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Potential curves splitting in the two-Coulomb-centre problem with different charges

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Abstract

The consistent scheme for obtaining quasiclassical (WKB) expansions for solutions of the quasiangular equation in the quantum mechanical two-Coulomb-centre problem is developed. In the framework of this scheme, the quasiclassical angular Coulomb spheroidal wave functions for large distances between the fixed positive charges (nuclei) are constructed for the under-barrier motion of the negative particle (electron). The quasiclassical expression for the exchange interaction ΔE of potential curves at the points of their quasicrossing is found.

1 Introduction

The bound state problem for the negative charged particle (electron or muon) moving in a 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-centre problem are used as a basis for the three-body problem in the adiabatic representation [3]. Nowadays, a lot of data obtained by solving these equations by means of numerical and asymptotic methods for different limiting cases are available. Interesting results were obtained for both the problem of the molecular hydrogen ion H_2^+ (see, for instance, [2, 4] and references therein) and the problem of two centres with strongly differing charges [5, 6, 7, 8, 9]. This problem was also considered for the Dirac equation within the asymptotic methods in [10, 11]. 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 [12] and arbitrary dimensions [13, 14].

In this article, we provide the combined approach to solve the quantum two-Coulomb-centre Z_1eZ_2 problem. An important peculiarity of our approach is the application of various methods for constructing the asymptotic expansions of the radial and angular Coulomb sphreoidal wave function (CSWF) in different areas of the electron motion. The perturbation theory can be used to determine the local behaviour of the solutions of the Z_1eZ_2 problem near a certain nucleus. However, the application of the standard perturbation theory leads to infinite sums of complicated form (this is the well-known perturbation theory feature and for the two-Coulomb-centre problem it was discussed in [15, 16]). Therefore, in order to remove the mentioned deficiencies, it is worthwhile to use the slightly modified perturbation theory [17] here.

We propose to employ the quasiclassical approach (Wentzel–Kramers–Brillouin method) to construct the asymptotic expansions of the angular CSWF in the internuclear region. This approach allows us to obtain analytic solutions, but for this problem 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 [18, 19, 20], whose solutions depend on this region of internuclear distances.

The paper is organized as follows. In Sec. 2, we give the basic equations of the Z_1eZ_2 problem in the spheroidal system of coordinates and present the CSWF for the near a certain nucleus region of the electron motion in terms of the modified perturbation theory [17]. In Sec. 3, the consistent scheme for obtaining WKB expansions for solutions of the quasiangular equation in the Z_1eZ_2 problem is elaborated. Using the Firsov surface integral method [21], in Sec. 4 we calculate the first three terms of the asymptotic behaviour of the exchange interaction potential of an ion with an atom for the general nonresonance case. In Sec. 5, the final results are discussed.

2 Basic equations and the perturbation theory results

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:

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

where r_1 and r_2 are the distances from the electron to nuclei 1 and 2, $E(R)$ is the electron energy and R is the distance between the nuclei. The Schrödinger equation (1) is separable in the prolate spheroidal coordinates:

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

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

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

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

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 $V(\eta, R)$

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

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

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:

$$\lambda_\xi = \lambda_\eta. \tag{7}$$

When R is much larger than the size of electron shells centred 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 $\lambda_\xi, \lambda_\eta$.

In order to find simple expansions in powers of $1/R$ of the wave function of a hydrogen-like atom in the field of point charge, one can employ the modified scheme of perturbation theory [17]. Hereby, within terms of order R^{-3} the function ψ of formula (3) can be expressed in the form

$$\psi^{pert}(\mu, \nu) = CU^{pert}(\mu)V^{pert}(\nu), \tag{8}$$

where

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

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

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

and for $p = 1, 2, 3$ all the $c_{n_i+k}^{(p)}$ coefficients have been derived in terms of the modified scheme of perturbation theory [17].

