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Asymptotic theory of the one- and two-electron processes in slow collisions of atomic ions with diatomic molecules

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We apply the asymptotic method and a semiclassical coupled-channel approach to study the one- and two-electronic processes occurring in the course of slow collisions between multiply charged atomic ion and diatomic molecules with two active electrons. The matrix elements responsible for different processes of single and double electron transfer are calculated asymptotically correctly (for large distances R between interacting particles) in the framework of the nonperturbative Landau-Herring approach. The methods are applied for study of single and double electron transfer in H_2+He^{2+} collisions at impact energies 0.1–30 keV/amu. Our calculations are in fairly good agreement with available experimental data and theoretical calculations of other authors.

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I. INTRODUCTION

The collision processes of multiply charged ions (MCI) with molecules have recently attracted considerable interest in view of their observed role in generation of the x-ray and euv radiation in the cometary atmospheres interacting with the solar wind [1–3] and in certain astrophysical environments [4], and in the cooling of divertor plasmas of magnetic fusion devices [5]. The understanding of the collision dynamics of a MCI–molecule collision system is at the same time an intrinsically challenging problem involving, generally, more than one electron and many mutually coupled reaction channels from both the discrete and continuum electronic and vibrational spectra. An *ab initio* numerical approach to determining the adiabatic eigenstates of such a system, as well as the corresponding nonadiabatic couplings between them, both needed for description of its low-energy collision dynamics, is obviously a formidable computational task. Development of special analytic methods for solving the electronic eigenvalue problem and for calculating the coupling matrix elements in the asymptotic region (i.e., for large internuclear separations R), which could provide accurate boundary conditions for the numerical solutions at finite R, would therefore be highly desirable. Since at low collision energies the large internuclear separations play a dominant role in the collision dynamics, one can construct an asymptotic approach to atomic collision processes based on the accurate knowledge of the asymptotic behavior of adiabatic states of the collision system and the corresponding coupling interactions (see, e.g., [6,7]).

The exact asymptotic determination of one-electron exchange coupling interactions between adiabatic states in the asymptotic region of internuclear separations has been pioneered by Landau [8] and Herring [9,10] (see also [11]). Its generalization to two-electron exchange interactions in the two Coulomb center systems has been done in [12–14]. The Landau-Herring method has been widely applied in the last four decades for calculation of one- and two-electron exchange coupling interactions in ion-atom and atom-atom systems which are responsible for many inelastic processes in these collision systems. The results of these studies have been reviewed in [15].

The electron-exchange interactions and corresponding processes in ion-molecule collision systems have so far been much less investigated by the asymptotic method. The only existing study is that for the one-electron exchange in the $Z_1+(eZZ)$ system [16], where Z and Z_1 are either bare nuclei or some effective ion core charges. The obtained general results for the one-electron exchange interaction in this system were used in [16] to calculate the electron capture cross section in the slow $He^{2+}+H_2{}^+$ collisions.

In the present paper we shall employ the asymptotic method to study the electron-exchange interactions and the dynamics of corresponding inelastic low-energy collision processes in the $A_2^{(Z_a-2)+}+B^{Z_b+}$ collision system, where Z_a and Z_b are the effective charges of the molecular core $A_2^{Z_a+}$ and of the ion B^{Z_b+}. The most important one- and two-electron exchange processes in this system are the following.

(i) nondissociative single electron captures (NDSEC):

$$A_2^{(Z_a-2)+}(e_1,e_2)+B^{Z_b+}\rightarrow A_2^{(Z_a-1)+}(e_2)+B^{(Z_b-1)+}(e_1), \quad (1)$$

(ii) two-electron capture (TEC):

$$A_2^{(Z_a-2)+}(e_1,e_2)+B^{Z_b+}\rightarrow A_2^{Z_a+}+B^{(Z_b-2)+}(e_1,e_2), \quad (2)$$

(iii) single electron capture with simultaneous target excitation:

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$$A_2^{(Z_a-2)+}(e_1,e_2) + B^{Z_b+} \rightarrow A_2^{(Z_a-1)+^*}(e_2) + B^{(Z_b-1)+}(e_1). \quad (3)$$

If process (3) leads to electron transition to a dissociative state of the molecular ion $A_2^{(Z_a-1)+^*}$ then process (3) is referred to as dissociative single electron capture (DSEC). In the case when the capture in reaction (1) leads to creation of an excited ionic state $B^{(Z_b-1)+^*}$ then one should take into account also the following processes:

$$A_2^{(Z_a-1)+}(e_2) + B^{(Z_b-1)+^*}(e_1) \rightarrow A_2^{Z_a+} + B^{(Z_b-2)+}(e_1,e_2), \quad (4)$$

$$A_2^{(Z_a-1)+}(e_2) + B^{(Z_b-1)+^*}(e_1) \rightarrow A_2^{(Z_a-1)+^*}(e_2) + B^{(Z_b-1)+}(e_1). \quad (5)$$

Processes (1) and (4) and Eqs. (1) and (5) are two-step processes, in which the first step, Eq. (1), is governed by a one-electron exchange interaction, while the second step, Eq. (4) or Eq. (5), is governed by a two-electron exchange interaction.

The right-hand side of reaction (3) may not necessarily appear as a final reaction state but rather an intermediary state formed in the first half of the collision. In that case, a second one-electron capture transition from the target $A_2^{(Z_a-1)+^*}$ to the ion $B^{(Z_b-1)+}$ may take place in the second half of the collision (two-step or sequential TEC),

$$A_2^{(Z_a-1)+^*}(e_2) + B^{(Z_b-1)+}(e_1) \rightarrow A_2^{Z_a+} + B^{(Z_b-2)+}(e_1,e_2). \quad (6)$$

While processes (1) and (6) involve only one one-electron exchange interaction, studied in our recent work [16], processes (2)–(5) involve two-electron exchange interactions of different types, the calculation of which within the asymptotic Landau-Herring method will be the subject of the present study.

It should be noted that provided the collision energy is sufficiently large, all processes (1)–(6) may be involved in the collision dynamics. Therefore, a coupled-channel approach has to be employed when studying the dynamics of $A_2^{(Z_a-2)+}(e_1,e_2)+B^{Z_b+}$ collision system. In the present paper we shall employ such an approach to calculate the cross sections for one- and two-electron capture processes in $\mathrm{He}^{2+}+\mathrm{H}_2$ collision system by making use of the two-electron coupling interactions calculated in the present paper and the one-electron couplings obtained in [16].

The paper is organized as follows. In the next section we study the general structure and R dependence of the two-electron exchange interaction in the asymptotic region of large distances R between colliding particles. In Sec. III we describe the method of deriving the asymptotic form of one-electron three-center wave function of the quasimolecule $A_2^{Z_a+}+B^{(Z_b-2)+}$ in different regions of configuration space and present its results. The same method is used in Sec. IV to derive the asymptotic expression of one-electron wave function of the quasimolecule $A_2^{(Z_a-2)+}+B^{Z_b+}$. The results of these two sections are used in Sec. V to calculate the asymptotically exact two-electron exchange interactions (two-electron nonadiabatic couplings) responsible for the two-electron processes (2)–(5). The obtained analytical results on electronic couplings are used in Sec. VI for close-coupling calculations of the total and partial cross sections of one- and two-electron capture processes in the $\mathrm{He}^{2+}+\mathrm{H}_2$ collision system in energy range 0.1–30 keV/amu. Our concluding remarks are given in Sec. VII. Atomic units ($\hbar = m_e = e^2 = 1$) will be used throughout this paper, unless explicitly stated otherwise.

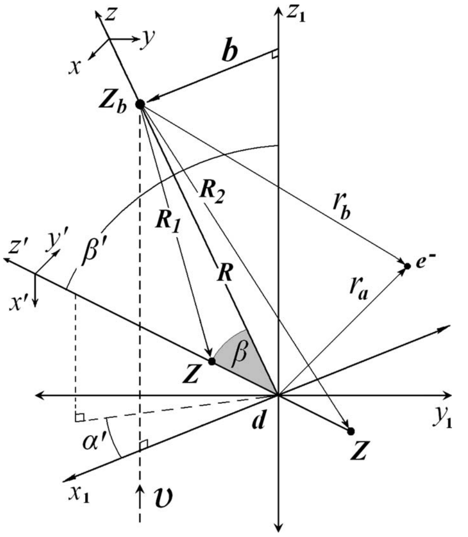

FIG. 1. Geometry of the colliding system and used notation.

II. TWO-ELECTRON EXCHANGE INTERACTION OF MULTIPLE CHARGED IONS WITH DIATOMIC MOLECULES

Let Ψ_a and Ψ_b be the perturbed two-electron wave functions describing the motion of the two electrons when they are dominantly localized around the molecular $A_2^{Z_a+}$ and atomic B^{Z_b+} core, respectively. The two-electron exchange interaction $H^{(if)}$ is defined then by [15]

$$H^{(if)} = \langle \Psi_b | H_{el} | \Psi_a \rangle - \langle \Psi_b | \Psi_a \rangle \langle \Psi_a | H_{el} | \Psi_a \rangle, \quad (7)$$

where H_{el} is the electronic Hamiltonian of the system $[A_2B]^{(Z_a+Z_b-2)+}$ that parametrically depends on the distance R between $A_2^{Z_a+}$ and B^{Z_b+}, internuclear separation d of the diatomic $A_2^{Z_a+}$, and the angle β between vectors $\mathbf{R}$ and $\mathbf{d}$ (see Fig. 1). We shall use the symbol Q to designate the set of these three parameters: $\{R,d,\beta\} \equiv Q$. We assume that the molecular particle A_2 has the H_2-type structure, i.e., consist from two identical nuclei with charge Z and two electrons (i.e., $Z_a = 2Z$). (This assumption can be removed by introducing the "two active electrons" approximation and an effective ionic core charge Z_a^{eff}). Therefore, electronic Hamiltonian H_{el} can be represented in the form

$$H_{el} = -\frac{\Delta_{\mathbf{r}_1}}{2} - \frac{\Delta_{\mathbf{r}_2}}{2} + V_a(\mathbf{r}_{1a}) + V_a(\mathbf{r}_{2a}) + V_b(r_{1b}) + V_b(r_{2b}) + \frac{1}{r_{12}}, \quad (8)$$

where indices 1, 2 stand for the electrons, a,b for heavy particles, $\mathbf{r}_{ia}$ ($\mathbf{r}_{ib}$) is the radius vector from center of mass of $A_2^{Z_a+}$ (B^{Z_b+}) particle to ith electron ($i=1,2$), r_{12} is the distance between the two electrons, R_1 and R_2 are the distances from nuclei B^{Z_b+} to each of the centers of the fragment $Z+Z$. The interaction potentials V_a and V_b of ith electron with the cores $A_2^{Z_a+}$ and B^{Z_b+}, respectively, have the following asymptotic behavior:

$$V_{a,b}(\mathbf{r}) \underset{r\to\infty}{\sim} -Z_{a,b}/r. \tag{9}$$

Let us consider now the exchange interaction $H^{(20)}$ that is responsible for the direct two-electron capture reaction (2). The properly symmetrized two-electron wave function Ψ_a of the initial configuration $A_2^{(Z_a-2)+}+B^{Z_b+}$ can be written in the form

$$\Psi_a = \frac{1}{\sqrt{2}}[\Psi_{1a}(\mathbf{r}_1,\mathbf{r}_2) + (-1)^{\Sigma}\Psi_{2a}(\mathbf{r}_1,\mathbf{r}_2)]\chi^{(1,2)}_{\Sigma M_{\Sigma}}, \tag{10}$$

where Σ and M_Σ are the total spin of the electron pair and its projection on the $\mathbf{R}$ axis, $\chi^{(1,2)}_{\Sigma M_\Sigma}$ is the two-electron spin wave function, and $\Psi_{1a}(\mathbf{r}_1,\mathbf{r}_2)$ and $\Psi_{2a}(\mathbf{r}_1,\mathbf{r}_2)\equiv\Psi_{1a}(\mathbf{r}_1\leftrightarrows\mathbf{r}_2)$ are the two-electron coordinate wave functions. The wave function Ψ_b of the final configuration $A_2^{Z_a+}+B^{(Z_b-2)+}$ has the following representation:

$$\Psi_b = \frac{1}{\sqrt{2}}\sum_{m_1m_2} C^{LM_L}_{\ell_1m_1\ell_2m_2}[\Psi_{1b}(\mathbf{r}_1,\mathbf{r}_2) + (-1)^{S}\Psi_{2b}(\mathbf{r}_1,\mathbf{r}_2)]\chi^{(1,2)}_{SM_S}, \tag{11}$$

where L and S are, respectively, the total orbital and spin momenta (centered on B^{Z_b+} particle) of the two electrons, and M_L and M_S are their projections on the $\mathbf{R}$ axis, ℓ_i and m_i $(i=1,2)$ are the electron orbital momentum and its projection on the $\mathbf{R}$ axis, the symbol $C^{LM_L}_{\ell_1m_1\ell_2m_2}$ designates the Clebsch-Gordan coefficients in the convenience of Ref. [17], and $\Psi_{2b}(\mathbf{r}_1,\mathbf{r}_2)\equiv\Psi_{1b}(\mathbf{r}_1\leftrightarrows\mathbf{r}_2)$. Substituting Eqs. (10) and (11) into expression (7) one obtains

$$H^{(20)} = \frac{1}{2}\sum_{m_1m_2} C^{LM_L}_{\ell_1m_1\ell_2m_2}[(-1)^{S}H_1^{(20)} + H_2^{(20)}], \tag{12}$$

where

$$H_1^{(20)} = \langle\Psi_{2b}|H_{el}|\Psi_{1a}\rangle + \langle\Psi_{1b}|H_{el}|\Psi_{2a}\rangle - \langle\Psi_a|H_{el}|\Psi_a\rangle(S_{1b,2a}+S_{2b,1a}), \tag{13}$$

$$H_2^{(20)} = \langle\Psi_{1b}|H_{el}|\Psi_{1a}\rangle + \langle\Psi_{2b}|H_{el}|\Psi_{2a}\rangle - \langle\Psi_a|H_{el}|\Psi_a\rangle(S_{1b,1a}+S_{2b,2a}), \tag{14}$$

$$S_{k\lambda,k'\lambda'} = \langle\Psi_{k\lambda}|\Psi_{k'\lambda'}\rangle, \quad k,k'=1,2; \quad \lambda,\lambda'=a,b. \tag{15}$$

The calculation of the leading asymptotic term of exchange interaction $H^{(20)}$ requires determination of the correct asymptotic (at $R\to\infty$) behavior of the two-electron wave functions $\Psi_{k\lambda}$ $(k=1,2,\ \lambda=a,b)$. However, even a qualitative analysis of their asymptotic behavior allows to determine some important properties of the matrix elements $H_1^{(20)}$ and $H_2^{(20)}$.

We introduce the coordinate system $\{x,y,z\}$ with its origin placed in the center of the ion B^{Z_b+} and z axis oriented along the vector $\mathbf{R}$, and the coordinate system $\{x',y',z'\}$ rigidly bound to the vector $\mathbf{d}$, with its origin placed in the midpoint of the distance d and axis z' oriented along the molecular bond $\mathbf{d}$ (see Fig. 1).

