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Quasicrossings of potential curves in the two-Coulomb-center problem

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Abstract. The quasiclassical expression for the exchange interaction ΔE of potential curves at the points of their quasicrossing is found by means of the combined approach for solving the quantum mechanical two-Coulomb-center Z_1eZ_2 problem. It can be used further for the calculation of cross sections of charge exchange processes between hydrogen or hydrogen-like atoms and bare nuclei.

1 Introduction

The bound state problem for the negative charged particle (electron or muon) moving in the field of two positive charges Z_1 and Z_2 (the so-called Z_1eZ_2 problem) is the crucial quantum mechanical problem having a rich history [1,2]. This problem plays the same fundamental role in solving various problems of molecular physics as the hydrogen atom problem in atomic physics. In the atomic collision theory, the solutions of the two-Coulomb-center problem are used as a basis for the three-body problem in the adiabatic representation [3].

An important feature of the considered problem is its separability in the prolate spheroidal coordinate system for the Schrödinger equation. The Heun-class confluent equations [4] obtained herewith have two regular and one irregular singularities leading to many specific properties of their solutions. Nowadays, a lot of data obtained by solving these equations by means of numerical and asymptotic methods for different limiting cases are available. New results were obtained for both the problem of the molecular hydrogen ion H_2^+ (see, for instance, [2,5–8] and references therein) and the problem of two centers with differing charges [9–15]. Large-distance expansions for the H_2^+ system were thoroughly studied in [16–18] in the context of their analyticity, convergency and summability. In [19], the algebraic perturbation theory was extended to the case of homonuclear many-electron systems. It is based on explicit use of the generators of the SO(2,1) Lie algebra. However, only σ-states are here considered for which the azimuthal quantum number is zero. The two-Coulomb-center problem was also considered for the Dirac equation within the asymptotic methods in [20,21]. At the same time, in a series of papers the Z_1eZ_2 problem was studied at small R in the spaces of both reduced [22] and arbitrary dimensions [23,24].

In order to solve many problems arising in the theory of slow atomic collisions, e.g. for calculation of the matrix element $\Delta(R)$ of the exchange interaction between a hydrogen atom (or H-like ion) and a bare nucleus, it is necessary to know the two-center radial and angular Coulomb spheroidal wave functions (CSWF) [1]. In the general non-resonant case ($Z_1 \neq Z_2$), the exchange matrix element $\Delta(R)$ was determined formerly [25,26] under the condition requiring that the two-Coulomb-center spheroidal wave function must tend to the one-center parabolic wave function when an electron approaches one of the nuclei. The correct result for the exchange energy splitting $\Delta E = 2\Delta(R)$ at the quasicrossing points can actually be obtained only (see [27]) when the wave functions of the zeroth order 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 the one-center parabolic and spheroidal wave functions of a hydrogen atom differ essentially from each other. To be more specific, at large distances from the nucleus, a set of several Coulomb parabolic wave functions makes a contribution to the asymptotic behavior of a CSWF. This circumstance makes it difficult to apply the comparison equation method [1,9,11,12] to determine the mentioned asymptotic behavior (see, for instance, [27]).

In this paper, we use the combined approach [15] to solve the quantum two-Coulomb-center Z_1eZ_2 problem in the case of large internuclear distances R. An important peculiarity of this approach is the application of various methods to constructing the asymptotic expansions of the radial and angular CSWF in different areas of the electron motion. The perturbation theory can be used to determine the local behavior of the solutions of the Z_1eZ_2 problem

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near a certain nucleus. However, the application of the standard perturbation theory [28] leads to infinite sums of complicated form. In connection with this, in a number of papers [29–31] the schemes of perturbation theory, which allow one to obtain analytic expressions, have been proposed.

In order to construct the asymptotic expansions of the angular CSWF in the internuclear region, we propose to employ the quasiclassical approach (the WKB method). This approach allows us to obtain analytic solutions, but for this problem (see (21)) it is limited to asymptotically large internuclear distances R. These distances should be so large that the quantum penetrability of the potential barrier separating atomic particles should be much smaller than unity. A great number of problems can be pointed out [32–34], whose solutions depend 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, basing on our previous paper [15], we shortly describe the procedure for obtaining the asymptotic expansions (at large R) of the two-Coulomb-center quasiradial and quasiangular wave functions up to terms of the third order in $1/R$ by means of the modified perturbation theory. Additionally, the WKB expansions for solutions of the quasiangular equation in the Z_1eZ_2 problem are provided. Using the Firsov surface integral method [35], in Section 4 we calculate the first three terms of the asymptotic behavior of the exchange interaction potential of an ion with an atom for the general nonresonance case. In Section 5, the final results of the paper and further studies of the Z_1eZ_2 problem are discussed.

2 Basic equations

The time-independent Schrödinger equation ($\hbar = |e| = m_e = 1$)

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

describing 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, permits complete separation of variables in the prolate spheroidal coordinates

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

Here r_1 and r_2 are the distances from the electron to the corresponding charges, the vector $\vec{r} = (x,y,z)$ connects the center of segment R with an electron having the binding energy $E(R)$. Replacing the wave function $\Psi\left(\vec{r},R\right)$ by the product function

$$\Psi\left(\vec{r},R\right) = \frac{U\left(\xi,R\right)}{\sqrt{\xi^2-1}}\frac{V\left(\eta,R\right)}{\sqrt{1-\eta^2}}\frac{\mathrm{e}^{\pm im\phi}}{\sqrt{2\pi}}$$
$$= \frac{\psi\left(\xi,\eta,R\right)}{\sqrt{(\xi^2-1)(1-\eta^2)}}\frac{\mathrm{e}^{\pm im\phi}}{\sqrt{2\pi}}, \quad m = 0,1,\ldots, \qquad (3)$$

and using new variables

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

we obtain the system of ordinary differential equations for the radial $U(\xi,R)$ and angular $V(\eta,R)$ Coulomb spheroidal functions:

