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Asymptotic properties of the three-Coulomb-center problem eZ_1ZZ

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An analytic study is presented of the asymptotic properties of the three-Coulomb-center problem eZ_1ZZ. The electron energies and wave functions of this system, where e designates an electron and Z, Z_1 are bare nuclei, are calculated asymptotically exactly for large distances L between the fragments of a quasimolecular system. The electron exchange interaction between eZZ and Z_1 fragments is also calculated asymptotically exactly and used to estimate the electron-capture cross section in slow collisions of $Z=1$ and $Z_1=2,3,4$ systems.

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I. INTRODUCTION

Solutions of the Schrödinger equation with two- and three-Coulomb-center potentials are of considerable interest from the point of view of various problems related to few-body systems, particularly when considering their collision dynamics in an adiabatic approximation. In molecular physics these systems play the same fundamental role as the hydrogen atom in atomic physics. The results obtained on the two-center Coulomb problem eZ_1Z_2 have found numerous applications in the physics of slow ion- (atom-) molecule collisions, the spectroscopy of complex chemical compounds, etc. [1–3].

The three-center $eZ_1Z_2Z_3$ Coulomb problem has received much less attention in the past than the two-center Coulomb problem. The reason for this is certainly related to the fact that, while in the case of the two-center Coulomb problem the Schrödinger equation allows a separation of variables in prolate spheroidal coordinates (due to the higher dynamical symmetry of the system), such a separation of variables is not possible in the case of the three-center Coulomb problem. Studies of the $eZ_1Z_2Z_3$ system have so far been limited to the use of approximate analytical methods only [4–6].

The question of the existence of a variable separation operator Λ, commuting with the Hamiltonian of an n- $(n>2)$ center Coulomb system, was studied for $n=4$ in [7] and in the general case in [8]. It has been shown [8] that in all cases when there is an operator Λ that commutes with the Hamiltonian ($\Lambda=L+O$, where O is an operator depending on intercenter separations and the charges) the problem is reduced to the one- and two-center problems. That means that the Schrödinger equation of the $eZ_1Z_2Z_3$ system is not separable in any orthogonal coordinate system and, therefore, its solution necessarily deals with partial differential equations. This fact substantially complicates all specific calculations of adiabatic electronic wave functions [molecular orbitals (MO's)] and energies [potential energy surfaces (PES's)] for a given system. The lack of a separation of variables in the $eZ_1Z_2Z_3$ problem introduces complexity even in approximate analytical treatments of the problem. These treatments usually address the asymptotic properties of the system at large and small intercenter distances. However, for many physical problems, knowledge of these properties is highly useful and sometimes sufficient for their adequate description.

The aim of present article is to undertake an asymptotic study of the discrete spectrum of the $eZ_1Z_2Z_3$ system with $Z_2=Z_3=Z$. The electronic Hamiltonian of this system depends on three coordinates: Q_1, Q_2, and Q_3 (further designated by the symbol Q), which determine the configuration of the nuclear triangle Z_1ZZ. These coordinates are chosen to represent the distance L of nucleus Z_1 to the center of mass of identical charges $Z+Z$, the distance R between the identical nuclei, and the angle β between the vectors $\mathbf{R}$ and $\mathbf{L}$ (see Fig. 1). However, as a matter of convenience of calculations, in each considered part of configuration space we shall introduce and use the most natural coordinates that facilitate the asymptotic solution of the eZ_1ZZ problem. The results obtained will then be written in L, R, and β coordinates, in which they acquire a more transparent physical meaning.

The article is organized as follows. In the next section, after a brief summary of some of the known properties of the eZ_1ZZ system, asymptotic formulas for the energies of the eZ_1ZZ system in the form of power expansions in L are presented. In Sec. III, the method of constructing the

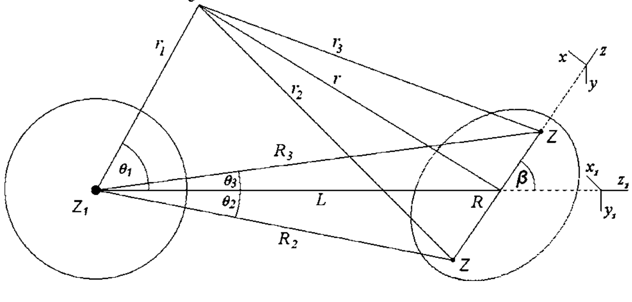

FIG. 1. Geometry of the quasimolecule eZ_1ZZ and the notation used.

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asymptotic form of the one-electron three-center wave function in different regions of configuration space is described and its results presented. As an application of the obtained wave functions, the leading term of the asymptotic (with respect to L) expansion of the electron exchange interaction in the eZ_1ZZ system is derived.

In Sec. IV, the expression obtained for the exchange interaction is generalized so as to take into account the velocity of the relative motion of colliding particles. The obtained asymptotic expressions for the potential energy surfaces, as functions of L and β, are illustrated on the system $H_2^+(R=2a_0)+He^{2+}$, a_0 being the Bohr radius. Furthermore, the obtained asymptotic results on the PES and electron-exchange interaction are used in this section to calculate the electron-capture cross sections in slow collisions of H_2^+ ions with nuclei He^{2+}, Li^{3+}, and Be^{4+} by using the coupled-channel formalism. Some concluding remarks are given in Sec. V.

Atomic units will be used in this work, unless otherwise explicitly indicated.

II. FORMULATION OF THE PROBLEM AND BASIC RELATIONS

The three-Coulomb-center quantum-mechanical problem $eZ_1Z_2Z_3$ consists in finding the eigenfunctions and eigenenergies of the electron in the field of three fixed nuclei with charges Z_1, Z_2, and Z_3. For the case $Z_2=Z_3=Z$ considered here, the corresponding Schrödinger equation has the form

$$H\Psi \equiv \left(-\frac{1}{2}\Delta_{\mathbf{r}_e} - \frac{Z_1}{r_1} - \frac{Z}{r_2} - \frac{Z}{r_3}\right)\Psi(\mathbf{r}_e;Q) = E(Q)\Psi(\mathbf{r}_e;Q), \tag{1}$$

where $\mathbf{r}_e$ is the radius vector of the electron in an arbitrary coordinate system, r_i is the electron distance from the ith nucleus ($i=1,2,3$), and $E(Q)$ and $\Psi(\mathbf{r}_e;Q)$ are the electron energy and the wave function, respectively, which parametrically depend on coordinates $Q_1=L$, $Q_2=R$, $Q_3=\beta$, and $Q=(L,R,\beta)$.

In the present article we shall be interested in the asymptotic solutions of Eq. (1) for large L, such that the condition $L \gg R$ is always satisfied. More specifically, we shall be particularly interested in the asymptotic configurations when the electron is bound either on the nucleus Z_1 or in the field of $Z+Z$ charges. Keeping in mind the above-mentioned asymptotic configurations, the solutions (MO's) of Eq. (1) can be divided into two classes: Ψ_I orbitals, which asymptotically correspond to the interaction of hydrogenlike atomic ions eZ_1, and Ψ_{II} orbitals, which asymptotically corresponds to the interaction of a hydrogenlike molecular ion eZZ with the nucleus Z_1. The molecular energies $E(Q)$ of the system can similarly be divided into two classes E_I (E_{II}), which at ($L\to\infty$) go over into the energies of the isolated hydrogenlike atomic (molecular) ion eZ_1 (eZZ).

This asymptotic classification of the solutions of Eq. (1) allows a convenient characterization of quasimolecular states by sets of quantum numbers: the I-labeled states ($R_{2,3}\to\infty$, $0\leqslant r_1<\infty$) can be characterized by the parabolic quantum numbers $I=[n_1,n_2,m]$, while the II-labeled states ($R_{2,3}\to\infty$, $0\leqslant r_{2,3}<\infty$) can be characterized by the set of spheroidal quantum numbers $II=[k,q,m_2]$. The quantum numbers k, q, and m_2 are related to the number of nodes of the wave function of the molecular ion eZZ along the prolate spheroidal coordinates ξ, η, and φ [1]. Usually, for classification of the states of the eZZ system, instead of k, q, and m_2, the spherical quantum numbers of the united atom limit, $II=[N'\ell_2m_2]$ ($N'=k+q+m_2+1$, $\ell_2=q+m_2$), are used, together with the parity quantum number $p=(-1)^{\ell_2}$ ($p\equiv g$, for ℓ_2 even, and $p\equiv u$, for ℓ_2 odd).

It is well known that for large internuclear distances $L\to\infty$ ($0\leqslant R<\infty$), the asymptotic series for the energy of the system eZ_1ZZ contains two types of series that have different functional dependences on L: one of them is a pure power series in L, and the other contains a multiplicative factor that exponentially decreases with increasing L. The pure power series results from multipole expansion of the energy of bound electrons (in eZ_1 or eZZ) due to electrostatic interaction with the distant perturber ($Z+Z$ or Z_1, respectively).

The series containing exponential factors arises from the delocalized electron motion in the field of two asymptotic nuclear arrangements and describes the electron-exchange interaction between these two arrangements. Normally, the contribution of the latter series to the total electron energy is (exponentially) small, but it is the one that removes the degeneracy of the energies that may occur at certain internuclear distances (for states of the same symmetry) in the multipole-expansion approximation (avoided energy crossings). By their physical nature, these exchange interaction series are responsible for electron-exchange effects in the dynamics of a slow collision.

In the present section we shall discuss power expansions of the energy of the eZ_1ZZ system only, postponing the discussion of the exchange interaction series to Sec. III. For the system eZ_1pp ($p=H^+$) these expansions were considered in [4,5]. What follows is a slight generalization of the results of [4,5].

We consider the following asymptotic ($L\to\infty$, $0\leqslant R<\infty$) arrangements of the system eZ_1ZZ:

$$eZ_1ZZ \xrightarrow[L\to\infty]{} \begin{array}{ll} \nearrow eZ_1+Z+Z & \text{(a)}, \\ \searrow eZZ+Z_1 & \text{(b)}. \end{array} \tag{2}$$

To these arrangements we associate the labels I [for (2a)] and II [for (2b)]. We start the asymptotic energy calculations with the arrangement (2a), placing the coordinate origin at the center Z_1 (i.e., assigning $\mathbf{r}_e\equiv\mathbf{r}_1$) and taking the polar axis along the vector $\mathbf{L}$. At large separation between the fragments eZ_1 and $Z+Z$, the operator of electrostatic electron interaction with the two identical nuclei can be expanded in multipoles, the first three terms of the expansion being ($r_1^{-1}R_{2,3}\gg 1$)

$$\begin{aligned} V(\mathbf{r}_1) = &-\left(\frac{Z}{R_2}+\frac{Z}{R_3}\right) - \left(\frac{Z\cos\theta_2}{R_2^2}+\frac{Z\cos\theta_3}{R_3^2}\right)r_1\cos\theta_1 \\ &- \left(\frac{Z\sin\theta_2}{R_2^2}+\frac{Z\sin\theta_3}{R_3^2}\right)r_1\sin\theta_1\cos\varphi_1 \\ &+ w(\mathbf{r}_1), \quad w(\mathbf{r}_1)\sim O(R_{2,3}^{-3}), \end{aligned} \tag{3}$$

with

$$H = H_1^{(0)} + V(\mathbf{r}_1) = -\frac{1}{2}\Delta_{\mathbf{r}_1} - \frac{Z_1}{r_1} + V(\mathbf{r}_1). \qquad (4)$$

Here r_1, θ_1, and φ_1 are the spherical coordinates of the electron in the coordinate system $\{x_1, y_1, z_1\}$, R_2 and R_3 are the distances of Z_1 to identical nuclei, and θ_2 and θ_3 are the angles between the polar axis and vectors $\mathbf{R}_2$ and $\mathbf{R}_3$. The coordinates $R_{2,3}$ and $\theta_{2,3}$ are related to L, R, and β by

$$R_{2,3} = (L^2 \mp RL\cos\beta + R^2/4)^{1/2},$$

$$\cos\theta_{2,3} = \left(L \mp \frac{R\cos\beta}{2}\right)(L^2 \mp RL\cos\beta + R^2/4)^{-1/2}. \qquad (5)$$