As well known, the transition from $\{x,y,z\}$ to $\{x',y',z'\}$ is determined by three Euler's angles α,β,γ [17]. As far as the relative orientation of the axes (x,x') and (y,y') are not fixed beforehand, it is customary to orient them so that the corresponding Euler's angles are equal to zero, $\alpha=\gamma=0$. We denote by $\Psi_{1a}^{(0)}$ the two-electron wave function of the diatomic $A_2^{(Z_a-2)+}$ and consider its asymptotic form when one electron is far away from the core $A_2^{Z_a+}$ and other electron is kept close to it:

$$\Psi_{1a}^{(0)}(\mathbf{r}_{1a},\mathbf{r}_{2a}) \underset{r_{1a}\gg r_{2a}\gg 1}{\sim} \varphi_a(\mathbf{r}_{1a})\varphi_a^{(0)}(\mathbf{r}_{2a}), \tag{16}$$

where the one-electron orbitals φ_a and $\varphi_a^{(0)}$ are defined by their asymptotic behavior

$$\varphi_a(\mathbf{r}_{1a}) \underset{r_{1a}\gg 1}{\sim} A_1(\theta_{1a})r_{1a}^{(Z_a-1)/\alpha_1-1}\exp(-\alpha_1 r_{1a})\frac{e^{i\mu_1\phi_{1a}}}{\sqrt{2\pi}}, \tag{17}$$

$$\varphi_a^{(0)}(\mathbf{r}_{2a}) \underset{r_{2a}\gg 1}{\sim} A_2(\theta_{2a})r_{2a}^{Z_a/\alpha_2-1}\exp(-\alpha_2 r_{2a})\frac{e^{i\mu_2\phi_{2a}}}{\sqrt{2\pi}}. \tag{18}$$

Here $\alpha_1^2/2$ and $\alpha_2^2/2$ are, respectively, the first and second ionization potentials of diatomic $A_2^{(Z_a-2)+}$, μ_i $(i=1,2)$ is the projection of ith electron orbital momentum on the molecular axis $\mathbf{d}$, and $\{r_{ia},\theta_{ia},\phi_{ia}\}$ are the spherical coordinates of ith electron in the coordinate system $\{x',y',z'\}$. The asymptotic coefficients $A_1(\theta_{1a})$ and $A_2(\theta_{2a})$ are quite easy to calculate or, alternatively, their values can be taken from literature (see, for example, Refs. [18,19]). A similar asymptotic expression can be written for the two-electron wave function $\Psi_{1b}^{(0)}$ of the atomic particle $B^{(Z_b-2)+}$:

$$\Psi_{1b}^{(0)}(\mathbf{r}_{1b},\mathbf{r}_{2b}) \underset{r_{1b}\gg r_{2b}\gg 1}{\sim} \varphi_b(\mathbf{r}_{1b})\varphi_b^{(0)}(\mathbf{r}_{2b}), \tag{19}$$

where the one-electron wave functions $\varphi_b(\mathbf{r})$ and $\varphi_b^{(0)}(\mathbf{r})$ have the following asymptotic forms:

$$\varphi_b(\mathbf{r}_{1b}) \underset{r_{1b}\gg 1}{\sim} B_1 r_{1b}^{(Z_b-1)/\beta_1-1}\exp(-\beta_1 r_{1b})Y_{\ell_1}^{m_1}(\theta_{1b},\phi_{1b}), \tag{20}$$

$$\varphi_b^{(0)}(\mathbf{r}_{2b}) \underset{r_{2b}\gg 1}{\sim} B_2 r_{2b}^{Z_b/\beta_2-1}\exp(-\beta_2 r_{2b})Y_{\ell_2}^{m_2}(\theta_{2b},\phi_{2b}). \tag{21}$$

Here $\beta_1^2/2$ and $\beta_2^2/2$ are, respectively, the first and second ionization potentials of the ion $B^{(Z_b-2)+}$, $Y_\ell^m(\theta,\phi)$ are the normalized spherical harmonics, $\{r_{ib},\theta_{ib},\phi_{ib}\}$ are the spherical coordinates of ith electron in the coordinate system $\{x,y,z\}$. The coefficients B_1 and B_2 are determined by linking the asymptotic expressions (19) and (21) with the corresponding Hartree-Fock wave functions [18,20]. Since $\Psi_{2b}^{(0)}(\mathbf{r}_1,\mathbf{r}_2)=\Psi_{1b}^{(0)}(\mathbf{r}_1\leftrightarrows\mathbf{r}_2)$ and $\Psi_{2a}^{(0)}(\mathbf{r}_1,\mathbf{r}_2)=\Psi_{1a}^{(0)}(\mathbf{r}_1\leftrightarrows\mathbf{r}_2)$ the same asymptotic properties must be true also for the wave functions $\Psi_{2b}^{(0)}(\mathbf{r}_1,\mathbf{r}_2)$ and $\Psi_{2a}^{(0)}(\mathbf{r}_1,\mathbf{r}_2)$ for $r_2\gg r_1\gg 1$. Using expressions (13)–(21) one can estimate the asymptotic behavior of the exchange interactions $H_1^{(20)}$ and $H_2^{(20)}$:

$$H_1^{(20)} \underset{R\to\infty}{\sim} \exp[-(\alpha_1+\beta_1)R], \tag{22}$$

$$H_2^{(20)} \underset{R\to\infty}{\sim} \exp[-(\alpha_1+\alpha_2+\beta_1+\beta_2)R/2], \tag{23}$$

which are responsible for different mechanisms of the two-electron capture referred to as "crossing transitions" $\{|\alpha_1\mu_1\rangle\to|\beta_2\ell_2m_2\rangle,|\alpha_2\mu_2\rangle\to|\beta_1\ell_1m_1\rangle\}$ [Eq. (22)], and "parallel transitions" $\{|\alpha_1\mu_1\rangle\to|\beta_1\ell_1m_1\rangle,|\alpha_2\mu_2\rangle\to|\beta_2\ell_2m_2\rangle\}$ [Eq. (23)], respectively [14,15].

In the present paper we shall consider the case when the first ionization potentials of any of colliding partners $A_2^{(Z_a-2)+}$, $B^{(Z_b-2)+}$ is smaller then any of the second ionization potentials of these particles (i.e., $\alpha_2,\beta_2>\alpha_1,\beta_1$). This inequality implies that Z_a and Z_b are not considerably different from each other. Under this condition, the matrix element $H_1^{(20)}$ dominates in the asymptotic region $R\to\infty$ and one can neglect the term $H_2^{(20)}$ in Eq. (12).

From the structure of the matrix element (13) it can be seen that the integrals $\langle\Psi_{2b}|H_{el}|\Psi_{1a}\rangle$ and $\langle\Psi_{1b}|H_{el}|\Psi_{2a}\rangle$ are determined by the configuration when the electrons are well separated, i.e., when the "outer" weakly bound electron is localized near the distant perturbing ion-core center, while the "inner" strongly bound electron is localized near its own ion-core center. This circumstance allows to represent the two-electron coordinate wave functions Ψ_{1a}, Ψ_{2b} as product of corresponding one-electron orbitals:

$$\Psi_{1a}(\mathbf{r}_1,\mathbf{r}_2)=\varphi_a^{(0)}(\mathbf{r}_2)\varphi_{ab}(\mathbf{r}_1), \tag{24}$$

$$\Psi_{2b}(\mathbf{r}_1,\mathbf{r}_2)=\varphi_b^{(0)}(\mathbf{r}_1)\varphi_{ba}(\mathbf{r}_2), \tag{25}$$

where $\varphi_{ab}(\mathbf{r}_1)$ is the wave function of the outer electron of molecule $A_2^{(Z_a-2)+}$ near the atomic core B^{Z_b+}, $\varphi_a^{(0)}(\mathbf{r}_2)$ is the electron wave function of the ground state of ion $A_2^{(Z_a-1)+}$; $\varphi_{ba}(\mathbf{r}_2)$ is the wave function of the outer electron of atom $B^{(Z_b-2)+}$ in the vicinity of molecular core $A_2^{Z_a+}$, and $\varphi_b^{(0)}(\mathbf{r}_1)$ is the ground-state wave function of atomic ion $B^{(Z_b-1)+}$. The wave functions $\Psi_{1b}(\mathbf{r}_1,\mathbf{r}_2)$ and $\Psi_{2a}(\mathbf{r}_1,\mathbf{r}_2)$ can be written in a similar way.

The exchange interactions $H^{(if)}$ that govern the two-electron transitions in processes (3)–(5) have similar properties: their leading R-dependent term has form (22) and is determined by the configuration when the transient electrons are well separated. In this configuration, wave functions (24) and (25) provide an asymptotically accurate representation of electronic motion.

Obviously, for large values of R, the functions Ψ_{ka} and Ψ_{kb} $(k=1,2)$ only slightly differ from the unperturbed molecular $\Psi_{ka}^{(0)}$ and atomic $\Psi_{kb}^{(0)}$ wave functions. However, this small difference is very important because it essentially determines the correct asymptotic form of the exchange interaction. Hence, the correct determination of the wave functions Ψ_{ka} and Ψ_{kb} $(k=1,2)$ is crucial for calculation of the exchange matrix element. In the next two sections we shall determine these functions asymptotically exactly in the configuration regions giving the main contribution to the exchange interactions for the $(Z+Z)+B^{(Z_b-2)+}$ and $A_2^{(Z_a-2)+}+B^{Z_b+}$ asymptotic arrangements [hereinafter the symbol $(Z+Z)$ designates the system of two identical Coulomb centers with charges Z placed at a certain fixed distance from each other]. The calculation of two-electron exchange interactions will be postponed to Sec. V.

III. ONE-ELECTRON THREE-CENTER WAVE FUNCTION OF THE SYSTEM $(Z+Z)+B^{(Z_b-2)+}$

To calculate the one-electron wave function φ_{ba} of the system $(Z+Z)+B^{(Z_b-2)+}$ we apply Landau-Herring method, which originally was proposed for calculation of the one-electron exchange energy ΔE between electronic states of the quasimolecular system $[A_2B]^{(Z_A+Z_B-1)+}$. The exchange interaction ΔE can be expressed (see [8–11]) in terms of a surface integral over the midplane S that divides the electron localization in the initial and final states of reactions similar to Eq. (1) or Eq. (6) (in this case $Z_B=Z_b$, $Z_A=Z_a-1$). If Φ_a and Φ_b are, respectively, the electronic wave functions of the quasimolecules $A_2^{(Z_A-1)+}+B^{Z_B+}$ and $A_2^{Z_A+}+B^{(Z_B-1)+}$, then

$$\Delta E=\int_S d\mathbf{S}(\Phi_a^*\nabla\Phi_b-\Phi_b^*\nabla\Phi_a). \tag{26}$$

In the Landau-Herring method for calculation of surface integral (26) the wave function Φ_a (Φ_b) is taken in the form $\Phi_a^{(0)}\chi_a$ $(\Phi_b^{(0)}\chi_b)$, where $\Phi_a^{(0)}$ $(\Phi_b^{(0)})$ is the wave function of the isolated $A_2^{(Z_A-1)+}$ $(B^{(Z_B-1)+})$ particle and χ_a (χ_b) is a function that takes into account the electron interactions with the perturbing center B^{Z_B+} $(A_2^{Z_A+})$ and is calculated asymptotically exactly in the region of configurational space where the electron interactions with the two centers have the same order of magnitude [15,21]. Hence, the general idea of the Landau-Herring method is to identify the asymptotic (large intercenter distances) regions of configuration space where certain interactions are strong (with respect to others, treated as perturbations), to solve the Schrodinger equation for electronic motion asymptotically exactly in those regions, and by smoothly connecting corresponding the solutions to obtain an asymptotically exact solution of the problem. We shall apply these ideas to determine the correct asymptotic form of one-electron three-center wave function φ_{ba} of atomic ion $B^{(Z_b-2)+}$ in the vicinity of distant Coulomb centers $(Z+Z)$. We assume that the condition $R\gg d$ is satisfied, with R considered as being large with respect to characteristic distances of bound electronic states.

Let us designate by symbols $\{r_a,\theta_a,\phi_a\}$ and $\{r_b,\theta_b,\phi_b\}$ the spherical coordinates of the electron in the $\{x',y',z'\}$ and $\{x,y,z\}$ coordinate systems, respectively. In the "one active electron" approximation, the wave function φ_{ba} of the three-center quasimolecular system $(Z+Z)+B^{(Z_b-2)+}$ satisfies the following Schrodinger equation:

$$\left[-\frac{1}{2}\Delta+V_b'(r_b)-\frac{Z}{|\mathbf{r}_b-\mathbf{R}_1|}-\frac{Z}{|\mathbf{r}_b-\mathbf{R}_2|}\right]\varphi_{ba}(\mathbf{r}_b)=E_b\varphi_{ba}(\mathbf{r}_b). \tag{27}$$

Here $V_b'(r_b)$ is the interaction potential of the electron with the atomic core $B^{(Z_b-1)+}$, which at large distances r_b has a pure Coulomb form

$$V_b'(r_b) \underset{r_b\to\infty}{\sim} -(Z_b-1)/r_b. \tag{28}$$

At $R\to\infty$, the electronic energy E_b of the quasimolecular system $(Z+Z)+B^{(Z_b-2)+}$ goes over into the electron binding energy $E_b^{(0)}$ of isolated atomic ion $B^{(Z_b-2)+}$:

$$E_b \underset{R\to\infty}{\sim} E_b^{(0)} \equiv -\beta_1^2/2. \tag{29}$$

It is convenient to introduce three regions of electronic motion, I, II, and III (near each of the two asymptotic nuclear arrangements and in between), where φ_{ba} is dominantly determined by different parts of electronic Hamiltonian. By solving the Schrodinger Eq. (27) in these three configuration regions separately (under the conditions $R_{1,2}\to\infty$) and linking smoothly the obtained solutions, one obtains an asymptotically correct expression for the wave function φ_{ba} at large distances ($R_{1,2}\gg 1$, $0\leq R<\infty$).

Under the condition $R_{1,2}\gg 1$, the wave function φ_{ba} in the region I $\{r_b\ll\min[R_1,R_2]\}$ must go over into the unperturbed atomic wave function φ_b:

$$\varphi_{ba}(\mathbf{r}_b) \underset{r_b\ll\min[R_1,R_2]}{\sim} \varphi_b(\mathbf{r}_b), \tag{30}$$

which satisfies the Schrodinger equation

$$\left[-\frac{1}{2}\Delta + V_b'(r_b) - E_b^{(0)}\right]\varphi_b(\mathbf{r}_b) = 0. \tag{31}$$

The asymptotic solution of Eq. (31) for $r_b\beta_1\gg 1$ is given by expression (20). Assuming that the atomic parameters B_1 and β_1 are known, we can proceed to the derivation of electron wave function of the quasimolecule $(Z+Z)+B^{(Z_b-2)+}$ in the region II ($r_a\sim r_b\sim R/2$), far from each of the cores $A_2^{Z_a+}$ and B^{Z_b+}. Using the zeroth approximation (29) for the electronic energy, we can write the three-center Schrodinger Eq. (27) in the form

$$\left[-\frac{1}{2}\Delta + V_b'(r_b) - E_b^{(0)} + W_b\right]\varphi_{ba}(\mathbf{r}_b) = 0, \tag{32}$$

where the perturbation W_b is given by

$$W_b = W_{b1} + W_{b2}, \quad W_{bj}(\mathbf{r}_b;\mathbf{R}_j) = \frac{Z}{R_j} - \frac{Z}{|\mathbf{r}_b - \mathbf{R}_j|}, \quad j=1,2. \tag{33}$$

Since in the region II for $R_{1,2}\to\infty$ the interaction potential of the electron with any of the centers is small (i.e., $W_b \ll E_b^{(0)}$), we can represent the zeroth approximation of the correct asymptotic expression for φ_{ba} as

$$\varphi_{ba}(\mathbf{r}_b) = \varphi_b(\mathbf{r}_b)\chi_b(\mathbf{r}_b), \tag{34}$$

where the corrective function χ_b takes into account the long-range interaction with distant Coulomb pair $(Z+Z)$. Substituting expression (34) into Eq. (32), and keeping in mind that wave function $\varphi_b(\mathbf{r}_b)$ satisfies Eq. (31), we obtain the following equation for χ_b:

$$\left[-\frac{\Delta}{2} - \frac{\nabla\varphi_b}{\varphi_b}\nabla + W_b\right]\chi_b(\mathbf{r}_b) = 0, \tag{35}$$

with the boundary condition $\chi_b(\mathbf{r}_b) \underset{r_b\to 0}{\to} 1$. Let us expand Eq. (35) and its solution χ_b in inverse powers of $R_{1,2}$. The leading term of this expansion can be obtained by neglecting in Eq. (35) the terms containing second derivatives (i.e., the Laplacian Δ) and keeping the dominant term of the product only,

$$\frac{\nabla\varphi_b}{\varphi_b}\nabla \simeq -\beta_1[1+O(R_{1,2}^{-1})]\frac{\partial}{\partial r_b}. \tag{36}$$

Equation (36) results from differentiating the exponential factor $\exp(-\beta_1 r_b)$ in φ_b only. Equation (35) then reduces to

$$\beta_1\frac{\partial\chi_b}{\partial r_b} + \chi_b W_b = 0. \tag{37}$$

After elementary integrations of Eq. (37), with taking into account the boundary condition for χ_b at $r_b\to 0$, one obtains

$$\chi_b(\mathbf{r}_b) = \chi_{b1}(\mathbf{r}_b;\mathbf{R}_1)\chi_{b2}(\mathbf{r}_b;\mathbf{R}_2), \tag{38}$$

$$\chi_{bj}(\mathbf{r}_b;\mathbf{R}_j) = \exp\left(-\frac{Zr_b}{\beta_1 R_j}\right) \times\left[\frac{r_b - R_j\cos\theta_{bj} + |\mathbf{r}_b - \mathbf{R}_j|}{R_j(1-\cos\theta_{bj})}\right]^{Z/\beta_1}, \quad j=1,2, \tag{39}$$

where θ_{bj} is the angle between the vectors $\mathbf{r}_b$ and $\mathbf{R}_j$. Under the condition $d\to 0$, expression (39) reduces to the well known expression for corrective function $\chi_b^{(0)}$ [7,15]

$$\chi_b(\mathbf{r}_b) \underset{d\to 0}{\sim} \chi_b^{(0)}(\mathbf{r}_b) = \exp\left(-\frac{2Zr_b}{\beta_1 R}\right) \times\left[\frac{r_b - R\cos\theta_b + |\mathbf{r}_b - \mathbf{R}|}{R(1-\cos\theta_b)}\right]^{2Z/\beta_1}, \tag{40}$$

which describes the effects of distortion of the atomic wave function $\varphi_b(\mathbf{r}_b)$ by the Coulomb center with charge $2Z$. Let us now perform a continuation of the electron wave function φ_{ba} from region II into the region III, close to the perturbing centers $(Z+Z)$. First we note that the derived corrective functions $\chi_{b1}(\mathbf{r}_b;\mathbf{R}_1)$ and $\chi_{b2}(\mathbf{r}_b;\mathbf{R}_2)$ are not valid near the centers $(Z+Z)$, since they diverge for $\mathbf{r}_b=\mathbf{R}_1$ and $\mathbf{r}_b=\mathbf{R}_2$, correspondingly. The reason for this is that Eq. (37) is also not valid in the region near the perturbing centers, where the second derivatives of the wave function cannot be neglected. We solve this problem by using the asymptotically exact representation of the Green's function of three-center Schrodinger Eq. (32).