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

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

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:

$$U(0) = 0, \ U(\mu) \xrightarrow[\mu\to\infty]{} 0, \quad V(0) = 0, \ V(R) = 0. \qquad (7)$$

The pair of one-dimensional boundary value problems for the radial $U(\xi,R)$ and angular $V(\eta,R)$ Coulomb spheroidal functions is equivalent to the original problem (1) provided that the separation constants are equal:

$$\lambda_1 = \lambda_2. \qquad (8)$$

In order to make the content of this paper clearer, we shall briefly discuss the main features of the Z_1eZ_2 problem in the asymptotic region with respect to the intercenter separation. In the limit $R\to\infty$, the potential curves $E(R)$ of the two-Coulomb-center problem go over into the energy levels of an isolated (e,Z_1) or (e,Z_2) atom, and the wave functions corresponding to them – into the hydrogen-like functions of these atoms in parabolic coordinates. For this reason, it is convenient to classify the eigenfunctions and energies $E_j(R)$ of the Z_1eZ_2 problem with respect to the parabolic quantum numbers of the states of the (e,Z_1) and (e,Z_2) atoms, respectively: $j = [nn_1n_2m]$ and $j' = [n'n_1'n_2'm']$. In the asymptotic region $R\to\infty$, the wave functions $\Psi_j(\vec{r},R)$ and $\Psi_{j'}(\vec{r},R)$ corresponding to the eZ_1 and eZ_2 potential curves are concentrated around each of the centers Z_1 and Z_2, and for the potential curves

$E_j(R)$ and $E_{j'}(R)$ asymptotic expansions in inverse powers of R are valid. The asymptotic expansion of $E_j(R)$ (or $E_{j'}(R)$) describes the motion of the electron in the Coulomb well deformed slightly by the presence of the second charge; it is the expansion in multipoles of the energy of the electrostatic interaction of the atom with the point charge and can be obtained by perturbation theory (see Sect. 3.1). The possibility of the classically allowed motion of the electron with a given energy in the second well is not taken into account here because the transition of the electron from one Coulomb well to another is a deeply under-barrier transition and gives exponentially small (in R) corrections to $E_j(R)$ and $E_{j'}(R)$. The exponentially small corrections play a fundamental part in the cases when in the power-law approximation two potential curves with $n_1 = n_1'$ and $m = m'$ intersect with decreasing distance between the centers. As expected, the allowance for the exponential corrections gives a quasicrossing instead of an exact crossing and it enables one to calculate (see Sect. 4) the resulting splitting of the potential curves. It should be noted that when there is a state with a given energy only in one well, the exponential corrections to $E_j(R)$ and $E_{j'}(R)$ are quadratic with respect to the exponentially small corrections in the case of quasicrossing of two potential curves. This is explained by the fact that in the first case these corrections arise only when taking into account twofold under-barrier transitions (from the original well into the other and back again), whereas in the second case, due to the presence of the bound state there are simple "exchange" transitions in both wells.

When $Z_1 = Z_2$, both wells are identical. In this case, there exist pairs of even (g) and odd (u) states (with respect to the inversion of the electron coordinates). The potential curves of these states converge as $R \to \infty$. At finite but large R, the wave functions are given as a sum and difference of the wave functions centered on the left- and right-hand nuclei [1]. Thus, the problem considered is reduced to the determination of the left- and right-hand-side states.

Hereinafter, for the definition we shall consider the left-hand-side states. The transfer from the left-hand side center Z_1 to the right-hand side one Z_2 can be 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 center satisfy the condition $n_1' + n_2' + m + 1 = n'$.

3 The wave functions of the problem

3.1 The perturbation theory

In the theoretical description of the hydrogen-like atom behavior in the field of point charge, we first need to develop perturbation theory for large internuclear distances R. Despite the fact that this problem has been investigated for many years, the problem of building the perturbation theory schemes, allowing to obtain simple analytical expressions for the wave function remains actual. One of these schemes was developed in [36] and applied in our previous paper [15] in order to obtain third-order (in R^{-1}) corrections to energies and wave functions of bounded states.

The formal scheme of these calculations consists in the following steps. First, we represent the original differential operator L of equations (5) and (6) in the form $L = L_0 + L_1/R$. The limiting differential operator L_0 is obtained from the original operator L by tending R to infinity. After this, we expand the functions $U(\mu)$ and $V(\nu)$ in the basic functions $u_{n_1}^{(0)}(\mu)$ and $v_{n_2}^{(0)}(\nu)$, which are defined as solutions of the equations $L_0^{(\mu)} u_{n_1}^{(0)}(\mu) = 0$ and $L_0^{(\nu)} v_{n_2}^{(0)}(\nu) = 0$, respectively. These solutions can be expressed in terms of the well-known special functions. Note that in the framework of this scheme we consider the energy as a parameter and the separation constants $\lambda_{1,2}$ as eigenvalues of the corresponding operators (energetic parameter γ can be found from Eq. (8)).

