions $u_{n_1}^{(0)}(\mu)$ and $v_{n_2}^{(0)}(\nu)$. The values of these matrix elements are given in Appendix A. Relation (15) allows calculating corrections of any order to the eigenvalue and eigenfunction.

We represent the separation constant and expansion coefficients in (14) in the forms

$$\lambda_i = \lambda_{n_i}^{(0)} + \lambda_{n_i}^{(1)} + \lambda_{n_i}^{(2)} + \lambda_{n_i}^{(3)} + \ldots, \qquad c_{n_i'} = c_{n_i'}^{(0)} + c_{n_i'}^{(1)} + c_{n_i'}^{(2)} + c_{n_i'}^{(3)} + \ldots, \tag{16}$$

where $\lambda^{(k)}_{n_i}$ and $c^{(k)}_{n'_i}$ are quantities of the respective R^{-k+1} and R^{-k} orders.

To determine the corrections to the nth eigenvalue and eigenfunction, we set $c^{(0)}_{n_i} = 1$ and $c^{(0)}_{n'_i} = 0$ for $n'_i \neq n_i$. To find the first-order approximation, we substitute expansions (16) in Eq. (15) and keep only terms of the order of unity. The obtained equation with $n'_i = n_i$ gives

$$\lambda^{(1)}_{n_i} = \frac{1}{2}\left\{(2n_i + m + 1)\left[2n_i + m + 1 - 2\frac{Z_1 \pm Z_2}{\gamma}\right] + 1 - m^2\right\}. \tag{17}$$

From Eq. (15) with $n'_i \neq n_i$, we find the coefficients

$$c^{(1)}_{n'_i} = \pm\frac{2n_i + m + 1 - 2(Z_1 \pm Z_2)/\gamma}{4\gamma R(n_i - n'_i)}\frac{\langle n'_i|\rho^0_i|n_i\rangle}{\langle n'_i|\rho^{-1}_i|n'_i\rangle}. \tag{18}$$

The coefficients $c^{(1)}_{n_1}$ and $c^{(1)}_{n_2}$ can be determined from the normalization conditions for the wave function $u_{n_1}(\mu) = u^{(0)}_{n_1}(\mu) + u^{(1)}_{n_1}(\mu)$ and $v_{n_2}(\nu) = v^{(0)}_{n_2}(\nu) + v^{(1)}_{n_2}(\nu)$, keeping only the terms proportional to R^{-1},

$$c^{(1)}_{n_i} = \pm\frac{2n_i + m + 1 - 2(Z_1 \pm Z_2)/\gamma}{4\gamma R}. \tag{19}$$

To determine the second-order corrections, we substitute the expansions $\lambda_i = \lambda^{(0)}_{n_i} + \lambda^{(1)}_{n_i} + \lambda^{(2)}_{n_i}$ and $c_{n'_i} = c^{(0)}_{n'_i} + c^{(1)}_{n'_i} + c^{(2)}_{n'_i}$ in Eq. (15) and consider terms of the order of R^{-1}. The obtained equation with $n'_i = n_i$ gives

$$\begin{aligned}\lambda^{(2)}_{n_i} = {} & \pm\frac{1}{8\gamma R}\left\{\left[2n_i + m + 1 - 2\frac{Z_1 \pm Z_2}{\gamma}\right]\left[2(2n_i + m + 1)\frac{Z_1 \pm Z_2}{\gamma} - \right.\right.\\ & \left.\left. - 8n_i(n_i + m + 1) - (m+1)(m+3)\right] - (2n_i + m + 1)(1 - m^2)\right\}.\end{aligned} \tag{20}$$