Consider the one-electron three-center Green's function $G_a(\mathbf{r}_a;\mathbf{r}_a'|Q)$,

$$\left[-\frac{\Delta}{2}+V_b'(|\mathbf{r}_a-\mathbf{R}|)-\frac{Z}{|\mathbf{r}_a+\mathbf{d}/2|}-\frac{Z}{|\mathbf{r}_a-\mathbf{d}/2|}-E_b\right]$$
$$\times G_a(\mathbf{r}_a;\mathbf{r}_a'|Q)=\delta(\mathbf{r}_a-\mathbf{r}_a'). \quad (41)$$

Using a procedure similar to the one used for obtaining the wave function $\varphi_{ba}(\mathbf{r}_b)$ one can obtain a corrective function $\bar{\chi}_a(\mathbf{r}_a)$ which allows one to represent $G_a(\mathbf{r}_a;\mathbf{r}_a'|Q)$ in the form

$$G_a(\mathbf{r}_a;\mathbf{r}_a'|Q)=G_a^{(0)}(\mathbf{r}_a;\mathbf{r}_a'|d)\bar{\chi}_a(\mathbf{r}_a)\bar{\chi}_a(\mathbf{r}_a'), \quad (42)$$

where $G_a^{(0)}(\mathbf{r}_a;\mathbf{r}_a'|d)$ is the Green's function for the potential of two Coulomb centers, $(Z+Z)$,

$$\left[-\frac{\Delta}{2}-\frac{Z}{|\mathbf{r}_a+\mathbf{d}/2|}-\frac{Z}{|\mathbf{r}_a-\mathbf{d}/2|}-E_b^{(0)}\right]G_a^{(0)}(\mathbf{r}_a;\mathbf{r}_a'|d)$$
$$=\delta(\mathbf{r}_a-\mathbf{r}_a'). \quad (43)$$

The two Coulomb center Green's function $G_a^{(0)}(\mathbf{r}_a;\mathbf{r}_a'|d)$ was the subject of our recent study [22], the results of which will be used here. We outline briefly only those results from [22] which are needed in our further derivations.

To take into account the specific of noncentral field of the fragment $(Z+Z)$ it is convenient to introduce the spheroidal coordinate system $\{\xi,\eta,\phi_a\}$ with the foci placed in the charge centers of the system $(Z+Z)$:

$$\xi=(|\mathbf{r}_a+\mathbf{d}/2|+|\mathbf{r}_a-\mathbf{d}/2|)/d, \quad 1\le\xi<\infty,$$

$$\eta=(|\mathbf{r}_a+\mathbf{d}/2|-|\mathbf{r}_a-\mathbf{d}/2|)/d, \quad -1\le\eta\le 1. \quad (44)$$

The Green's function $G_a^{(0)}(\mathbf{r}_a;\mathbf{r}_a'|d)\equiv G_a^{(0)}(\xi,\eta,\phi_a;\xi',\eta',\phi_a|d)$ can be represented in form of an expansion over the complete orthonormalized system of oblate angular spheroidal functions $\bar{S}_{m\ell}(p_b,\eta)$ [22,23]:

$$G_a^{(0)}(\xi,\eta,\phi_a;\xi',\eta',\phi_a'|d)$$
$$=\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}G_{m\ell}(\xi,\xi';E_b^{(0)})\bar{S}_{m\ell}(p_b,\eta)\bar{S}^*_{m\ell}(p_b,\eta')\frac{e^{im(\phi_a-\phi_a')}}{2\pi}, \quad (45)$$

where $p_b=\beta_1 d/2$. The angular spheroidal function $\bar{S}_{m\ell}(p,\eta)$ is the solution of the differential equation

$$\left\{\frac{d}{d\eta}\left[(1-\eta^2)\frac{d}{d\eta}\right]+\left[\lambda_{m\ell}-p^2(1-\eta^2)-\frac{m^2}{1-\eta^2}\right]\right\}\bar{S}_{m\ell}(p,\eta)$$
$$=0, \quad (46)$$

and can be represented as expansion over the associated Legendre polynomials, $P^m_{m+s}(\eta)$ [23],

$$\bar{S}_{m\ell}(p,\eta)=N_{m\ell}(p)\sum_{s=0,1}^{\infty}{}'c_s^{m\ell}(p)P^m_{m+s}(\eta), \quad (47)$$

with the normalization factor

$$N_{m\ell}(p)=\left\{\sum_{s=0,1}^{\infty}{}'[c_s^{m\ell}(p)]^2\frac{2(2m+s)!}{s!\,(2m+2s+1)}\right\}^{-1/2}. \quad (48)$$

The prime indicates that the sum is to be taken over the integer values of s having the same parity as the number $\ell-|m|$. The separation constant $\lambda_{m\ell}$, as well as coefficients $c_s^{m\ell}$, are calculated numerically. The radial Green's function $G_{m\ell}(\xi,\xi';E_b^{(0)})$ can be expressed by two linearly independent solutions, $\Pi^{(1)}_{m\ell}(p_b,\xi)$ and $\Pi^{(2)}_{m\ell}(p_b,\xi)$, of the equation

$$\left\{\frac{d}{d\xi}\left[(\xi^2-1)\frac{d}{d\xi}\right]+\left[-\lambda_{m\ell}-p_b^2(\xi^2-1)+2p_b\alpha\xi\right.\right.$$
$$\left.\left.-\frac{m^2}{\xi^2-1}\right]\right\}\Pi_{m\ell}(p_b,\xi)=0, \quad (49)$$

with the following asymptotic behavior

$$\Pi^{(1)}_{m\ell}(p_b,\xi)\underset{\xi\to\infty}{\sim}(2p_b\xi)^{-\alpha-1}\exp(p_b\xi), \quad (50)$$

$$\Pi^{(2)}_{m\ell}(p_b,\xi)\underset{\xi\to\infty}{\sim}(2p_b\xi)^{\alpha-1}\exp(-p_b\xi), \quad (51)$$

where $\alpha=2Z/\beta_1$. The radial Green's function $G_{m\ell}(\xi,\xi';E_b^{(0)})$ is then given by

$$G_{m\ell}(\xi,\xi';E_b^{(0)})=\frac{8Z}{\alpha}\Pi^{(1)}_{m\ell}(p_b,\xi_<)\Pi^{(2)}_{m\ell}(p_b,\xi_>), \quad (52)$$

where $\xi_<=\min(\xi,\xi')$ and $\xi_>=\max(\xi,\xi')$. Using the confluent hypergeometric functions of the first $\Phi(a,c;x)$ and second $\Psi(a,c;x)$ kind [24] we introduce the basis functions $R^{(1,2)}_{\tau\mu}(x)$,

$$R^{(1)}_{\tau\mu}(x)=x^{\mu}e^{-x}\Phi(-\tau+\mu+1,2\mu+2;2x), \quad (53)$$

$$R^{(2)}_{\tau\mu}(x)=x^{\mu}e^{-x}\Psi(-\tau+\mu+1,2\mu+2;2x). \quad (54)$$

The two linearly independent solutions $\Pi^{(1)}_{m\ell}(p_b,\xi)$ and $\Pi^{(2)}_{m\ell}(p_b,\xi)$ can be represented in terms of $R^{(1)}_{\tau\mu}(x)$ and $R^{(2)}_{\tau\mu}(x)$ as the following expansions:

$$\Pi^{(1,2)}_{m\ell}(p_b,\xi)=\left(\frac{\xi-1}{\xi+1}\right)^{m/2}\sum_{s=-\infty}^{\infty}h^{(1,2)}_{sm\ell}(p_b)R^{(1,2)}_{\alpha,s+\nu_{m\ell}}[p_b(\xi+1)]. \quad (55)$$

The parameter $\nu_{m\ell}$ is to be determined from the requirement of convergence of expansions (55) for $1<\xi<\infty$. The procedure of calculation of $\nu_{m\ell}$ is described in detail in [22,25]. The coefficients $h^{(1)}_{sm\ell}(p_b)$ and $h^{(2)}_{sm\ell}(p_b)$ [26] satisfy the following recurrence relations [for the sake of brevity we have dropped indices $m\ell$ in designations for $h^{(1,2)}_{sm\ell}(p_b)$]:

$$p_b\kappa_s h^{(1)}_{s-1}+(\rho_s-\lambda_{m\ell})h^{(1)}_s-p_b\zeta_s h^{(1)}_{s+1}=0, \quad (56)$$

$$-p_b\tilde{\kappa}_s h^{(2)}_{s-1}+(\tilde{\rho}_s-\lambda_{m\ell})h^{(2)}_s+p_b\tilde{\zeta}_s h^{(2)}_{s+1}=0, \quad (57)$$

where

$$\kappa_s = \frac{2[(s+\nu_{m\ell})^2-\alpha^2](s+\nu_{m\ell}+m)}{(s+\nu_{m\ell})(2s+2\nu_{m\ell}-1)(2s+2\nu_{m\ell}+1)},$$

$$\rho_s = \tilde{\rho}_s = (s+\nu_{m\ell})(s+\nu_{m\ell}+1),$$

$$\zeta_s = 2(s+\nu_{m\ell}+1)(s+\nu_{m\ell}+1-m), \tag{58}$$

$$\tilde{\kappa}_s = \frac{4(s+\nu_{m\ell}-\alpha)(s+\nu_{m\ell}+m)}{2s+2\nu_{m\ell}-1}, \tag{59}$$

$$\tilde{\zeta}_s = \frac{(s+\nu_{m\ell}+\alpha+1)(s+\nu_{m\ell}-m+1)}{2s+2\nu_{m\ell}+3}.$$

From the known asymptotic behavior of $\Pi^{(1)}_{m\ell}(p_b,\xi)$ and $\Pi^{(2)}_{m\ell}(p_b,\xi)$ [see Eqs. (50) and (51)] one can derive the following normalization conditions for the coefficients $h^{(1)}_s(p_b)$ and $h^{(2)}_s(p_b)$:

$$\sum_{s=-\infty}^{\infty} h^{(1)}_s \frac{\Gamma(2s+2\nu_{m\ell}+2)}{2^{s+\nu_{m\ell}}\Gamma(s+\nu_{m\ell}+1-\alpha)} = 1, \quad \sum_{s=-\infty}^{\infty} 2^{-s-\nu_{m\ell}} h^{(2)}_s = 1. \tag{60}$$

For the purposes of obtaining φ_{ba} in the vicinity of the centers $(Z+Z)$, we need the asymptotic form of the function $G^{(0)}_a(\mathbf{r}_a;\mathbf{r}'_a|d)$ when one of its arguments is large (for instance, for $r'_a \gg r_a \sim 1$). Using the leading term of the asymptotic expansion for spheroidal coordinates ξ' and η',

$$\xi' = \frac{2r'_a}{d} + O\left(\frac{1}{r'_a}\right), \quad \eta' = \cos\theta'_a\left[1+O\left(\frac{1}{r'_a}\right)\right], \tag{61}$$

and inserting in Eq. (45) the asymptotic form (51) for $\Pi^{(2)}_{m\ell}(p_b,\xi)$, we obtain the following expression of $G^{(0)}_a(\mathbf{r}_a;\mathbf{r}'_a|d)$ at $r'_a \gg r_a \sim 1$:

$$\begin{aligned} G^{(0)}_a(\xi,\eta,\phi_a;\xi',\eta',\phi'_a|d) \underset{r'_a\gg r_a}{\approx} & \; 4\beta_1(2\beta_1 r'_a)^{2Z/\beta_1-1}\exp(-\beta_1 r'_a) \\ & \times \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell} \Pi^{(1)}_{m\ell}(p_b,\xi)\bar{S}_{m\ell}(p_b,\eta) \\ & \times \frac{e^{im\phi_a}}{\sqrt{2\pi}}\Phi^*_{m\ell}(p_b;\theta'_a,\phi'_a). \end{aligned} \tag{62}$$

Here we use the following notation:

$$\Phi_{m\ell}(p_b;\theta'_a,\phi'_a) \equiv \bar{S}_{m\ell}(p_b,\cos\theta'_a)\frac{e^{im\phi'_a}}{\sqrt{2\pi}}. \tag{63}$$

In the transition from $\{x',y',z'\}$ to $\{x,y,z\}$ coordinate system, the angular functions $\Phi_{m\ell}(p_b;\theta'_a,\phi'_a)$ are transformed as [17]:

$$\begin{aligned} \Phi_{m\ell}(p_b;\theta'_a,\phi'_a) = & \; N_{m\ell}(p_b)\sum_{s=0,1}^{\infty}{}' c^{m\ell}_s(p_b)\sum_{m'=-(m+s)}^{m+s} D^{s+|m|}_{m'm}(0,\beta,0) \\ & \times P^{m'}_{m+s}(\cos\theta'_b)\frac{e^{im'\phi'_b}}{\sqrt{2\pi}}, \end{aligned} \tag{64}$$

where $D^{s+|m|}_{m'm}$ are the Wigner's D functions [17]. Obviously, the asymptotic expression (62), as well as the function $G^{(0)}_a(\mathbf{r}_a;\mathbf{r}'_a|d)$ itself, does not take into account the effects of the long-range Coulomb part of the potential $V'_b(r_b)$ of atomic core $B^{(Z_b-1)+}$. These effects can be accounted for by the same method used for the determination of the long-range effects of the potential of two centers $(Z+Z)$ on the wave function $\varphi_{ba}(\mathbf{r}_b)$ in the region II. Therefore, we define a three-center Green's function $G_a(\mathbf{r}_a;\mathbf{r}'_a|Q)$ as the product

$$G_a(\mathbf{r}_a;\mathbf{r}'_a|Q) = G^{(0)}_a(\mathbf{r}_a;\mathbf{r}'_a|d)\bar{\chi}_a(\mathbf{r}'_a). \tag{65}$$

Substituting expression (65) into Eq. (41) [using the asymptotic behavior (62) for $G^{(0)}_a$ in the variable r'_a and neglecting the second derivatives], we obtain the following equation for $\bar{\chi}_a(\mathbf{r}'_a;Q)$:

$$\alpha_1\frac{\partial\bar{\chi}_a}{\partial r'_a} + \left[\frac{Z}{R_1}+\frac{Z}{R_2}-\frac{Z_b-1}{|\mathbf{r}'_a-\mathbf{R}|}\right]\bar{\chi}_a = 0, \tag{66}$$

with the boundary condition $\bar{\chi}_a(\mathbf{r}'_a) \underset{r'_a\to 0}{\longrightarrow} 1$. The solution $\bar{\chi}_a(\mathbf{r}'_a)$ can be obtained in the same way as $\chi_b(\mathbf{r}_b)$ [see Eq. (38)]. Under the condition $R_{1,2}\sim R \gg d/2$ expression for $\bar{\chi}_a(\mathbf{r}'_a)$ is simplified to

$$\begin{aligned} \bar{\chi}_a(\mathbf{r}'_a) \approx \bar{\chi}^{(0)}_a(\mathbf{r}'_a) = & \exp\left(-\frac{2Zr'_a}{\alpha_1 R}\right) \\ & \times\left[\frac{|\mathbf{r}'_a-\mathbf{R}|+r'_a+R\cos\theta'_b}{R(1+\cos\theta'_b)}\right]^{(Z_b-1)/\alpha_1}, \end{aligned} \tag{67}$$

where θ'_b is the angle between the vectors $\mathbf{r}'_a$ and $\mathbf{R}$. The function $G_a(\mathbf{r}_a;\mathbf{r}'_a|Q)$ should be symmetric with respect to the permutation of its arguments, i.e., for $\mathbf{r}_a \leftrightarrows \mathbf{r}'_a$, $G_a(\mathbf{r};\mathbf{r}'_a|Q) = G^*_a(\mathbf{r}'_a;\mathbf{r}_a|Q)$. Hence, we should also "correct" the zeroth order expression (65) in the region II by the long-range factor $\bar{\chi}_a(\mathbf{r}_a)$: $G_a(\mathbf{r}_a;\mathbf{r}'_a|Q) = G^{(0)}_a(\mathbf{r};\mathbf{r}'_a|d)\bar{\chi}_a(\mathbf{r}_a)\bar{\chi}_a(\mathbf{r}'_a)$. However, since we are determining the wave function $\varphi_{ba}(\mathbf{r}_a)$ in the region III, where $r_a \sim 1$, due to the boundary condition for $\bar{\chi}_a$ we have $\bar{\chi}_a(\mathbf{r}_a) \approx 1$, and the asymptotic representation (65) is correct.