For the normalization constant C from the condition $\int |\Psi|^2 dV = 1$ one can obtain

$$\begin{aligned} C(R) = \frac{4\gamma^{1/2}}{R}\Bigg\{ & \sum_{i=1}^{2} \Bigg[\langle n_i|\rho_i^{-1}|n_i\rangle \left(1 + 2c_{n_i}^{(1)} + 2c_{n_i}^{(2)} + 2c_{n_i}^{(3)}\right) \\ & + \sum_{k=-1}^{1} \left(|c_{n_i+k}^{(1)}|^2 + 2c_{n_i+k}^{(1)} c_{n_i+k}^{(2)}\right) \langle n_i+k|\rho_i^{-1}|n_i+k\rangle \Bigg] \\ & + \frac{1}{4\gamma^2 R^2} \sum_{i=1}^{2} \langle n_i|\rho_i^{1}|n_i\rangle \left(1 - 2c_{n_i}^{(1)}\right) - \frac{\langle n_1|\rho_1^2|n_1\rangle - \langle n_2|\rho_2^2|n_2\rangle}{8\gamma^3 R^3} \Bigg\}^{-1/2}. \end{aligned} \tag{9}$$

3 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. Let us find the quasiclassical asymptotic behaviour of the angular wave function $V_I(\nu)$ centred on atom (e, Z_1) in the classically fobidden region. For this purpose, we rewrite the quasiangular equation (6) in the form of the one-dimensional Schrödinger equation:

$$V_I'' - \frac{q_I^2}{\hbar^2} V_I = 0 \tag{10}$$

where $q_I = \sqrt{2(U_{eff} - E)}$ 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. In the under-barrier region, the quantity q_I is real and coincides with the quasiangular momentum of a classical particle within imaginary unit i, $q_I^2(\nu) > 0$ at $\nu_2 < \nu < \nu_3$.

Representing the solution of (10) in the form of the expansion in powers of $\hbar$:

$$V_I^{quas} = \mathrm{e}^{S/\hbar}, \quad S = \sum_{k=-1}^{\infty} \hbar^k S_k, \tag{11}$$

substituting (11) into (10) 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 $S_k(\nu)$

$$\left(S'_{-1}\right)^2 = q_I^2; \tag{12}$$

$$2S'_{-1}S'_0 + S''_{-1} = 0; \tag{13}$$

$$2S'_{-1}S'_k + S''_{k-1} + \sum_{j=0}^{k-1} S'_j S'_{k-j-1} = 0, \quad k = 1, 2, \ldots. \tag{14}$$

As a solution of (12) we choose the function $S_{-1}(\nu) = -\int_{\nu_2}^{\nu} q_I(\nu')d\nu'$ corresponding to exponential damping of V^{quas} in the under-barrier region. The equation for S_0 is solved in the closed species $S_0 = \ln(C_0/\sqrt{q})$, and the solutions of all the next equations of the recurrent system (14) are expressed by means of quadratures

$$S_k = \int \frac{1}{2q}\left(S''_{k-1} + \sum_{j=0}^{k-1} S'_j S'_{k-j-1}\right) d\nu + C_k, \quad C_k = \text{const}, \quad k = 1, 2, \ldots. \tag{15}$$

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 given in Sec. 2 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} (9) in powers of $1/\nu$:

$$V_I^{quas}(\nu) \xrightarrow[\nu_2 \ll \nu \ll \nu_m]{} V_I^{pert}(\nu) \tag{16}$$

For satisfaction of (16), it is necessary that the internuclear distance be much larger than that at which the potential barrier in the quasiangular equation disappears, i.e.

$$R \gg R_0 = \left[2(\tilde{Z}_1 + \tilde{Z}_2) + \sqrt{4\tilde{Z}_1^2 + \gamma^2(1-m^2)} + \sqrt{4\tilde{Z}_2^2 + \gamma^2(1-m^2)}\right]/2\gamma^2. \tag{17}$$

Therefore, the solution of the quasiangular equation (10) in the quasiclassical approximation, which satisfies the boundary condition (16), is of the form (hereinafter $\hbar = 1$)

$$V_I^{quas} = \frac{C_0}{\sqrt{q_I}} \exp\left[-\int_{\nu_2}^{\nu} q_I d\nu' + S_1 + S_2\right] \tag{18}$$

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

$$S_1 = -\frac{\tilde{Z}_1}{4\gamma^3\nu^2}\left(1 + \frac{17\tilde{Z}_1}{6\gamma^2\nu}\right) + \frac{\tilde{Z}_2}{4\gamma^3(R-\nu)^2}\left(1 + \frac{17\tilde{Z}_2}{6\gamma^2(R-\nu)}\right)$$

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

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

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

Thus, the obtained formula (18) determines the quasiclassical asymptotic behaviour of solutions of the quasiangular equation (10) when $\hbar\to 0$ and is valid in the under-barrier region $\nu_2<\nu<\nu_3$.

The final expression for the wave function $\Psi_I(\vec{r},R)$ centred on the atom of (e,Z_1) has the form (3) where

$$\psi_I(\mu,\nu)=C_I(R)\,U^{pert}(\mu)\,V_I^{quas}(\nu), \tag{21}$$

and the normalization constant $C_I(R)$ is still given by formula (9).