Omitting the details of these calculations, which can be found in [15], we write the solutions of the quasiradial (5) and quasiangular (6) equations in the following form:

$$U^{pert}(\mu) = f_{n_1}^{(0)}(\mu) + \sum_{p=1}^{3} \sum_{k=-p}^{p} c_{n_1+k}^{(p)} f_{n_1+k}^{(0)}(\mu), \tag{9}$$

$$V^{pert}(\nu) = f_{n_2}^{(0)}(\nu) + \sum_{p=1}^{3} \sum_{k=-p}^{p} c_{n_2+k}^{(p)} f_{n_2+k}^{(0)}(\nu), \tag{10}$$

$$f_{n_i}^{(0)}(x) = \sqrt{\frac{(n_i+m)!}{n_i!(m!)^2(2n_i+m+1)}}\,(2\gamma x)^{(m+1)/2} \times \mathrm{e}^{-\gamma x} F(-n_i,\, m+1,\, 2\gamma x), \tag{11}$$

where $F(\alpha, \beta, z)$ is the confluent hypergeometric function and for $p = 1, 2, 3$ all the $c_{n_i+k}^{(p)} \sim R^{-p}$ coefficients have been calculated in [15]. The important feature of (9) and (10) is the finite number of terms in every order of R^{-1}.

The energetic parameter γ, as was mentioned above, can be determined from (8). Taking into account that $n_1 + n_2 + m + 1 = n$, we arrive at the expression

$$\gamma = \gamma_0 + \frac{\gamma_1}{R} + \frac{\gamma_2}{R^2} + \frac{\gamma_3}{R^3} + \cdots, \tag{12}$$

where

$$\gamma_0 = \frac{Z_1}{n},\ \gamma_1 = \frac{nZ_2}{Z_1},\ \gamma_2 = -\frac{n^2 Z_2}{2Z_1^3}\Big[3(n_1 - n_2)Z_1 + nZ_2\Big],$$
$$\gamma_3 = \frac{Z_2 n^3}{2Z_1^5}\Big\{Z_1^2\left[6(n_1 - n_2)^2 + 1 - n^2\right] + 3Z_1 Z_2 n(n_1 - n_2) + Z_2^2 n^2\Big\}. \tag{13}$$

The energy $E = -\gamma^2/2$ and (12) give the well-known [1] multipole expansion for the energy of electrostatic interaction of the atom eZ_1 with the remote point charge Z_2. Note also that for γ_3 there is a misprint in formula (4.60) [1].

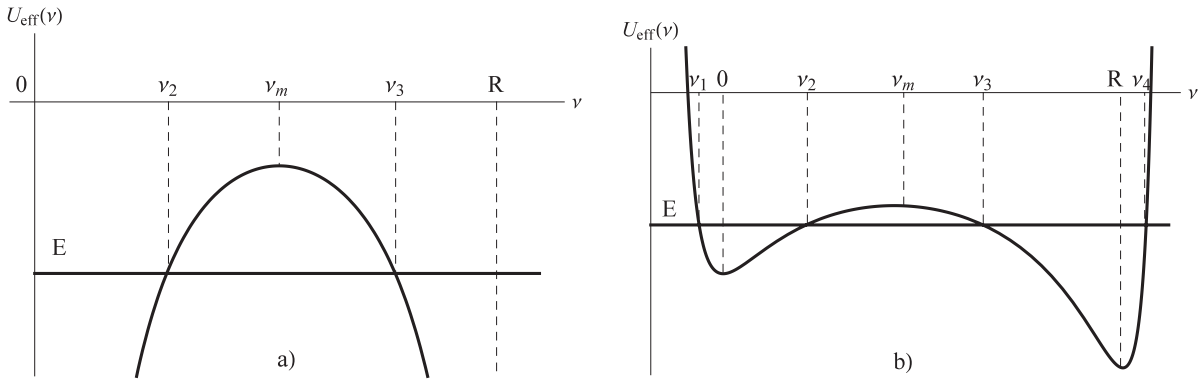

Fig. 1. The effective potential energy $U_{eff}(\nu)$: (a) when $m = 0$ and $m = 1$, (b) when $m > 1$.

Herewith, the function ψ from formula (3) within $O(R^{-4})$ is of the form

$$\psi^{pert}(\mu, \nu, R) = C(R)U^{pert}(\mu)V^{pert}(\nu), \qquad (14)$$

where the formula for the normalization constant C can also be found in [15].

The functions (3), (14) and (10) describe the electron behavior in the main distribution region of electron density, where the ratios μ/R and ν/R are small quantities. The idea of the used asymptotic method consists in the fact that when an electron moves far away from both centers, the exchange energy is determined mainly by the region in the vicinity of the internuclear axis R. Therefore, next we shall consider the under-barrier motion of an electron when an electron is located far from both Coulomb centers (nuclei).

The main idea of the asymptotic method we used is based on the idea that when the electron is far from the nuclei the exchange-interaction energy is determined mainly by the electron distribution region close to the internuclear axis R. Previously [36,37], the solution of the quasiangular equation (6) in the aforementioned region has been obtained only in the limiting case $R \gg 2n^2/Z_1$ for the internuclear distances sufficiently larger than the sizes of electron shells of the atom (e, Z_1) and ion (e, Z_2). However, the well-known asymptotic Landau–Herring method [38], applied in [37], has a small applicability domain because of approximations used for calculating the so-called correction functions. Thus, in the next subsection, we shall consider the quasiclassical approximation (the WKB method), applied to the quasiangular equation (6). This approach is suitable also in the region of not too large distances, where the wave functions of every center overlap.

Therefore, the condition of the motion quasiclassicality will be used below only with respect to the quasiangular variable ν saving the perturbation solution of the problem for quasiradial variable μ. This fact allows us to express the matrix element of the exchange interaction [34], which characterizes the charge transfer process between the hydrogen-like ions and bare nuclei, in terms of quasiclassical penetrability of the potential barrier separating two potential wells (see Fig. 1) in the quasiangular equation (6).

3.2 WKB solutions of the quasiangular equation in inter-center region

In order to calculate the splitting of the potential curves at the points of quasicrossing, it is necessary to determine the electron wave function (3) in the internuclear region. The interaction with another nucleus is not small here, so it cannot be considered as a small perturbation. Solutions of (6) for a large number of zeros of the eigenfunctions $V(\nu)$ 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, Heading [39], Fröman [40], Ponomarev [41], Berry and Mount [42]).