To find φ_{ba} in the region III, we multiply Eq. (27) by G_a and Eq. (41) by φ_{ba}, subtract the results from one another, and integrate over the half-space Ω containing centers $(Z+Z)$. Using the Gauss theorem, we transform the obtained volume integral into a surface integral and come to the following representation:

$$\begin{aligned} \varphi_{ba}(\mathbf{r}_a) = -\frac{1}{2}\int_S & d\mathbf{S}[\varphi_{ba}(\mathbf{r}'_a)\nabla G_a(\mathbf{r}_a;\mathbf{r}'_a|Q) \\ & - G_a(\mathbf{r}_a;\mathbf{r}'_a|Q)\nabla\varphi_{ba}(\mathbf{r}'_a)], \end{aligned} \tag{68}$$

where S is the plane enclosing the volume Ω. For the surface S one can use a plane perpendicular to the internuclear axis $\mathbf{R}$ placed somewhere in asymptotic region II $(r_a \sim R/2)$.

Using the asymptotic expressions for the functions $\varphi_{ba}(\mathbf{r}_a)$ [see Eqs. (34) and (39)] and $G_a(\mathbf{r}_a;\mathbf{r}'_a|Q)$ [see Eqs. (62), (65), and (67)] obtained earlier, we calculate surface integral (68) for large distances R by the method described in

[15]. The final asymptotic expression for the three-center wave function $\varphi_{ba}(\mathbf{r}_a)$ in the region III close to centers $(Z+Z)$ is obtained in the form

$$\varphi_{ba}(\mathbf{r}_a)=\mathbf{D}_a(\beta_1,R)\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{+\ell}T^{\ell}_{mm_1}(p_b,\beta)\Pi^{(1)}_{m\ell}(p_b,\xi)\times\bar{S}_{m\ell}(p_b,\eta)\frac{e^{im\phi_a}}{\sqrt{2\pi}},\tag{69}$$

$$\mathbf{D}_a(\beta_1,R)=2B_1|m_1|\,!\left(\frac{2}{\beta_1}\right)^{|m_1|}(2\beta_1)^{2Z/\beta_1}B^{m_1}_{\ell_1}\times e^{-2Z/\beta_1-\beta_1R}R^{[(Z_b-1)+2Z/\beta_1]-|m_1|-1},\tag{70}$$

where the following notation is used:

$$T^{\ell}_{mm_1}(p_b,\beta)=N_{m\ell}(p_b)\sum_{s=0,1}^{\infty}{}'(-1)^{s+|m_1|+|m|}\times c^{m\ell}_s(p_b)B^{m_1}_{s+|m|}C^m_sD^{s+|m|}_{m_1m}(0,\beta,0),\tag{71}$$

$$B^m_\ell=\frac{1}{2^{|m|}|m|!}\sqrt{\frac{2\ell+1}{2}\frac{(\ell+|m|)!}{(\ell-|m|)!}},$$

$$C^m_s=\sqrt{\frac{2(s+2|m|)!}{(2s+2|m|+1)s!}}.\tag{72}$$

Under the condition $d\to0$ $(p_b\to0)$ the coefficient $c^{m\ell}_s$ has the following behavior $c^{m\ell}_s\to\delta_{s,\ell-|m|}$. Using the asymptotic (at $p_b\to0$) relations for oblate angular $\bar{S}_{m\ell}(p_b,\eta)$ and Coulomb radial $\Pi^{(1)}_{m\ell}(p_b,\xi)$ spheroidal functions, one obtains directly that the three-center wave function $\varphi_{ba}(\mathbf{r}_a)$ for $d\to0$ reduces to the well known asymptotic expression for the two-center electron wave function of the atom $B^{(Z_b-2)+}$ near the bare nucleus with charge $2Z$ [15]:

$$\varphi_{ba}(\mathbf{r}_a)\underset{d\to0}{=}\mathbf{D}_a(\beta_1,R)\sum_{\ell=m_1}^{\infty}\frac{\Gamma(\ell+1-\alpha)2^{\ell}}{\Gamma(2\ell+2)}\times R^{(1)}_{\alpha\ell}(\beta_1r_a)(-1)^{\ell+m_1}B^{m_1}_{\ell}Y^{m_1}_{\ell}(\theta_a,\phi_a).\tag{73}$$

IV. ONE-ELECTRON THREE-CENTER WAVE FUNCTION OF THE QUASIMOLECULE $A_2^{(Z_a-2)+}+B^{Z_b+}$

In the present section we shall study the asymptotic behavior of the one-electron wave function φ_{ab} of the molecular ion (or molecule) $A_2^{(Z_a-2)+}$ in the vicinity of the ionic center B^{Z_b+}. In the one active electron approximation, the wave function φ_{ab} satisfies the following Schrodinger equation:

$$\left[-\frac{\Delta}{2}+V'_a(\mathbf{r}_a)+V_b(r_b)\right]\varphi_{ab}(\mathbf{r}_a)=E_a\varphi_{ab}(\mathbf{r}_a).\tag{74}$$

Let E_a be the electron energy of the quasimolecule $A_2^{(Z_a-2)+}+B^{Z_b+}$ which at $R\to\infty$ goes over into the electron binding energy $E_a^{(0)}$ of the isolated diatomic $A_2^{(Z_a-2)}$:

$$E_a\underset{R\to\infty}{\sim}E_a^{(0)}\equiv-\alpha_1^2/2.\tag{75}$$

The effective potential $V'_a(\mathbf{r}_a)$ has the following asymptotic behavior:

$$V'_a(\mathbf{r}_a)\underset{r_a\to\infty}{\sim}-(Z_a-1)/r_a.\tag{76}$$

Under the condition $R_{1,2}\gg1$, the wave function φ_{ab} must go over into the unperturbed molecular wave function φ_a:

$$\varphi_{ab}(\mathbf{r}_a)\underset{r_a\ll\min[R_1,R_2]}{\sim}\varphi_a(\mathbf{r}_a),\tag{77}$$

where the asymptotic behavior of the φ_a is determined by Eq. (17). It is convenient to represent the coefficient $A_1(\theta)$ [see Eq. (17)] as an expansion over the normalized associated Legendre polynomials $\Theta^m_\ell(\theta)$ $[\Theta^m_\ell(\theta)=\sqrt{2\pi}Y^m_\ell(\theta,\varphi)e^{-im\varphi}]$:

$$A_1(\theta)=\sum_{s=0,1}^{\infty}a_s^{\alpha_1\mu_1}\Theta^{\mu_1}_{s+|\mu_1|}(\theta).\tag{78}$$

In order to calculate the electron wave function φ_{ab} in the underbarrier region near atomic ion B^{Z_b+} we employ the one-electron Green's function for the one-center potential $V_b(r_b)$ that satisfies the equation

$$\left[-\frac{1}{2}\Delta+V_b(r_b)-E_a^{(0)}\right]G_b^{(0)}(\mathbf{r}_b;\mathbf{r}'_b|d)=\delta(\mathbf{r}_b-\mathbf{r}'_b).\tag{79}$$

We shall consider here the case when the energy $E_a^{(0)}$ is not equal to any of the energy levels of the ion $B^{(Z_b-1)+}$ at infinite separation of $A_2^{(Z_a-2)+}$ and $B^{(Z_b-1)+}$. (The case of accidental resonance should be considered separately. One should use standard perturbation theory to remove accident degeneracy by accounting higher order corrections to the corresponding energy therm [8]). We note also, that in the case of symmetrical colliding systems the method applied here for calculation of the exchange interaction should be slightly modified. Resonant two-electron exchange interaction in the symmetric system is expressed in terms of the energy splitting $\Delta E=E_g-E_u$ of symmetrical (gerade) and antisymmetrical (ungerade) electronic states, the symmetry being defined with respect to reflection of all electronic coordinates in the plane perpendicular to the internuclear axis. The resulting expression for the matrix element is then expressed similar to Eq. (26) surface integral (albeit in six-dimensional configurational space of the electronic coordinates). For a more detailed description of the resonance two-electron transfer we refer readers to Refs. [15,27].

For an arbitrary spherically symmetric potential $V_b(r_b)$, the Green's function $G_b^{(0)}(\mathbf{r}_b;\mathbf{r}'_b|d)$ can be expanded in spherical harmonics Y^m_ℓ [15,23]:

$$G_b^{(0)}(\mathbf{r}_b;\mathbf{r}'_b|d)=-\frac{2}{r_br'_b}\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}g_\ell(\mathbf{r}_b;\mathbf{r}'_b|d)Y^m_\ell(\theta_b,\varphi_b)\times Y^{m*}_\ell(\theta'_b,\varphi'_b),\tag{80}$$

where $g_\ell(\mathbf{r}_b;\mathbf{r}'_b|d)$ is the one-dimensional radial Green's function, which can be written as [15,23]

$$g_\ell(\mathbf{r}_b;\mathbf{r}'_b|d) = -\frac{1}{2\alpha_1} f_{1\ell}(r_<) f_{2\ell}(r_>), \tag{81}$$

$$\frac{d^2 f_{i\ell}}{dr_b^2} + 2\left[E_b^{(0)} - V_b(r_b) - \frac{\ell(\ell+1)}{2r_b^2}\right] f_{i\ell} = 0, \quad i=1,2. \tag{82}$$

Here $r_< = \min(r_b, r'_b)$, $r_> = \max(r_b, r'_b)$. The functions $f_{1\ell}$ and $f_{2\ell}$ are the solutions of Eq. (82) and have the following asymptotic forms:

$$f_{1\ell} \underset{r_b\to\infty}{=} r_b^{-Z_b/\alpha_1} \exp(\alpha_1 r_b), \quad f_{2\ell} \underset{r_b\to\infty}{=} r_b^{Z_b/\alpha_1} \exp(-\alpha_1 r_b). \tag{83}$$

For the purposes of obtaining φ_{ab} in the vicinity of atomic ion $B^{(Z_b-2)+}$, we need the asymptotic form of the function $G_b^{(0)}(\mathbf{r}_b;\mathbf{r}'_b|d)$ when one of its arguments is large. For instance, for $r'_b \gg r_b \sim 1$, $G_b^{(0)}(\mathbf{r}_b;\mathbf{r}'_b|d)$ can be obtained by inserting in Eq. (80) the asymptotic form (83) for $f_{2\ell}$,

$$G_b^{(0)}(\mathbf{r}_b;\mathbf{r}'_b|d) \underset{r'_b\gg r_b}{\approx} \alpha_1^{-1} r_b'^{Z_b/\alpha_1-1} e^{-\alpha_1 r'_b} \times \sum_{\ell,m} \frac{f_{1\ell}(r_b)}{r_b} Y_\ell^m(\theta_b,\varphi_b) Y_\ell^{m*}(\theta'_b,\varphi'_b). \tag{84}$$

As in the derivations in the previous section, we should correct the wave function φ_a and the Green's function $G_b^{(0)}(\mathbf{r}_b;\mathbf{r}'_b|d)$ in the region II by the corresponding corrective functions to take into account their perturbations by the distant atomic ion B^{Z_b+} and molecular ion $A_2^{(Z_a-1)+}$, respectively, namely,

$$\varphi_{ab}(\mathbf{r}_a) = \varphi_a(\mathbf{r}_a)\chi_a(\mathbf{r}_a). \tag{85}$$

$$G_b(\mathbf{r}_b;\mathbf{r}'_b|Q) = G_b^{(0)}(\mathbf{r}_b;\mathbf{r}'_b|d)\bar{\chi}_b(\mathbf{r}_b). \tag{86}$$

The analytic expressions for $\bar{\chi}_b$ and χ_a can be obtained in the same way as those for $\bar{\chi}_a$ and χ_b, Eqs. (39) and (67), respectively. Therefore, we present here only the final results:

$$\bar{\chi}_b(\mathbf{r}_b) = \exp\left(-\frac{Z_b r_b}{\alpha_1 R}\right)\left[\frac{r_b + |\mathbf{R}+\mathbf{r}_b| - R\cos\theta_b}{R(1-\cos\theta_b)}\right]^{(Z_a-1)/\alpha_1}, \tag{87}$$

$$\chi_a(\mathbf{r}_a) = \exp\left(-\frac{Z_b r_a}{\alpha_1 R}\right)\left[\frac{r_a + |\mathbf{R}-\mathbf{r}_a| + R\cos\theta_a}{R(1+\cos\theta_a)}\right]^{Z_b/\alpha_2}. \tag{88}$$

The integral relation for the solutions of Eq. (74) can be obtained in the same way as in the case for function φ_{ba}. We will not repeat the derivation procedure but give only the final result

$$\varphi_{ab}(\mathbf{r}_b) = \mathbf{D}_b(\alpha_1,R)\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}(-1)^{\ell+m+1} \times \widetilde{T}_\ell^{m\mu_1}(\beta,R)\frac{f_{1\ell}(r_b)}{r_b}Y_\ell^m(\theta_b,\varphi_b), \tag{89}$$

where

$$\mathbf{D}_b(\alpha_1,R) = e^{-Z_b/\alpha_1} R^{[(Z_a-1)+Z_b/\alpha_1]-1} e^{-\alpha_1 R}, \tag{90}$$

$$\widetilde{T}_\ell^{m\mu_1}(\beta,R) = \frac{2^{|m|}|m|!}{R^{|m|}\alpha_1^{|m|+1}} \sum_{s=0,1}^{\infty} a_s^{\alpha_1\mu_1} B_\ell^m B_{s+|\mu_1|}^m D_{m\mu_1}^{s+|\mu_1|}(0,\beta,0). \tag{91}$$

The three-center one-electron wave function φ_{ba}, derived in the previous section, satisfies the Schrödinger Eq. (27) with an asymptotic accuracy, i.e., up to terms that decrease strongly at $R\to\infty$ ($R_{1,2}\sim R$). Similarly, the three-center one-electron wave function φ_{ab} satisfies the Schrödinger Eq. (74) with the same asymptotic accuracy. With these two wave functions we can construct the two-electron wave functions $\Psi_{k\lambda}(\mathbf{r}_1,\mathbf{r}_2)$, $k=1,2$; $\lambda=a,b$ [see Eqs. (24) and (25)] needed for calculation of two-electron exchange interactions in processes (2)–(5).

V. ASYMPTOTIC EXPRESSIONS FOR TWO-ELECTRON EXCHANGE INTERACTIONS

In the present section we calculate analytically the asymptotically exact expressions for two-electron exchange interactions that govern processes (2)–(5). An important property of two-electron wave functions $\Psi_{k\lambda}(\mathbf{r}_1,\mathbf{r}_2)$ is their orthogonality, $\langle\Psi_{kb}|\Psi_{k'a}\rangle=0$, $k'\neq k$, $k,k'=1,2$ (see [15]). Therefore, only the interelectronic interaction r_{12}^{-1} will give a nonzero contribution to the two-electron exchange intearctions. Since the leading contribution to the exchange interaction comes from the configuration region when the two electrons are well separated, one can employ a multipole expansion of the interaction r_{12}^{-1}.

