PHYSICAL REVIEW A VOLUME 48, NUMBER 6 DECEMBER 1993

Theoretical investigations of charge exchange with ion excitation in atomic collisions at thermal energies

Andrey K. Belyaev*
Department of Chemistry, University of California, Berkeley, California 94720

(Received 14 May 1992)

The process of charge exchange with ion excitation is investigated theoretically. The multielectron and multichannel model for the process under consideration is proposed. The formulas for two-electron exchange coupling are obtained and discussed. The model is applied to the investigation of charge exchange with ion excitation in collisions of helium ions with mercury atoms at thermal energies. The matrix elements of exchange coupling, the adiabatic potential energies, the partial cross section, and the partial rate constant for the process under consideration are calculated. The matrix elements of exchange coupling in this case are mainly determined by electron-core interactions. The effective potentials are used for these interactions. The calculated partial rate constant for excitation of $\mathrm{Hg}^+(7p\ ^2P_{3/2})$ agrees with experimental data.

PACS number(s): 34.70.+e, 82.30.Fi, 34.50.Fa

I. INTRODUCTION

Ever since the 1930s, when Manley and Duffendack [1] studied experimentally processes of charge exchange with ion excitation, there has been interest in this kind of reaction:

$$A^+ + M \rightarrow A + M^+(f) + \Delta E_f \ , \tag{1.1}$$

where A^+, A, M denote the ground states of an ion and atoms, respectively, $M^+(f)$ is an excited state of an ion M^+, numbered by index f, and ΔE_f is the energy defect. In practice A is usually an atom of noble gas and M is a metal atom. The special feature of these reactions is that at least two electrons change their wave functions during transitions. In the literature the process (1.1) is called "charge exchange with ion excitation," to distinguish it from a process of charge transfer into an excited state: $A^+ + M \rightarrow A^* + M^+$.

Intensive, mainly experimental, investigations of these processes have been carried out since the 1960's when the role of these processes as the pumping mechanism for several transitions in ionic lasers became clear (see, for example, [2–5] and references therein). It has been determined that the exothermic processes under consideration could occur efficiently at thermal energies. However, experimental data were few, and often contradictory, and this fact stimulated renewed interest [6–16] both experimentally and theoretically in processes (1.1).

Despite a great number of works concerning processes of charge exchange with ion excitation, up to now there was no clear understanding of this kind of reaction neither experimentally nor theoretically. For instance, previous theoretical approaches did not provide reliable partial cross sections and partial rate constants; there exist discrepancies both between experimental and calculated data, and between the calculations of different authors.

Putting aside discussion of experimental methods and results, it should be mentioned that quantities measured directly are rate constants and that experimental data of different approaches are substantially distinguished from each other, especially for partial rate constants, although partial values are of prominent importance in analyses of laser level pumping. Recently measurements of Ref. [14] have obtained agreement with the results of Sadeghi and co-workers [6] in $\mathrm{He}^+ + \mathrm{Cd}$ collisions, however, the partial rate constants for some states have discrepancies up to factors of 6. This fact suggests that some partial rate constants are measured quite accurately. So the data of Refs. [6,14] for $\mathrm{He}^+ + \mathrm{Cd}$ collisions, as well as ones of Ref. [7] and Ref. [13] for $\mathrm{He}^+ + \mathrm{Zn}$ and $\mathrm{He}^+ + \mathrm{Hg}$ collisions, respectively, are assumed to be the most reliable experimental data.

The previous theoretical treatments [2,8–15] being asymptotic should be best applicable for excitation of states with the smallest energy defects, because of the largest internuclear distances. But the main result of applying the previous theoretical approaches to concrete processes is that calculated partial rate constants for excitation of states with the smallest energy defects are much smaller than experimental values. For instance, the pronounced discrepancies are 8000–95 000 [12,14] for excitation of the $\mathrm{Cd}^+(9p)$ states in $\mathrm{He}^+ + \mathrm{Cd}$ collisions and at least 50 [13] for excitation of the $\mathrm{Hg}^+(7p\ ^2P_{3/2})$ state in $\mathrm{He}^+ + \mathrm{Hg}$ collisions.

This result is a consequence of the fact that the previous theoretical approaches were applied to the processes, for which the main prerequisite of the models are not fulfilled. The point is that practically all previous theoretical interpretations, except of [12] (see below), have tacitly assumed that in nonadiabatic regions the main maximum of the wave function for the excited electron is far from the nucleus of an incoming ion. However, the consideration of wave functions and analysis of exchange couplings presented below in the present work show that this assumption is not fulfilled.

Thus, it is necessary to study theoretically processes of charge exchange with ion excitation. In connection with this, Sec. II presents a theoretical approach, which has

1050-2947/93/48(6)/4299(8)/$06.00

been begun in Ref. [16]. Section III contains the results of applying this theoretical approach to collisions of helium ions with mercury atoms at thermal energies. Section IV presents an asymptotic limit for processes (1.1).

Throughout the paper atomic units ($m_e = e = \hbar = 1$) are used unless stated otherwise.