From Eq. (15) in the case $n'_i \neq n_i$, we find

$$\begin{aligned}c^{(2)}_{n'_i} = {} & \pm\frac{1}{2\gamma R(n'_i - n_i)}\left\{\left(\lambda^{(1)}_{n_i} - \frac{1-m^2}{2}\right)c^{(1)}_{n'_i} \mp \right.\\ & \mp\frac{1}{2\gamma\langle n'_i|\rho^{-1}_i|n'_i\rangle}\left[\frac{1}{R}\left(\lambda^{(1)}_{n_i} - \frac{3(1-m^2)}{4}\right)\langle n'_i|\rho^0_i|n_i\rangle + \right.\\ & \left.\left. + \left(\frac{\lambda^{(0)}_{n_i}}{R} \mp (Z_1 \pm Z_2)\right)\left(\sum_{n''_i}\langle n'_i|\rho^0_i|n''_i\rangle\, c^{(1)}_{n''_i} \mp \frac{\langle n_i|\rho^1_i|n'_i\rangle}{2\gamma R}\right)\right]\right\}.\end{aligned} \tag{21}$$

From the normalization conditions for the wave function $u_{n_1} = u^{(0)}_{n_1} + u^{(1)}_{n_1} + u^{(2)}_{n_1}$ and $v_{n_2} = v^{(0)}_{n_2} + v^{(1)}_{n_2} + v^{(2)}_{n_2}$, keeping only terms of the order of R^{-2}, we obtain

$$\begin{aligned}c^{(2)}_{n_i} = {} & \frac{1}{8\gamma^2 R^2}\left\{\frac{m^2-1}{2} - \left[2n_i + m + 1 - 2\frac{Z_1 \pm Z_2}{\gamma}\right]\left[2n_i + m + 3 + \frac{4n_i(n_i + m)}{2n_i + m + 1} + \right.\right.\\ & \left.\left. + \frac{2n_i + m + 1 - 2(Z_1 \pm Z_2)/\gamma}{4}\big(2n_i(n_i + m + 1) + m + 4\big)\right]\right\}.\end{aligned} \tag{22}$$

Calculating higher-order corrections does not involve principal difficulties. For the third-order corrections, we obtain

$$\lambda_{n_i}^{(3)} = \frac{1}{16\gamma^2 R^2}\left\{ \frac{(2n_i+m+1)[2n_i+m+1-2(Z_1\pm Z_2)/\gamma]^3}{2} - \right.$$

$$- \frac{[2n_i+m+1-2(Z_1\pm Z_2)/\gamma]^2}{2} \times$$

$$\times \left[2(2n_i+m+1)\frac{Z_1\pm Z_2}{\gamma} - 36n_i(n_i+m+1) - (5m+13)(m+1)\right] +$$

$$+ (2n_i+m+1)\left[2n_i+m+1-2\frac{Z_1\pm Z_2}{\gamma}\right]\left[2(2n_i+m+1)\frac{Z_1\pm Z_2}{\gamma} + 2(3-m^2)\right] +$$

$$\left. + (1-m^2)[8n_i(n_i+m+1)+(m+1)(m+3)]\right\}, \tag{23}$$

$$c_{n_i'}^{(3)} = \pm\frac{1}{2\gamma R(n_i-n_i')}\left\{-\lambda_{n_i}^{(2)}c_{n_i'}^{(1)} - \left(\lambda_{n_i}^{(1)} - \frac{1-m^2}{2}\right)c_{n_i'}^{(2)} \pm \right.$$

$$\pm \frac{1}{\langle n_i'|\rho_i^{-1}|n_i'\rangle}\left[\frac{\lambda_{n_i}^{(2)}}{2\gamma R}\langle n_i|\rho_i^0|n_i'\rangle \mp \frac{Z_1\pm Z_2\mp\lambda_{n_i}^{(0)}/R}{2\gamma}\sum_{n_i''} c_{n_i''}^{(2)}\langle n_i''|\rho_i^0|n_i'\rangle + \right.$$

$$+ \left(\frac{\lambda_{n_i}^{(1)}}{2\gamma R} - \frac{3(1-m^2)}{8\gamma R}\right)\sum_{n_i''}\langle n_i'|\rho_i^0|n_i''\rangle\, c_{n_i''}^{(1)} + \frac{Z_1\pm Z_2\mp\lambda_{n_i}^{(0)}/R}{4\gamma^2 R}\sum_{n_i''} c_{n_i''}^{(1)}\langle n_i''|\rho_i^1|n_i'\rangle \mp$$