A. Coupling interaction for direct two-electron exchange

We shall calculate the two-electron exchange interaction $H^{(20)}(Q)$ that is responsible for the direct two-electron capture process (2) by using the general representation for exchange interaction (7). The wave function Ψ_a of the initial configuration $A_2^{(Z_a-2)+}+B^{Z_b+}$ is represented by Eqs. (10) and (24), with φ_{ab} given by Eqs. (89)–(91). The wave function Ψ_b of the final configuration $A_2^{Z_a+}+B^{(Z_b-2)+}$ is represented by Eqs. (11) and (25) with φ_{ba} given by Eqs. (69)–(71). Therefore, the coupling interaction $H^{(20)}(Q)$ can be written as

$$H^{(20)}(Q) = (-1)^S \sum_{m_1 m_2} C_{\ell_1 m_1 \ell_2 m_2}^{LM_L} \langle \varphi_b^{(0)}(\mathbf{r}_{1b})\varphi_{ba}(\mathbf{r}_{2a})| \times H_{el}|\varphi_{ab}(\mathbf{r}_{1b})\varphi_a^{(0)}(\mathbf{r}_{2a})\rangle. \tag{92}$$

In the dipole-dipole approximation, the interaction r_{12}^{-1} has the form

$$\left(\frac{1}{r_{12}}\right)^{dd} = -\frac{8\pi}{3R^3}\sum_{q=-1}^{+1}\frac{r_{2a}Y_1^q(\theta_{2a},\phi_{2a})r_{1b}Y_1^{-q}(\theta_{1b},\phi_{1b})}{(1+q)\,!\,(1-q)!}. \tag{93}$$

Representing the spherical harmonic $Y_1^q(\theta_{2a},\phi_{2a})$ in the coordinate system $\{x',y',z'\}$ by

$$Y_\ell^q(\theta_{2a},\phi_{2a}) = \sum_{j=-\ell}^{+\ell} D_{qj}^{\ell *}(0,\beta,0)Y_\ell^j(\theta'_{2a},\phi'_{2a}), \tag{94}$$

we obtain the leading (at $R\to\infty$) asymptotic term of the exchange interaction $H^{(20)}(Q)$:

$$H^{(20)}(Q) = \frac{8\pi(-1)^{S+1}}{3R^3}\sum_{m_1m_2}C^{LM_L}_{\ell_1m_1\ell_2m_2} \times\sum_{q=-1}^{+1}\sum_{k=-1}^{+1}\frac{D^1_{qk}(0,\beta,0)}{(1-q)\,!\,(1+q)!}H^{(k)}_{ba}(Q)H^{(q)}_{ab}(Q), \tag{95}$$

where

$$H^{(k)}_{ba}(Q) = \langle\varphi_a^{(0)}(\mathbf{r}_{2a})|r_{2a}Y_1^k(\theta'_{2a},\phi'_{2a})|\varphi_{ba}(\mathbf{r}_{2a})\rangle, \tag{96}$$

$$H^{(q)}_{ab}(Q) = \langle\varphi_{ab}(\mathbf{r}_{1b})|r_{1b}Y_1^{-q}(\theta_{1b},\phi_{1b})|\varphi_b^{(0)}(\mathbf{r}_{1b})\rangle. \tag{97}$$

The technique of calculation of matrix elements $H^{(k)}_{ba}$ and $H^{(q)}_{ab}$ is described in Appendix A.

Due to the presence of infinite sums over the angular quantum numbers in expressions (69) and (89) it is obvious that the leading asymptotic term of exchange interaction (92) will be determined by dipole terms in expansion for r_{12}^{-1}. However, that is not always the case for the exchange interactions that are responsible for processes (3)–(5), where different bound-bound transitions may be involved. In the cases when the corresponding dipole transition is either forbidden or has negligibly small value, one has to use the quadrupole terms in the multipole expansion for r_{12}^{-1}.

B. Exchange interaction that corresponds to electron capture with excitation (or dissociative excitation) of molecular ion

We now calculate the two-electron exchange interaction $H^{(21)}(Q)$ that is responsible for process (3): one-electron capture by the projectile B^{Z_b+} with simultaneous excitation (or dissociative excitation) of the resulting diatomic $A_2^{(Z_a-1)+}$. Two-electron wave function Ψ_a of the initial configuration is given by the same formulas as in the previous subsection. The final two-electron wave function Ψ_b describes the quasimolecule $A_2^{(Z_a-1)+^*}+B^{(Z_b-1)+}$. Taking into account that in this configuration electrons are well separated, we represent Ψ_b as

$$\Psi_b = \frac{1}{\sqrt{2}}[\varphi_b^{(0)}(\mathbf{r}_{1b})\varphi_a^{(1)}(\mathbf{r}_{2a}) + (-1)^S\varphi_b^{(0)}(\mathbf{r}_{2b})\varphi_a^{(1)}(\mathbf{r}_{1a})], \tag{98}$$

where $\varphi_a^{(1)}(\mathbf{r})$ is the wave function of excited (bound or dissociative) state of molecular ion $A^{(Z_a-1)+^*}$. Using the previously obtained results for Ψ_a and Ψ_b, dipole approximation (93) for r_{12}^{-1} and Eq. (7) for the exchange interaction, we represent the $H^{(21)}(Q)$ as

$$H^{(21)}(Q) = -\frac{8\pi}{3R^3}\sum_{q=-1}^{+1}\sum_{k=-1}^{+1}\frac{D^1_{qk}(0,\beta,0)}{(1-q)\,!\,(1+q)!}H^{(k)}_{a[1]}(d)H^{(q)}_{ab}(Q), \tag{99}$$

$$H^{(k)}_{a[1]}(d) = \langle\varphi_a^{(0)}(\mathbf{r}_{2a})|r_{2a}Y_1^k(\theta'_{2a},\phi'_{2a})|\varphi_a^{(1)}(\mathbf{r}_{2a})\rangle. \tag{100}$$

In the case of dipole forbidden transitions in the molecular ion, we have to use the quadrupole term in the multipole expansion of r_{12}^{-1} (keeping, however, the dipole term for the transitions in the atomic ion),

$$\left(\frac{1}{r_{12}}\right)^{qd} = -\frac{4\pi}{\sqrt{5}R^4}\sum_{q=-1}^{+1}[r_{2a}^2Y_2^q(\theta_{2a},\phi_{2a})r_{1b}Y_1^{-q}(\theta_{1b},\phi_{1b})](\delta_{1|q|} + \sqrt{3}\delta_{0q}). \tag{101}$$

Hereinafter, $\delta_{nn'}$ is the Kronecker's delta symbol. Calculating exchange interaction (7) with previously obtained wave functions Ψ_a, Ψ_b and electron-electron interaction in form (101), one obtains for $H^{(21)}(Q)$

$$H^{(21)}(Q) = -\frac{4\pi}{\sqrt{5}R^4}\sum_{q=-1}^{+1}\sum_{k=-2}^{+2}D^2_{qk}(0,\beta,0)H^{(k)}_{a[2]}(d)H^{(q)}_{ab}(Q)(\delta_{1|q|} + \sqrt{3}\delta_{0q}), \tag{102}$$

$$H^{(k)}_{a[2]}(d) = \langle\varphi_a^{(0)}(\mathbf{r}_{2a})|r_{2a}^2Y_2^k(\theta'_{2a},\phi'_{2a})|\varphi_a^{(1)}(\mathbf{r}_{2a})\rangle. \tag{103}$$

The matrix elements $H^{(k)}_{a[1]}(d)$ and $H^{(k)}_{a[2]}(d)$, responsible, respectively, for the dipole and quadrupole bound-bound transitions in molecular ion $A_2^{(Z_a-1)+}$, are calculated in Appendix B.

C. Exchange interaction that corresponds to electron capture with ion deexcitation

In this subsection we calculate the leading term of the two-electron exchange interaction $H^{(10)}(Q)$ between the initial $A_2^{(Z_a-1)+}+B^{(Z_b-1)+^*}$ and final $A_2^{Z_a+}+B^{(Z_b-2)+}$ state of process (4). The two-electron wave function Ψ_a can be represented in symmetrized form,

$$\Psi_a = \frac{1}{\sqrt{2}}[\varphi_a^{(0)}(\mathbf{r}_{1a})\varphi_b^{(1)}(\mathbf{r}_{2b}) + (-1)^S\varphi_a^{(0)}(\mathbf{r}_{2a})\varphi_b^{(1)}(\mathbf{r}_{1b})], \tag{104}$$

where $\varphi_b^{(1)}$ is the electron wave function of the excited state of atomic ion $B^{(Z_b-1)+^*}$. The final state two-electron wave function Ψ_b is the same as in Sec. V A and is given by expression (11). Substituting expressions (104) and (11) for Ψ_a and Ψ_b, respectively, into Eq. (7) and using dipole approximation (93) for the electron-electron interaction, we obtain the leading (at $R\to\infty$) asymptotic term for $H^{(10)}(Q)$,

$$H^{(10)}(Q) = -\frac{8\pi}{3R^3}\sum_{m_1m_2} C^{LM_L}_{\ell_1m_1\ell_2m_2}\sum_{q=-1}^{+1}\sum_{k=-1}^{+1}\frac{D^1_{qk}(0,\beta,0)}{(1-q)\,!\,(1+q)!} \times H^{(k)}_{ba}(Q)H^{(q)}_{b[1]}, \tag{105}$$

$$H^{(q)}_{b[1]} = \langle\varphi^{(1)}_b(\mathbf{r}_{1b})|r_{1b}Y^{-q}_1(\theta_{1b},\phi_{1b})|\varphi^{(0)}_b(\mathbf{r}_{1b})\rangle. \tag{106}$$

In order to account bound-bound transitions that are forbidden in dipole approximation we use dipole-quadrupole term in the expansion for r^{-1}_{12}: $(r^{-1}_{12})^{dq} = -(r^{-1}_{12})^{qd}(2a \rightleftarrows 1b, q \to -q)$. The matrix element $H^{(10)}(Q)$ in this case takes the following form:

$$H^{(10)}(Q) = \frac{4\pi}{\sqrt{5}R^4}\sum_{m_1m_2} C^{LM_L}_{\ell_1m_1\ell_2m_2} \times \sum_{q=-1}^{+1}\sum_{k=-1}^{+1} D^1_{qk}(0,\beta,0)(\delta_{1|q|} + \sqrt{3}\,\delta_{0q})H^{(k)}_{ba}(Q)H^{(q)}_{b[2]}, \tag{107}$$

$$H^{(q)}_{b[2]} = \langle\varphi^{(1)}_b(\mathbf{r}_{1b})|r^2_{1b}Y^{-q}_2(\theta_{1b},\phi_{1b})|\varphi^{(0)}_b(\mathbf{r}_{1b})\rangle. \tag{108}$$

The matrix elements $H^{(q)}_{b[1,2]}$ are calculated in Appendix B.

D. Exchange interaction that corresponds to electron bound-bound transitions on different particles (excitation transfer)

We consider here the exchange interaction $H^{(11)}(Q)$ that is responsible for the two-electron excitation transfer process (5), i.e., when bound-bound transitions simultaneously take place in the parent particles. The wave function Ψ_a of the initial state $A_2^{(Z_a-1)+} + B^{(Z_b-1)+^*}$ is given by Eq. (104), while the wave function Ψ_b of the final state $A_2^{(Z_a-1)+^*} + B^{(Z_b-1)+}$ is given by Eq. (98). In the case of dipole-dipole transitions, we obtain for $H^{(11)}(Q)$ the following expression:

$$H^{(11)}(Q) = -\frac{8\pi}{3R^3}\sum_{q=-1}^{+1}\sum_{k=-1}^{+1}\frac{D^1_{qk}(0,\beta,0)}{(1-q)\,!\,(1+q)!}H^{(k)}_{a[1]}(d)H^{(q)}_{b[1]}. \tag{109}$$

In the case of quadrupole-dipole (101) approximation for r^{-1}_{12}, we have for $H^{(11)}(Q)$,

$$H^{(11)}(Q) = -\frac{4\pi}{\sqrt{5}R^4}\sum_{q=-1}^{+1}\sum_{k=-2}^{+2} D^2_{qk}(0,\beta,0)(\delta_{1|q|} + \sqrt{3}\,\delta_{0q})H^{(k)}_{a[2]}(d)H^{(q)}_{b[1]}, \tag{110}$$

while in the case of dipole-quadrupole $(r^{-1}_{12})^{dq}$ approximation for r^{-1}_{12}, we have

$$H^{(11)}(Q) = \frac{4\pi}{\sqrt{5}R^4}\sum_{q=-1}^{+1}\sum_{k=-2}^{+2} D^2_{qk}(0,\beta,0)(\delta_{1|q|} + \sqrt{3}\,\delta_{0q})H^{(k)}_{a[1]}(d)H^{(q)}_{b[2]}. \tag{111}$$

VI. CROSS-SECTION CALCULATIONS

In the present section we shall apply the results obtained in the previous sections to study the basic electron-transfer processes in slow collisions of $H_2(1\sigma_g^2)$ with He^{2+}. This collision system has been subject to many experimental and theoretical studies for several decades (see Refs. [28–40] and references therein) in view of its relative structural simplicity and the importance of its collision processes in magnetic fusion and astrophysical plasmas [4,5]. However, the experimental data as well as theoretical calculations of the cross sections for these processes are often in disagreement with each other (see [28,38] and reference therein) and further investigations of the dynamics of $H_2 + He^{2+}$ collision system is, therefore, necessary.

The previous studies of collision processes in $H_2 + He^{2+}$ collision system indicate that at low collision energies the most important are the processes

$$\text{NDSEC:}\quad H_2(1\sigma_g^2) + He^{2+} \to H_2{}^+(1\sigma_g) + He^+, \tag{112}$$

$$\text{DSEC:}\quad H_2(1\sigma_g^2) + He^{2+} \to H + H^+ + He^+, \tag{113}$$

$$\text{TEC:}\quad H_2(1\sigma_g^2) + He^{2+} \to 2H^+ + He. \tag{114}$$

In the present section we shall employ a close-coupling treatment of the collision dynamics in $H_2 + He^{2+}$ system which accounts simultaneously for both the direct processes (112)–(114) and the two-step processes of type (4)–(6). We shall use the semiclassical version of the close-coupling method [41] whereby the position vector $\mathbf{R}$ of incident ion with respect to the center of mass of diatomic target follows a classical straight-line trajectory, $\mathbf{R} = \mathbf{b} + \mathbf{v}t$, with an impact parameter $\mathbf{b}$ and constant velocity $\mathbf{v}$. The direction of $\mathbf{v}$ defines the z_1 axis of the laboratory reference frame $\{x_1, y_1, z_1\}$. The center of mass of diatomic molecule is placed at the origin of the coordinate system $\{x_1, y_1, z_1\}$ and the orientation of the molecular bond vector $\mathbf{d}$ is specified by the set of two angles $\{\alpha', \beta'\}$ $(0 \le \alpha' \le 2\pi,\ 0 \le \beta' \le \pi)$ (see Fig. 1). The internal degrees of freedom of triatomic collision system are treated quantum mechanically and described by the wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{d}, t)$, which is a solution of the equation

$$(H_{el} + T_d - i\,\partial/\partial t|_{\mathbf{d},r_i})\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{d}, t) = 0, \tag{115}$$

where $\mathbf{r}_i$ $(i = 1, 2)$ denotes the electronic coordinates, $H_{el}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{d}, \mathbf{R})$ is the fixed-nuclei Born-Oppenheimer electronic Hamiltonian, and T_d is the kinetic rotational-vibrational operator of the molecule H_2. The wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{d}, t)$ is expanded, for each $\mathbf{d}$, in terms of the eigenfunctions $\{\phi_i\}$ of the operator H_{el}:

$$H_{el}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{d}, \mathbf{R})\phi_i(\mathbf{r}_1, \mathbf{r}_2; \mathbf{d}, \mathbf{R}) = \varepsilon_i(\mathbf{R}, \mathbf{d})\phi_i(\mathbf{r}_1, \mathbf{r}_2; \mathbf{d}, \mathbf{R}), \tag{116}$$

$$\Psi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{d},t) = d^{-1}Y_{JM}(\hat{\mathbf{d}})\chi_0(d)\sum_j a_j(t;\mathbf{d})\phi_j(\mathbf{r}_1,\mathbf{r}_2;\mathbf{d},\mathbf{R}) \times \exp\left(-i\int_{t_0}^{t}\varepsilon_j dt'\right), \tag{117}$$

where $d^{-1}Y_{JM}(\hat{\mathbf{d}})\chi_0(d)$ is the initial rovibrational wave function of the molecule H_2. In the present low-energy calculations we shall neglect the electron momentum transfer effects during the collision.