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

$$V'' - \frac{q^2}{\hbar^2}V = 0, \qquad (15)$$

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

$$U_{eff}(\nu) = -\frac{\tilde{Z}_1}{\nu} - \frac{\tilde{Z}_2}{R-\nu} + \frac{\hbar^2\left(m^2-1\right)}{8\nu^2(1-\nu/R)^2}, \qquad (16)$$

$$\tilde{Z}_{1,2} = \left[\pm(Z_1 - Z_2) - \lambda_2/R\right]/2. \qquad (17)$$

Here the Planck constant $\hbar$ is restored explicitly and the following notation is introduced (see also Fig. 1): ν_i $(i = \overline{1,4})$ are the turning points being solutions of the equation $q(\nu) = 0$, ν_m is the point where the effective potential reaches a maximum. Moreover, the quantity q is real and up to the factor of the imaginary unit i coincides with the quasiangular momentum of a classical particle, $q^2(\nu) > 0$ at $\nu_2 < \nu < \nu_3$.

In [15], a recurrent scheme for obtaining the WKB-expansions for solutions of the quasiangular equation (15)

in the under-barrier region was developed. The quasiclassical formulas for a quasiangular function V^{quas} obtained are of the form (hereinafter $\hbar = 1$):

$$V^{quas}(\nu) = \frac{C_0}{\sqrt{q(\nu)}} \exp\left[-\int_{\nu_2}^{\nu} q(\nu')d\nu' + S_1(\nu) + S_2(\nu) + \mathrm{O}(R^{-4})\right], \quad (18)$$

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

$$S_1 = \frac{\tilde{Z}_1\tilde{Z}_2}{2\gamma^5 R^3}\ln\frac{\nu}{R-\nu} - \frac{\tilde{Z}_1}{4\gamma^3\nu^2}\left[1+\frac{17\tilde{Z}_1}{6\gamma^2\nu}\right] + \frac{\tilde{Z}_2}{4\gamma^3(R-\nu)^2}\left[1+\frac{17\tilde{Z}_2}{6\gamma^2(R-\nu)}\right] - \frac{\tilde{Z}_1\tilde{Z}_2}{4\gamma^5R^2}\left[\frac{3R+\nu}{\nu^2} - \frac{4R-\nu}{(R-\nu)^2}\right] + \frac{m^2-1}{16\gamma^3 R}\left[\frac{R+\nu}{\nu^3} - \frac{2R-\nu}{(R-\nu)^3}\right] + C_1, \quad (19)$$

$$S_2 = \frac{\tilde{Z}_1}{4\gamma^4\nu^3} + \frac{\tilde{Z}_2}{4\gamma^4(R-\nu)^3} + C_2. \quad (20)$$

The integration constants C_0, C_1, and C_2 have been found by exact matching $V^{quas}(\nu) \xrightarrow[\nu_2 \ll \nu \ll \nu_m]{} V^{pert}(\nu)$; they are given in Appendix B of [15]. Note also that, in the expression for C_0 there is a misprint: the additional factor $\sqrt{\gamma}[n_2!(n_2+m)!(2n_2+m+1)]^{-1/2}$ was omitted.

Here we restrict ourselves only to the found terms S_{-1}, S_0, S_1, and S_2 because the consideration of the higher-order corrections does not usually improve the agreement between the results of the WKB method and the exact solution. As it is known [38–42], the reason for this is that the formal series in powers of $\hbar$ is not convergent but only asymptotic. The presence of the logarithmic term in (19) suggests that expression (18) has a nonphysical singularity at the location point $\nu = R$ of another nucleus, which is not surprising: the potential of another nucleus cannot be considered here as a small perturbation.

At some value R_0 of the internuclear distance, the influence of the cores on each other becomes too strong, and the wave functions centered on each nucleus overlap, which leads to the disappearance of the potential barrier in the quasiangular equation (15). Therefore, the condition of applicability of the WKB-function (18) requires the internuclear distance to be much larger than R_0, i.e.

$$R \gg R_0 = \frac{1}{2\gamma^2}\left[2(\tilde{Z}_1+\tilde{Z}_2) + \sqrt{4\tilde{Z}_1^2+\gamma^2(1-m^2)} + \sqrt{4\tilde{Z}_2^2+\gamma^2(1-m^2)}\right]. \quad (21)$$

When this requirement is fulfilled, the polarization shift of the electron energy (see (12) and (13)) is small compared to the binding energy of an electron in the isolated atom eZ_1.

In the under-barrier region, the final expression for the wave function $\Psi_j(\vec{r}, R)$ centered on the atom of (e, Z_1) is of the form

$$\Psi_j(\vec{r}, R) = C(R)\frac{R^2}{4}\frac{U_j^{pert}(\mu)}{\sqrt{\mu(R+\mu)}}\frac{V_j^{quas}(\nu)}{\sqrt{\nu(R-\nu)}}\frac{\mathrm{e}^{\pm im\phi}}{\sqrt{2\pi}}, \quad (22)$$

where $U_j^{pert}(\mu)$ and $V_j^{quas}(\nu)$ are given by (9) and (18), respectively. The expression for the wave function $\Psi_{j'}(\vec{r}, R)$ centered on the ion (e, Z_2) can be derived from (9), (18), and (22) by making the replacements $Z_1 \leftrightarrow Z_2$, $n_i \to n_i'$, $\nu \to R-\nu$, $\phi \to -\phi$.