$$\left.\left. \mp \frac{\lambda_{n_i}^{(1)}+m^2-1}{4\gamma^2R^2}\langle n_i|\rho_i^1|n_i'\rangle \mp \frac{Z_1\pm Z_2\mp\lambda_{n_i}^{(0)}/R}{8\gamma^3R^2}\langle n_i|\rho_i^2|n_i'\rangle\right]\right\}, \tag{24}$$

$$c_{n_i}^{(3)} = \pm\frac{m^2-1}{32\gamma^3R^3}(2n_i+m+1-4\langle n_i|\rho_i^1|n_i\rangle) \pm$$

$$\pm \frac{2n_i+m+1-2(Z_1\pm Z_2)/\gamma}{64\gamma^3R^3}\big[(33-m^2)\big(2n_i(n_i+m+1)+m+4\big)+56\big] \pm$$

$$\pm \frac{[2n_i+m+1-2(Z_1\pm Z_2)/\gamma]^2}{32\gamma^3R^3}\big[(2n_i+m+1)\big(2n_i(n_i+m+1)+m-1\big) +$$

$$+ 10\langle n_i|\rho_i^1|n_i\rangle\big] \pm \frac{[2n_i+m+1-2(Z_1\pm Z_2)/\gamma]^3}{128\gamma^3R^3}[6n_i(n_i+m+1)+3m+10]. \tag{25}$$

The parameter γ can be determined from (8). Taking $n_1+n_2+m+1=n$ into account, we obtain

$$\gamma = \gamma_0 + \frac{\gamma_1}{R} + \frac{\gamma_2}{R^2} + \frac{\gamma_3}{R^3} + \ldots, \tag{26}$$

where

$$\gamma_0 = \frac{Z_1}{n}, \qquad \gamma_1 = \frac{nZ_2}{Z_1}, \qquad \gamma_2 = -\frac{n^2Z_2}{2Z_1^3}[3(n_1-n_2)Z_1+nZ_2],$$
$$\gamma_3 = \frac{Z_2n^3}{2Z_1^5}\{Z_1^2[6(n_1-n_2)^2+1-n^2]+3Z_1Z_2n(n_1-n_2)+Z_2^2n^2\}. \tag{27}$$

The energy $E=-\gamma^2/2$ and (26) give the well-known multipole expansion [1] for the energy of electrostatic interaction of the atom eZ_1 with the remote point charge Z_2. We also note that there is a misprint in formula (4.60) for γ_3 in [1].

The transfer from the left center Z_1 to the right center Z_2 in the formulas given above is realized by the changes $Z_1 \leftrightarrow Z_2$, $n_i \to n'_i$, $\nu \to R-\nu$, and $\phi \to -\phi$. The parabolic quantum numbers n'_1 and n'_2 of the right center satisfy the condition $n'_1 + n'_2 + m + 1 = n'$.

We have thus shown that applying the modified perturbation theory scheme [25] allows obtaining simple expansions in powers of $1/R$ for the wave function of a hydrogen-like atom in the field of a point charge. Moreover, up to terms of the order of R^{-3}, the function ψ in formula (3) becomes

$$\psi^{\text{pert}}(\mu,\nu) = C\, U^{\text{pert}}(\mu) V^{\text{pert}}(\nu), \tag{28}$$

where

$$\begin{aligned} U^{\text{pert}} &= f^{(0)}_{n_1}(\mu) + \sum_{p=1}^{3}\sum_{k=-p}^{p} c^{(p)}_{n_1+k} f^{(0)}_{n_1+k}(\mu), \\ V^{\text{pert}} &= f^{(0)}_{n_2}(\nu) + \sum_{p=1}^{3}\sum_{k=-p}^{p} c^{(p)}_{n_2+k} f^{(0)}_{n_2+k}(\nu), \end{aligned} \tag{29}$$

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

and all the coefficients $c^{(p)}_{n_i+k}$ for $p = 1, 2, 3$ were derived above.