As functions of the zeroth-order approximation it is naturally to use linear combinations of the Coulomb parabolic functions [9] $\varphi_{n_1n_2m}(\mu,\nu,\varphi_1)$:

$$\Psi_I^{(0)} = \sum_{n_1'n_2'm'} a_{n_1'n_2'm'}(R_2,R_3,\theta_2,\theta_3)\varphi_{n_1'n_2'm'}(\mu,\nu,\varphi_1), \qquad (6)$$

$$\varphi_{n_1n_2m}(\mu,\nu,\varphi_1) = \frac{\sqrt{2}Z_1^{3/2}}{n^2} f_{n_1m}\left(\frac{Z_1\mu}{n}\right) f_{n_2m}\left(\frac{Z_1\nu}{n}\right)\frac{e^{im\varphi_1}}{\sqrt{2\pi}}, \qquad (7)$$

where

$$f_{pm}(\rho) = \frac{1}{|m|!}\sqrt{\frac{(p+|m|)!}{p!}}\Phi(-p,|m|+1,\rho)e^{-\rho/2}\rho^{|m|/2}, \qquad (8)$$

$\Phi(\cdots)$ is the confluent hypergeometric function of the first kind [10], n is the principal quantum number, and $\mu = r_1(1+\cos\theta_1)$ and $\nu = r_1(1-\cos\theta_1)$ are the parabolic coordinates. The energies E_I of the system eZ_1+Z+Z and expansion coefficients $a_{n_1n_2m}$ can be obtained as a solution of the secular equation

$$\sum_{n_1'n_2'm'} [\langle n_1n_2m|V|n_1'n_2'm'\rangle - (E_I - E_1^{(0)})\delta_{n_1n_1'}\delta_{n_2n_2'}\delta_{mm'}]a_{n_1'n_2'm'} = 0, \qquad (9)$$

where $E_1^{(0)} = -Z_1^2/2n^2$ is the energy of the unperturbed atom eZ_1 in a state with fixed principal quantum number $n = n_1 + n_2 + |m| + 1$. The analytic expressions for the matrix elements $\langle n_1n_2m|V|n_1'n_2'm'\rangle$ in the basis of parabolic functions (7) can be easily calculated (see, e.g., [4]). Then, by equating to zero the determinant of the system (9), one obtains the corrections to the energy levels in the first approximation of perturbation theory [4]:

$$E_I(Q) \equiv E_{n_1n_2m}(R_2,R_3,\tilde{\gamma}) = -\frac{Z_1^2}{2n^2} - \left(\frac{Z}{R_2} + \frac{Z}{R_3}\right) + \frac{3Zn\Delta}{2Z_1}\left(\frac{1}{R_2^4} + \frac{1}{R_3^4} + \frac{2\cos\tilde{\gamma}}{R_2^2R_3^2}\right)^{1/2}, \qquad (10)$$

where $\Delta = n_1 - n_2$ is the "electric quantum number" and $\tilde{\gamma}$ is the angle between the vectors $\mathbf{R}_2$ and $\mathbf{R}_3$. For $\tilde{\gamma}=0$ and $R_2 = R_3$, Eq. (10) goes over into the known formula for the linear Stark effect [9,11].

Let us now consider the asymptotic behavior of the E_{II} power energy series, corresponding to the asymptotic arrangement (2b) and correlating at $L\to\infty$ with the energy levels of a hydrogenlike molecular ion eZZ. At sufficiently large distances between the fragments Z_1 and eZZ, when the condition $L \gg R$ is satisfied, it is possible to consider that the nucleus Z_1 interacts with the molecular ion eZZ as a whole. To calculate this interaction to the first order of perturbation theory, the above-described asymptotic method can be applied in somewhat extended form. This extension consists in the substitution of atomic the electron density distribution and atomic multipole momentum with those for the molecular ion and in taking into account that to the different projections of electronic angular momentum of eZZ ion on the vector $\mathbf{R}$ there are different corresponding energies. In implementing this extension, we follow the ideas of [4,5].

For describing the electron motion and relative position of nuclei in the quasimolecule $eZZ+Z_1$, we introduce two systems of prolate spheroidal coordinates with origin at the midpoint of the interval R and focal points at its ends:

$$\xi = (r_2 + r_3)/R, \quad \eta = (r_2 - r_3)/R, \quad \varphi = \arctan(y/x), \qquad (11)$$

$$\tilde{\xi} = (R_2 + R_3)/R, \quad \tilde{\eta} = (R_2 - R_3)/R, \quad \tilde{\varphi} = 0,$$

$$1 \leqslant \xi < \infty, \quad -1 \leqslant \eta \leqslant 1, \quad 0 \leqslant \varphi < 2\pi,$$

$$1 \leqslant \tilde{\xi} < \infty, \quad -1 \leqslant \tilde{\eta} \leqslant 1. \qquad (12)$$

The prolate spheroidal coordinates $\tilde{\xi}$, $\tilde{\eta}$ can be expressed in terms of coordinates L, R, and β as

$$\tilde{\xi} = [(L^2 - LR\cos\beta + R^2/4)^{1/2} + (L^2 + LR\cos\beta + R^2/4)^{1/2}]R^{-1},$$

$$\tilde{\eta} = [(L^2 - LR\cos\beta + R^2/4)^{1/2} - (L^2 + LR\cos\beta + R^2/4)^{1/2}]R^{-1}. \qquad (13)$$

For the asymptotic arrangement (2b), the electronic Hamiltonian can be written as

$$H = H_2^{(0)} + V_1,$$

$$H_2^{(0)} = -\frac{1}{2}\Delta_{\mathbf{r}} - \frac{Z}{r_2} - \frac{Z}{r_3},$$

$$V_1 = -\frac{Z_1}{|\mathbf{L}+\mathbf{r}|} \equiv -\frac{Z_1}{r_1}. \qquad (14)$$

Following the standard procedures, we expand the wave function $\Psi_{II}(\mathbf{r};Q)$ as

$$\Psi_{II}(\mathbf{r};Q) = \Psi_i(\xi,\eta,\varphi;\tilde{\xi},\tilde{\eta},R) = \sum_j \sum_{m_j} a_{ijm_j}(\tilde{\xi},\tilde{\eta},R)\phi_{jm_j}(\xi,\eta,\varphi;R), \qquad (15)$$

with ϕ_{jm_j} being the wave functions of the discrete spectrum of the quantum-mechanical eZZ problem:

$$\phi_{jm_j}(\xi,\eta,\varphi;R) = N_{jm_j}(R)\Pi_{jm_j}(\xi;R)S_{jm_j}(\eta;R)\frac{\exp(im_j\varphi)}{\sqrt{2\pi}}. \tag{16}$$

Here $N_{jm_j}(R)$ is the normalization constant, m_j is the projection of the electron orbital momentum on the internuclear axis $\mathbf{R}$, and j designates the set of all remaining quantum numbers [1,11]. Various expansions for the radial Coulomb $\Pi_{jm_j}(\xi;R)$ and angular $S_{jm_j}(\eta;R)$ spheroidal functions can be found in [1,3]. For the perturbation V_1 we use the Neumann expansion [12]:

$$V_1 = -\frac{2Z_1}{R}\sum_{n=0}^{\infty}(2n+1)\sum_{k=0}^{n}(-1)^k\varepsilon_k\left[\frac{(n-k)!}{(n+k)!}\right]^2 \times P_n^k(\tilde{\eta})P_n^k(\eta)P_n^k(\xi_<)Q_n^k(\xi_>)\cos k\varphi, \tag{17}$$

where $\varepsilon_k = 2-\delta_{k0}$, P_n^k and Q_n^k are the associated Legendre polynomials of first and second kind, respectively, and $\xi_<$ ($\xi_>$) are the smaller (larger) of the coordinates $\tilde{\xi}$ and ξ.

After substituting Eqs. (15) and (17) into Eq. (1), multiplying the result from the left by $\phi^*_{im_i}$, and carrying out the integration over electronic coordinates, we obtain an infinite system of coupled equations for the coefficients a_{ijm_j} [analogous to Eq. (9)]. The energy eigenvalues $E_{II}(Q)$ are then obtained by equating to zero the determinant of that system. For sufficiently large distances between the nucleus Z_1 and the eZZ ion, when the condition $\tilde{\xi}\approx 2L/R \gg 1$ is satisfied, in the second approximation of perturbation theory for potential energy surfaces of $eZZ+Z_1$ quasimolecules, we obtain

$$E_{II}(Q) \equiv E_i(\tilde{\xi},\tilde{\eta},R) = \varepsilon_i(R) - \frac{2Z_1}{R\tilde{\xi}}\left\{1+\frac{1}{3\tilde{\xi}^2}\left[1+\left(\frac{R}{2}\right)^3(3\tilde{\eta}^2 - 1)A_{ii}^{(20)}(R)\right]\right\} - \frac{8Z_1^2}{(R\tilde{\xi})^4}[(1-\tilde{\eta}^2)\alpha_i^{\perp}(R)+\tilde{\eta}^2\alpha_i^{\parallel}(R)], \tag{18}$$

where the components of the polarizability tensor parallel and perpendicular to the molecular axis $\alpha^{\parallel}(R)$ and $\alpha^{\perp}(R)$ of the eZZ ion are determined by the formulas

$$\alpha_i^{\parallel}(R) = \frac{R^8}{128}\sum_j{}' \frac{[A_{ij}^{(10)}(R)]^2}{\varepsilon_j(R)-\varepsilon_i(R)},$$

$$\alpha_i^{\perp}(R) = \frac{R^8}{256}\sum_j \frac{[A_{ij}^{(11)}(R)]^2}{\varepsilon_j(R)-\varepsilon_i(R)}, \tag{19}$$

$$A_{ij}^{(n\mu)}(R) = N_{ij}(R)\left\{\int_{-1}^{1}S_i(\eta;R)P_n^{\mu}(\eta)S_j(\eta;R)d\eta\int_1^{\infty}\Pi_i(\xi;R)P_n^{\mu}(\xi)\Pi_j(\xi;R)\xi^2 d\xi - \int_{-1}^{1}S_i(\eta;R)P_n^{\mu}(\eta)S_j(\eta;R)\eta^2 d\eta\int_1^{\infty}\Pi_i(\xi;R)P_n^{\mu}(\xi)\Pi_j(\xi;R)d\xi\right\}. \tag{20}$$

Here $\mu = |m_i - m_j|$, $N_{ij}(R) = N_i(R)N_j(R)$, and $\varepsilon_i(R)$ are the energies of the hydrogenlike molecular ion eZZ [here we have omitted the subscript m_j in the functions $\Pi_{jm_j}(\xi;R)$, $S_{jm_j}(\eta;R)$, and normalization constant N_{jm_j}]. The prime on the summation sign in Eq. (19) indicates that for $\alpha_i^{\parallel}(R)$ the term with $j=i$ in the sum should be omitted. Equation (18) applies for states of the molecular ion eZZ with projection of electron orbital momentum $m_j=0$ and for nuclear configurations for which the condition $R^2A_{ij}^{(1)}(R) \ll \xi^2[\varepsilon_j(R)-\varepsilon_i(R)]$ is satisfied.

It should be emphasized that the electron wave functions, determined by Eqs. (6) and (15), describe the electronic motion in the regions of configuration space where its interaction with the other fragment(s) can be treated as a perturbation. There are, however, regions in configuration space where this assumption does not hold and where the electron wave function has to be determined by nonperturbative methods. These regions are obviously related to the delocalized (underbarrier) electron motion and to the previously mentioned exponentially small corrections to the electronic energy. In the next section we consider the electronic motion in these regions and construct the corresponding asymptotic three-center electron wave function.