Substitution of Eq. (117) into the Schrodinger Eq. (115) and integration of the resulting system of differential equations for amplitudes $a_k(t;\mathbf{d})$,

$$i\frac{da_k}{dt} = \sum_{\substack{j=1\\ j\neq k}} a_j H_{jk} \exp\left[-i\int_{t_0}^{t}(\varepsilon_j-\varepsilon_k)dt'\right], \tag{118}$$

yields, after summation over all final vibrational states $\{\chi_f\}$ and averaging over initial $\hat{\mathbf{d}}$ orientations, the cross section for transition to a given electronic channel $\{\phi_f\}$:

$$\sigma_f(v) = \frac{1}{4\pi}\int d\mathbf{b}\int d\mathbf{d}|\chi_0(d)|^2 P_f(b,\mathbf{d}), \tag{119}$$

where the probability $P_f(b,\mathbf{d})$ for electron capture into a given final state is defined in the standard way as $P_f(b,\mathbf{d}) = |a_f(t\to\infty;\mathbf{d})|^2$. In the present calculations we neglect the vibrational motion of the H_2 bond, hence the amplitudes $a_f(t\to\infty;\mathbf{d})$ [i.e the probability $P_f(b,\mathbf{d})$] of Eq. (118) are calculated at the equilibrium distance $d=1.4$ a.u. of H_2 molecule,

$$\sigma_f(v) = \frac{1}{2}\int_0^{\pi}\sin\beta' d\beta'\int_0^{2\pi}d\alpha'\int_0^{\infty}bP_f(b,\alpha',\beta';d_0)db, \tag{120}$$

where the dependence on the initial (and fixed) molecular bond orientation (α', β'; see Fig. 1) is explicitly indicated [42]. The cross section $\sigma_f(v,\beta')$ as function of the angle β' between the molecular bond and the direction of velocity vector is defined as

$$\sigma_f(v,\beta') = \frac{1}{2\pi}\int_0^{2\pi}d\alpha'\int_0^{\infty}2\pi bP_f(b,\alpha',\beta';d_0)db. \tag{121}$$

In the coupled state calculations of the cross sections of reactions (112)–(114) we shall use the diabatic three-center basis consisting of the two-electron three-center wave functions of types (10), (11), (98), and (104). We designate by a_1 and $\phi_1(\mathbf{r}_1,\mathbf{r}_2;\mathbf{d},\mathbf{R})$ the amplitude and the wave function of initial state $He^{2+}+H_2(1\sigma_g^2)$, respectively, and by a_j and $\phi_j(\mathbf{r}_1,\mathbf{r}_2;\mathbf{d},\mathbf{R})$ ($j=2,\ldots,N$) the amplitudes and wave functions of the final states of reactions (112)–(114). In Table I we give the list of asymptotic ($R\to\infty$) electronic energies of the quasimolecular states included in present calculations [configuration $He^+(1s)+H_2{}^+(1s\sigma)$, since its energy much lower than energy of entrance channel, were not included in calculation and given only for reference]. The exact values of the energies of the states involved in the calculations have been taken from the NIST database [43] for the He states, from Ref. [44] for $H_2(1\sigma_g^2)$ state, and from calculations by the method of chain fractions [23] for $H_2{}^+$.

TABLE I. Electronic energies of the system $[HeH_2]^{2+}$ at $d=d_0=1.4$ a.u. and infinite separation $R\to\infty$.

State		E (a.u.)
$He^+(n=2)+H_2{}^+(4s\sigma)$		−0.6107
…		
$He^+(n=2)+H_2{}^+(1s\sigma)$		−1.7840
$He^{2+}+H_2(1\sigma_g^2)$		−1.8479
…	…	
…	$He(1s3p)+H_2^{2+}$	−2.0551
…	$He(1s3d)+H_2^{2+}$	−2.0556
…	$He(1s3s)+H_2^{2+}$	−2.0613
$He^+(1s)+H_2{}^+(4s\sigma)$		−2.1107
$He^+(1s)+H_2{}^+(4p\pi)$		−2.1195
…	$He(1s2p)+H_2^{2+}$	−2.1238
…	…	
$He^+(1s)+H_2{}^+(4d\pi)$		−2.1260
$He^+(1s)+H_2{}^+(4d\sigma)$		−2.1276
$He^+(1s)+H_2{}^+(4p\sigma)$		−2.1353
	$He(1s2s)+H_2^{2+}$	−2.1460
$He^+(1s)+H_2{}^+(3s\sigma)$		−2.1893
$He^+(1s)+H_2{}^+(3p\pi)$		−2.2093
$He^+(1s)+H_2{}^+(3d\pi)$		−2.2247
$He^+(1s)+H_2{}^+(3d\sigma)$		−2.2283
$He^+(1s)+H_2{}^+(3p\sigma)$		−2.2487
$He^+(1s)+H_2{}^+(2s\sigma)$		−2.3949
$He^+(1s)+H_2{}^+(2p\pi)$		−2.4563
$He^+(1s)+H_2{}^+(2p\sigma)$		−2.6121
	$He(1s^2)+H_2^{2+}$	−2.9036
$He^+(1s)+H_2{}^+(1s\sigma)$		−3.2843

The system of differential equations (118) has been solved with the initial conditions

$$|a_k(t=t_0)| = \delta_{1k}, \quad k=1,2,\ldots,N, \tag{122}$$

by using the backward differentiation formula algorithm [45,46], for a given set of fixed parameters: velocity v, impact parameter b, and angles α' and β' of the molecular bond orientation (see Fig. 1). In order to obtain orientation-averaged cross sections $\sigma_f(v)$ [as well as $\sigma_f(v,\beta')$] we calculated the cross sections $\sigma_f(v,\mathbf{d})$ for 140 basic orientations of the molecular bond $\mathbf{d}$ (14 different values of the angle α' at each of ten values of angle β') for a given velocity v. System of equations (118) was integrated in the interval corresponding to maximal projectile-target separation of $R_0=50$ a.u.; i.e., the projectile starts at the coordinate $z_1^i=-\sqrt{R_0^2-b^2}$ and the trajectory is followed until the projectile reaches the coordinate $z_1^f=-z_1^i$. We have assumed that if the electron remains (at $z_1=z_1^f$) in the initial $H_2{}^+$ molecular orbital $1\sigma_g$, the H_2^+ ion does not dissociate, leading to NDSEC process (112), and if the electron is found in any of the excited states of H_2^+ ion the time evolution of the collision system leads to DSEC process (113). In the framework of adopted asymptotic approach, the diabatic potentials ($\varepsilon_j \equiv H_{jj}$) of the initial H_{11} and the final (H_{nn}^{SEC} for NDSEC and DSEC, and H_{nn}^{TEC} for TEC channels, respectively) configurations to the lowest order of accuracy at large distances R can be represented as

$$H_{11} = -\frac{\alpha_1^2}{2} - \frac{\alpha_2^2}{2} + Z_b\left(\frac{Z_a}{2R_1} + \frac{Z_a}{2R_2} - \frac{2}{R}\right) + O(R^{-2}), \tag{123}$$

$$H_{nn}^{\text{SEC}} = -\frac{\alpha_2^2}{2} - \frac{\beta_2^2}{2} + (Z_b - 1)\left(\frac{Z_a}{2R_1} + \frac{Z_a}{2R_2} - \frac{1}{R}\right) + O(R^{-2}), \tag{124}$$

$$H_{nn}^{\text{TEC}} = -\frac{\beta_1^2}{2} - \frac{\beta_2^2}{2} + (Z_b - 2)\left(\frac{Z_a}{2R_1} + \frac{Z_a}{2R_2}\right) + O(R^{-2}). \tag{125}$$

The detailed procedure for calculation of nondiagonal coupling matrix element $H^{(if)}$ responsible for two-electron processes (2)–(5) is given in Sec. V and Appendixes A and B.

The coupling matrix elements H_{AB} responsible for one-electron processes (1) and (6) in the colliding system $A_2^{(Z_a-2)+} + B^{Z_b+}$ are related to calculation of surface integral (26) ($2H_{AB} \approx \Delta E$). Asymptotic representation of these types of matrix elements has been studied in our recent work [16]. We omit the details of calculations and present here only the final results for H_{AB}. We have considered two cases: (i) the projectile B^{Z_b+} is the bare nucleus with charge Z_b and (ii) the projectile B^{Z_b+} is an atomic ion with closed shell electronic configuration and an effective core charge Z_b. For H_{AB} in the case (i) we have

$$\begin{aligned}H_{AB} = {} & \frac{(2Z_b)^{3/2}}{2n^2} 2^{2|m_2|+n_1}\left(\frac{Z_b}{n}\right)^{n_2+|m_2|} \exp\left[-\frac{R}{2}\left(\frac{Z_b}{n} + \alpha_1\right)\right. \\ & \left. - \frac{1}{2}\left(\frac{nZ_a}{Z_b} + \frac{Z_b}{\alpha_1}\right)\right] R^{n_2 + Z_a/\alpha_1} \\ & \times \left(\frac{Z_b}{n} + \alpha_1\right)^{-|m_2|} \sqrt{\frac{(n_1 + |m_2|)!}{(n_2 + |m_2|)\,!\,n_1\,!\,n_2!}} \\ & \times \sum_{s=|m_2|}^{\infty} a_s^{\alpha_1\mu_1} D_{m_2\mu_1}^{s+|\mu_1|}(0,\beta,0) B_{s+\mu_1}^{m_2},\end{aligned} \tag{126}$$

where the set of parabolic quantum numbers $[nn_1n_2m_2]$ describes electronic wave function of the ion $B^{(Z_b-1)+}$ [16]. For H_{AB} in the case (ii) we have

$$\begin{aligned}H_{AB} = {} & B_2 B_{\ell_2}^{m_2} \frac{2^{2|m_2|!}|m_2|!}{(\alpha_1 + \beta_2)^{m_2}} R^{(Z_a - 1/\alpha_1) + (Z_b/\beta_2) - |m_2| - 1} \\ & \times \exp\left[-\frac{R(\alpha_1 + \beta_2)}{2}\right] \exp\left[-\frac{1}{2}\left(\frac{Z_a - 1}{\beta_2} + \frac{Z_b}{\alpha_1}\right)\right] \\ & \times \sum_{s=|m_2|}^{\infty} a_s^{\alpha_1\mu_1} D_{|m_2|\mu_1}^{s+\mu_1}(0,\beta,0) B_{s+\mu_1}^{m_2}.\end{aligned} \tag{127}$$

In the present calculations of NDSEC process (112) we shall use the matrix element given by Eq. (126). The coefficients $a_s^{\alpha_1\mu_1}$ [see Eq. (78)] of the asymptotic behavior of the one-electron orbital in $H_2(1\sigma_g^2)$ molecule have been calculated by matching (in the region $r_a' \gtrsim 2$ a.u.) asymptotic expression (17) with the Coulson ground-state orbital $\psi_{1s\sigma}^{H_2}$ [47]. The result is (see Ref. [48]) $a_0^{\alpha_1 0} = 2.327$, $a_2^{\alpha_1 0} = 0.283$, $a_4^{\alpha_1 0} = 0.017$, $a_{s \geq 6}^{\alpha_1 0} \sim 0$. For the asymptotic coefficient B_2 of the wave function of electron motion in the field of the bare nucleus we use for this orbital its Coulomb asymptotic form [see Eq. (2.13) of Ref. [15]].

The one-electron process (6) of the TEC and DSEC interaction is governed by the one-electron exchange interaction similar to Eq. (127):

$$\begin{aligned}H_{AB} = {} & B_1 B_{\ell_1}^{m_1} \frac{2^{2|m_1|!}|m_1|!}{(\alpha_2 + \beta_1)^{|m_1|}} R^{(Z_a/\alpha_2) + (Z_b - 1/\beta_1) - |m_1| - 1} \\ & \times \exp\left[-\frac{R(\alpha_2 + \beta_1)}{2}\right] \\ & \times \exp\left[-\frac{1}{2}\left(\frac{Z_a}{\beta_1} + \frac{Z_b - 1}{\alpha_2}\right)\right] \\ & \times \sum_{s=|m_1|}^{\infty} a_s^{\alpha_2\mu_2} D_{|m_1|\mu_2}^{s+\mu_2}(0,\beta,0) B_{s+\mu_2}^{m_1}.\end{aligned} \tag{128}$$

The required asymptotic factor $A_2(\theta_{2a})$ (i.e., the coefficients $a_s^{\alpha_2\mu_2}$) [see Eq. (18)] of the wave function of H_2^+ ion in this case can be calculated in the same way as the coefficient $A_1(\theta_{1a})$ [see Eq. (78)] of the asymptotic wave function of $H_2(1\sigma_g^2)$. The values of coefficients $a_s^{\alpha_2\mu_2}$ for the ground and excited states of molecular ion H_2^+ (at $d = 1.4$ a.u.) included in present calculations are given in Table II. The corresponding wave functions of the H_2^+ electronic states were calculated by the method of chain fractions described in [23]. Finally, we give here the asymptotic normalization coefficients B_1 [see Eq. (20)] for the valence electron wave function of He: $B_1[1s^2] = 2.87$, $B_1[1s2s] = -0.35$, $B_1[1s2p] = 0.2$, $B_1[1s3s] = 0.02$, $B_1[1s3p] = -0.015$, and $B_1[1s3d] = 0.009$.

It is well known (see Ref. [49]) that the postcollision interaction (PCI) (i.e., the interaction of the intermediate reaction products) may exert a significant influence on the collision dynamics. In the case of charge-transfer processes studied in the present paper long-range Coulomb interaction of H_2^+ and He^+ products of the NDSEC process (112) can induce electronic excitation of the H_2^+ ion and thereby contribute to the DSEC process, namely,

TABLE II. Coefficients $a_s^{\alpha_2\mu_2}=\bar{a}_s^{\alpha_2\mu_2}\times 10^n$ of expansion (78) calculated for the wave functions of hydrogen molecular ion $H_2{}^+$ for the ground and some excited states.

State	Coeff.							
	$\bar{a}_\delta^{\alpha_2\mu_2}$	n	$\bar{a}_{\delta+2}^{\alpha_2\mu_2}$	n	$\bar{a}_{\delta+4}^{\alpha_2\mu_2}$	n	$\bar{a}_{\delta+6}^{\alpha_2\mu_2}$	n
$1s\sigma$	4.67	0	4.79	−1	2.46	−2	1.1	−3
$2s\sigma$	−9.29	−1	−2.56	−2	−3.7	−4	−1.1	−5
$2p\sigma$	1.63	0	5.57	−2	1.36	−3	1.3	−5
$2p\pi$	9.74	−1	2.12	−2	7.7	−4		
$3s\sigma$	1.13	−1	1.29	−3	2.3	−6		

$$He^+(n)+H_2{}^+(1\sigma_g)\rightarrow He^+(n)+H_2{}^+(n'\lambda'). \qquad (129)$$

This PCI excitation mediated contribution to the DSEC process is negligible in the low-energy (adiabatic) region, but with increasing the projectile velocity it becomes important. In order to estimate the contribution of this PCI mechanism to DSEC, we shall employ a simple "one-electron" model in which the perturbing atomic ion He^+ is treated as the point-like Coulomb charge. In this case, the single electron excitation process can be considered as being caused by the following effective potential [50]:

$$V(\mathbf{r}_a,\mathbf{R})=-(Z_b-1)/|\mathbf{R}-\mathbf{r}_a|, \qquad (130)$$

where (as in previous sections) $\mathbf{r}_a$ is the radius vector of the molecular electron with respect to the center of the molecule [note that, formally, the potential $V(\mathbf{r}_a,\mathbf{R})$ coincides with $V_b'(r_b)$ given by Eq. (28)]. Assuming a strong coupling only between the initial and final states in excitation process (129) we can use the leading multipole (dipole or quadrupole) approximation for interaction (130). Hence, the coupling matrix element,

$$H_{ex}(Q)=\langle\varphi_a^{(0)}(\mathbf{r}_a)|V(\mathbf{r}_a,\mathbf{R})|\varphi_a^{(1)}(\mathbf{r}_a)\rangle, \qquad (131)$$

responsible for electronic excitation (129) can easily be constructed from the matrix elements $H_{a[1]}^{(k)}(d)$ and $H_{a[2]}^{(k)}(d)$ [see Eqs. (100) and (103)].

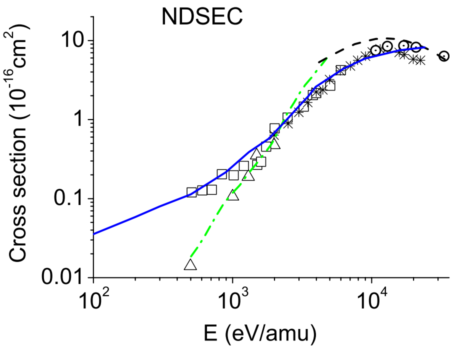

FIG. 2. (Color online) Cross sections for NDSEC into $He(2\ell)+H_2{}^+(1\sigma_g)$: △, Ref. [29]; dash-dotted line, theoretical result of Ref. [28]. Cross sections for NDSEC into $He(2p)+H_2{}^+(1\sigma_g)$: □ Ref. [31]; ∗, Ref. [32]. Total NDSEC cross section: ⊙, Ref. [30]; dashed line, theoretical result of Ref. [28]; solid line, present results.

In the present close-coupling calculations for total cross sections σ_f of reactions (112)–(114) we have included the entrance channel $He^{2+}+H_2(1\sigma_g^2)$ and the most important exit channels: two NDSEC channels $He^+(n=2,m=0)+H_2{}^+(1s\sigma)$, 6 TEC channels $He(1s^2,1s2\ell,1s3\ell,m=0)+H_2^{2+}$, and 13 DSEC channels $He^+(1s)+H_2{}^+(n=2,3,4)$. All the processes (1)–(6) are involved in the population of these configurations. We have included also 13 DSEC channels $He^+(n=2)+H_2{}^+(n=2,3,4)$ which can only be populated through mechanism (129) as the second step after NDSEC process.

Our results for the total cross section of NDSEC process (112) (see Fig. 2) agree fairly well with the experimental data of Refs. [29–32] in a rather wide range of collision energies. In the same figure we have plotted the results of molecular orbital close-coupling calculations of Ref. [28]. Since we have neglected the effects of electron momentum transfer, our results become less reliable when the collision energy is larger than ∼20 keV/amu.