II. THEORY

The important point in theoretical investigations of collisions in both nonadiabatic approach and coupled-channel equations is the calculation of the matrix elements of exchange couplings H_{if}:

$$H_{if} = \langle \Psi_i(1,2,3,\ldots)|\hat{H}_e(1,2,3,\ldots)|\Psi_f(1,2,3,\ldots)\rangle \ , \tag{2.1}$$

where $\Psi_{i,f}$ are basis multielectron antisymmetrized complete (coordinate and spin) wave functions of the initial and final quasimolecular states, respectively; $\hat{H}_e(1,2,3,\ldots)$ is the multielectron electronic Hamiltonian of the quasimolecule.

In Hund's case (c), when the total angular momentum J of the molecule is quantized along the axis of the molecule, wave functions Ψ_i and Ψ_f are written as

$$\Psi_i(1,2,3,\ldots;J_i,\Omega) = \hat{A}\sum C'\Phi_M(\mathbf{r}_1,\mathbf{r}_2)\Phi_{M^{2+}}(\mathbf{r}_\alpha,\ldots)\varphi_{A^+}(\mathbf{r}_3)\Phi_{A^{2+}}(\mathbf{r}_\beta,\ldots)\delta_{\mu_1\lambda_1}\delta_{\mu_2\lambda_2}\delta_{\mu_3\lambda_3}\cdots \ , \tag{2.2}$$

$$\Psi_f(1,2,3,\ldots;J_f,\Omega) = \hat{A}\sum C''\varphi_{M^+(f)}(\mathbf{r}_1)\Phi_{\mathrm{M}^{2+}}(\mathbf{r}_\alpha,\ldots)\Phi_{\mathrm{A}}(\mathbf{r}_2,\mathbf{r}_3)\Phi_{\mathrm{A}^{2+}}(\mathbf{r}_\beta,\ldots)\delta_{\mu'_1\lambda_1}\delta_{\mu'_2\lambda_2}\delta_{\mu'_3\lambda_3}\cdots \ . \tag{2.3}$$

Here $J_{i,f}$ are the total angular momenta of an initial and a final state, respectively; Ω is their projection upon the molecular axis; $\hat{A}$ is the operator of antisymmetrization for all electrons under consideration; C', C'' denote all necessary Clebsch-Gordan coefficients; $\varphi(\mathbf{r})$ and Φ are a single- and a many-electron (nonantisymmetrized) coordinate wave functions, respectively; $\delta_{\alpha\beta}$ is the Kroneker symbol; μ is projection of the spin of an electron; λ is spin variable. The summation in Eqs. (2.2) and (2.3) is carried out on all projections, except of Ω.

An expression for exchange coupling derived by substituting Eqs. (2.2) and (2.3) into Eq. (2.1) depends on whether valence electrons of an atom, M are equivalent. Neglecting terms which correspond to the transition of three and more electrons, in the case of equivalent valence electrons in an atom M Eq. (2.1) becomes

$$H_{if} = Ch_{if} \ , \tag{2.4}$$

where

$$h_{if} = \langle \Phi_M(\mathbf{r}_1,\mathbf{r}_2)|\hat{H}_e(1,2)|\varphi_A(\mathbf{r}_1)\varphi_{M^+(f)}(\mathbf{r}_2)\rangle \ , \tag{2.5}$$

$\hat{H}_e(1,2)$ being the two-electron electronic Hamiltonian of the quasimolecule, C being some coefficient dependent on the quantum numbers of the examined states and overlapping integrals of other electrons. This coefficient appears due to quantum addition of angular momenta, antisymmetrization of electrons, and the summation over spin variables. It can be explicitly determined for concrete processes. From here on $\langle\ \rangle$ means integrating over coordinate variables only.

So the problem is reduced to consideration of two electrons, but the presence of others leads to a correct coefficient C in Eq. (2.4). For instance, in $\mathrm{He}^+ + \mathrm{Cd}$, Zn, Hg collisions three electrons should be taken into account [11,12].

In order to calculate matrix elements h_{if}, and hence H_{if} let us use linear combination of atomic orbitals (LCAO) as a first approximation. It is well known (see, for example, [17]) that LCAO does not provide a strict asymptotic expression on the exchange coupling for single-electron transfer, but at interatomic distances R near 10 a.u. an error is about 10%, and for smaller distances LCAO can be more accurate than an asymptotic approach. Single-electron atomic orbitals can be calculated, for instance, in the Hartree-Fock [18] and the Coulombic [19] approximations for ground and excited states, respectively; for example $\varphi_A(\mathbf{r})$ is a solution of the following Schrödinger equation:

$$\hat{H}_A(1)\varphi_A(\mathbf{r}) = E_A\varphi_A(\mathbf{r}) \ , \tag{2.6}$$

$\hat{H}_A(1)$ being the single-electron Hamiltonian of an atom A.