III. ASYMPTOTIC FORM OF THE EXCHANGE INTERACTION OF A HYDROGENLIKE MOLECULAR ION INTERACTING WITH A NUCLEUS

For the calculation of the charge-exchange probabilities of a hydrogenlike molecular ion eZZ interacting with a fully stripped ion Z_1,

$$eZZ + Z_1 \to eZ_1 + Z + Z, \tag{21}$$

under the condition that collision velocities be not very small, and when during the characteristic interaction time the rotation of the molecular ion axis $\mathbf{R}$ can be neglected, it is necessary to know the matrix element $\Delta(Q)$ of the exchange interaction of the diabatic electronic states of the quasimolecular systems $eZZ+Z_1$ and eZ_1+Z+Z. If the electron binding energies $E_{II}^{(0)}$ and $E_I^{(0)}$ of the molecular ion eZZ and, respectively, the nucleus Z_1 do not differ considerably from each other, the exchange interaction $\Delta(Q)$ can be expressed in terms of a surface integral over the S surface that divides the electron localization in the initial and final states of reaction (21) [13]:

$$\Delta(Q)=\int_S d\mathbf{S}(\Psi_{\rm I}^{*}\,\boldsymbol{\nabla}\,\Psi_{II}-\Psi_{II}^{*}\,\boldsymbol{\nabla}\,\Psi_{\rm I}). \qquad (22)$$

Here, as in the previous sections, the electronic wave functions Ψ_I and Ψ_{II} at infinite distances L go over into the wave functions $\Psi_I^{(0)}$ and $\Psi_{II}^{(0)}$ of the hydrogenlike eZ_1 ion and the molecular eZZ ion, respectively, while at finite L they take into account the influence of the other fragment.

For an asymptotic (at large L) calculation of the surface integral (22) it is necessary to know the electron wave functions $\Psi_I^{(0)}$ and $\Psi_{II}^{(0)}$ in the internuclear region far from both fragments Z_1 and $Z+Z$. The potential of the two identical Coulomb centers can be represented there as the sum of a pure Coulomb part $-Z'/r$ (with a total charge $Z'=2Z$) and a short-range component:

$$V_s(\mathbf{r})=\frac{Z'}{r}-\frac{Z}{|\mathbf{r}+\mathbf{R}/2|}-\frac{Z}{|\mathbf{r}-\mathbf{R}/2|}.$$

According to this partition we shall rewrite the Schrödinger equation (1) of the eZ_1ZZ problem in the form

$$\left(-\frac{\Delta}{2}-\frac{Z_1}{r_1}-\frac{Z'}{r}+V_s\right)\Psi_i=E_i\Psi_i,\quad i={\rm I},II, \qquad (23)$$

which is more convenient for solving it using various approximations. Considering this equation in the asymptotic region $r_1\sim r\sim L/2$ to within the terms of the order of $O(R^2/L^3)$, the short-range potential V_s in Eq. (23) can be neglected. In this case, the variables in the remaining Schrödinger equation (23) (with the switched off interaction V_s) can be separated into prolate spheroidal coordinates:

$$\xi_1=\frac{r_1+r}{L}\quad(1\leqslant\xi_1<\infty),\quad \eta_1=\frac{r_1-r}{L}\quad(-1\leqslant\eta_1\leqslant1),$$
$$\varphi_1=\arctan\left(\frac{y_1}{x_1}\right)\quad(0\leqslant\varphi_1<2\pi), \qquad (24)$$

and the corresponding electron wave functions can be represented as a product

$$\Psi_i(\xi_1,\eta_1,\varphi_1;L)=C_i(L)\Pi_i(\xi_1,L)\Xi_i(\eta_1,L)\frac{\exp(im_i\varphi_1)}{\sqrt{2\pi}}. \qquad (25)$$

Here $C_i(L)$ is the normalization constant, and the meaning of the indices $i=I,II$ is the same as in the previous section. The functions $\Pi_i(\xi_1,L)$ and $\Xi_i(\eta_1,L)$, which are usually referred to as radial and angular Coulomb spheroidal functions (CSF's), respectively, satisfy the following system of coupled differential equations [1,11]:

$$\frac{d}{d\xi_1}(\xi_1^2-1)\frac{d\Pi_i}{d\xi_1}+\left[\frac{E_iL^2}{2}(\xi_1^2-1)+(Z_1+Z')L\xi_1-\frac{m_i^2}{\xi_1^2-1}+\lambda_i\right]\Pi_i=0,$$

$$\frac{d}{d\eta_1}(1-\eta_1^2)\frac{d\Xi_i}{d\eta_1}+\left[\frac{E_iL^2}{2}(1-\eta_1^2)+(Z'-Z_1)L\eta_1-\frac{m_i^2}{1-\eta_1^2}-\lambda_i\right]\Xi_i=0, \qquad (26)$$

where λ_i is the separation constant in the spheroidal coordinates (24), which depends on L and on the complete set of quantum numbers $i=I,II$.

The main contribution to the surface integral (22) at asymptotically large distances L gives the part of the surface S with a small area near the axis $\mathbf{L}$ only, where $\xi_1-1\leqslant L^{-1}$ and $\eta_1\sim0$. The solution of the system of equations (26) in this area can be derived using the well-known technique of "corrective functions" (CF's) introduced in [13]. We shall determine the zeroth-order approximation for $\Psi_I(\xi_1,\eta_1,\varphi_1;L)$ as a product of the one-center CSF $\Psi_I^{(0)}$ and a long-range corrective function χ_I:

$$\Psi_{\rm I}(\xi_1,\eta_1,\varphi_1;L)=\Psi_{\rm I}^{(0)}(\xi_1,\eta_1,\varphi_1;L)\chi_{\rm I}(\xi_1,\eta_1)$$
$$=\Psi_{\rm I}^{(0)}\chi_1(\xi_1)\chi_2(\eta_1), \qquad (27)$$

where the one-center CSF $\Psi_I^{(0)}$ is given by

$$\Psi_{\rm I}^{(0)}=C_{\rm I}^{(0)}(L)\Pi_{\rm I}^{(0)}(\xi_1,L)\Xi_{\rm I}^{(0)}(\eta_1,L)\frac{\exp(im_1\varphi_1)}{\sqrt{2\pi}}, \qquad (28)$$

and the radial $\Pi_I^{(0)}$ and angular $\Xi_I^{(0)}$ functions satisfy the system of equations (26) with $Z'\equiv2Z=0$. Under the condition of large L, we shall use in Eqs. (26) the asymptotic expansion for the separation constant λ_I as a series in powers of L [1,14]: $\lambda_I=-Z'L+\lambda_I^{(0)}+O(L^{-1})$, where $\lambda_I^{(0)}$ is the separation constant of this system for $Z'=2Z=0$. Substituting the expression (27) into (26) and taking into account the terms proportional to L only, we obtain for the corrective functions χ_1 and χ_2 the following differential equations of the first order:

$$\frac{Z_1}{n}\chi_1'+\left(\frac{Z'}{2}-\frac{Z'}{\xi_1+1}\right)\chi_1=0,\quad \frac{Z_1}{n}\chi_2'+\left(\frac{Z'}{2}+\frac{Z'}{\eta_1-1}\right)\chi_2=0. \qquad (29)$$

Here n is the principal quantum number defined by $E_I^{(0)}=-Z_1^2/2n^2$. The solution of these equations satisfying to condition $\chi_I=\chi_1\chi_2\to1$ at $\xi_1\to1$ and $\eta_1\to-1$ is given by the expression

$$\chi_{\rm I}=\chi_1(\xi_1)\chi_2(\eta_1)=\left(\frac{1+\xi_1}{1-\eta_1}\right)^{nZ'/Z_1}\exp\left(-\frac{nZ'}{2Z_1}(\xi_1+\eta_1)\right). \qquad (30)$$

As can be seen from Eq. (30), the corrective function χ_I contains only one parameter: the ratio nZ'/Z_1. This results in an interesting consequence in the case of a Coulomb degeneracy. The degenerate hydrogenlike electronic states at $L=R_{2,3}=\infty$ on the ion Z_1 undergo a linear Stark effect: their energy [according to Eq. (10)] shifts from the original level by a value of the order of L^{-2} (at $L\approx R_{2,3}\gg R/2$). This shift, being of higher order of smallness, can be neglected when deriving the corrective function χ_I. However, when the degeneracy is removed, one should use the "correct" representation for the wave functions $\Psi_I^{(0)}$ of the zero approximation, which differ considerably in the spherical, parabolic, and prolate spheroidal coordinates. All these wave functions, having the same principal quantum number n, are corrected (multiplied) by the same CF χ_I in the internuclear region $r \sim r_1 \sim L/2$, as χ_I depends only on the zeroth-order energy value of the perturbed ion eZ_1.

Since the CF χ_I is identical for all states having the same principal quantum number n, for deriving the correct asymptotic form of three-center wave function Ψ_I one should use the correct "intra-atomic" wave functions $\Psi_I^{(0)}$ of the zeroth-order approximation. However, this problem is a nontrivial one for the following reasons.

One can represent the CSF $\Psi_I^{(0)}$ with certain principal and magnetic quantum numbers n and m_1 as a linear combination of the parabolic wave functions $\varphi_{n_1 n_2 m_1}(\nu_1, \mu_1, \varphi_1)$ with parabolic quantum numbers n_1 and n_2:

$$\begin{aligned}\Psi_{\mathrm{I}}^{(0)} &= \Psi_{n_{\xi_1} n_{\eta_1} m_1}^{(0)}(\xi_1, \eta_1, \varphi_1; L)\\ &= \sum_{n_1+n_2=n-|m_1|-1} U_{n_1 n_2}^{n_{\xi_1} n_{\eta_1}}(L)\, \varphi_{n_1 n_2 m_1}(\nu_1, \mu_1, \varphi_1). \qquad (31)\end{aligned}$$

Here n_{ξ_1} and n_{η_1} are the quantum numbers which determine the zeros of the one-center radial and angular CSF's, $\Pi_I^{(0)}(\xi_1, L)$ and $\Xi_I^{(0)}(\eta_1, L)$, respectively, inside appropriate intervals, and $n_{\xi_1} + n_{\eta_1} + |m_1| + 1 = n$. Under the condition of large, but finite L, the spheroidal coordinates (24) in the intra-atomic region are close to the parabolic ones ν_1, μ_1: $\xi_1 \to 1 + \mu_1/L$ and $\eta_1 \to -1 + \nu_1/L$, where $\nu_1 = r_1(1+\cos\theta_1)$ and $\mu_1 = r_1(1-\cos\theta_1)$.

Closed expressions for the transformation coefficients $U_{n_1 n_2}^{n_{\xi_1} n_{\eta_1}}(L)$, which specify the expansion (31) of one-center CSF $\Psi_{n_{\xi_1} n_{\eta_1} m_1}^{(0)}$ over the parabolic basis $\varphi_{n_1 n_2 m_1}$, are obtained in [15]. We shall not present here their rather cumbersome expressions, but rather we shall mention only their most important properties in the context of our further calculations.