We now normalize the total wave function $\Psi(\vec{r}, R)$ given by (3) and (28) up to and including terms of order of R^{-3}. For the normalization constant C, we finally obtain

$$\begin{aligned} C(R) = \frac{4\gamma^{1/2}}{R}\Bigg\{ &\sum_{i=1}^{2}\Bigg[\langle n_i|\rho_i^{-1}|n_i\rangle(1 + 2c^{(1)}_{n_i} + 2c^{(2)}_{n_i} + 2c^{(3)}_{n_i}) + \\ &+ \sum_{k=-1}^{1}(|c^{(1)}_{n_i+k}|^2 + 2c^{(1)}_{n_i+k}c^{(2)}_{n_i+k})\langle n_i+k|\rho_i^{-1}|n_i+k\rangle\Bigg] + \\ &+ \frac{1}{4\gamma^2R^2}\sum_{i=1}^{2}\langle n_i|\rho_i^{1}|n_i\rangle(1 - 2c^{(1)}_{n_i}) - \frac{\langle n_1|\rho_1^2|n_1\rangle - \langle n_2|\rho_2^2|n_2\rangle}{8\gamma^3R^3}\Bigg\}^{-1/2}. \end{aligned} \tag{30}$$

The obtained functions (3), (28), and (29) describe the electron behavior in the main region of distribution of the electron density.

Our next task is to find the two-center wave function in the internuclear region where the electron is far from both Coulomb centers (nuclei). Previously in [26], the solution of quasiangular equation (6) in this region has been obtained only in the limit case $R \gg 2n^2/Z_1$. Unfortunately, the well-known asymptotic Landau–Herring method [27], used in [26], has a small applicability domain because of the approximations used to calculate the so-called correction functions. Therefore, to find the quasiangular wave function $V(\nu)$ under the potential barrier, in the next section, we use the semiclassical approximation (the WKB method), which can also be applied in the region of not too large distances between nuclei. In this case, we use the condition that the motion is semiclassical only for the quasiangular variable ν, keeping the perturbative solution of the Z_1eZ_2 problem for the quasiradial variable μ. This allows expressing the matrix element of the exchange interaction [22], characterizing the charge transfer process between hydrogen-like ions and bare nuclei, in terms of the semiclassical penetrability of the potential barrier separating the potential wells (see Fig. 1) in quasiangular equation (6).

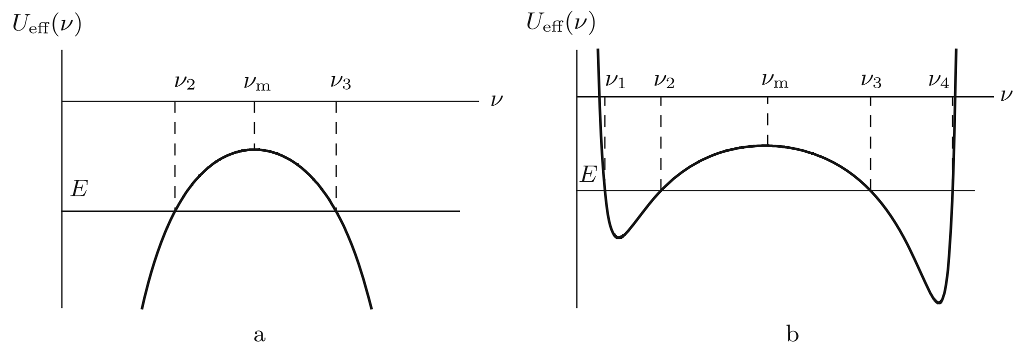

Fig. 1. The effective potential energy $U_{\text{eff}}(\nu)$ of quasiangular equation (31) for (a) $m = 0$ and 1 and (b) $m > 1$.