In Tables 1 and 2, for the quasimolecule Z_1eZ_2 with $Z_1 = 3$ and $Z_2 = 1$, we present the results of numerical calculations for quasiangular wave functions corresponding to the ground state ($n_1 = n_2 = m = 0$) and the first ($n_1 = m = 0$, $n_2 = 1$) excited σ-states. The calculations of the wave functions is performed by expressions (10), in which a different number ($p = 1, 2, 3$) of corrections is taken into account, and by quasiclassical formulas (18)–(20). In the last column, we also present the results of exact numerical calculation of the Z_1eZ_2 problem taken from [37]. As it is seen from the tables, the accuracy of our asymptotic formulas (10) increases with p. The quasiclassical wave function V^{quas} is in better agreement with the numerical wave functions in the region of its validity $2\gamma\nu_2 \ll \rho_2 \ll 2\gamma\nu_3$. In connection with this, an essential and favorable fact is that exchange splitting of the potential curves ΔE can be represented in the form of the surface integral (23) in which a surface crossing internuclear axis in the under-barrier region can be chosen as S where the quasiclassical wave function (18)–(20) is known with higher accuracy than the perturbation solution (10).

4 Splitting of the potential curves at the quasicrossing points

In order to calculate the probabilities of charge transfer processes between a hydrogen or hydrogen-like atom and a bare nucleus, it is necessary to know the exchange matrix element $\Delta(R) = \Delta E(R)/2$ between the states of the transferring electron of atom (e, Z_1) and ion (e, Z_2). In the case when the binding energies of an electron in the atom and ion differ slightly, the calculation of the exchange splitting $\Delta E(R)$ of the potential curves at the quasicrossing points can be carried out using the Firsov surface integral [35]

$$\Delta E = \oint_S \left(\Psi_j^*\vec{\nabla}\Psi_{j'} - \Psi_{j'}^*\vec{\nabla}\Psi_j\right)\cdot d\vec{S}. \quad (23)$$

Here Ψ_j and $\Psi_{j'}$ are the electron wave functions of the quasimolecule (Z_1, e, Z_2), which turns in the separated nuclei limit ($R \to \infty$) into the wave functions of the hydrogen-like atoms (e, Z_1) and (e, Z_2), respectively; $d\vec{S} = \vec{n}dS$; S is the surface enclosing the half-space containing nuclei Z_1; $\vec{n}$ is the surface normal to S.

Table 1. The quasiangular wave functions of the quasimolecule Z_1eZ_2 with $Z_1 = 3$ and $Z_2 = 1$ corresponding to the ground state ($n_1 = n_2 = m = 0$), $R = 2$ a.u. The wave function V_p^{pert}, calculated by means of perturbation theory and defined by (10), including terms of the second ($p = 2$) and third ($p = 3$) orders of R^{-1}, and the quasiclassical wave function V^{quas} (18)–(20) are compared with the results of exact calculations V^{num} [37].

ρ_2	$V_2^{pert}(\rho_2)$	$V_3^{pert}(\rho_2)$	$V^{quas}(\rho_2)$	$V^{num}(\rho_2)$
0.00	0.000 00	0.000 00	–	0.000 00
0.20	0.412 67	0.412 59	–	0.412 33
0.40	0.527 01	0.526 91	–	0.526 62
0.60	0.582 84	0.582 74	–	0.582 48
0.80	0.607 71	0.607 62	–	0.607 39
1.00	0.613 49	0.613 42	–	0.613 24
1.25	0.603 71	0.603 66	–	0.603 54
1.50	0.582 04	0.582 02	–	0.581 97
1.75	0.553 28	0.553 29	–	0.553 29
2.00	0.520 53	0.520 56	–	0.520 60
2.50	0.450 64	0.450 71	–	0.450 83
3.00	0.382 19	0.382 27	0.397 75	0.382 43
3.50	0.319 53	0.319 61	0.319 43	0.319 81
4.00	0.264 36	0.264 42	0.260 61	0.264 63
4.50	0.216 95	0.216 99	0.212 56	0.217 20
5.00	0.176 91	0.176 91	0.172 77	0.177 11
5.50	0.143 50	0.143 47	0.139 87	0.143 66
6.00	0.115 89	0.115 83	0.112 81	0.116 01
6.50	0.093 25	0.093 16	0.090 68	0.093 32
7.00	0.074 79	0.074 68	0.072 66	0.074 81
7.50	0.059 82	0.059 69	0.058 07	0.059 80
8.00	0.047 73	0.047 58	0.046 30	0.047 66
9.00	0.030 19	0.030 02	0.029 28	0.030 02
10.00	0.018 96	0.018 79	0.018 55	0.018 62
11.00	0.011 83	0.011 67	0.012 46	0.011 12

As an integration surface in (23) we choose the surface defined by the equation $\eta = \text{const}$. Let us find the values of exchange splitting ΔE of the eZ_1 and eZ_2 potential curves in close vicinity to the quasicrossing points, where the quasimomenta q_j and $q_{j'}$ of the electron centered on the atoms (e, Z_1) and (e, Z_2), respectively, are approximately equal: $q_j \approx q_{j'}$. Then, substituting the wave function Ψ_j in the form (3), (22) and a similar expression for $\Psi_{j'}$ into (23), we obtain

$$\begin{aligned}\Delta E &= CC'\frac{R^3}{8}\left(V_j^{quas}\frac{dV_{j'}^{quas}}{d\nu} - V_{j'}^{quas}\frac{dV_j^{quas}}{d\nu}\right)\\ &\quad\times\int_0^\infty \frac{U_j^{pert}(\mu)U_{j'}^{pert}(\mu)}{\mu(R+\mu)}d\mu\\ &= CC'C_0C_0'\mathrm{e}^{C_1+C_1'}\\ &\quad\times\mathrm{e}^{C_2+C_2'}\frac{R^3}{8}\mathrm{e}^{-J}\int_0^\infty \frac{U_j^{pert}(\mu)U_{j'}^{pert}(\mu)}{\mu(R+\mu)}d\mu. \quad (24)\end{aligned}$$

Here $J = \int_{\nu_2}^{\nu_3} q(\nu)d\nu$ is the barrier integral, and the constants $C'(R)$ and $C_i'(R)$ can be derived from the expressions for $C(R)$ and $C_i(R)$ (see [15]) by making the replacements $Z_1 \leftrightarrow Z_2$, $n_i \to n_i'$. Thus, in the case of $q_j = q_{j'}$ the exchange interaction energy does not depend on the choice of the integration surface S position and, as expected, up to the pre-exponential factor is determined by the quasiclassical penetrability of the potential barrier separating two Coulomb centers in the quasiangular equation (6).