Matrix elements of exchange coupling h_{if}, Eq. (2.5), could be calculated by direct integration of all terms in the two-electron Hamiltonian $\hat{H}_e(1,2)$ with a known two-electron wave function $\Phi_M(\mathbf{r}_1,\mathbf{r}_2)$. However, in this case very accurate operators of electron-core interactions should be used, otherwise it could lead to an error in the determination of matrix elements. The more reliable way is to pick out dominant terms, using properties of wave functions and Hamiltonians. Dominant terms, and hence, representation of the Hamiltonian $\hat{H}_e(1,2)$ depend on wave functions of valence electrons. Respecting calculations of coupling matrix elements for the process (1.1), there exist two different cases with regard to shapes of valence electrons' wave functions along the molecular axis, as depicted in Fig. 1. The distinction between them is that the main maximum of the wave function for the excited electron in M^{+*} is far from [case (a), Fig. 1(a)] or near to [case (b), Fig. 1(b)] a nucleus of an ion A^+.

In case (a) a "final" representation of $\hat{H}_e(1,2)$ can be used, that is, picking out the "final" Hamiltonians $\hat{H}_A(1)$ and $\hat{H}_{M^+}(2)$ from $\hat{H}_e(1,2)$. In case (b) it is better to use an "initial" representation of the electronic Hamiltonian, that is, to pick out the "initial" Hamiltonian $\hat{H}_M(1,2)$, which is the Hamiltonian of two valence electrons in an atom M,

$$\hat{H}_e(1,2)=\hat{H}_M(1,2)+\hat{V}_{1A^+}+\hat{V}_{2A^+}+\hat{V}_{A^+M^{2+}} , \tag{2.7}$$

where $\hat{V}_{\alpha\beta}$ is the operator of the interaction between particles α and β. Taking into account that $\Phi_M(\mathbf{r}_1,\mathbf{r}_2)$ is the eigenfunction of $\hat{H}_M(1,2)$, Eq. (2.5) leads to

$$\begin{aligned} h_{if}=&\langle \Phi_M(\mathbf{r}_1,\mathbf{r}_2)|\hat{V}_{1A^+}+\hat{V}_{2A^+}|\varphi_A(\mathbf{r}_1)\varphi_{M^+(f)}(\mathbf{r}_2)\rangle \\ &+\langle \Phi_M(\mathbf{r}_1,\mathbf{r}_2)|\varphi_A(\mathbf{r}_1)\varphi_{M^+(f)}(\mathbf{r}_2)\rangle[\tilde{E}_M+V_{A^+M^{2+}}] , \end{aligned} \tag{2.8}$$

$\tilde{E}_M$ being the energy of two electrons in an atom M.

The last equation could be written as

$$\begin{aligned} h_{if}=&\langle \Phi_i(\mathbf{r}_1,\mathbf{r}_2)|\hat{V}_{1A^+}+\hat{V}_{2A^+}|\Phi_f(\mathbf{r}_1,\mathbf{r}_2)\rangle \\ &+\langle \Phi_i(\mathbf{r}_1,\mathbf{r}_2)|\Phi_f(\mathbf{r}_1,\mathbf{r}_2)\rangle[\tilde{E}_M+V_{A^+M^{2+}}] , \end{aligned} \tag{2.9}$$

which is a generalization of an equation for a matrix element of single-electron exchange coupling for the case of two electrons.

Thus, the mechanism of a transition in this case corresponds to the interaction of valence electrons with a core A^+. That is, both electrons, being initially in the same atom and equivalent, transfer simultaneously from one core to the other due to attraction to the latter, but only one of them could be bound with an ion of a noble gas, because a negative ion of a noble gas does not exist [20]; the latter electron thus has to be bound with the metal ion but in an excited state.

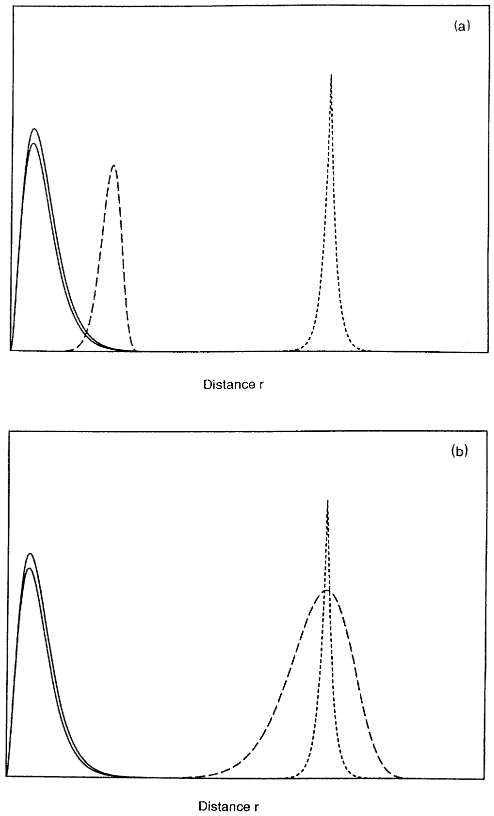

FIG. 1. The schematic plot of valence electrons' wave functions via an electron coordinate r along the internuclear axis before (solid lines) and after (dashed and dotted lines) a transition: (a) the main maximum of an excited electron wave function (the dashed line) is far from an incoming ion A^+; (b) the main maximum of an excited electron wave function is near to an incoming ion A^+. A wave function of the ground state in an atom A is depicted by the dotted line.