4. Semiclassical solutions of the quasiangular equation in the region between nuclei

Although the perturbation theory allows solving fundamental problems connected with expansions of the eigenvalues $\lambda_{1,2}(R)$ and eigenfunctions $U(\mu)$ and $V(\nu)$ in powers of $1/R$, determining the next terms of these expansions encounters rapidly increasing numerical difficulties. Solutions of Eqs. (5) and (6) at large R can be represented in a quite simple compact form using the WKB method (or semiclassical approximation), which was developed and became known as one of the most effective approximate methods for solving quantum mechanical problems (see, e.g., [28]–[31]). The WKB method allows obtaining uniform estimates for eigenfunctions at arbitrarily large internuclear distances R. Another advantage of semiclassical asymptotic expansions is their simplicity. Moreover, in contrast to perturbation theory, the semiclassical approximation is not restricted by the smallness of the interaction and hence has a wider applicability domain, which permits studying qualitative laws for the behavior and properties of quantum mechanical systems. Below, we construct semiclassical solutions of the quasiangular equation in the classically forbidden region.

We rewrite quasiangular equation (6) in the form of the one-dimensional Schrödinger equation

$$V'' - \frac{q^2}{\hbar^2} V = 0, \tag{31}$$

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

$$U_{\text{eff}}(\nu) = -\frac{\widetilde{Z}_1}{\nu} - \frac{\widetilde{Z}_2}{R-\nu} + \frac{\hbar^2(m^2-1)}{8\nu^2(1-\nu/R)^2}, \qquad \widetilde{Z}_{1,2} = \frac{\pm(Z_1 - Z_2) - \lambda/R}{2}.$$

Here, the dependence on the Planck constant $\hbar$ is explicitly restored, and we introduce the following notation (see Fig. 1): ν_i ($i = \overline{1,4}$) are the turning points, and ν_{m} is the point where the effective potential U_{eff} reaches a maximum. Moreover, the quantity q is real and coincides with the quasiangular momentum of a classical particle up to the imaginary unit i, $q(\nu) > 0$ at $\nu_2 < \nu < \nu_3$. We represent the solution of (31) in the form of an expansion in powers of $\hbar$,

$$V^{\text{semi}} = e^{S/\hbar}, \qquad S = \sum_{k=-1}^{\infty} \hbar^k S_k. \tag{32}$$

Substituting this equation in (31) and equating the coefficients of like powers of $\hbar$ to zero, we obtain a recursive system of first-order differential equations for the unknown functions $S_k(\nu)$,

$$(S'_{-1})^2 = q^2, \tag{33}$$

$$2S'_{-1}S'_0 + S''_{-1} = 0, \tag{34}$$

$$2S'_{-1}S'_k + S''_{k-1} + \sum_{j=0}^{k-1} S'_j S'_{k-j-1} = 0, \quad k = 1, 2, \ldots. \tag{35}$$

As a solution of (33), we choose the function

$$S_{-1}(\nu) = -\int_{\nu_2}^{\nu} q(\nu')\,d\nu', \tag{36}$$

corresponding to exponential damping of $V^{\rm semi}(\nu)$ in the under-barrier region. The equation for S_0 is solved in closed form: $S_0 = \log(C_0/\sqrt{q})$. The solutions of all the subsequent equations in recursive system (35) are expressed in quadratures:

$$S_k = \int \frac{1}{2q}\biggl(S''_{k-1} + \sum_{j=0}^{k-1} S'_j S'_{k-j-1}\biggr)d\nu + C_k, \qquad C_k = \text{const}, \quad k = 1, 2, \ldots. \tag{37}$$

For further consideration, it is convenient to introduce two ranges for ν: $0 \le \nu \ll \nu_{\rm m}$ and $\nu_2 \ll \nu \ll \nu_3$. Formulas (29) obtained in Sec. 3 hold in the first range, and we use the semiclassical approach to find the quasiangular function $V(\nu)$ determining the behavior of an electron in the under-barrier region $\nu_2 < \nu < \nu_3$. We note that where these ranges overlap, the results obtained by the perturbation theory and by the semiclassical approximation coincide. This allows finding the integration constants C_k from the condition for matching the semiclassical solution $V^{\rm semi}$ given (32) with the asymptotic expansion of $V^{\rm pert}$ given by (29):

$$V^{\rm semi}(\nu) \xrightarrow[\nu_2 \ll \nu \ll \nu_{\rm m}]{} V^{\rm as}(\nu). \tag{38}$$