Formula (24) determines the magnitude of the exchange splitting of the potential curves ΔE, but it is limited by the condition $R > R_0$ (see (21)). At the distances between the centers $R < R_0$, i.e., for $|E_j(R)| < |U_{eff}(\nu_m)|$ the electron moves on the generalized orbit embracing two nuclei, so we cannot separate the electron motion between different potential wells, and it makes no sense to consider the exchange interaction energy at these distances.

For the expansion of the barrier integral J in positive powers of R_0/R the value of the turning points ν_i, $(i = \overline{1,4})$ with respect to the asymptotic parameter R should be fixed: $\nu_{1,2} = \mathrm{O}(1)$, $\nu_{3,4} = \mathrm{O}(R)$. Let us consider a point ν_0 dividing the integration domain $\nu_2 \leqslant \nu \leqslant \nu_3$ into the domain $\nu_2 \leqslant \nu \leqslant \nu_0$ where the Coulomb potential $-\tilde{Z}_1/\nu$ dominates and the domain $\nu_0 \leqslant \nu \leqslant \nu_3$ where the potential $-\tilde{Z}_2/(R-\nu)$ dominates. Since in the first domain $\nu_2 \leqslant \nu \leqslant \nu_0$ the Coulomb potential of the charge $\tilde{Z}_1$ prevails, we choose it as a basic potential and expand the quasimomentum q in the potential of the remote nucleus $\tilde{Z}_2$. In the second domain $\nu_0 \leqslant \nu \leqslant \nu_3$, we consider the Coulomb potential of the charge $\tilde{Z}_2$ as a basic potential, assuming the potential of the remote nucleus $\tilde{Z}_1$ as weak perturbation. The result of the integral J thus obtained does not depend on the choice of the point ν_0

Table 2. The quasiangular wave functions of the quasimolecule Z_1eZ_2 with $Z_1 = 3$ and $Z_2 = 1$ corresponding to the excited state ($n_1 = m = 0$, $n_2 = 1$), $R = 8$ a.u. The wave function V_p^{pert}, calculated by means of perturbation theory and defined by (10), including terms of the second ($p = 2$) and third ($p = 3$) orders of R^{-1}, and the quasiclassical wave function V^{quas} (18)–(20) are compared with the results of exact calculations V^{num} [37].

ρ_2	$V_2^{pert}(\rho_2)$	$V_3^{pert}(\rho_2)$	$V^{quas}(\rho_2)$	$V^{num}(\rho_2)$
0.00	0.000 00	0.000 00	–	0.000 00
0.20	0.183 52	0.183 20	–	0.183 07
0.40	0.178 00	0.177 72	–	0.177 71
0.60	0.134 02	0.133 85	–	0.134 00
0.80	0.073 68	0.073 65	–	0.073 96
1.00	0.007 15	0.007 26	–	0.007 71
1.50	−0.155 09	−0.154 62	–	−0.153 94
2.00	−0.286 67	−0.285 95	–	−0.285 17
2.50	−0.379 22	−0.378 37	–	−0.377 61
3.00	−0.435 38	−0.434 51	–	−0.433 83
3.50	−0.461 46	−0.460 67	–	−0.460 10
4.00	−0.464 44	−0.463 80	–	−0.463 35
4.50	−0.450 75	−0.450 30	–	−0.449 98
5.00	−0.425 82	−0.425 60	–	−0.425 40
6.00	−0.358 52	−0.358 74	–	−0.358 75
7.00	−0.285 74	−0.286 33	−0.344 67	−0.286 52
8.00	−0.219 18	−0.220 03	−0.238 78	−0.220 36
9.00	−0.163 44	−0.164 43	−0.173 31	−0.164 89
10.00	−0.119 26	−0.120 29	−0.125 39	−0.120 85
12.00	−0.060 51	−0.061 41	−0.063 76	−0.062 10
14.00	−0.029 30	−0.029 97	−0.031 37	−0.030 71
16.00	−0.013 72	−0.014 17	−0.015 14	−0.014 90
18.00	−0.006 27	−0.006 55	−0.007 28	−0.007 25
20.00	−0.002 81	−0.002 97	−0.003 58	−0.003 67
22.00	−0.001 23	−0.001 33	−0.001 98	−0.002 07

Table 3. Adiabatic energy splittings ΔE at quasicrossing points R_c in the system (p, e, Z_2).