In the expansion (31), which represents the one-center CSF $\Psi_{n_{\xi_1} n_{\eta_1} m_1}^{(0)}$ as a linear combination of $n_{\xi_1} + n_{\eta_1} + 1$ Coulomb parabolic functions $\varphi_{n_1 n_2 m_1}$ (where $n_1 + n_2 = n_{\xi_1} + n_{\eta_1}$), one of the coefficients $U_{n_1 n_2}^{n_{\xi_1} n_{\eta_1}}(L)$ is of the order of $O(1)$ and the remaining are small, proportional to L^{-k} $(k \geqslant 1)$. It means that in the vicinity of the Coulomb center Z_1, the CSF $\Psi_{n_{\xi_1} n_{\eta_1} m_1}^{(0)}$ tends to one of the parabolic functions with quantum numbers $n_1 = n_{\xi_1}$ and $n_2 = n_{\eta_1}$ at $L \to \infty$. In the internuclear region $r_1 \sim r \sim L/2$ near to the axis $\mathbf{L}$, the contribution to the asymptotic wave function $\Psi_{n_{\xi_1} n_{\eta_1} m_1}^{(0)}$ gives $n_{\xi_1} + 1$ parabolic functions $\varphi_{n_1 n_2 m_1}$ with quantum numbers $n_1 = 0, 1, 2, \ldots, n_{\xi_1}$ and $n_2 = n_{\xi_1} + n_{\eta_1} - n_1$. This circumstance results in a rather cumbersome analytic expression for the exchange interaction $\Delta(Q)$.

Thus, in the case of a degeneracy of the initial and final states in electron-capture reactions in the eZ_1ZZ system, we meet the problem of the exact determination of hydrogenlike functions $\Psi_{n_{\xi_1} n_{\eta_1} m_1}^{(0)}$ in the spheroidal coordinates (24). In the general case, this problem has not been solved until now. However, in a number of particular cases it is possible to obtain approximate analytic expressions for these functions. Recently, the one-center CSF's have been studied extensively in the region of large distances L between the fragments, when the quantum numbers n_{ξ_1} and n_{η_1} are not too large (see, for example, [16,17] and references therein). In this region, the leading asymptotic terms of radial $\Pi_{n_1 n_2 m_1}^{(0)}(\xi_1, L)$ and angular $\Xi_{n_1 n_2 m_1}^{(0)}(\eta_1, L)$ CSF's are determined by the expressions [16–18]

$$\begin{aligned}\Pi_{n_1 n_2 m_1}^{(0)}(\xi_1, L) &= \exp\left\{-\frac{Z_1 L}{2n}(\xi_1 - 1)\right\}(\xi_1^2 - 1)^{|m_1|/2}(\xi_1 + 1)^{n_2}\\ &\quad\times \Phi\left(-n_1, |m_1| + 1; \frac{Z_1 L}{n}(\xi_1 - 1)\right)[1 + O(L^{-1})],\end{aligned} \qquad (32)$$

$$\begin{aligned}\Xi_{n_1 n_2 m_1}^{(0)}(\eta_1, L) &= \exp\left\{-\frac{Z_1 L}{2n}(1 + \eta_1)\right\}(1 - \eta_1^2)^{|m_1|/2}(1 - \eta_1)^{n_1}\\ &\quad\times \Phi\left(-n_2, |m_1| + 1; \frac{Z_1 L}{n}(1 + \eta_1)\right)[1 + O(L^{-1})].\end{aligned} \qquad (33)$$

We note that above asymptotic expressions are correct under the condition of sufficiently large L and in the region of electron coordinates near the $\mathbf{L}$ axis, where $(\xi_1 - 1) \leqslant L^{-1}$ and $|\eta_1| \leqslant L^{-1}$. If $\eta_1 \sim 0$, the argument of the degenerated hypergeometric function $\Phi(a, b; t)$ in Eq. (33) has a large value. Therefore, it is necessary to take into account only the leading terms of the asymptotic expansion of $\Phi(a, b; t)$ at $t \to \infty$ [10]. Having this in mind, for the normalized electron wave function Ψ_I we obtain the following asymptotic expression in the coordinate region $(\xi_1 - 1) \leqslant L^{-1}$ and $\eta_1 \sim 0$:

$$\begin{aligned}\Psi_{\mathrm{I}} &= C_{\mathrm{I}} \exp\left\{-\left(\frac{Z_1 L}{n} + \frac{nZ'}{Z_1}\right)\frac{(\xi_1 + \eta_1)}{2}\right\}(\xi_1 - 1)^{|m_1|/2}\, \Phi\left(-n_1, |m_1| + 1; \frac{Z_1 L}{n}(\xi_1 - 1)\right)\\ &\quad\times (1 - \eta_1^2)^{|m_1|/2}(1 + \eta_1)^{n_2}(1 - \eta_1)^{n_1 - nZ'/Z_1}\frac{\exp(im_1\varphi_1)}{\sqrt{2\pi}}[1 + O(L^{-1})],\end{aligned} \qquad (34)$$

$$C_{\mathrm{I}} = (-1)^{n_2}\frac{\sqrt{2}}{|m_1|!}\frac{Z_1^{3/2}}{n^2}2^{-n_2 - |m_1|/2 + nZ'/Z_1}\left(\frac{Z_1 L}{n}\right)^{n_2 + |m_1|}\sqrt{\frac{(n_1 + |m_1|)!}{n_1!\,n_2!\,(n_2 + |m_1|)!}}. \qquad (35)$$

We note that apart from the earlier used "laboratory" coordinate system $\{x_1, y_1, z_1\}$, with the z_1 axis directed along the vector **L**, it is convenient to introduce the "molecular" coordinate system $\{x, y, z\}$ rigidly connected with the vector **R**, since the coordinates of the electron and the system $Z+Z$ are most conveniently defined in this coordinate system (see Fig. 1). It is customary to place the origin of the coordinate system $\{x, y, z\}$ in the midpoint of the interval R and to orient the z axis along the molecular axis **R**. The transition from coordinate system $\{x, y, z\}$ to the $\{x_1, y_1, z_1\}$ system is determined by the three Euler's angles α, β, and γ (see, e.g., [19]). As far as the relative orientation of the axes (x, x_1) and (y, y_1) are not fixed beforehand, it is customary to place these pairs of axes in the mutually perpendicular planes (see Fig. 1), so that the corresponding Euler's angles are equal to zero, $\alpha = \gamma = 0$.

The important simplifying factor in calculating the exchange interaction matrix element (22) is the possibility to represent the normalized eigenfunctions of the molecular ion eZZ at large distances $r \gg 1$ in the form (one-center-type wave function)

$$\Psi_{II}^{(0)}(\mathbf{r}) = A_{\alpha_2}^{m_2\ell_2}(\theta) r^{2Z/\alpha_2 - 1} e^{-\alpha_2 r} \frac{\exp(i m_2 \varphi)}{\sqrt{2\pi}}. \tag{36}$$

Here θ and φ are the spherical angles of the vector **r** in the molecular coordinate system $\{x, y, z\}$, m_2 is the projection of the electron orbital momentum ℓ_2 on the molecular axis **R**, $\alpha_2 = \sqrt{-2E_{II}^{(0)}(R)}$, and $E_{II}^{(0)}(R) \equiv \varepsilon_{N'\ell_2 m_2}(R)$ is the electron binding energy in the molecular ion eZZ. For the sake of convenience of calculations, we represent $A_{\alpha_2}^{m_2\ell_2}(\theta)$ as an expansion over the normalized associated Legendre polynomials $\bar{P}_\ell^m(\cos\theta)$:

$$A_{\alpha_2}^{m_2\ell_2}(\theta) = \sum_{s=0,1}^{\infty}{}' d_s^{m_2\ell_2} \bar{P}_{s+|m_2|}^{m_2}(\cos\theta),$$

$$\bar{P}_\ell^m(\cos\theta) e^{im\varphi}/\sqrt{2\pi} \equiv Y_\ell^m(\theta, \varphi). \tag{37}$$

Here $Y_\ell^m(\theta, \varphi)$ are the normalized spherical harmonics [10] and the prime on the sum symbol designates that the summation is carried out over those s having the same parity as the number δ:

$$\delta = \begin{cases} 0, & \ell_2 - |m_2|, \quad \text{even}, \\ 1, & \ell_2 - |m_2|, \quad \text{odd}. \end{cases}$$

In Table I we give the values of the coefficients $d_s^{m_2\ell_2}$ for the ground and first three excited states of the molecular hydrogen ion H_2^+ (at $R=2$ a.u.), obtained by matching the asymptotic expression (36) for the wave functions with the exact electron wave functions calculated by the algorithm described in [1]. The wave function matching was performed in the region of electron distances $2a < r < 3a$ for the ground-state wave function and in the region $2a < r < 4a$ for the excited-state wave functions, where the value of a is of order of the equilibrium internuclear distance of $H_2^+(1s\sigma)$ in its ground vibrational state.

We shall now calculate the exchange interaction (22) in $\{x, y, z\}$ coordinates. In the transition from $\{x, y, z\}$ to $\{x_1, y_1, z_1\}$ coordinates, expression (37) for the asymptotic coefficient $A_{\alpha_2}^{m_2\ell_2}(\theta)$ is transformed as [19]

$$A_{\alpha_2}^{m_2\ell_2}(\theta) \frac{e^{im_2\varphi}}{\sqrt{2\pi}} = \sum_{s=0,1}^{\infty}{}' \sum_{k=-(s+|m_2|)}^{s+|m_2|} d_s^{m_2\ell_2} \times D_{km_2}^{s+|m_2|}(0, \beta, 0) Y_{s+|m_2|}^k(\bar{\theta}, \bar{\varphi}), \tag{38}$$

where $D_{mm'}^j(\alpha, \beta, \gamma)$ is the Wigner D function and $\bar{\theta}$ and $\bar{\varphi}$ are the spherical angles of the vector **r** in the $\{x_1, y_1, z_1\}$ coordinate system (note that the angles $\bar{\varphi}$ and φ_1 have obviously the same meaning). The angles θ, φ and $\bar{\theta}, \bar{\varphi}$ are mutually related by [19]

$$\cos\theta = \cos\bar{\theta}\cos\beta + \sin\bar{\theta}\sin\beta\cos\bar{\varphi},$$

$$\cot\varphi = \cot\bar{\varphi}\cos\beta - \frac{\cot\bar{\theta}\sin\beta}{\sin\bar{\varphi}}.$$

The leading term of the asymptotic form of the unperturbed molecular wave function $\Psi_{II}^{(0)}$ in the coordinate region far from the Coulomb centers $Z+Z$, which makes the main contribution to the surface integral (22), can be represented, according to Eqs. (36)–(38) and (24), in a factorized form

$$\Psi_{II}^{(0)} = \left[\frac{L(1-\eta_1)}{2}\right]^{Z'/\alpha_2 - 1} \exp\left\{-\frac{\alpha_2 L}{2}(1-\eta_1)\right\} \times \exp\left\{-\frac{\alpha_2 L}{2}(\xi_1 - 1)\right\} \sum_{s=0,1}^{\infty}{}' \sum_{k=-(s+|m_2|)}^{s+|m_2|} d_s^{m_2\ell_2} \times D_{km_2}^{s+|m_2|}(0, \beta, 0) Y_{s+|m_2|}^k(\bar{\theta}, \bar{\varphi}). \tag{39}$$

TABLE I. Coefficients $d_s^{m_2\ell_2} = \bar{d}_s^{m_2\ell_2} \times 10^n$ of the expansion (37) calculated for the wave functions of the hydrogen molecular ion H_2^+ for the ground and first three excited states.