Writing the two-electron wave function as a product of single-electron wave functions $\Phi_M(\mathbf{r}_1,\mathbf{r}_2)=\varphi_M(\mathbf{r}_1)\varphi_M(\mathbf{r}_2)$, the coupling matrix element is found to be in the "initial" representation,

$$\begin{aligned} H_{if}=C\Big\{&S_2\langle\varphi_M(\mathbf{r}_1)|\hat{V}_{1A^+}|\varphi_A(\mathbf{r}_1)\rangle+S_1\langle\varphi_M(\mathbf{r}_2)|\hat{V}_{2A^+}|\varphi_{M^+(f)}(\mathbf{r}_2)\rangle+[\varphi_M\varphi_A|\varphi_M\varphi_{M^+(f)}] \\ &-S_1[\varphi_M\varphi_{M^+(f)}|\varphi_M\varphi_M]-S_2[\varphi_M\varphi_A|\varphi_M\varphi_M]+S_1S_2[2E_m+V_{A^+M^{2+}}]\Big\} , \end{aligned} \tag{2.10}$$

where Slater's notation for a two-electron integral $[ab|cd]=\langle a(\alpha)c(\beta)|\hat{V}_{\alpha\beta}|b(\alpha)d(\beta)\rangle$ is used; E_M is the energy of one electron in a ground state of an atom M; $S_1=\langle\varphi_M(\mathbf{r}_1)|\varphi_A(\mathbf{r}_1)\rangle$ and $S_2=\langle\varphi_M(\mathbf{r}_2)|\varphi_{M^+(f)}(\mathbf{r}_2)\rangle$ are the overlap integrals for the exchanged and excited electrons, respectively.

In comparison with Eq. (2.8), Eq. (2.10) has some additional terms, which appear due to the fact that a product of single-electron wave functions is not an exact eigenfunction of the two-electron Hamiltonian.

It should be pointed out that calculations by means of both "initial" and "final" representations of the electronic Hamiltonian $\hat{H}_e$, as well as direct integration of all terms in it, must yield the same result for H_{if}. But "initial" representation and, hence, Eq. (2.10) are more preferable for analyzing and computing matrix elements in case (b), as Eq. (2.10) has the dominant terms, which are the two first terms.

The important point is a choice of the electron-core interactions, as the particles under consideration are multielectronic. Coulombic potentials could be taken to estimate matrix elements (in this case an analytic expression for the main term of exchange coupling can be evaluated). But a more accurate result is obtained by using effective potentials derived from single-electron Schrödinger equations, Eq. (2.6), with known energy and a known wave function calculated, say, in the Hartree-Fock approximation, that is,

$$\hat{V}_{iA^+} = V^{\mathrm{eff}}_{A^+}(r) = E_A + \frac{\Delta\varphi_A(\mathbf{r})}{2\varphi_A(\mathbf{r})} , \tag{2.11}$$

where Δ is Laplacian. In accordance with the fact that the Hartree-Fock approximation does not provide a correct asymptotic behavior of a wave function, the correct asymptotic behavior of potentials should be used.

Thus, in the case when the main maximum of the wave function for an excited electron in a metal ion is near an incoming ion nucleus, and when valence electrons in a metal atom are equivalent, the matrix elements of exchange coupling can be calculated by means of Eqs. (2.10) and (2.11) and strict expansion of interelectron interaction [19].

III. RESULTS AND DISCUSSIONS

In the present paper the process of charge exchange of helium ions (A=He) on mercury atoms (M=Hg) with excitation of mercury ions is investigated at thermal energies:

$$\begin{aligned}&\mathrm{He}^+(1s\,{}^2S_{1/2}) + \mathrm{Hg}(6s^2\,{}^1S_0)\\ &\qquad \to \mathrm{He}(1s^2\,{}^1S_0) + \mathrm{Hg}^+(nlj\,{}^2L_J) + \Delta E_{nlj} ,\end{aligned} \tag{3.1}$$

where l,j and L,J are the quantum numbers of orbital and total angular momenta for an excited electron and the excited state, respectively; n is a principle quantum number of an excited electron in a mercury ion, ΔE_{nlj} is the energy defect for excitation of a $\mathrm{Hg}^+(nlj)$ state.