For (38) to be satisfied, it is necessary that the internuclear distance be much larger than the distance at which the potential barrier in quasiangular equation (31) disappears, i.e.,

$$R \gg R_0 = \frac{1}{2\gamma^2}\Bigl[2(\widetilde{Z}_1 + \widetilde{Z}_2) + \sqrt{4\widetilde{Z}_1^2 + \gamma^2(1-m^2)} + \sqrt{4\widetilde{Z}_2^2 + \gamma^2(1-m^2)}\Bigr]. \tag{39}$$

If this requirement is met, then the polarization shift of the electron energy (see (26) and (27)) is small compared with the binding energy of an electron in the isolated atom eZ_1.

Therefore, the solution of quasiangular equation (31) in the semiclassical approximation satisfying boundary condition (38) has the form (here and hereafter, we set $\hbar = 1$)

$$V^{\rm semi} = \frac{C_0}{\sqrt{q}} \exp\Bigl[-\int_{\nu_2}^{\nu} q(\nu')\,d\nu' + S_1 + S_2\Bigr], \tag{40}$$

where the semiclassical corrections S_1 and S_2 are determined by the formulas

$$S_1 = -\frac{\widetilde{Z}_1}{4\gamma^3\nu^2}\biggl(1 + \frac{17\widetilde{Z}_1}{6\gamma^2\nu}\biggr) + \frac{\widetilde{Z}_2}{4\gamma^3(R-\nu)^2}\biggl(1 + \frac{17\widetilde{Z}_2}{6\gamma^2(R-\nu)}\biggr) +$$
$$+ \frac{m^2-1}{16\gamma^3}\biggl(\frac{1}{\nu^3} + \frac{1}{\nu^2 R} - \frac{1}{R(R-\nu)^2} - \frac{1}{(R-\nu)^3}\biggr) + \frac{\widetilde{Z}_1\widetilde{Z}_2}{2\gamma^5 R^3}\log\frac{\nu}{R-\nu} +$$

$$+\frac{\widetilde{Z}_1\widetilde{Z}_2}{4\gamma^5 R}\left(\frac{3}{(R-\nu)^2}-\frac{3}{\nu^2}+\frac{1}{R}\left[\frac{1}{R-\nu}-\frac{1}{\nu}\right]\right)+C_1, \tag{41}$$

$$S_2=\frac{\widetilde{Z}_1}{4\gamma^4\nu^3}+\frac{\widetilde{Z}_2}{4\gamma^4(R-\nu)^3}+C_2, \tag{42}$$

and the expressions for the integration constants C_0, C_1, and C_2 are given in Appendix B. The next terms $S_3, S_4, \ldots$ of expansion (32) are determined in the same way. But we restrict ourself to only the found terms S_{-1}, S_0, S_1, and S_2 because considering corrections of higher orders in $\hbar$ usually does not improve the agreement between the results of the WKB method and the exact solution. The reason for this, as is known [27]–[31], is that the formal series in powers of $\hbar$ is not convergent but only asymptotic.

The obtained formula (40) thus determines the semiclassical asymptotic behavior of solutions of quasiangular equation (31) as $\hbar \to 0$ and holds in the under-barrier region $\nu_2 < \nu < \nu_3$.

Although formulas (40)–(42) differ essentially from perturbation theory formulas (29), applying them to concrete problems does not encounter obstacles because the quantities S_k included in V^{semi} given by (31) are determined in terms of quadratures in (37).

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

$$\psi(\mu,\nu)=C(R)\,U^{\text{pert}}(\mu)\,V^{\text{semi}}(\nu) \tag{43}$$

and the normalization constant $C(R)$ is still given by formula (30).

5. Conclusions

We have obtained asymptotic expressions for the two-center quasiradial and quasiangular wave functions at large internuclear distances R using a modified perturbation theory. We showed that the corrections to the wave functions in each order of R^{-1} can be expressed by a finite number of Coulomb wave functions with a modified charge. We derived simple analytic expressions for the first, second, and third corrections to quasiradial and quasiangular functions, which are needed for stating the boundary conditions in the adiabatic representation of the three-body problem [1].