State \ Coeff.	$1s\sigma$	n	$2s\sigma$	n	$2p\sigma$	n	$2p\pi$	n
$\bar{d}_\delta^{m_2\ell_2}$	4.353±0.034	0	−7.950±0.763	−1	1.946±0.012	0	8.74±0.09	−1
$\bar{d}_{\delta+2}^{m_2\ell_2}$	7.076±0.318	−1	−3.95±0.31	−2	1.20±0.10	−1	3.0±0.27	−2
$\bar{d}_{\delta+4}^{m_2\ell_2}$	4.66±0.86	−2	−9.22±0.64	−4	4.32±0.98	−3	7.7±2.3	−4
$\bar{d}_{\delta+6}^{m_2\ell_2}$	2.37±0.90	−3	−1.92±0.62	−5	1.11±0.55	−4		

In the coordinate region $(\xi_1-1)\leq L^{-1}$ and $\eta_1\sim 0$ of interest here, the electronic wave function $\Psi_{II}=C_{II}\Pi_{II}(\xi_1,L)\Xi_{II}(\eta_1,L)e^{im_2\bar{\varphi}}(2\pi)^{-1/2}$ satisfies to the system of equations (26), where now $m_i=m_2$, $E_{II}=-\alpha_2^2/2-Z_1/L$, and $\lambda_{II}=L(\alpha_2-Z_1-Z')+Z_1/\alpha_2+O(L^{-1})$. According to the method used above, we shall search for the functions $\Pi_{II}(\xi_1,L)$ and $\Xi_{II}(\eta_1,L)$ as products:

$$\Pi_{II}(\xi_1,L)=\exp\left\{-\frac{\alpha_2 L}{2}(\xi_1-1)\right\}\bar{\chi}_1(\xi_1), \tag{40}$$

$$\Xi_{II}(\eta_1,L)=\exp\left\{-\frac{\alpha_2 L}{2}(1-\eta_1)\right\}(1-\eta_1)^{Z'/\alpha_2-1}\bar{\chi}_2(\eta_1). \tag{41}$$

By substituting Eqs. (40) and (41) into Eq. (26) and keeping in the equation for $\bar{\chi}_2(\eta_1)$ the terms proportional to L, but in the equation for $\bar{\chi}_1(\xi_1)$ keeping also the terms of the order of unity, we arrive at a system of two ordinary differential equations of the first order for the CF's $\bar{\chi}_1(\xi_1)$ and $\bar{\chi}_2(\eta_1)$. The solution of this system, which satisfies the boundary condition $\chi_{II}\equiv\bar{\chi}_1(\xi_1)\bar{\chi}_2(\eta_1)\rightarrow 1$ at $\xi_1\rightarrow 1$ and $\eta_1\rightarrow 1$, can be represented as

$$\chi_{II}(\xi_1,\eta_1)=\left(\frac{1+\xi_1}{1+\eta_1}\right)^{Z_1\alpha_2}\exp\left\{-\frac{Z_1}{2\alpha_2}(\xi_1-\eta_1)\right\}. \tag{42}$$

With this expression for χ_{II}, the leading term of the asymptotic form of Ψ_{II} at $L\rightarrow\infty$ is

$$\Psi_{II}=C_{II}\exp\left\{-\frac{1}{2}\left(\alpha_2 L+\frac{Z_1}{\alpha_2}\right)(\xi_1-\eta_1)\right\}$$
$$\times(1-\eta_1)^{2Z/\alpha_2-1}\left(\frac{1+\xi_1}{1+\eta_1}\right)^{Z_1/\alpha_2}\frac{e^{im_2\bar{\varphi}}}{\sqrt{2\pi}}[1+O(L^{-1})]. \tag{43}$$

Matching expression (43) with the asymptotic form (39) of the unperturbed electron wave function $\Psi_{II}^{(0)}$ in the region sufficiently far from the Coulomb centers $Z+Z$, we find the normalizing factor C_{II} in the form

$$C_{II}\frac{e^{im_2\bar{\varphi}}}{\sqrt{2\pi}}=\left(\frac{L}{2}\right)^{2Z/\alpha_2-1}\sum_{s=0,1}^{\infty}{}'\sum_{k=-(s+|m_2|)}^{s+|m_2|}d_s^{m_2\ell_2}$$
$$\times D_{km_2}^{s+|m_2|}(0,\beta,0)Y_{s+|m_2|}^{k}(\bar{\theta},\bar{\varphi}). \tag{44}$$

As integration surface in Eq. (22) we take the surface of the paraboloid $\eta_1=\text{const}$. Then, by substituting into Eq. (22) the expressions (34) and (43) for the wave functions Ψ_I and Ψ_{II}, respectively, and having in mind that $\bar{\varphi}\equiv\varphi_1$, we obtain the final expression for the exchange interaction $\Delta(Q)$:

$$\Delta(L,R,\beta)=2^{|m_1|+n_1+(2Z-Z_1)(nZ_1^{-1}-\alpha_2^{-1})}\exp\left[-\frac{L}{2}\left(\frac{Z_1}{n}+\alpha_2\right)-\frac{1}{2}\left(\frac{2nZ}{Z_1}+\frac{Z_1}{\alpha_2}\right)\right]\frac{(2Z_1)^{3/2}}{n^2}\left(\frac{Z_1}{n}\right)^{n_2+|m_1|}\left(\frac{Z_1}{n}+\alpha_2\right)^{-|m_1|}L^{n_2+2Z/\alpha_2}$$
$$\times\sqrt{\frac{(n_1+|m_1|)!}{n_1!n_2!(n_2+|m_1|)!}}\sum_{s=0,1}^{\infty}{}'d_s^{m_2\ell_2}D_{m_1m_2}^{s+|m_2|}(0,\beta,0)\frac{1}{|m_1|!}\sqrt{\frac{(2s+2|m_2|+1)(s+|m_1|+|m_2|)!}{2(s+|m_2|-|m_1|)!}}. \tag{45}$$

From Eq. (45) it follows that from the n^2 states with the same principal quantum number n the dominant contribution to the exchange interaction $\Delta(L,R,\beta)$ at asymptotically large L gives the state with $n_1=m_1=0$,

$$\Delta(L,R,\beta)=2^{(2Z-Z_1)(nZ_1^{-1}-\alpha_2^{-1})}\frac{(2Z_1)^{3/2}}{n^2(n-1)!}\left(\frac{Z_1}{n}\right)^{n-1}\exp\left[-\frac{L}{2}\left(\frac{Z_1}{n}+\alpha_2\right)-\frac{1}{2}\left(\frac{2nZ}{Z_1}+\frac{Z_1}{\alpha_2}\right)\right]L^{n+2Z/\alpha_2-1}$$
$$\times\sum_{s=0,1}^{\infty}{}'d_s^{m_2\ell_2}D_{0m_2}^{s+|m_2|}(0,\beta,0)\sqrt{s+|m_2|+1/2}. \tag{46}$$

IV. APPLICATIONS OF $\Delta(L,R,\beta)$: ELECTRON-CAPTURE CROSS SECTION FOR Z_1+H_2^+ COLLISIONS (Z_1=2,3,4)

As an application of the obtained result for $\Delta(L,R,\beta)$ we shall calculate the cross section for electron capture in slow collisions of H_2^+ with bare nuclei Z_1 ($Z_1=2,3,4$):

$$\mathrm{H}_2^+ + \mathrm{He}^{2+}\rightarrow 2\mathrm{H}^+ + \mathrm{He}^+, \tag{47a}$$

$$\mathrm{H}_2^+ + \mathrm{Li}^{3+}\rightarrow 2\mathrm{H}^+ + \mathrm{Li}^{2+}, \tag{47b}$$

$$\mathrm{H}_2^+ + \mathrm{Be}^{4+}\rightarrow 2\mathrm{H}^+ + \mathrm{Be}^{3+}, \tag{47c}$$

within the framework of a semiclassical coupled-channel formalism [20]. These reactions play an important role in both fusion and astrophysical plasmas [21], and reaction (47a) have been the subject of several recent studies [22–27].

The large experimental values of the total cross sections of reaction (47a) (several times 10^{-16} cm^2 at the collision velocity of $\simeq 1$ a.u. [22,23]) suggest that electron capture takes place at large distances between colliding particles.

That justifies the use of the derived asymptotic form of the coupling interaction $\Delta(L,R,\beta)$ for a theoretical study of these processes.

In the coupled-state cross-section calculations for reactions (47) we shall use the diabatic two-center basis [wave functions of the types (34) and (43)] and designate by a_1 and Ψ_1 the amplitude and wave function of the initial state $Z_1+H_2^+(1s\sigma)$, respectively, and by a_j and Ψ_j $(j=2,\ldots,N)$ the amplitudes and wave functions of the final states of the system $2H^+ + eZ_1[nn_1n_2m]$. The following parabolic final states were included in present calculations: [1000], [2100], [2010], [3200], [3110], [3020], [4030]. Following the standard scheme [20,22], we expand the electron wave function ψ_{el} of the colliding system in terms of the diabatic (in our case) states Ψ_k,

$$\psi_{el} = \sum_{k=1}^{N} a_k \Psi_k \exp\left[-\frac{i}{v}\int_{z_0}^{z} E_k^{(d)} dz'\right], \tag{48}$$

and for the transitions amplitudes a_k we obtain the system of coupled differential equations

$$\frac{da_k}{dz} = -\frac{i}{v}\sum_{\substack{n=1\\ n\neq k}}^{N} a_n H_{nk} \exp\left[-\frac{i}{v}\int_{z_0}^{z}(E_n^{(d)} - E_k^{(d)})dz'\right], \tag{49}$$

where v is the relative collision velocity, $z=\sqrt{L^2-\rho^2}$, ρ is the impact parameter, and z_0 is a constant to be defined later.

In the framework of the adopted asymptotic approach, the diabatic PES $E_k^{(d)} \equiv H_{kk}$ of the initial $(k=1)$ $Z_1+H_2^+(1s\sigma)$ and final $(k=2,\ldots,N)$ $2H^+ + eZ_1[nn_1n_2m]$ states in reactions (47) can be determined (within the same accuracy as that for the exchange interaction) by the expressions (10) and (18)–(20), respectively. We note that the asymptotic expressions (10) and (18)–(20) represent the electronic energy only; to obtain the values for H_{kk} one should add the potential energy of the Coulomb interaction between the system's fragments $Z+Z$ and Z_1: $H_{kk}=E_{I,II}+Z_1Z/R_2+Z_1Z/R_3$. The nondiagonal coupling matrix element H_{nk} $(n\neq k)$ is related to the exchange interaction $\Delta(L,R,\beta)$ by the relation [13] $\Delta(L,R,\beta)\approx 2H_{nk}$.

The system of coupled equations (49) does not take into account the electron momentum transfer in reactions (47) as the diabatic two-center functions Ψ_k do not include any additional factors describing the electron translational motion during the collision [22]. As is well known, the effects of electron translational factors (ETF's) may significantly affect the magnitude of the cross section for collision velocities $v \geqslant 1.0$ a.u. [22].

For inclusion of electron momentum transfer effects in electron-capture reactions many recipes have been proposed (see, for example, [29–31] and references therein). One of them, proposed in [31] and followed in the present work, is based on modifications of the electron-exchange interaction (45). This modification leads to the concept of the "dynamical" exchange interaction $\widetilde{\Delta}(Q,v)$ [31].