Within the nonadiabatic approach [21] adiabatic potential energies U are obtained by finding roots of the secular equation

$$\det|\underline{H} - U\underline{S}| = 0 , \tag{3.2}$$

where $\underline{H}$ is a matrix of the electronic Hamiltonian $\hat{H}_e$ in a basis set $\{\Psi\}$ of antisymmetrized complete wave functions and $\underline{S}$ is a matrix of overlap integrals in the same basis set. In the internuclear distances range of interest for process (3.1) several initial and final wave functions should be taken into account [22]. The basis set $\{\Psi\}$ is divided into several sets:

$$\{\Psi\} = \{\{\Psi_1\},\{\Psi_f\},\{\Psi_m\}\} , \tag{3.3}$$

where $\{\Psi_i\}$ is a basis set of wave functions describing the initial states of the quasimolecule, $\{\Psi_f\}$ and $\{\Psi_m\}$ are the same for final and intermediate states, respectively. Using Eq. (3.3), a matrix $\underline{H}$ can be represented by the following:

$$\underline{H} = \begin{bmatrix} \underline{H}^{ii} & \underline{H}^{if} & \underline{H}^{fm} \\ \underline{H}^{fi} & \underline{H}^{ff} & \underline{H}^{fm} \\ \underline{H}^{mi} & \underline{H}^{mf} & \underline{H}^{mm} \end{bmatrix} , \tag{3.4}$$

where $\underline{H}^{ii}$ is a submatrix for determining initial potential calculated without taking into account final and intermediate states, $\underline{H}^{if}$ is a submatrix of exchange couplings between initial and final states and so on. The utility of representing matrix $\underline{H}$ in the form of Eq. (3.4) is the opportunity to use some submatrices calculated by means of simplified basis wave functions (say, single-electron ones) and to compute others by using more complicated wave functions.

The initial wave function Ψ_i correlates to the multiconfiguration wave function Ψ_{Hg} of a mercury atom $\mathrm{Hg}(6s^2\,{}^1S_0)$ in the ground state. It can be expressed through the following Slater determinants [23]:

$$\Psi_{\mathrm{Hg}} = C_1(6s^2_{1/2}) + C_2(6p^2_{1/2}) + C_3(6p^2_{3/2}) . \tag{3.5}$$

At the first approximation a basis set $\{\Psi_i\}$ for the quasimolecule $(\mathrm{HeHg})^+$ can be restricted by the only initial wave function because the configuration weight coefficient C_1 is close to unity. So the matrix $\underline{H}^{ii}$ in Eq. (3.4) consists of the only matrix element H_{ii} and the polarization potential may be used for this element in process (3.1) at internuclear distances $R > 4$ a.u. [22]. The matrix $\underline{H}^{ff}$ has been calculated [22] by means of the pseudopotential method with a quasimolecular basis set of Hund's "c" type of coupling. Twelve final wave functions corresponding to an interaction of a helium atom in a ground state with a mercury ion in excited states from $\mathrm{Hg}^+(7s)$ to $\mathrm{Hg}^+(8p)$ at an infinite internuclear separation have been taken into account.

The exchange-coupling matrix elements H_{if} for process (3.1) have been examined by using "initial" and "final" representations of the electronic Hamiltonian, as well as by direct integration of all terms in it, and results of calculations coincide with each other [it should be mentioned that using Coulombic potentials instead of effective ones leads to an error of about 15% in Eq. (2.10) and to other values of exchange couplings in direct integrating]. But the calculations show that an "initial" representation picks out dominant terms which are the first two terms in Eq. (2.10), while results in a "final" representation and direct integrating are close to a mutual cancellation of terms. This is because in process (3.1) case (b) is realized. As an example, the wave functions of valence electrons before and after a transition corresponding to excitation of the $\mathrm{Hg}^+(7p\,{}^2P_{3/2})$ state are shown in Fig. 2 along the molecular axis (the internuclear distance R approximately corresponds to a nonadiabatic region). Single-electron coordinate wave functions have been calculated in the Hartree-Fock [18,24] and the Coulombic [19] approximations. It is seen that the main maximum of the wave function for an excited electron in a mercury ion is near a helium nucleus.

So in the examined case the "initial" representation is preferable and the dominant terms of H_{if} correspond to interactions of valence electrons with a helium ion. Matrix elements of interelectron interaction, which have been assumed to be dominant in previous models, are not really dominant ones and exchange couplings of the previous calculations were therefore diminished.

Thus, in the present work the calculations of exchange-coupling matrix elements H_{if} and, hence, a matrix $\underline{H}^{if}$ have been carried out by means of Eq. (2.10) with the coefficient [11]

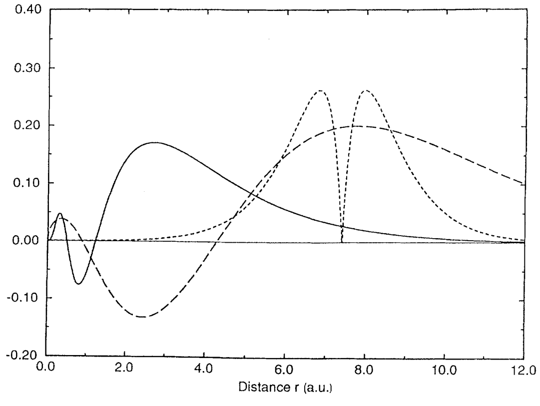

FIG. 2. The coordinate wave functions of the valence electrons in the ground state of a mercury atom (the solid line), in the ground state of a helium atom (the dotted line), and in the excited $Hg^+(7p3/2)$ state (the dashed line). A mercury nucleus is in the zero point. The internuclear distance equals 7.4 a.u.

$$C = \langle \varphi_{A^+} | \varphi_A \rangle \begin{bmatrix} 1/2 & L & J \\ \Omega & 0 & \Omega \end{bmatrix}$$

(the brackets denote the Clebsch-Gordan coefficient) and the effective potential $V^{\text{eff}}_{A^+}(r)$, Eq. (2.11), for electron-core interaction. Interelectron interaction is accounted for according to the strict expansion [19]. The calculated matrix elements have greater theoretical accuracy in comparison with the previous ones and the present calculations provide exchange couplings greater than in the previous calculations.