4 Splitting of the potential curves at the pseudocrossing points

In order to calculate the probabilities of charge transfer processes between a hydrogen or hydrogen-like atom and 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 and ion. In the case when the binding energies of an electron in the atom (e,Z_1) and ion (e,Z_2) 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 [21]

$$\Delta E=\oint_S\left(\Psi_I^*\vec{\nabla}\Psi_{II}-\Psi_{II}^*\vec{\nabla}\Psi_I\right)\cdot d\vec{S}. \tag{22}$$

Here Ψ_I and Ψ_{II} 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 function of the hydrogen-like atom (e,Z_1) and the wave function of the ion (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.

As an integration surface in (22) we choose the paraboloid of revolution $\eta=$ 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, when the quasimomenta q_I and q_{II} of the electron centred on the atom (e,Z_1) and ion (e,Z_2), respectively, are approximately equal: $q_I\approx q_{II}$. Then, substituting the wave function Ψ_I in the form (3), (21) and a similar expression for Ψ_{II} into (22), we obtain the following expression for the exchange splitting of the potential curves:

$$\Delta E = \frac{2\gamma^2\,(-1)^{n_2+n_2'}\,(2\gamma R)^{n_2+n_2'+m+1}\,\mathrm{e}^{-\gamma R}}{[n\,n'\,n_2!\,(n_2+m)!\,n_2'!\,(n_2'+m)!]^{1/2}}\left\{1-\frac{A_2+A_2'}{2\gamma R}-\frac{A_1}{2\gamma^2 R}\left(\frac{Z_1}{n}+\frac{Z_2}{n'}\right)\right.$$
$$-\frac{1}{2\gamma R}\left[\frac{A_2^2+A_2'^2}{4}+A_2A_2'+\frac{1-m^2}{2}\right]+c_{n_1}^{(1)}\left(\frac{A_2}{2n}+\frac{A_2'}{2n'}-2\right)\left[c_{n_1}^{(1)}+\right.$$
$$+\frac{1+2n_1(n_1+m)/A_1}{4\gamma R}-\frac{c_{n_2}^{(1)}}{A_2 n}(4T_2+m^2+3)+\frac{c_{n_2'}^{\prime(1)}}{A_2' n'}(4T_2'+m^2+3)\Big]$$
$$+A_1\left[\frac{|c_{n_2}^{(1)}|^2}{2n}+\frac{|c_{n_2'}^{\prime(1)}|^2}{2n'}-\frac{\langle n_1|\rho_1|n_1\rangle}{4\gamma^2R^2}\left(\frac{A_2}{n}+\frac{A_2'}{n'}\right)\right]+\frac{(A_2+A_2')^2}{4\gamma^2R^2}$$
$$+\frac{A_2^3+A_2'^3-24(T_2+T_2')-(m^2+1)(A_2+A_2')-16(m^2+2)}{16\gamma^2R^2}$$
$$-\frac{A_1}{4\gamma^2R^2}\left(\frac{3T_2+m^2+2}{n}+\frac{3T_2'+m^2+2}{n'}\right)+\frac{3T_1+m^2-1}{4\gamma^2R^2}$$
$$+\left(\frac{Z_1-Z_2}{2\gamma^2R}\right)^2\left(A_2+A_2'+2+\frac{m^2-1}{2}\left[\frac{A_2}{T_2}+\frac{A_2'}{T_2'}\right]\right)$$
$$\left.+\frac{Z_1-Z_2}{4\gamma^3R^2}\left(4(T_2'-T_2)+\langle n_2|\rho_2|n_2\rangle-\langle n_2'|\rho_{2'}|n_2'\rangle\right)\right\}. \tag{23}$$