In Fig. 3(a) we show the calculated total cross section for DSEC reaction (113). For collision energies below 3 keV/amu the results of present calculations are in very good accord with theoretical calculations of Ref. [28]. In the same figure we show the experimental data of Refs. [29,30]. We also compare our DSEC cross section with the total cross

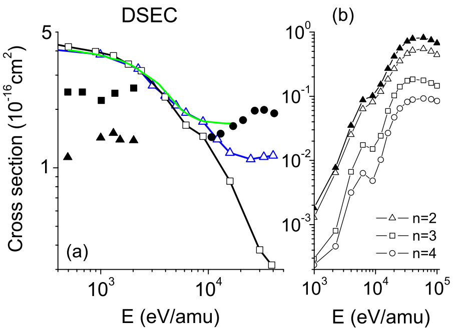

FIG. 3. (Color online) (a) Total DSEC cross section. Experimental results: ▲, Ref. [29]; ●, Ref. [30]; ■, experimental data of Ref. [33] for total cross section of the single electron capture. Theoretical results: solid line, *ab initio* calculation of Ref. [28]; —△—, present calculations with account of PCI; —□—, present calculations with switched off PCI. (b) Present calculation for cross sections of the electronic excitation of the $H_2{}^+$ ion (see explanation in text); —▲—, total cross section; lines with open symbols, total cross sections of the electronic excitation into the individual final states of $H_2{}^+(n)$.

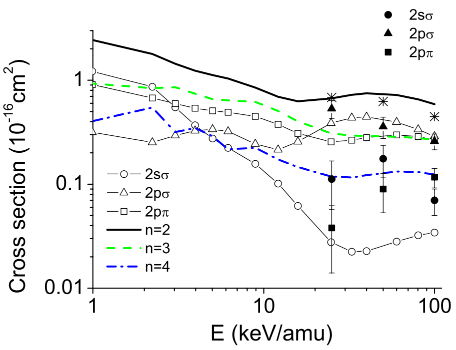

FIG. 4. (Color online) Total cross sections for population of the specific DSEC states. Present calculations: lines with open symbols, cross sections for population of the individual DSEC states $H_2^+(n=2)$; solid line, total cross section for population of $H_2^+(n=2)$ states; dashed line, total cross section for population of $H_2^+(n=3)$ states; dash-dotted line, total cross section for population of $H_2^+(n=4)$ states. Experiment: symbols, population of the specific DSEC states $H_2^+(2s\sigma,2p\sigma,2p\pi)$, Ref. [51]; $*$, sum of the partial cross sections from Ref. [51] for population into the $H_2^+(2s\sigma,2p\sigma,2p\pi)$ states.

section for single electron capture of Ref. [33] since the NDSEC cross section is very small at low collision energies and can be neglected. The present results support the conclusions of experimental [29,30] and theoretical [28] findings that DSEC is the dominant process at low energies in this collision system. However, with increasing the collision velocity our total DSEC cross section underestimates the experimental results of Ref. [30] by a factor of 2. To study the relative contribution of the different mechanisms (namely, the effect of PCI) to the total DSEC cross section we have carried out a model close-coupling calculations including the entrance channel, two NDSEC channels $\mathrm{He}^+(n=2,m=0)+H_2^+(1s\sigma)$, and 13 DSEC channels $\mathrm{He}^+(n=2)+H_2^+(n=2,3,4)$. The result of this model calculation is presented in Fig. 3(b) and demonstrates that total cross sections of the capture into the DSEC states through mechanism (129) rapidly increase with increasing of collision energy.

To estimate this effect in the entire picture of reactions (112)–(114) we have "switched off" in the calculations the matrix elements (131) responsible for the PCI [i.e., we have excluded all $\mathrm{He}^+(n=2)+H_2^+(n=2,3,4)$ channels]. The resulting total DSEC cross sections are presented in Fig. 3(a) and demonstrate that neglecting of the postcollision interactions leads to significant underestimation of the DSEC cross section at energies above ~10 keV/amu.

In Fig. 4 we show the resulting DSEC cross sections leading to population of individual excited states of molecular ion H_2^+. The main contribution to the DSEC cross section comes from electron capture with excitation (of the second electron) to the low-lying levels of H_2^+. In the same figure we show the experimental data of Ref. [51] on the relative contributions of some dissociative channels into DSEC process (113). Our calculation for total cross section of the DSEC into $H_2^+(n=2)$ states is in fairly good agreement with experimental data.

In Fig. 5 we compare the probabilities of TEC, DSEC, and NDSEC at two impact energies 0.5 and 9.0 keV/amu.

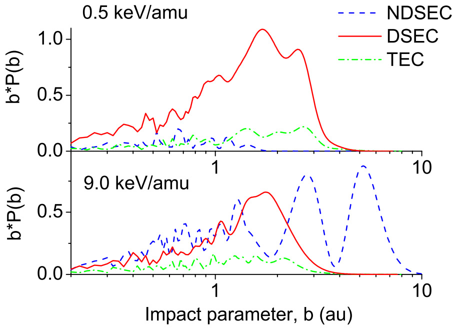

FIG. 5. (Color online) $bP(b)$ as function of b for impact energies 0.5 and 9.0 keV/amu. Solid line, probability of DSEC; dashed line, probability of NDSEC; dot-dashed line, probability of TEC.

The main contribution to TEC and DSEC at both collision energies gives almost the same impact parameter range, $b\sim 1-4$ a.u. In contrast to this, the high impact parameters play no role in NDSEC state population at low collision velocities, while at higher velocities ($v\gtrsim 0.7$ a.u.) the large impact parameters give the dominant contribution to NDSEC. These results are also in accord with the theoretical calculations of Ref. [28].

In Fig. 6 we show the total cross sections for TEC reaction (114). The result of present calculations is in a satisfactory overall agreement with the experimental data of Refs. [33–39]. The present result does not reproduce adequately well the minimum of experimental cross section near 4 keV/amu. In the same figure we show also the results of theoretical calculations of Refs. [28,34,40]. For collision energies $\lesssim 2$ keV/amu our calculations are in good agreement with the theoretical results of [40]. In Fig. 7(a) we give the cross sections for capture into specific TEC states. For low and intermediate collision energies the capture into $\mathrm{He}(1s2\ell)$ and $\mathrm{He}(1s3\ell)$ states gives the dominant contribution in the total TEC cross section. Our calculations also show that the main product of reaction (114) at high collision velocities is the ground state of $\mathrm{He}(1s^2)$. In Fig. 7(b) we compare our TEC cross section for capture into $\mathrm{He}(1s2p)$ final state with the experimental data of Ref. [31] and theoretical data of Ref. [28].

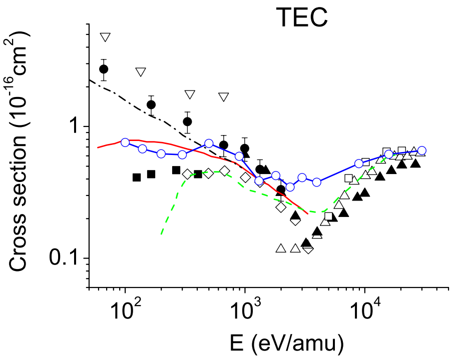

FIG. 6. (Color online) Total TEC cross section. Experimental results: ◇, Ref. [33]; ■, Ref. [34]; ▽, Ref. [35]; △, Ref. [36]; ▲, Ref. [37]; ●, Ref. [38]; □, Ref. [39]. Theory: dashed line, Ref. [28]; dash-dotted line, Ref. [40]; solid line, Ref. [34]; —○—, present calculation.

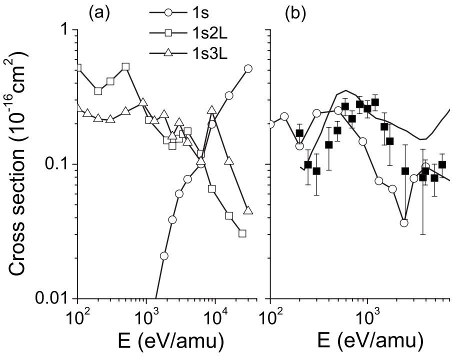

FIG. 7. (a) Present calculations for total cross sections into specific TEC states. (b) TEC cross sections into He($1s2p$). ■, experimental results of Ref. [31]; solid line, theoretical result of Ref. [28]; —○—, present calculation.

In Figs. 8–10 we show the β'-dependent cross section $\sigma_f(v,\beta')$, calculated using Eq. (121), for total DSEC, TEC, and TEC into He($1s2p$) processes, respectively. The orientation effects for capture into NDSEC channels are negligible and are not shown here. For the collision energy range covered by the present study, the DSEC reaction (see Fig. 8) is favored when H_2 molecular bond is oriented at the angle $\pi/4$ with respect to the direction of the projectile velocity vector. For the TEC (see Fig. 9), the most favorable for the process is the perpendicular orientation of molecular bond with respect to the projectile velocity vector. However, the situation for TEC into He($1s2p$) is changed (see Fig. 10) and the two-electron capture is most probable when $\beta'=\pi/4$.

VII. CONCLUSIONS

In the present work we have developed the asymptotic theory of the three-center two-electron system $[A_2B]^{(Z_a+Z_b-2)+}$ in the discrete spectrum. Closed form asymptotic expressions for different one- and two-electron exchange matrix elements between an atomic ion and a homonuclear diatomic molecule have been derived. The derived electron exchange interactions are valid also in the case of atomic ions with closed outer electronic shell and homonuclear diatomics with two valence electrons. Within the "two-active-electron" approximation, the obtained results can easily be generalized to many-electron outer shell diatomics by using the fractional parentage scheme for constructing the many-electron wave function and summing over the possible combinations of transferred electrons. We have applied the developed asymptotic theory to study the one- and two-electron exchange processes in slow collisions of hydrogen molecule $H_2[X^1\Sigma_g^+]$ with He^{2+} ion. The cross sections of these processes have been calculated by employing the semiclassical close-coupling method with the analytic asymptotic expressions for the one- and two–electron coupling matrix elements obtained in the present and our previous work [16]. The results of our calculations for the total and state-selective cross sections of reactions (112)–(114) are in good overall agreement with the experimental data and with the *ab initio* molecular orbital close-coupling calculations of other authors.

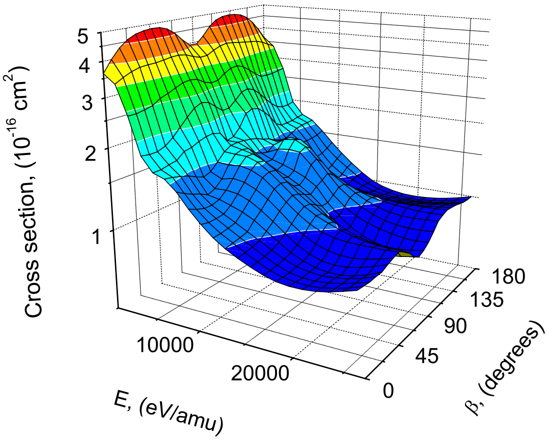

FIG. 8. (Color online) Present calculation of the total cross section $\sigma_f(v,\beta')$ of DSEC reaction as a function of collision energy and orientation angle β'.

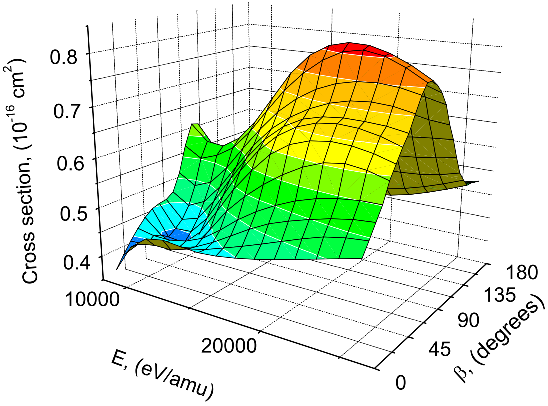

FIG. 9. (Color online) Same as in Fig. 8 but for total TEC cross section.

The influence of the postcollision interaction on the charge-transfer processes (112)–(114) has been studied. We have found that PCI has a negligible effect on the total NDSEC and TEC cross sections. However, this interaction does affect the DSEC. At the collision energies $E<10$ keV/amu the DSEC almost entirely is governed by the direct two-electron process of type (3). With increasing the collision energy, the main contribution to DSEC comes from elec-

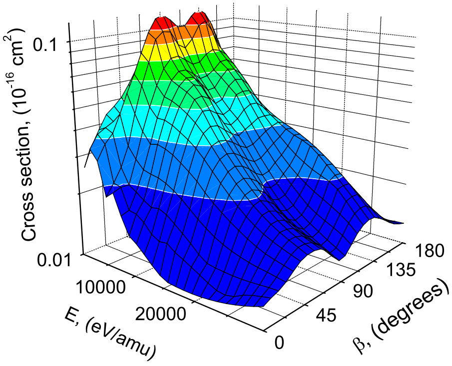

FIG. 10. (Color online) Same as in Fig. 8 but for TEC cross section into He($1s2p$) final state.

tronic excitation process (129) due to long-range interaction of the H_2^+ and He^+ ions.

We have performed a detailed study of the dependence of calculated cross sections on the initial orientation of molecular bond. We found that while the probability of one-electron processes is almost independent of this orientation, the probability of two-electron processes shows a significant dependence on the molecular bond orientation.

APPENDIX A

We calculate here the two-electron matrix elements $H_{ba}^{(k)}$ and $H_{ab}^{(q)}$ [see Eqs. (96) and (97)]. The normalized ground-state wave function $\varphi_a^{(0)}$ of the isolated molecular ion eZZ can be obtained as residue from the asymptotic expression of the radial part of two-center Green's function (45) at small values of parameter $p_a = d\sqrt{-\varepsilon_a^{00}(d)}/2$. The result is

$$\varphi_a^{(0)}(\xi,\eta) = 2(2Z)^{3/2}\exp(-p_a\xi)\bar{S}_{00}(p_a,\eta)(2\pi)^{-1/2}, \quad \text{(A1)}$$

where $\varepsilon_a^{00}(d)$ is the ground-state electronic energy of the ion eZZ and $\bar{S}_{m\ell}(p_a,\eta)$ is given by Eq. (47). For electronic wave function of molecular ion $H_2^+(1s\sigma)$ at internuclear separation $d=1.4$ a.u., the coefficients $c_s^{00}(p_a)$ of expansion (47) have the values $c_2^{00}=0.145\,29c_0$, $c_4^{00}=0.003\,192\,5c_0$, and $c_6^{00}(p_a)\approx 0$; c_0 is arbitrary constant [see Eq. (48)].

Writing the operators of dipole transitions in the spheroidal coordinates,

$$r_{2a}Y_1^0(\theta',\phi') = \frac{d}{4}\sqrt{\frac{3}{\pi}}\xi\eta, \quad r_{2a}Y_1^{\pm 1}(\theta',\phi') = \mp\frac{d}{4}\sqrt{\frac{3(\xi^2-1)(1-\eta^2)}{2\pi}}e^{\pm i\phi'}, \quad \text{(A2)}$$

and integrating in Eq. (96) with Eq. (A1) for $\varphi_a^{(0)}$ and Eq. (69) for φ_{ba}, we obtain the matrix element $H_{ba}^{(k)}$ in the form

$$H_{ba}^{(0)} = \frac{R^4(2Z)^{3/2}}{8}\mathbf{D}_a(\beta_1,R)\sum_{\ell=0}^{\infty}\omega_\ell^{(0)}(\beta)[J_\ell^{(2)}K_\ell^{(1)} - J_\ell^{(1)}K_\ell^{(2)}], \quad \text{(A3)}$$

$$H_{ba}^{(1)} = -H_{ba}^{(-1)} = \frac{R^4Z^{3/2}}{4}\mathbf{D}_a(\beta_1,R)\sum_{\ell=1}^{\infty}\omega_\ell^{(1)}(\beta)[I_\ell^{(1)}M_\ell^{(2)} - I_\ell^{(2)}M_\ell^{(2)}], \quad \text{(A4)}$$

where the following notation has been used:

$$\omega_\ell^{(0)}(\beta) = \sum_{s=0}^{\infty}(-1)^{s+m_1}\frac{c_s^{0\ell}(p_b)}{N_{0\ell}(p_b)}B_s^{m_1}\sqrt{\frac{2}{2s+1}}D_{m_10}^{s}(0,\beta,0),$$

$$\omega_\ell^{(1)}(\beta) = \sum_{s=0}^{\infty}(-1)^{s+m_1+1}\frac{c_s^{1\ell}(p_b)}{N_{1\ell}(p_b)}B_{s+1}^{m_1} \times\sqrt{\frac{2(s+2)!}{(2s+3)s!}}D_{m_11}^{s+1}(0,\beta,0).$$

The radial and angular integrals $I_\ell^{(i)}$, $J_\ell^{(i)}$, $K_\ell^{(i)}$, and $M_\ell^{(i)}$ ($i=1,2$) are given by

$$J_\ell^{(i)} = \int_1^{\infty}\Pi_{0\ell}^{(1)}(p_b,\xi)e^{-p_a\xi}\xi^{2i-1}d\xi,$$

$$I_\ell^{(i)} = \int_1^{\infty}\Pi_{1\ell}^{(1)}(p_b,\xi)e^{-p_a\xi}\sqrt{\xi^2-1}\,\xi^{2i-2}d\xi, \quad \text{(A5)}$$

$$K_\ell^{(i)} = \int_{-1}^{+1}d\eta\bar{S}_{00}(p_a,\eta)\,\eta^{2i-1}\bar{S}_{0\ell}(p_b,\eta),$$

$$M_\ell^{(i)} = \int_{-1}^{+1}d\eta\bar{S}_{00}(p_a,\eta)\,\eta^{2i-2}\bar{S}_{1\ell}(p_b,\eta), \quad \text{(A6)}$$

and obtained in closed analytical form by tedious but straightforward calculations.