The matrices $\underline{H}^{if}$, $\underline{H}^{ii}$, $\underline{H}^{ff}$ and $\underline{S}$ calculated by this manner allow us to compute the adiabatic potential energies of a quasimolecule $(HeHg)^+$. The most important adiabatic and diabatic potentials for process (3.1) are shown in Fig. 3. It should be pointed out that at internuclear distances $R > 4$ a.u. the initial diabatic potential (curve 1 in Fig. 3) intersects four final diabatic potentials (curves 2–5 in Fig. 3; the diabatic potentials 4 and 5 coincide with the respective adiabatic potentials). But due to strong exchange coupling between initial $He^+ + Hg$ and final $He + Hg^+(7s_{1/2})$ states at $R < 7$ a.u. the adiabatic potentials are considerably distinguished from the diabatic potentials [especially the initial and final $He + Hg^+(7p_{1/2})$, $He + Hg^+(7s_{1/2})$ potentials] and at $R > 4$ a.u. there exist only two nonadiabatic regions, corresponding to quasi-intersections of the initial and $He + Hg^+(7p_{3/2,1/2})$ final states.

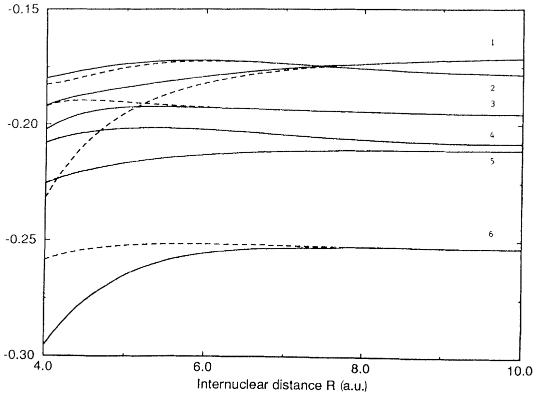

FIG. 3. The adiabatic (solid lines) and diabatic (dashed lines) potential energies of the quasimolecule $(HeHg)^+$. Curves 1 correspond to the $He^+ + Hg$ interaction; curves 2, $He + Hg^+(7p3/2)$; curves 3, $He + Hg^+(7p1/2)$; curves 4, $He + Hg^+(6d5/2)$; curves 5, $He + Hg^+(6d3/2)$; curves 6, $He + Hg^+(7s1/2)$ interaction at infinite internuclear distances. The energies are evaluated from the state $He + Hg^{2+}$ at $R \to \infty$.

In order to analyze the electronic Hamiltonian matrix in the vicinity of the intersection of the initial $He^+ + Hg$ and final $He + Hg^+(7p_{3/2})$ diabatic potentials ($R \approx 7.44$ a.u.) let us transfer to the diabatic basis set $\{\chi\}$

$$\chi_1 = \Psi'_i \ , \tag{3.6a}$$

$$\chi_k = \sum_f a_{kf}(R) \Psi'_f , \quad k > 1 , \tag{3.6b}$$

where $\Psi' = S^{-1/2}\Psi$ is a basis set of orthogonal wave functions, $\underline{a}$ is the matrix of eigenfunctions for the matrix $(\underline{H}^{ff})'$ of the electronic Hamiltonian in $\{\Psi'\}$ representation. The off-diagonal elements $(H_{if})_\chi$ have the meaning of the matrix elements of exchange coupling in $\{\chi\}$ representation and can be written in terms of the matrix elements H_{if} in $\{\Psi\}$ representation as

$$(H_{if})_\chi = \sum_{n,m,k} S_{in}^{-1/2} H_{nm} S_{mk}^{-1/2} a_{kf}(R) \ . \tag{3.7}$$

Analysis shows that the exchange couplings $(H_{if})_\chi$ are mainly determined by a destroyed s wave due to substantial mixing of the final wave functions by interatomic interaction, not only between wave functions of the fine structure but also between the ones of different configurations, and due to sufficiently large magnitudes of exchange couplings H_{if}, especially between the initial and $He + Hg^+(ns)$ states. In the examined vicinity the off-diagonal matrix elements $(H_{if})_\chi$ are much smaller than differences of diagonal ones in the same representation, except of $(H_{1\,7p_{3/2}})_\chi$ (the index nlj indicates correlation of the quasimolecular and the atomic states). Moreover, a minimum of the adiabatic splitting in the nonadiabatic region $\Delta = 3.006 \times 10^{-4}$ a.u. is in excellent agreement with double exchange coupling $2(H_{1\,7p_{3/2}})_\chi = 2.996 \times 10^{-4}$ a.u. obtained from Eq. (3.7) at the same internuclear distance. So the consideration here can be restricted by two wave functions χ_1 and $\chi_{7p_{3/2}}$.