Here $A_i = 2n_i+m+1$, $A_i' = 2n_i'+m+1$, $T_i = 2n_i(n_i+m+1)+m$, $T_i' = 2n_i'(n_i'+m+1)+m$, and expression for the $c_{n_2'}^{\prime(1)}$ can be obtained from the expansion coefficient $c_{n_2}^{(1)}$, derived by means of the perturbation theory, putting $Z_1 \leftrightarrow Z_2$, $n_2 \to n_2'$. In the resonance case ZeZ, formula (23) gives the difference between the energies of gerade and ungerade states and coincides with the results of [22, 15, 26, 23, 24]. It should be noted also that the formulae for H_2^+ in [1, 15] 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 [15, 27] within the comparison equation method and given then in [1], it should be noted that the pre-exponential factor in [15, 27] 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 parameter $\beta = (Z_2-Z_1)/(-2E)^{1/2} = n_2'-n_2$. The formulae obtained in these papers give the correct result only in the case of equal charges when β is equal to zero. When using different parts of the asymptotic series, the same difference between the potential curves at the quasicrossing points can be represented by various formulae of the form

$$\Delta E = T\delta(n_2, n_2', m, p), \tag{24}$$

where δ is determined by formula (4.36) from [1]. Komarov and Slavyanov [23] proposed to determine T by differentiating the expression $E = -(Z_2-Z_1)^2/(2\beta^2)$

with respect to indices, which gives

$$T_{KS} = 2\frac{(Z_2 - Z_1)^2}{(n_2' - n_2)^3}. \tag{25}$$

Power [15] 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:

$$T_P = \frac{\partial E_1}{\partial n_2} + \frac{\partial E_2}{\partial n_2'}. \tag{26}$$

This result is presented in [1].

Ponomarev [25] noticed that the dependence of the $\beta(E)$ on the energy should be considered when differentiating the eZ_1- and eZ_2-energies. Following his ideas, the following result was obtained in [6, 7]:

$$T_{PKS} = \frac{\frac{\partial E_1}{\partial n_2}}{\sqrt{1 + \frac{\partial \beta}{\partial E_1}\frac{\partial E_1}{\partial n_2}}} + \frac{\frac{\partial E_2}{\partial n_2'}}{\sqrt{1 - \frac{\partial \beta}{\partial E_2}\frac{\partial E_2}{\partial n_2'}}}. \tag{27}$$

The numerical values of pre-exponential factor, given by these formulae, differ from each other. The most consistent appears formula (27). One can easily show that the expressions for the splitting of potential curves (24), (26) and (24), (27) are different due to the terms of the order of $O(R^{-2})$.

It is of interest to estimate the limits of applicability and practical accuracy of the asymptotic formula (23) for ΔE by its comparison with the results of numerical integration of a Z_1eZ_2 problem. In Table 1 we compare the exact numerical values of ΔE_{num} [28] in the Z_1eZ_2 system ($Z_1 = 1$, $4 \le Z_2 \le 7$) with the values given by the Bogush ΔE_B [16] (obtained within the comparison equation method in terms of formula 25 and using specific, based on the substraction of energies determination of ΔE), Komarov and Slavyanov ΔE_{KS} [1] (obtained within the comparison equation method in terms of formula 26) and our (23) formulae (Nlm are spherical quantum numbers in the limit of the united atom ($R = 0$)). The value of γ was calculated using the expressions obtained by means of the perturbation theory, 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 developed here.

Table 1: 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	ΔE_{KS}	ΔE_{num}	ΔE_B
4	$(4,3,0) - (3,2,0)$	7.76	6.66(−2)	6.56(−2)	6.94(−2)	–
5	$(5,4,0) - (4,3,0)$	12.92	4.07(−3)	6.09(−3)	4.25(−3)	4.16(−3)
6	$(6,5,0) - (5,4,0)$	21.4	2.40(−5)	3.37(−5)	–	2.41(−5)
7	$(7,6,0) - (6,5,0)$	31.9	2.06(−8)	2.44(−8)	–	2.14(−8)

Note that the range of applicability and accuracy of asymptotic expansion (23) for ΔE decrease when we substitute the expansion for γ to (23) and make additional expansion in powers of $1/R$. This can be explained by the expansion of exponent $e^{-\gamma R}$ 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 formula (23) and substituting into it the value of γ calculated by means of the perturbation theory.

5 Conclusions

The new approach to construction of the two-Coulomb-centre wave function in the internuclear region at large distances between the centres is proposed. The asymptotic expressions for the quasiradial and quasiangular functions obtained here 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 bare nucleus. The comparison of ΔE (23) with the results of exact numerical calculations [28] shows that the domain of applicability of our asymptotic formula (formally valid under the condition (17)) 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 centres where the matrix element $\Delta(R) = \Delta E/2$ of the exchange interaction demonstrates different behaviour 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 (23) for the exchange splitting ΔE becomes the limiting expression [23] 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 [23] is inapplicable because the exchange splitting of energetic terms (23) differs from the asymptotic result [23] by the value of the order of Z_2/R. The asymptotic theory [23] 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 $R \gg 2n^2/Z_1$.

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