Let us calculate now the matrix elements $H_{ab}^{(q)}$ [Eq. (97)]. We shall consider the two cases: the one-electron wave function $\varphi_b^{(0)}$ describe (i) the bound state in the field of bare nuclei and given by Eq. (B1) (see Appendix B); (ii) the bound state of screened potential (B7) and given by expression (B8). We shall give here only the final expression for $H_{ab}^{(q)}$ ($q=-1,0,1$) omitting the details of calculations. For the case (i) we have

$$H_{ab}^{(q)} = \frac{2Z_b^{3/2}}{\sqrt{\pi}}\left(\frac{2}{\alpha_1}\right)^{1+|q|} \times(2\alpha_1)^{2+Z_b/\alpha_1}\frac{\Gamma(2-Z_b/\alpha_1)}{(Z_b+\alpha_1)^5}R^{[(Z_a-1)+Z_b/\alpha_1]-|q|-1} \times e^{-\alpha_1R-Z_b/\alpha_1}{}_2F_1\left(2-Z_b/\alpha_1,5;4;\frac{2\alpha_1}{\alpha_1+Z_b}\right) \times\sum_{s=0}^{\infty}a_s^{\alpha_1\mu_1}D_{q\mu_1}^{s+|\mu_1|}(0,\beta,0)B_{s+|\mu_1|}^{q}B_1^{q}. \quad \text{(A7)}$$

For the case (ii) we have the following expression:

$$H_{ab}^{(q)} = \sqrt{\frac{3}{\pi}}\frac{2^{|q|-2}}{\alpha_1^{1+|q|}}e^{-\alpha_1R-Z_b/\alpha_1}R^{[(Z_a-1)+Z_b/\alpha_1]-|q|-1} \times\sum_{\ell=|q|}^{\infty}\sum_{s=0}^{\infty}(-1)^{\ell+1+q}D_{q\mu_1}^{s+|\mu_1|}(0,\beta,0)a_s^{\alpha_1\mu_1}B_\ell^{q}B_{s+|\mu_1|}^{q} \times C_{\ell010}^{\ell_20}C_{\ell q1-q}^{\ell_2m_2}\sqrt{\frac{(2\ell+1)(2n-p-1)!}{(2\ell_2+1)Z_bp!}} \times\frac{(2\alpha_1)^{\kappa_1}\Gamma(1+S_\ell-Z_b/\alpha_1)}{\Gamma(2S_\ell+2)\Gamma(2S_{\ell_2}+2)}$$

$$\sum_{k=0}^{p}\frac{(-p)_k}{(2S_{\ell_2}+2)_k}\left(\frac{2Z_b}{n}\right)^{2+S_{\ell_2}+k}\frac{\Gamma(\kappa_2)}{k!}\left(\frac{n}{Z_b-\alpha_1 n}\right)^{\kappa_2}{}_2F_1\left(\kappa_2,\kappa_1;2+2S_\ell,\frac{2n\alpha_1}{n\alpha_1-Z_b}\right), \tag{A8}$$

where $\kappa_1=1+S_\ell+Z_b/\alpha_1$ and $\kappa_2=4+k+S_\ell+S_{\ell_2}$. The symbols n and p designated the principal quantum number and the number of nodes, respectively, of the radial wave function (B8), expression for S_ℓ is given in Appendix B. Following the above described algorithm, the two-electron exchange interactions $H^{(20)}$ for the direct two-electron capture from the molecule H_2 to He^{2+} ion resulting in formation of specific $He(1s,n\ell)$ states have the form

$$\begin{aligned}H^{(20)}[2H^+ + He(1s^2)] = 62.32e^{-2.406R}R^{0.05657}\\ \times(1+0.334\cos 2\beta\\ +0.0185\cos 4\beta),\end{aligned}$$

$$\begin{aligned}H^{(20)}[2H^+ + He(1s2s)] = 0.00352e^{-1.602R}R^{3.378}\\ \times(1+0.322\cos 2\beta\\ +0.0284\cos 4\beta).\end{aligned}$$

APPENDIX B

We shall calculate the matrix elements $H^{(q)}_{b[1]}$, $H^{(q)}_{b[2]}$ [see Eqs. (106) and (108)] and $H^{(k)}_{a[1]}(d)$, $H^{(k)}_{a[2]}(d)$ [see Eqs. (100) and (103)]. Consider transitions in the field of pure Coulomb center Z_b, atomic ion B^{Z_b+}, and molecular ion $A_2^{Z_a+}$. We shall use the primes to indicate the excited states of the correspondent ion.

1. Transitions in the Coulomb field of the bare nuclei Z_b

It is convenient to use parabolic coordinate system $\{\mu,\nu,\varphi\}$ with axis z directed along the vector $\mathbf{R}$. The bounded state electron wave function $\phi_{nn_1m}(\mathbf{r}_b)$ of the ion eZ_b in this coordinates has the form

$$\begin{aligned}\phi_{nn_1m}(\mathbf{r}_b) = N_{nn_1m}\nu^{m/2}\mu^{m/2}e^{-Z_b/2n(\nu+\mu)}F(-n_1,m+1,Z_b\mu/n)\\ \times F(-n_2,m+1,Z_b\nu/n)\frac{e^{im\varphi}}{\sqrt{2\pi}},\end{aligned} \tag{B1}$$

where the normalization constant N_{nn_1m} given by

$$N_{nn_1m}=\frac{\sqrt{2}Z_b^{3/2}}{(|m|\,!\,n)^2}\left(\frac{Z_b}{n}\right)^{|m|}\sqrt{\frac{(n_1+|m|)\,!\,(n_2+|m|)!}{n_1\,!\,n_2!}}. \tag{B2}$$

Through the symbol $[nn_1n_2m]$ we designate the set of parabolic quantum numbers. We assume that the wave function of the final state $\varphi_b^{(0)}(\mathbf{r}_b)$ has zero orbital momentum projection, i.e., $\varphi_b^{(0)}(\mathbf{r}_b)=\phi_{nn_10}(\mathbf{r}_b)$. We shall consider two cases for initial state wave function $\varphi_b^{(1)}(\mathbf{r}_b)$ which are characterized by zero and nonzero orbital momentum projection: (i) $\varphi_b^{(1)}=\phi_{n'n'_10}$ and (ii) $\varphi_b^{(1)}=\frac{1}{\sqrt{2}}(\phi_{n'n'_1+1}+\phi_{n'n'_1-1})$, respectively.

After elementary integration with hydrogenlike wave functions (B1) in the parabolic coordinates we come to following expressions for matrix element of the bound-bound transitions for the case (i):

$$\begin{aligned}H^{(q)}_{b[1]}=\frac{\delta_{0q}}{16}\sqrt{\frac{3}{\pi}}N_{nn_10}N_{n'n'_10}\\ \times\sum_{s=0}^{n'_1}\sum_{k=0}^{n'_2}\frac{(-n'_1)_s(-n'_2)_k}{(s\,!\,k!)^2}\left(\frac{Z_b}{n'}\right)^{s+k}(I^{(\mu)}_{s+2}I^{(\nu)}_{k}-I^{(\mu)}_{s}I^{(\nu)}_{k+2}),\end{aligned} \tag{B3}$$

and for the case (ii) we have

$$\begin{aligned}H^{(q)}_{b[1]}=\frac{-q}{16}\sqrt{\frac{3}{\pi}}N_{nn_10}N_{n'n'_1q}\\ \times\sum_{s=0}^{n'_1}\sum_{k=0}^{n'_2}\frac{(-n'_1)_s(-n'_2)_k}{(s+1)\,!\,s\,!\,(k+1)\,!\,k!}\left(\frac{Z_b}{n'}\right)^{s+k}(I^{(\mu)}_{s+2}I^{(\nu)}_{k+1}\\ +I^{(\mu)}_{s+1}I^{(\nu)}_{k+2}).\end{aligned} \tag{B4}$$

The matrix elements of the quadrupole transitions $H^{(q)}_{b[2]}$ are represented in the following form. Case (i):

$$\begin{aligned}H^{(q)}_{b[2]}=\frac{\delta_{0q}}{32}\sqrt{\frac{5}{\pi}}N_{nn_10}N_{n'n'_10}\\ \times\sum_{s=0}^{n'_1}\sum_{k=0}^{n'_2}\frac{(-n'_1)_s(-n'_2)_k}{(s\,!\,k!)^2}\left(\frac{Z_b}{n'}\right)^{s+k}(I^{(\mu)}_{s}I^{(\nu)}_{k+3}\\ -3I^{(\mu)}_{s+1}I^{(\nu)}_{k+2}-3I^{(\mu)}_{s+2}I^{(\nu)}_{k+1}+I^{(\mu)}_{s+3}I^{(\nu)}_{k}),\end{aligned} \tag{B5}$$

and for the case (ii) we have

$$\begin{aligned}H^{(q)}_{b[2]}=\frac{-q}{32}\sqrt{\frac{15}{\pi}}N_{nn_10}N_{n'n'_1q}\\ \times\sum_{s=0}^{n'_1}\sum_{k=0}^{n'_2}\frac{(-n'_1)_s(-n'_2)_k}{(s+1)\,!\,s\,!\,(k+1)\,!\,k!}\left(\frac{Z_b}{n'}\right)^{s+k}(I^{(\mu)}_{s+3}I^{(\nu)}_{k+1}\\ -I^{(\mu)}_{s+1}I^{(\nu)}_{k+3}).\end{aligned} \tag{B6}$$

In the above formulas we used the following designations:

$$I^{(\mu)}_s=s\,!\left(\frac{2nn'}{Z_b(n-n')}\right)^{s+1}{}_2F_1\left(n_1+1,s+1;1;\frac{2n'}{n'-n}\right),$$

$$I^{(\nu)}_k=I^{(\mu)}_{s\to k}(n_1\to n_2).$$

2. Transitions in the field of atomic ion B^{Z_b+}

We shall calculate the matrix element of bound-bound transitions in the field of closed electronic shell atomic core B^{Z_b+} within conception of effective screened potential

$$V_{\text{eff}}(r)=-\frac{Z_b}{r}+\frac{A_\ell}{r^2}. \tag{B7}$$

The normalized wave function $\varphi^{(\text{eff})}_{n\ell m}(\mathbf{r}_b)$ in this potential reads [8]

$$\varphi_{n\ell m}^{(\mathrm{eff})}(\mathbf{r}_b)=\frac{2^{n-p}n^{-2}}{\Gamma(2n-2p)}\sqrt{\frac{\Gamma(2n-p)}{\Gamma(p+1)}}R_{n,n-p-1}^{(1)}(r_b/n)Y_\ell^m(\theta_b,\phi_b), \tag{B8}$$

where p is the number of nodes of the radial part of $\varphi_{n\ell m}^{(\mathrm{eff})}(\mathbf{r}_b)$. Empirical parameter A_ℓ is determined by fitting the ground-state energy in potential (B7) with corresponding experimental values. We assume that the final state wave function $\varphi_b^{(0)}(\mathbf{r}_b)$ with p nodes is given by $\varphi_b^{(0)}(\mathbf{r}_b)=\varphi_{nl0}^{(\mathrm{eff})}(\mathbf{r}_b)$, where $n=Z_b/\beta_2$ and $l=\ell_2$. Similarly as in previous subsection we shall consider the two cases for initial state p'-nodes wave function $\varphi_b^{(1)}(\mathbf{r}_b)$: (i) $\varphi_b^{(1)}(\mathbf{r}_b)=\varphi_{n'l'0}^{(\mathrm{eff})}(\mathbf{r}_b)$ and (ii) $\varphi_b^{(1)}(\mathbf{r}_b)=\frac{1}{\sqrt{2}}[\varphi_{n'l'+1}^{(\mathrm{eff})}(\mathbf{r}_b)+\varphi_{n'l'-1}^{(\mathrm{eff})}(\mathbf{r}_b)]$.

Using wave functions (B8) after elementary integrations, we come to the following expression for matrix elements of bound-bound transitions on atomic ion B^{Z_b+} in case (i):

$$H_{b[j]}^{(q)}=\sqrt{\frac{(2j+1)(2l'+1)}{\pi(2l+1)}}C_{l0j0}^{l'0}C_{l0jq}^{l'q}I_r^{(j)}, \tag{B9}$$

and in the case (ii):

$$H_{b[j]}^{(q)}=\sqrt{\frac{(2j+1)(2l+1)}{2\pi(2l'+1)}}C_{l0j0}^{l'0}C_{l0jq}^{l'q}I_r^{(j)}. \tag{B10}$$

The radial integral $I_r^{(j)}$ $(j=1,2)$ given by

$$\begin{aligned}I_r^{(j)}=&\sqrt{\frac{(2S_{l'}+p'+1)\,!\,(2S_l+p+1)!}{p'\,!\,p!}}\\&\times\frac{\beta_2'^{\,S_{l'}+2}\beta_2^{S_l+2}2^{S_{l'}+S_l+2}}{Z_b(2S_l+1)\,!\,(2S_{l'}+1)!}\sum_{k=0}^{p}\frac{(-p)_k(2\beta_2)^k}{(2S+2)_k k!}\frac{(\sigma_k-1)!}{(\beta_2-\beta_2')^{\sigma_k}}\\&\times{}_2F_1\left(2S_{l'}+2+p',\sigma_k;2S_{l'}+2,\frac{-2\beta_2'}{(\beta_2-\beta_2')}\right),\end{aligned} \tag{B11}$$

where $\sigma_k=3+S_{l'}+S_l+k+j$, $S_\ell=\frac{1}{2}[\sqrt{1+8A_\ell+4\ell(\ell+1)}-1]$, and $-\beta_2'^2/2$ is the electronic energy of the initial state $\varphi_b^{(1)}(\mathbf{r}_b)$.

3. Electron transitions on the hydrogenlike molecular ion *eZZ*

We shall calculate the matrix elements $H_{a[i]}^{(k)}$ $(i=1,2)$ in prolate spheroidal coordinate system $\{\xi,\eta,\phi_a\}$ [see Eq. (44)]:

$$\begin{aligned}H_{a[i]}^{(k)}=&\int_0^{2\pi}d\phi_a\int_{-1}^{+1}d\eta\int_1^{\infty}d\xi\left(\frac{d}{2}\right)^3(\xi^2-\eta^2)\varphi_a^{(0)}(\xi,\eta,\phi_a)\\&\times[V]\varphi_a^{(1)}(\xi,\eta,\phi_a),\end{aligned} \tag{B12}$$

where $[V]$ is the operator of dipole $(i=1)$ or quadrupole $(i=2)$ transitions written in spheroidal coordinates $\{\xi,\eta,\phi_a\}$. We calculate the three-dimensional integrals in Eq. (B12) using exact numerical one-electron wave functions $\varphi_a^{(0,1)}(\xi,\eta,\phi_a)$. Combining the corresponding matrix elements that are responsible for transitions near atomic ion [see Eq. (A7)] with the matrix elements of bound-bound transitions in Eq. (B12) we come to the expression for matrix elements of the two-electron processes of the electron transfer with simultaneous dissociation (in our case) of the molecular ion ${H_2}^+$:

$$\begin{aligned}H^{(21)}[\mathrm{He}^++{\mathrm{H}_2}^+(2s\sigma)]=&\,0.1575\frac{e^{-1.062R}}{R^{2.175}}(1+2.481\cos 2\beta\\&+0.237\cos 4\beta+0.013\cos 6\beta),\end{aligned}$$

$$\begin{aligned}H^{(21)}[\mathrm{He}^++{\mathrm{H}_2}^+(2p\sigma)]=&-4.6\frac{e^{-1.062R}}{R^{1.175}}\cos\beta(1\\&+0.197\cos 2\beta+0.0113\cos 4\beta).\end{aligned}$$

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