In accordance with this inference and that the exchange coupling $(H_{1\,7p_{3/2}})_\chi$ [Eq. (3.7)] is weakly changed and small, as well as that the Massey parameter has a low value (≈ 0.02), both the perturbation theory and the Landau-Zener model are valid and yield coincided results [21] in the nonadiabatic region of interest.

It is seen from Fig. 3 that the process (3.1) turns out to be a multichannel one. The probability P_f^F for a quasimolecule to transfer from an initial state i to a final state f in the case of F possible final channels during a double passage of the nonadiabatic regions is [11]

$$P_f^F=\{2p_f(1-p_f)\}\left\{\prod_{j=1}^{f-1}p_j\right\}\times\left\{1+\sum_{m=1}^{2(F-f)}\prod_{k=1}^{m}(-p_{f+[(k+1)/2]})\right\}, \qquad (3.8)$$

where p_k is the probability of a paired nonadiabatic transition during a single passage of the nonadiabaticity region related to the interaction of the U^i and U^k potential energies; square brackets denote the largest integer of a number. It should be mentioned that a similar expression for P_f^F but in a different form was obtained earlier by Salop and Olson [25] under the same prerequisites. Equation (3.8) has simple physical meaning, that is, the probability P_f^F is a product of three probabilities. The first set of curly brackets in Eq. (3.8) is the probability of a transition $i \rightarrow f$ in a two-channel approximation. The second set of curly brackets represents the probability for a quasimolecule to survive in initial state i in the interval (∞, R_f) [26]. The last set of curly brackets in Eq. (3.8) takes into account the presence of channels lying below channel f and takes on values from 0.5 to 1. Thus, neglecting the states lying below f may lead to a result overstated by a factor of 2, but neglecting the states lying above channel f may lead to a large error.

The total probability p_D for the quasimolecule to decay from the initial state is found to be

$$P_D=-2\sum_{m=1}^{2F}\prod_{k=1}^{m}(-p_{[(k+1)/2]}) \qquad (3.9)$$

and the probability P_S of the quasimolecule to survive in the initial state is

$$P_S=1+2\sum_{m=1}^{2F}\prod_{k=1}^{m}(-p_{[(k+1)/2]})\ . \qquad (3.10)$$

In the present work partial cross sections and partial rate constants are calculated by means of the formulas of Ref. [11]. Those formulas take into account the orbital effect in the attractive initial potential and the fact that the problem is multichannel. The partial values for excitation of $\mathrm{Hg}^+(7p\ ^2P_{3/2})$ (the state with the smallest energy defect $\Delta E_{7p_{3/2}}=0.267$ eV in $\mathrm{He}^+ + \mathrm{Hg}$ collisions) are presented in Figs. 4 and 5. The energy dependence of the cross section is about $\sigma(E) \sim E^{-1/2}$. In contrast, the partial rate constant is close to a constant value over a wide temperature interval, equals $K(T=1000\ \mathrm{K}) = 1.16\times10^{-10}\ \mathrm{cm}^3/\mathrm{s}$, and agrees well with the most reliable experimental value $K^{\mathrm{expt}}_{\mathrm{Hg}^+(7p_{3/2})}=(7\pm4)\times10^{-11}\ \mathrm{cm}^3/\mathrm{s}$ [13].

In the vicinity of the quasi-intersection of the initial $\mathrm{He}^+ + \mathrm{Hg}$ and final $\mathrm{He} + \mathrm{Hg}^+(7p_{1/2})$ potentials the Landau-Zener model is not completely correct and provides estimates greater than experimental data $K^{\mathrm{expt}}_{\mathrm{Hg}^+(7p_{1/2})}=(8\pm3)\times10^{-11}\ \mathrm{cm}^3/\mathrm{s}$ [13].

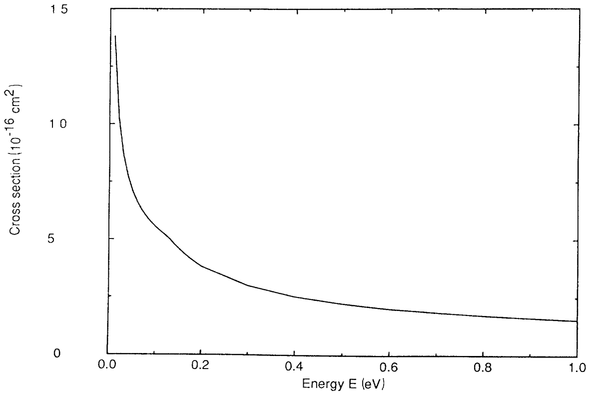

FIG. 4. The calculated energy dependence of the partial cross section for excitation of $\mathrm{Hg}^+(7p\ ^2P_{3/2})$ in $\mathrm{He}^+ + \mathrm{Hg}$ collisions.