Z_2	(Nlm)–$(N'l'm')$	R_c	ΔE (27)	ΔE_{KPS} [1]	ΔE_B [49]	ΔE_{num} [50]
4	$(4,3,0)$–$(3,2,0)$	7.76	6.66×10^{-2}	6.56×10^{-2}	–	6.94×10^{-2}
5	$(5,4,0)$–$(4,3,0)$	12.9	4.07×10^{-3}	6.09×10^{-3}	4.16×10^{-3}	4.25×10^{-3}
6	$(6,5,0)$–$(5,4,0)$	21.4	2.40×10^{-5}	3.37×10^{-5}	2.41×10^{-5}	–
7	$(7,6,0)$–$(6,5,0)$	31.9	2.06×10^{-8}	2.44×10^{-8}	2.14×10^{-8}	–
8	$(8,7,0)$–$(7,6,0)$	44.3	3.04×10^{-12}	4.51×10^{-12}	2.88×10^{-12}	–

and in the case $m > 1$ is of the form

$$
\begin{aligned}
J =& \gamma R + \frac{\tilde{Z}_1}{\gamma} \ln \frac{\nu_2 - \nu_1}{4eR} + \frac{\tilde{Z}_2}{\gamma} \ln \frac{\nu_4 - \nu_3}{4eR} \\
&+ \frac{\sqrt{m^2-1}}{2} \ln \frac{\left(\sqrt{\nu_2} + \sqrt{\nu_1}\right)\left(\sqrt{R-\nu_3} + \sqrt{R-\nu_4}\right)}{\left(\sqrt{\nu_2} - \sqrt{\nu_1}\right)\left(\sqrt{R-\nu_3} - \sqrt{R-\nu_4}\right)} \\
&- \frac{1}{\gamma^3 R}\left[\tilde{Z}_1\tilde{Z}_2 - \frac{(m^2-1)\gamma^2}{4}\right]\left[1 + \frac{3(\tilde{Z}_1 + \tilde{Z}_2)}{2\gamma^2 R}\right] \\
&\times \ln \frac{16eR^2}{(\nu_2 - \nu_1)(\nu_4 - \nu_3)} + \frac{(\tilde{Z}_1 - \tilde{Z}_2)^2}{2\gamma^3 R} \\
&+ \frac{(\tilde{Z}_1 + \tilde{Z}_2)(\tilde{Z}_1^2 - 4\tilde{Z}_1\tilde{Z}_2 + \tilde{Z}_2^2)}{4\gamma^5 R^2} + \mathrm{O}(R^{-3}), \qquad (25)
\end{aligned}
$$

where the effective charges $\tilde{Z}_{1,2}$ are determined by (17). Although the equation $q = 0$ allows finding the exact solutions, the asymptotic expressions for the turning points ν_i, $i = 1, 2, 3, 4$ up to the terms of the order of R^{-2} will be used below. In the cases $m = 0$ and $m = 1$, the barrier integral J can be determined in the same way.

The calculation of the quasiradial integral

$$
I_r = \int_0^\infty \frac{U_j^{pert}(\mu) U_{j'}^{pert}(\mu)}{\mu(R+\mu)} d\mu,
$$

from (24) presents no difficulties, too. Its value can be expressed in terms of the coefficients $c_{n_1}^{(k)}$ from the expansion (9) and the matrix elements $\langle n_1|\rho_1^k|n_1\rangle$ (see [15] for their explicit form):

$$
\begin{aligned}
I_r =& \frac{1}{R}\left\{\langle n_1|\rho_1^{-1}|n_1\rangle\left(1 + 2c_{n_1}^{(1)} + 2c_{n_1}^{(2)}\right) - \frac{\langle n_1|\rho_1^0|n_1\rangle}{2\gamma R}\right. \\
&\left. + \frac{\langle n_1|\rho_1|n_1\rangle}{4\gamma^2 R^2} + \sum_{k=-1}^{1} |c_{n_1+k}^{(1)}|^2 \langle n_1 + k|\rho_1^{-1}|n_1 + k\rangle\right\}. \qquad (26)
\end{aligned}
$$

Substituting (25) and (26), the values of normalization constants C, C', as well as formulas for the matching constants C_i, C'_i $(i = 0, 1, 2)$ (see [15]) into (24), we obtain the following expression for the exchange splitting of the potential curves:

$$\Delta E = \frac{2\gamma^2 (-1)^{n_2+n'_2} (2\gamma R)^{n_2+n'_2+m+1} \mathrm{e}^{-\gamma R}}{\sqrt{n\, n'\, n_2!\, (n_2+m)!\, n'_2!\, (n'_2+m)!}} \times \left\{ 1 - \frac{1}{2\gamma R}\left[\frac{A_2^2 + A_2'^2}{4} + A_2 A'_2 + \frac{1-m^2}{2}\right] - \frac{A_2 + A'_2}{2\gamma R} - \frac{A_1}{2\gamma^2 R}\left(\frac{Z_1}{n} + \frac{Z_2}{n'}\right) + \frac{(A_1-1)(A_2+A'_2)^2 + 2A_2A'_2(A_1-2)}{8\gamma^2 R^2} + \frac{A_2^3 + A_2'^3 + (A_2A'_2 - 4A_1 + 2m^2 - 6)(A_2 + A'_2)}{32\gamma^2 R^2} + \frac{[A_2^2 + A_2'^2 + 4A_2A'_2 + 2(1-m^2)]^2}{128\gamma^2 R^2} + \frac{A_1(3A_1 + 1 - m^2)}{4\gamma^2 R^2} + \mathrm{O}(R^{-3}) \right\}, \quad (27)$$

where $A_i = 2n_i + m + 1$, $A'_i = 2n'_i + m + 1$. Note that the formula (27) is valid for any value of $m = 0, 1, 2, \ldots$ In the resonance case ZeZ, formula (27) gives the difference between the energies of gerade and ungerade states and coincides with the results of [16–18] for $Z_1 = Z_2 = 1$ and of [26,43–46] for $Z_1 = Z_2 = Z$. It should be noted also that the formulas for H_2^+ in [1,26] contain a mistake in the terms of the order of R^{-2}.