In the framework of the semiclassical approach, we found an analytic expression for solutions of quasiangular equation (6) in the region of under-barrier electron motion. This approach, usually applicable for highly excited states, yields a precision of calculating the energy levels of the order of $1/n$ (where n is the principal quantum number of the electron state in an isolated atom eZ_1). Therefore, to study low-lying states, higher orders of the semiclassical approximation must be used; determining them using the recursive scheme developed here does not involve fundamental difficulties. We will use the asymptotic expressions for the quasiradial and quasiangular functions obtained here in our further investigations in calculating the matrix element of the exchange interaction characterizing the charge transfer process between a hydrogen-like atom (ion) and a multiply charged ion.

There are two ranges of distances between two Coulomb centers where the solutions of quasiangular equation (6) behave differently depending on the variation of the internuclear distance R and the quasiangular variable ν. In the range $R \gg 2n^2/Z_1$, semiclassical solution (40) for $V(\nu)$ becomes limit expression (29) obtained in the framework of the modified perturbation theory. In the range $R_0 < R < 2n^2/Z_1$, perturbation theory is inapplicable because it does not take the exact shape of the potential barrier formed by the two Coulomb centers into account. At the same time, calculations show that the semiclassical method used here correctly describes the electron motion both for intermediate internuclear distances $R_0 < R < 2n^2/Z_1$ and in the asymptotic limit $R \gg 2n^2/Z_1$.

Appendix A: The matrix elements

We present expressions for the matrix elements of the operators ρ_i^k for $k = -1, 0, 1, 2$ and $i = 1, 2$, where $\rho_1 = 2\gamma\mu$ and $\rho_2 = 2\gamma\nu$. The diagonal matrix elements have the forms

$$\langle n_i|\rho_i^{-1}|n_i\rangle = \frac{1}{2n_i + m + 1}, \qquad \langle n_i|\rho_i^0|n_i\rangle = 1,$$

$$\langle n_i|\rho_i^1|n_i\rangle = \frac{6n_i(n_i + m + 1) + (m + 1)(m + 2)}{2n_i + m + 1},$$

$$\langle n_i|\rho_i^2|n_i\rangle = \frac{1}{2n_i + m + 1}[(m + 1)(m + 2)(m + 3) + 12n_i(m + 2)(m + 3) + \\ + 30n_i(n_i - 1)(m + 3) + 20n_i(n_i - 1)(n_i - 2)].$$

The off-diagonal matrix elements have the forms

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

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

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

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

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

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

$$\langle n_i - 1|\rho_i^2|n_i\rangle = \langle n_i|\rho_i^2|n_i - 1\rangle = -3\left(\frac{n_i(n_i + m)}{(2n_i + m + 1)(2n_i + m - 1)}\right)^{1/2} \times \\ \times [5n_i(n_i + m) + m^2 + 1],$$

$$\langle n_i + 1|\rho_i^2|n_i\rangle = \langle n_i|\rho_i^2|n_i + 1\rangle = -3\left(\frac{(n_i + 1)(n_i + m + 1)}{(2n_i + m + 1)(2n_i + m + 3)}\right)^{1/2} \times \\ \times [5n_i(n_i + m + 1) + (m + 2)(m + 3)],$$

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

$$\langle n_i + 2|\rho_i^2|n_i\rangle = \langle n_i|\rho_i^2|n_i + 2\rangle = 3\left(\frac{(n_i + 1)(n_i + 2)(n_i + m + 1)(n_i + m + 2)}{(2n_i + m + 1)(2n_i + m + 5)}\right)^{1/2} \times \\ \times (2n_i + m + 3),$$

$$\langle n_i - 3|\rho_i^2|n_i\rangle = \langle n_i|\rho_i^2|n_i - 3\rangle = \\ = -\left(\frac{n_i(n_i - 1)(n_i - 2)(n_i + m)(n_i + m - 1)(n_i + m - 2)}{(2n_i + m + 1)(2n_i + m - 5)}\right)^{1/2},$$

$$\langle n_i+3|\rho_i^2|n_i\rangle = \langle n_i|\rho_i^2|n_i+3\rangle =$$
$$= -\left(\frac{(n_i+1)(n_i+2)(n_i+3)(n_i+m+1)(n_i+m+2)(n_i+m+3)}{(2n_i+m+1)(2n_i+m+7)}\right)^{1/2}.$$

We also note that there are misprints in the formulas for the matrix elements $\langle n_i|\rho_i^2|n_i\rangle$ and $\langle n_i+1|\rho_i^1|n_i\rangle$ in [25].