For the calculation of $\widetilde{\Delta}(Q,v)$ at $L\to\infty$ it is necessary to determine the electron wave function in the region between the fragments $Z+Z$ and Z_1 by taking into account the electron momentum transfer. In this region, the electron interaction with each of the ion fragments can be considered as Coulombic and the Shrödinger equation for the electron wave function in the field of two fragments, which move with a relative velocity v, has the form [32]

$$\left(-\frac{\Delta_{\mathbf{r}_c}}{2} - \frac{Z_1}{r_1} - \frac{Z'}{r} + V_s \pm \frac{i}{2}\mathbf{v}\cdot\boldsymbol{\nabla} + \frac{v^2}{8}\right)\Psi(Q;\mathbf{r}_c,v) = E(Q)\Psi(Q;\mathbf{r}_c,v), \tag{50}$$

where the vector $\mathbf{r}_c$ determines the position of the electron relative to the center of mass of colliding fragments, the sign ñ in front of the gradient term depends on the location of the electron between the nucleus Z_1 and the two identical nuclei $Z+Z$, and the other notation is the same as in Secs. II and III. Let us introduce the wave functions Φ_1 and Φ_2, which represent the exact solutions of the Shrödinger equation (50), but satisfy different initial conditions at $L\to\infty$ [31]:

$$\Phi_1 = F_1\Psi_I(Q;\mathbf{r}_1) \equiv \Psi_I(Q;\mathbf{r}_1)\exp[i\mathbf{v}\cdot\mathbf{r}_c/2], \tag{51}$$

$$\Phi_2 = F_2\Psi_{II}(Q;\mathbf{r}) = \Psi_{II}(Q;\mathbf{r})\exp[-i\mathbf{v}\cdot\mathbf{r}_c/2], \tag{52}$$

while the earlier introduced wave functions Ψ_I and Ψ_{II} satisfy the Shrödinger equation (23) for fixed nuclei. For the calculation of the dynamical exchange interaction we use the same expression (22), but now with the functions $\Phi_{1,2}$ [31]:

$$\widetilde{\Delta}(Q,v) = \int_S d\mathbf{S}(\Phi_1^*\boldsymbol{\nabla}\Phi_2 - \Phi_2^*\boldsymbol{\nabla}\Phi_1). \tag{53}$$

Introducing the standard definitions for the tangential v_τ and normal v_r components of the relative collision velocity v, $v_\tau = v\rho(\rho^2+v^2t^2)^{-1/2}$ and $v_r = v^2t(\rho^2+v^2t^2)^{-1/2}$, and representing the factors $F_{1,2}$, appearing in Eqs. (51) and (52) in the form

$$F_{1,2} = \exp\left(\pm\frac{1}{2}\left[iv_\tau\rho_c\sin\theta_c + iv_r\frac{\mathbf{r}_c\cdot\mathbf{L}}{L}\right]\right),$$

where ρ_c and θ_c are the polar radius and azimuthal angles in the integration plane S, we calculate the surface integral (53) by the same technique used previously to obtain Eq. (44):

$$\widetilde{\Delta}(Q,v) \equiv \widetilde{\Delta}(L,R,\beta,v) = 2^{|m_1|+n_1+(2Z-Z_1)(nZ_1^{-1}-\alpha_2^{-1})}\frac{(2Z_1)^{3/2}}{n^2}\left(\frac{Z_1}{n}\right)^{n_2+|m_1|}\left(\frac{Z_1}{n}+\alpha_2\right)^{-|m_1|}\frac{1}{\kappa}\exp\left[-\frac{\kappa L}{2}\left(\frac{Z_1}{n}+\alpha_2\right)-\frac{1}{2}\left(\frac{2nZ}{Z_1}+\frac{Z_1}{\alpha_2}\right)\right]$$
$$\times L^{n_2+2Z/\alpha_2}\left(\frac{(n_1+|m_1|)!}{n_1!n_2!(n_2+|m_1|)!}\right)^{1/2}\sum_{s=0,1}^{\infty}{}' d_s^{m_2\ell_2}D_{m_1m_2}^{s+|m_2|}(0,\beta,0)\frac{1}{|m_1|!}\sqrt{\frac{(2s+2|m_2|+1)(s+|m_1|+|m_2|)!}{2(s+|m_2|-|m_1|)!}}, \tag{54}$$

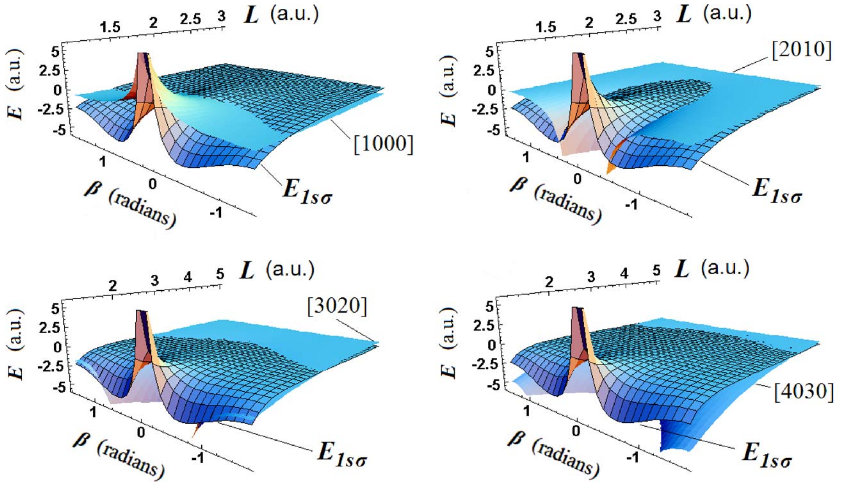

FIG. 2. (Color online) Diabatic PES of $He^{2+}+H_2^{+}(1s\sigma)$ (labeled by $E_{1s\sigma}$) and of $He^{+}[nn_1n_2m]+2H^{+}$ states (the later are labeled by their parabolic quantum numbers [1000], [2010], [3020], and [4030]).

where $\kappa=\sqrt{1+v_\tau^2/(\alpha_2+Z_1/n)^2}$. The obtained asymptotic expression for $\tilde{\Delta}(L,R,\beta,v)$ takes into account the effects of electron translational motion within the plane-wave representation of ETF's [see Eqs. (51) and (52)].

In the present close-coupling calculations we shall neglect any degrees of freedom related to the relative motion of the nuclei of the molecular ion. In other words, we use the *sudden* approximation, with the molecular internuclear vector **R** "frozen" [33]. This approximation treats the ion H_2^+ as a rigid system with a fixed internuclear separation, the value of which in the present calculations is taken to be the equilibrium distance $R=2$ a.u.

We turn now to the calculations of asymptotic diabatic PES (H_{kk}) of $H_2^{+}+He^{2+}$ system, Eqs. (10) and (18)–(20), needed for solving the dynamical equations (49). The electron energy $\varepsilon_0\equiv\varepsilon_{1s\sigma}$ and the parameter $A_{00}^{(20)}$ ($R=2$ a.u.) of $H_2^{+}(1s\sigma)$, calculated using the exact numerical wave functions of the *eZZ* system [1], have the values $\varepsilon_{1s\sigma}=-1.102\,634$ a.u. and $A_{00}^{(20)}=0.2025$. The components of polarizability tensor of the H_2^+ ion in its ground state with regard to the parallel $\alpha_0^{\parallel}(R)$ and perpendicular $\alpha_0^{\perp}(R)$ orientations of molecular vector **R** are given by

$$\alpha_0^{\tilde{\beta}}=2\langle\phi_0(\mathbf{r})|V_{\tilde{\beta}}(\mathbf{r})\tilde{G}_{E_0}(\mathbf{r};\mathbf{r}'|R)V_{\tilde{\beta}}(\mathbf{r}')|\phi_0(\mathbf{r}')\rangle,$$

where $\phi_0(\mathbf{r})$ is the wave function of the ground state of H_2^+, $\tilde{\beta}=\parallel,\perp$, $V_{\parallel}(\mathbf{r})=(R/2)\xi\eta$, and $V_{\perp}(\mathbf{r})=(R/2)\sqrt{(\xi^2-1)(1-\eta^2)}e^{\pm i\varphi}$. $\tilde{G}_{E_0}(\mathbf{r};\mathbf{r}'|R)$ in the above equation is the two-center reduced Green's function [34,35], which can be calculated from the partial expansions of two-center Coulomb Green's function obtained in [18]. It is more convenient, however, to use expression (19) for $\alpha_i^{\parallel,\perp}(R)$ calculations. The calculated polarizabilities for the ground and first three excited states of H_2^+ reproduce to within 2%–5% the results of [34], obtained by expansion of the two-center Coulomb Green's function over Sturmian functions. (We mention here also the recent calculations of H_2^+ polarizability [36].)

In Fig. 2 we show the diabatic PES of $He^{2+}+H_2^{+}(1s\sigma)$ and $2H^{+}+He^{+}[nn_1n_2m]$ in the states with parabolic quantum numbers $[n,0,n-1,0]$, $(n=1,2,3,4)$, respectively, calculated for $R=2$ a.u. and $Z_1=2$ using formulas (10) and (18)–(20).

The behavior of the initial $He^{2+}+H_2^{+}(1s\sigma)$ and final $2H^{+}+He^{+}[nn_1n_2m]$ channel PES suggests that the initial state is dominantly depopulated by transitions at the avoided crossings in the region $L=2-3$ a.u., leading to capture into the He^+ [2010] and [3020] final states. The intersection of the diabatic PES corresponding to the $He^{2+}+H_2^{+}(1s\sigma)$ and $2H^{+}+He^{+}$ [4030] states takes place at larger distances $L\sim4.5$ a.u. Due to the strong exponential decrease (with increasing L) of exchange coupling matrix elements for excited states [see Eqs. (45) and (54)], the population of He^+ [4030] final states is not expected to be significant. The diabatic PES for reactions (47b) and (47c) have a similar behavior as those in Fig. 2 and we do not present them here.

Now we turn to the calculations of the total and partial cross sections for reactions (47). The geometry of the Z_1+eZZ collision is shown in Fig. 3. We introduce the new coordinate system $\{x',y',z'\}$, in which the relative velocity is set parallel to the z' axis and the impact parameter ρ is directed along the x' axis. The center of mass of the molecular ion *eZZ* is placed at the origin of the Cartesian coordinate

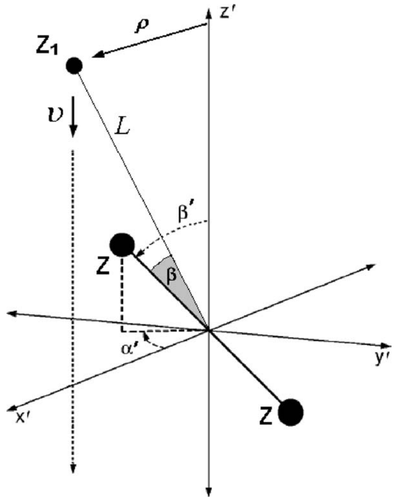

FIG. 3. Geometry of the Z_1+eZZ collision.

system $\{x', y', z'\}$, and its orientation is specified by the set of two angles $\{\alpha', \beta'\}$ $(0 \leqslant \alpha' \leqslant 2\pi,\ 0 \leqslant \beta' \leqslant \pi)$.

It is well known (see, for example, [22] and references therein) that the main contribution to the charge-exchange cross section at low and intermediate collision velocities comes from the peripheral (large impact parameter) collisions, allowing the use of straight-line classical trajectories for a description of the projectile-target relative motion, $L(t)=\sqrt{\rho^2+v^2t^2}$. The system of coupled differential equations (49) is then solved numerically for a given set of fixed parameters—impact parameter ρ, velocity v, target internuclear separation R, and molecular bond orientation $\{\alpha', \beta'\}$—and for the initial conditions

$$|a_k(t \to -\infty)| = \delta_{1k}, \quad k = 1,2, \ldots ,N. \tag{55}$$

The probabilities $P_k(R,\rho,\alpha',\beta')$ and partial cross sections $\sigma_k(R,\alpha',\beta')$ for electron capture into a given Stark state k are

$$P_k(R,\rho,\alpha',\beta') = |a_k(t \to +\infty)|^2,$$

$$\sigma_k(R,\alpha',\beta') = \int 2\pi\rho P_k(R,\rho,\alpha',\beta')d\rho. \tag{56}$$

The sum of the partial cross sections $\sigma_k(R,\alpha',\beta')$ over the nth Stark manifold is $\sigma_{[n]}(R,\alpha',\beta')$, while the total-capture cross section for a given molecular ion alignment is $\sigma_{tot}(R,\alpha',\beta')=\Sigma_{k=2}^{N}\sigma_k(R,\alpha',\beta')$. These cross sections have to be averaged over the orientations of the H_2^+ molecular axis:

$$\bar{\sigma}_{tot}(R,\beta') = \frac{1}{2\pi}\int_0^{2\pi} \sigma_{tot}(R,\alpha',\beta')d\alpha', \tag{57}$$

$$\bar{\sigma}_{tot}(R) = 1/2\int_0^{\pi} \sin\beta'\,\bar{\sigma}_{tot}(R,\beta')d\beta', \tag{58}$$

where $\bar{\sigma}_{tot}(R)$ is the alignment averaged total cross sections [25]. However, for averaging the total (or partials) cross sections by using formulas (57) and (58) it is necessary to perform calculations for about $\sim 10^2$ molecular orientations [25], which is a formidable computational effort. We have, therefore, chosen to compute the orientation-averaged cross sections by the method proposed and used in [37,38]. For the considered collision systems, it is necessary to consider at least three orientations of the H_2^+ molecular axis with respect to the direction of the incoming beam (see Fig. 3). These orientations yields a coarse set of grid points for rotational averaging. The three basic orientations place the molecular axis along the x', y', and z' coordinate axes. We label these three orientations by I $\{\alpha'=0,\ \beta'=0\}$, II $\{\alpha'=0,\ \beta'=\pi/2\}$, and III $\{\alpha'=\pi/2,\ \beta'=\pi/2\}$. The rotationally averaged target property $\bar{g}$ is then given by [37,38]

$$\bar{g} = \frac{1}{\pi}[(\pi-2)g^{(I)} + (g^{(II)} + g^{(III)})], \tag{59}$$

where $g^{(i)}$ is the property of interest at orientation i $(i=I,II,III)$. All cross-section results presented in this section are based on this averaging procedure, unless otherwise stated explicitly.