Addressing to the result for the splitting of the potential curves obtained previously in [26,47] and given then in [1], it should firstly be noted that the pre-exponential factor in [26,47] was derived incorrectly because the distance between the potential curves was calculated at not the same value of R but at the same value of the parameter $\beta = (Z_2 - Z_1)/(-2E)^{1/2} = n'_2 - n_2$. The formulas obtained in these papers give the correct result only in the case of equal charges when β is equal to zero. In the general nonresonant case $Z_1 \neq Z_2$, the exponential splitting of the potential curves at the quasicrossing points was obtained in [26,47] by differentiating with respect to indices of the power expansions (12) for the eZ_1- and eZ_2-energies. When using different parts of the asymptotic series, the same difference between the potential curves at the quasicrossing points can be represented by various formulas of the form

$$\Delta E = T\delta(n_2, n'_2, m, p), \quad (28)$$

where δ is determined by formula (4.36) from [1]. Komarov and Slavyanov [25,44] proposed to determine T by differentiating the expression $E = -(Z_2 - Z_1)^2/(2\beta^2)$ with respect to indices, which gives

$$T_{KS} = 2\frac{(Z_2 - Z_1)^2}{(n'_2 - n_2)^3}. \quad (29)$$

Power [26] criticized this expression and noted that it does not give a correct result for the splitting in the limiting case $Z_1 = Z_2$. Thus, Power proposed to differentiate the half-sum of the eZ_1- and eZ_2-energies with respect to indices:

$$T_P = \frac{\partial E_1}{\partial n_2} + \frac{\partial E_2}{\partial n'_2}. \quad (30)$$

This result is presented in [1].

Ponomarev [48] noticed that the dependence of $\beta(E)$ on the energy should be considered when differentiating the eZ_1- and eZ_2-energies. Following his ideas, the following result was obtained in [9,11]:

$$T_{PKS} = \frac{\frac{\partial E_1}{\partial n_2}}{\sqrt{1 + \frac{\partial \beta}{\partial E_1}\frac{\partial E_1}{\partial n_2}}} + \frac{\frac{\partial E_2}{\partial n'_2}}{\sqrt{1 - \frac{\partial \beta}{\partial E_2}\frac{\partial E_2}{\partial n'_2}}}. \quad (31)$$

The numerical values of pre-exponential factor, given by these formulas, differ from each other. The most consistent appears formula (31). One can easily show that the expressions for the splitting of potential curves (28), (30) and (28), (31) are different due to the terms of the order of $\mathrm{O}(R^{-2})$.

It is of interest to estimate the limits of applicability and practical accuracy of the asymptotic formula (27) for ΔE by its comparison with the results of numerical integration of a Z_1eZ_2 problem. In Table 3, we compare the values of ΔE in the Z_1eZ_2 system ($Z_1 = 1$, $4 \leqslant Z_2 \leqslant 8$) provided by our formula (27) with analytical results ΔE_{KPS} [1] and ΔE_B [49] as well as with the exact numerical calculations ΔE_{num} [50] (Nlm are spherical quantum numbers in the limit of the united atom ($R = 0$)). The value of γ was calculated using expansion (12), including the terms of the second order. As it is seen from the table, the values of ΔE are quite close to the exact ones. The proximity of these results convincingly demonstrates the usefulness of the WKB method in determining the two-Coulomb-center wave function.

Note that the range of applicability and accuracy of asymptotic expansion (27) for ΔE decrease when we substitute (12) to (27) and make additional expansion in powers of $1/R$. This can be explained by the expansion of exponent $\mathrm{e}^{-\gamma R}$ into converging series which should be subsequently terminated because the final expansion as a whole is asymptotic. Therefore, much better results can be obtained by directly using (27) and making the substitution of γ (12) calculated by means of perturbation theory.

5 Concluding remarks

– The asymptotic expressions for the quasiradial and quasiangular functions, obtained in our previous work [15], is used to calculate the matrix element of the one-electron exchange interaction potential determining the process of one-electron charge transfer between a hydrogen-like atom (ion) and a bare nucleus. The comparison of ΔE (27) with the results

of exact numerical calculations [50] shows that the domain of applicability of our asymptotic formula (formally valid under the condition (21)) is prolonged up to values $R > R_0$ even for small quantum numbers, $n = 1, 2$;

– there are two ranges of distances between the two Coulomb centers where the matrix element $\Delta(R) = \Delta E/2$ of the exchange interaction demonstrates different behavior depending on the variation of the internuclear distance R. Thus, in the range $R \gg 2n^2/Z_1$ and $Z_1 = Z_2$ formula (27) for the exchange splitting ΔE becomes the limiting expression [44] obtained in the framework of the comparison equation method. In the range $R_0 < R < 2n^2/Z_1$ (and also $Z_2 > Z_1$) the asymptotic theory [44] is inapplicable because the exchange splitting of potential curves (27) differs from the asymptotic result [44] by the value of the order of Z_2/R. The asymptotic theory [44] suggests the smallness of the Z_2/R in comparison with the electron binding energy; this requirement is not fulfilled in our case because these values are of the same order. Meanwhile, the calculations show that the proposed quasiclassical method describes the exchange splitting of the potential curves $\Delta E(R)$ both for intermediate internuclear distances $R_0 < R < 2n^2/Z_1$ and in the asymptotic limit $R \gg 2n^2/Z_1$;

– this paper is focused mainly on the case when the difference between charges $Z_1 - Z_2$ of the Coulomb centers are not so large ($\leqslant 7$). In our further studies we shall consider the case when the charge of one of the Coulomb centers Z_1 is small and the charge of the other one is large ($Z_2 \gg 1$) so that the difference $Z_2 - Z_1$ is also large. This situation occurs in the physically important case of charge exchange of the hydrogen atom on a multiply charged ion.

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Author contribution statement

All authors contributed equally to the paper.

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