Appendix B: The integration constants

The integration constants C_0, C_1, are C_2 are equal to

$$C_0 = (-1)^{n_2} e^{-\widetilde{Z}_1/\gamma} Q_+ Q_-, \qquad Q_\pm = \left(\frac{\widetilde{Z}_1}{\gamma} \pm \frac{\sqrt{m^2-1}}{2}\right)^{\{n_2+1/[1\pm\sqrt{(m-1)/(m+1)}]\}/2},$$

and

$$\begin{aligned}
C_1 = & -\frac{2n_2+m+1-2(Z_1-Z_2)/\gamma}{2\gamma R} + \\
& + \frac{(Z_1-Z_2)^2}{8\gamma^4 R^2}\left[\frac{(m^2-1)(2n_2+m+1)}{2n_2(n_2+m+1)+m+1} + 2(2n_2+m-3)\right] + \\
& + \frac{Z_1-Z_2}{4\gamma^3 R^2}[2\langle n_2|\rho_2^1|n_2\rangle - 2n_2(2n_2+2m-3) - m^2+3m+5] + \\
& + \frac{1}{8\gamma^2 R^2}\big[2n_2(n_2+1)(2n_2-11) + m^2(2n_2-3) + m\big(6n_2(n_2-3)-11\big) - 8\big],
\end{aligned}$$

$$\begin{aligned}
C_2 = & -\frac{(Z_1-Z_2)^3}{24\gamma^6 R^3[2n_2(n_2+m+1)+m+1]^2} \times \\
& \times \{2n_2^2(m+1)(98n_2m - 26n_2 + 47m^2 + 36m - 75) + \\
& + (m{+}1)^2[m(50n_2 + 22n_2m + 2m^2 + 7m + 8) - 100n_2 - 29] + \\
& + 8n_2^4(25m{+}9) + 80n_2^5\} + \\
& + \frac{(Z_1-Z_2)^2}{24\gamma^5 R^3[(2n_2(n_2+m+1)+m+1](2n_2+m+1)} \times \\
& \times \{(1+m)^2[9m(m^2+3m-9) - 152] + \\
& + 2n_2(m+1)(-385 - 386m + 27m^2 + 45m^3 - 771n_2 - 252mn_2 + 180m^2n_2) + \\
& + 144n_2^4(2n_2+5m-2) + 4n_2^3(6m-11)(30m+31)\} - \\
& - \frac{Z_1-Z_2}{48\gamma^4 R^3}\{21m^3 - 114m^2 - 413m - 254 + 168n_2^3 - n_2^2(6m^2 - 252m + 558) - \\
& - n_2(6m^3 - 126m^2 + 558m + 826)\} + \\
& + \frac{1}{96\gamma^3 R^3}\{128n_2^4 + 12(m^2-1)\langle n_2|\rho_2^1|n_2\rangle - 4n_2^3[3m^2 - 64m + 121] - \\
& - 6n_2^2[m(3m^2 - 35m + 121) + 183] - 2n_2m[m(3m^2 - 11m + 180) + 549] -
\end{aligned}$$

$$- 662n_2 - 133 - m[m(3m^2 + 59m + 254) + 331]\} + \frac{\widetilde{Z}_1 \widetilde{Z}_2}{2\gamma^5 R^3} \log(2\gamma R) -$$

$$- \frac{2n_2 + m + 1 - 2(Z_1 - Z_2)/\gamma}{32\gamma^3 R^3} [(2n_2(n_2 + m + 1) + m)(33 - m^2) + 56].$$

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