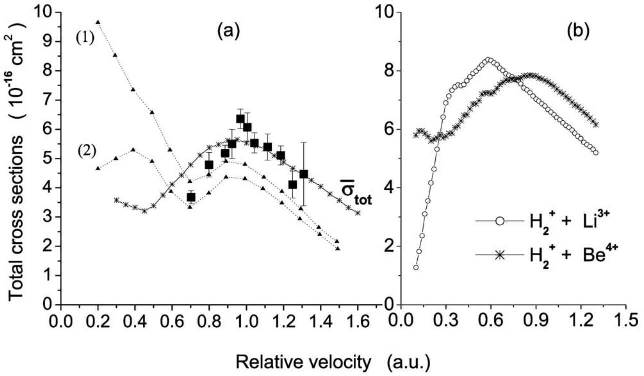

FIG. 4. The total cross sections for the charge exchange reactions (47). (a) Reaction (47a): experimental data (symbols) [23]. Solid line $\bar{\sigma}_{tot}$: present calculations. Dotted lines (1) and (2): theoretical results of Ref. [25]. (b) Present total cross sections for reactions (47b) and (47c).

For the numerical integration of the coupled equations (49) it is necessary to determine the dependence of angle β (see Figs. 1 and 3) on ρ and v. Using the properties of the Wigner D functions, one obtains

$$\cos\beta = \frac{\rho}{L(t)}\left[\frac{D^1_{-1,0}(\alpha',\beta',0)}{\sqrt{2}} + \frac{tv}{\rho}D^1_{0,0}(\alpha',\beta',0) - \frac{D^1_{+1,0}(\alpha',\beta',0)}{\sqrt{2}}\right]. \tag{60}$$

The coupled equations (49) were integrated in the interval corresponding to a projectile-target separation of ±20 a.u.; i.e., the projectile starts at a distance $z_0=20$ a.u., far from the target, and the trajectory is followed until the projectile is 20 a.u. far away from the target. The difference between the result obtained with this separation interval and that obtained with a separation of ±40 a.u. is negligible. The impact parameter ρ range included in the calculations was from 0.2 to 8.0 a.u. This range was divided into two parts. For close collisions, with ρ varying from 0.2 to 2.0 a.u., we used a step of 0.01 a.u., whereas for collisions with ρ varying from 2.0 to 8.0 a.u., we used a step of 0.1 a.u. The increase of the upper limit of ρ to 10.0 a.u. changes the calculated cross-section results for less than 0.1%. An overall check of the accuracy of the applied numerical procedure is obtained from the unitarity condition for $\Sigma P_k(R,\rho,\alpha',\beta')$, which was satisfied within the $10^{-8}-10^{-9}$ accuracy level for any of the velocity values and orientation angles considered.

The orientation-averaged total cross section $\bar{\sigma}_{tot}$ $(R=2$ a.u.) of reaction (47a), obtained by the numerical integration coupled equations (49), is shown in Fig. 4(a). The coupling matrix elements H_{jk} used in these calculations were calculated using Eq. (54), which takes into account the effects of electron translation factors. The agreement of the calculated cross section with experimental data of Ref. [23] can be considered quite satisfactory. In the same figure we show also the results of theoretical calculations performed in

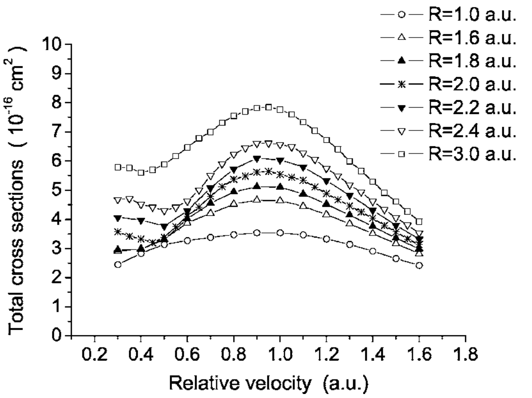

FIG. 5. The total orientation-averaged capture cross sections $\bar{\sigma}_{tot}(R)$ of reaction (47a) calculated for different H_2^+ internuclear distances R.

Ref. [25] within the framework of a many-body classical approach (the Kirschbaum-Wilets-Cohen model) introduced in [39] (line 1) and by using the nonperturbative semiclassical coupled-channel approach (line 2) employing the rovibrational *sudden* approximation. (In this approximation, the target molecular states are determined for fixed positions of the nuclei, while the electronic wave function is presented as a linear combination of traveling atomic capture states.)

In Fig. 4(b) we present also the results of the present calculations for the total capture cross sections of reactions (47b) and (47c). To the best of our knowledge no experimental data are presently available for these reactions.

In a number of recent publications [24–28] considerable attention has been given to the dependence of the total-capture cross section of reactions of type (47) on the value of the H_2^+ internuclear distance. The change of R is related to the molecular ion vibrations. We have performed such calculations for reaction (47a) by using the method described in the previous sections for a number of different values of R between $R=1$ a.u. and $R=3$ a.u. The results of these calculations are shown in Fig. 5. It is observed that with increasing R, the total cross section increases considerably, particularly for collision velocities around 1 a.u. This indicates that in more accurate cross-section calculations one should perform an additional averaging over the initial distribution of internuclear separations of H_2^+ (for example, employing a Frank-Condon weighting procedure, as used in [25]).

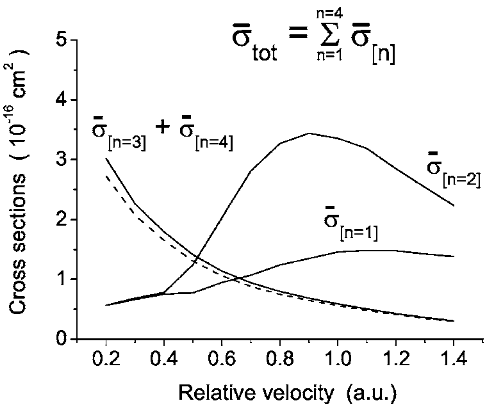

FIG. 6. The orientation-averaged partial cross sections $\bar{\sigma}_{[n]}$ ($R=2$ a.u.) for electron-capture reaction (47a) to states $He^+(n)$ with $n=1,2,3,4$. The dashed line is the capture cross sections to states with $n=3$.

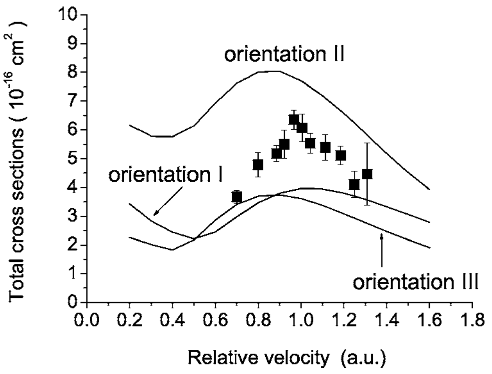

FIG. 7. The total cross sections $\sigma_{tot}(R,\alpha',\beta')\equiv\sigma_{tot}^{(i)}$ for electron-capture reaction (47a) for the three molecular bond orientations $i=I,II,III$.

The partial cross sections $\bar{\sigma}_{[n]}$ ($R=2$ a.u.) for electron capture to final states with principal quantum numbers $n=1,2,3,4$ are shown in Fig. 6. It can be seen that for collision velocities $v \geq 0.5$ a.u., the dominant contribution ($\sim 60\%$) to the total cross section $\bar{\sigma}_{tot}$ gives the capture channel He^+ ($n=2$). The same conclusion was reached also in the calculations of Refs. [23,25]. At lower velocities, the capture to He^+ ($n=2$) decreases significantly, and the capture to He^+ ($n=3$) becomes dominant. It should be noted, however, that in this velocity region our partial cross sections significantly disagree with those of Ref. [25].

The total cross section of reaction (47a) for the specific molecular orientations *I*, *II*, and *III* are shown in Fig. 7. The calculations show a significant dependence of the total cross section on the molecular orientation; therefore, we provide a more detailed study of this orientation effect. In Fig. 8, we show the cross section $\bar{\sigma}_{tot}(R,\beta')$ for the collision $H_2^+ + He^{2+}$ with averaging using the formula (57). For this averaging procedure we performed calculations for 40 different values of the angle α' at each of 10 values of angle β' (with totally 400 unique bond orientations for a given velocity v).

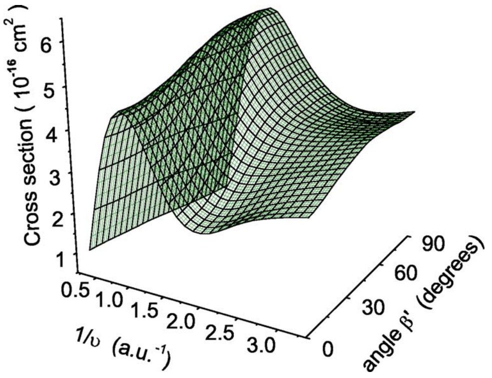

FIG. 8. (Color online) The total cross section $\bar{\sigma}_{tot}(R,\beta')$ of reaction (47a) as a function of collision velocity and orientation angle β' when the internuclear separation H_2^+ is 2 a.u.

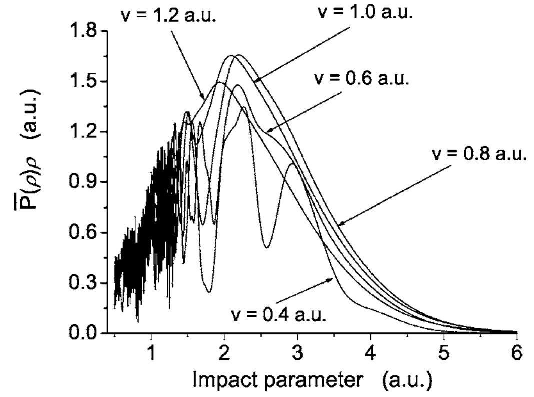

FIG. 9. Orientation-averaged probabilities $\bar{P}(\rho)$ for electron capture (47a) times the impact parameter ρ, as functions of ρ (in a.u.), for collision velocities $v=0.4$, 0.6, 0.8, 1.0, and 1.2 a.u.

We plot $\bar{\sigma}_{tot}(R,\beta')$ versus $1/v$ values to emphasize the oscillation of the total cross section at low velocities, which is very pronounced at $\beta' \sim 0$ but almost disappears at $\beta' \sim \pi/2$.

The obtained results regarding the alignment effects in $H_2^+ + He^{2+}$ collisions are in qualitative agreement with the experimental finding of Ref. [24] and the calculations of Refs. [25–27]. It appears that electron capture is favored when the molecular axis of the H_2^+ ion is perpendicular to the projectile velocity vector. The oscillation in total cross sections at low collision velocities was found also in the numerical integration of the time-dependent Schrödinger equation [26].

In Fig. 9 we show the electron-capture probabilities for reaction (47a) as a function of impact parameter for a number of collision velocities. It follows from this figure that the most important contribution to the capture cross section comes from the region of $\rho \sim 1-4$ a.u. The quantity $\bar{P}(\rho)\rho$ exhibits rapid oscillations at small impact parameter values and a sharp exponential decrease at high ρ, a behavior typical for all electron-capture reactions.

V. CONCLUSIONS

In the present article we have presented the results of an asymptotic study of the three-Coulomb-center problem eZ_1ZZ. We have obtained analytic results for the electron-exchange interaction between eZZ and Z_1 fragments of this system, as well as for its diabatic potential-energy surfaces. We have applied the obtained results in a close-coupling calculation of total and partial electron-capture cross sections in the $Z_1 + H_2^+$ ($Z_1 = 2,3,4$) collision systems and obtained a satisfactory agreement of the total cross section with available experimental data. For collision velocities $v \geqslant 0.5$ a.u. the electron capture dominantly populates the $n=2$ level of the product He^+ ion, whereas for the lower velocities the $n=3$ level is dominantly populated. We have also investigated the total cross-section dependence on the orientation of the H_2^+ molecular axis and found that the collisions with projectile velocity perpendicular to the molecular axis of H_2^+ give the largest contribution to the cross section.

APPENDIX

We shall calculate here the corrections to the energy coming from the terms proportional to $R_{2,3}^{-3}$. At large distances between the fragments $Z+Z$ and Z_1, the interaction potential $V(\mathbf{r}_1)$ [see Eq. (3)] can be considered as a small perturbation to the Hamiltonian $H_1^{(0)}$ which describes the motion of the electron in the field of nucleus Z_1. This justifies the application of the perturbation theory for the calculation of the higher correction to the $H_1^{(0)}$ energy terms and wave functions. Since the discrete n levels of a hydrogenlike ion are degenerate (with an degeneracy order of n^2), it is necessary to construct the correct wave functions of the zeroth-order approximation in the form (6), with coefficients determined from Eq. (9).

Substituting the energy terms (10) into Eq. (9), we find from its solution the expansion coefficients $a_{n_1 n_2 m}$ and, thus, the correct expression for zeroth-order wave functions. For the states with $n=2$, for instance, one obtains [4]

$$\psi_1^{(0)} = \sqrt{\frac{1}{2}}(\varphi_{001} + \varphi_{00-1}),$$

$$\psi_2^{(0)} = \frac{1}{\sqrt{2(A^2+B^2)}}[A(\varphi_{001} - \varphi_{00-1}) - iB(\varphi_{100} - \varphi_{010})],$$

$$\psi_{3,4}^{(0)} = \frac{1}{2\sqrt{(A^2+B^2)}}[(A \mp \sqrt{A^2+B^2})\varphi_{100} - (A \pm \sqrt{A^2+B^2})\varphi_{010} - iB(\varphi_{001} - \varphi_{00-1})]. \quad \text{(A1)}$$

To calculate the corrections for the energy terms proportional to $R_{2,3}^{-3}$ it is necessary to take into account the corresponding higher-order term w in the expansion of the interaction potential (3). It is convenient to represent w in parabolic coordinates [see Eqs. (6)–(8)]:

$$w = -\frac{C}{8}(\mu^2 - 4\mu\nu + \nu^2) + \frac{3D}{2}\sqrt{\mu\nu}(\mu - \nu)\sin\varphi_1 + \frac{3E}{4}\mu\nu\cos 2\varphi_1, \quad \text{(A2)}$$

where

$$A = \frac{\cos\theta_2}{R_2^2} + \frac{\cos\theta_3}{R_3^2}, \quad B = \frac{\sin\theta_2}{R_2^2} - \frac{\sin\theta_3}{R_3^2},$$

$$C = \frac{3\cos^2\theta_2 - 1}{R_2^3} + \frac{3\cos^2\theta_3 - 1}{R_3^3},$$

$$D = \frac{\cos\theta_2 \sin\theta_2}{R_2^3} - \frac{\cos\theta_3 \sin\theta_3}{R_3^3}, \quad E = \frac{\sin^2\theta_2}{R_2^2} + \frac{\sin^2\theta_3}{R_3^2}. \quad \text{(A3)}$$

By direct calculations one can show that the nondiagonal matrix element of the operator (A2) with the wave functions (A1) is zero. It is therefore sufficient to average this operator over the wave functions (A1) to obtain the corrections to the energy to terms proportional to $R_{2,3}^{-3}$. Performing the necessary integration, one obtains, for the energy terms with $n=2$,

$$E_1 = -\frac{Z_1^2}{8} - \frac{Z}{R_2} - \frac{Z}{R_3} + \frac{6Z}{Z_1^2}\left(\frac{1}{R_2^3} + \frac{1}{R_3^3}\right),$$

$$E_2 = -\frac{Z_1^2}{8} - \frac{Z}{R_2} - \frac{Z}{R_3} + \frac{6Z}{Z_1^2[R_2^{-4} + R_3^{-4} + 2R_2^{-2}R_3^{-2}\cos\tilde{\gamma}]}\left[\frac{1}{R_2^7} + \frac{1}{R_3^7} + \frac{2\cos\tilde{\gamma}}{(R_2R_3)^2}\left(\frac{1}{R_2^3} + \frac{1}{R_3^3}\right) + \frac{1-3\sin^2\tilde{\gamma}}{(R_2R_3)^3}\left(\frac{1}{R_2} + \frac{1}{R_3}\right)\right],$$

$$\begin{aligned}E_{3,4} = &-\frac{Z_1^2}{8} - \frac{Z}{R_2} - \frac{Z}{R_3} \pm \frac{3Z}{Z_1}\sqrt{\frac{1}{R_2^4} + \frac{1}{R_3^4} + \frac{2\cos\tilde{\gamma}}{R_2^2R_3^2}} - \frac{6Z}{Z_1^2[R_2^{-4} + R_3^{-4} + 2R_2^{-2}R_3^{-2}\cos\tilde{\gamma}]}\\ &\times\left[\frac{1}{R_2^7} + \frac{1}{R_3^7} + \frac{2\cos\tilde{\gamma}}{(R_2R_3)^2}\left(\frac{1}{R_2^3} + \frac{1}{R_3^3}\right) - \frac{1-3\cos^2\tilde{\gamma}}{2(R_2R_3)^3}\left(\frac{1}{R_2} + \frac{1}{R_3}\right)\right].\end{aligned} \tag{A4}$$

Using the same technique, one can determine the correct zeroth-order approximation for the wave functions of the states with $n=3$:

$$\begin{aligned}\psi_{1,3} = \frac{B}{2\sqrt{2}(A^2+B^2)}\Bigg(&\frac{-B}{\sqrt{2}}(\varphi_{002} + \varphi_{00-2}) + i(A \pm \sqrt{A^2+B^2})(\varphi_{011} - \varphi_{01-1}) \pm i(\mp A + \sqrt{A^2+B^2})(\varphi_{101} - \varphi_{10-1})\\ &+ \sqrt{2}B\varphi_{110} \pm \frac{B(-A \pm \sqrt{A^2+B^2})}{\sqrt{2}(\pm A + \sqrt{A^2+B^2})}\varphi_{200} \mp \frac{B(A \pm \sqrt{A^2+B^2})}{\sqrt{2}(A \mp \sqrt{A^2+B^2})}\varphi_{020}\Bigg),\end{aligned}$$

$$\psi_2 = \frac{1}{\sqrt{A^2+B^2}}\left(\frac{-A(\varphi_{002} - \varphi_{00-2})}{\sqrt{2}} - \frac{iB}{2}(\varphi_{011} + \varphi_{01-1} - \varphi_{101} - \varphi_{10-1})\right),$$

$$\psi_{4,6} = \frac{1}{2\sqrt{2(A^2+B^2)}}[\mp(\pm A + \sqrt{A^2+B^2})(\varphi_{011} + \varphi_{01-1}) + (A \mp \sqrt{A^2+B^2})(\varphi_{101} + \varphi_{10-1}) \mp i\sqrt{2}B(\varphi_{002} - \varphi_{00-2})],$$

$$\begin{aligned}\psi_{5,7} = \frac{1}{2\sqrt{2}(A^2+B^2)}[&\mp i\sqrt{2}AB(\varphi_{002} + \varphi_{00-2} - 2\varphi_{110}) + i\sqrt{2}B(\mp A + \sqrt{A^2+B^2})\varphi_{200} - i\sqrt{2}B(\pm A + \sqrt{A^2+B^2})\varphi_{020}\\ &+ (\mp A^2 \pm B^2 + A\sqrt{A^2+B^2})(\varphi_{10-1} - \varphi_{101}) + (\pm A^2 \mp B^2 + A\sqrt{A^2+B^2})(\varphi_{01-1} - \varphi_{011})],\end{aligned}$$

$$\psi_8 = \frac{1}{\sqrt{4A^4 + 4A^2B^2 + 3B^4}}[i\sqrt{2}AB(\varphi_{011} - \varphi_{01-1} - \varphi_{101} + \varphi_{10-1}) - (2A^2 - B^2)\varphi_{110} - B^2(\varphi_{200} + \varphi_{020})],$$

$$\psi_9 = \frac{1}{\sqrt{3}}(\varphi_{110} + \varphi_{002} + \varphi_{00-2}). \tag{A5}$$

The higher-order corrections to the energies can also be obtained by the same technique. For the sake of brevity, we present here only the results for the energies of σ states $[n_1, n_2, m=0]$:

$$E_{[200]} = -\frac{Z_1^2}{18} - \frac{Z}{R_2} - \frac{Z}{R_3} + \frac{9Z}{Z_1}\sqrt{\frac{1}{R_2^4} + \frac{1}{R_3^4} + \frac{2\cos\tilde{\gamma}}{R_2^2R_3^2}} - \delta E,$$

$$E_{[020]} = -\frac{Z_1^2}{18} - \frac{Z}{R_2} - \frac{Z}{R_3} - \frac{9Z}{Z_1}\sqrt{\frac{1}{R_2^4} + \frac{1}{R_3^4} + \frac{2\cos\tilde{\gamma}}{R_2^2R_3^2}} + \delta E,$$

$$E_{[110]} = -\frac{Z_1^2}{18} - \frac{Z}{R_2} - \frac{Z}{R_3} + \frac{\delta E}{2}, \tag{A6}$$

where δE is given by

$$\begin{aligned}\delta E = &\frac{72Z}{Z_1^2[R_2^{-4} + R_3^{-4} + 2R_2^{-2}R_3^{-2}\cos\tilde{\gamma}]}\\ &\times\left\{\frac{1}{R_2^7} + \frac{1}{R_3^7} + \frac{1}{2(R_2R_3)^3}\left[\left(\frac{1}{R_2} + \frac{1}{R_3}\right)(3\cos^2\tilde{\gamma} - 1)\right.\right.\\ &\left.\left.+ 4\left(\frac{R_3}{R_2^2} + \frac{R_2}{R_3^2}\right)\cos\tilde{\gamma}\right]\right\}.\end{aligned}$$

In the case of the isosceles triangle configuration ($R_2=R_3$, $\theta_2=\theta_3=\tilde{\gamma}/2$), formulas (A6) reproduce the corresponding results of [4].

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