It should be mentioned that the partial rate constants of the $\mathrm{Hg}^+(7p)$ states excitation are less than 10% of the total rate constant $K^{\mathrm{expt}}_{\mathrm{total}}=1.6\times10^{-9}\ \mathrm{cm}^3/\mathrm{s}$ [5] for decaying of helium ions in collisions with mercury atoms. In order to specify other excited states the potential energies should be calculated at internuclear distances $R<4$ a.u. In this region the basis set $\{\Psi\}$ should be increased by intermediate wave functions Ψ_m [16]. Because of the large polarizabilities of $\mathrm{He}(2\ ^1S)$ and $\mathrm{He}(2\ ^3S)$ the diabatic potentials of the $\mathrm{He}(2\ ^{1,3}S) + \mathrm{Hg}^+$ intermediate states intersect the diabatic potentials of both initial and final states. This could explain the excitation of the endothermic states [16] that have been experimentally observed in $\mathrm{He}^+ + \mathrm{Cd}$ collisions [14]. The other states which may be included in $\{\Psi_m\}$ correspond to the Beutler states, for instance, $\mathrm{He} + \mathrm{Hg}^+(5d^96s^2)$. There is some guess [10,14] that the diabatic potential of this state crosses both the initial and the final ones, but because of the large energy defect, ≈ 10 eV, it may be at small distances and the question of the potential behavior is still open. Excitation of the $\mathrm{Hg}^+(5d^96s^2)$ state has the rate constant $K^{\mathrm{expt}}_{\mathrm{Hg}^+(5d^96s^2)}=(4\pm1.5)\times10^{-10}\ \mathrm{cm}^3/\mathrm{s}$ [27] and cannot explain the total decaying of He^+ in collisions with Hg.

In accordance with Eq. (3.8) the transition probability and, hence, the partial rate constant of $\mathrm{Hg}^+(7p\ ^2P_{3/2})$ excitation may be decreased by the presence of additional nonadiabatic regions, but this could just improve agree-

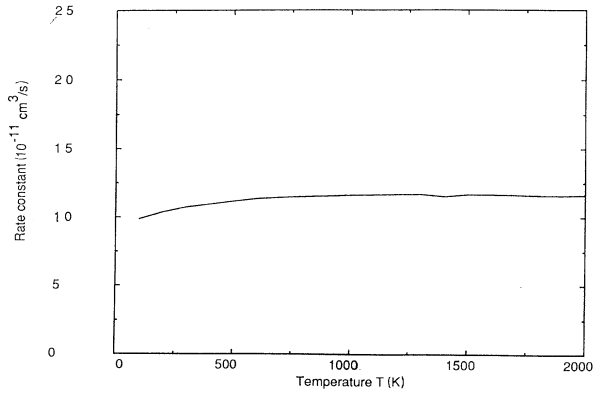

FIG. 5. The calculated temperature dependence of the partial rate constant for excitation of $\mathrm{Hg}^+(7p\ ^2P_{3/2})$ in $\mathrm{He}^+ + \mathrm{Hg}$ collisions.

ment between the theoretical and experimental data. The agreement of the calculated partial rate constant for excitation of $\mathrm{Hg}^+(7p\,^2P_{3/2})$ with the experimental value shows that the present approach provides the correct theoretical treatment of charge exchange with ion excitation at thermal energies.

Thus, the adiabatic potential energies of the $(\mathrm{HeHg})^+$ quasimolecule, the energy dependence of the partial cross section, and the temperature dependence of the partial rate constant for excitation of the $\mathrm{Hg}^+(7p\,^2P_{3/2})$ state in collisions of helium ions with mercury atoms at thermal energies calculated in the present work are sufficiently reliable and agree well with experimental data.

IV. CONCLUSION

In conclusion, let us briefly compare the derived theory with previous ones. In the previous models the exchange couplings have been mainly calculated by means of integrating interelectron interaction over some regions in six-dimensional (6D) configurational space with asymptotically corrected wave functions [9–11]. Multiconfiguration final wave functions have been taken into account in Ref. [15]. An attempt to take into account the operator $\hat{V}_{2A^+}$ has been made in Ref. [13]. The two-electron Holstein-Herring approach has also been used for the exchange interaction $\Delta=2H_{if}$ in terms of an integral over the midplane Σ_1 for an exchanged electron [8,12]

$$\Delta=\int d\mathbf{r}_2\int_{\Sigma_1} d\Sigma_1[\tilde{\Psi}_i\nabla_1\tilde{\Psi}_f-\tilde{\Psi}_f\nabla_1\tilde{\Psi}_i]\;, \tag{4.1}$$

where $\tilde{\Psi}_{i,f}$ are asymptotic analogs of $\Psi_{i,f}$ (for information about the many-electron asymptotic approximation see, for example, [28] and references therein). Reference [12] has examined two cases: low [in fact this is case (a) in Fig. 1(a)] and high (when an orbit radius is much greater than R) excited energies in $M^+(f)$. It has been shown [12] that in the first case the result of applying the Holstein-Herring approach coincides with the 6D integral of interelectron interaction [9–11,15]. In the second case, the exchange interaction has been calculated in the same manner with another corrected wave function [12].

As is mentioned above, Eqs. (2.9) and (2.10) do not provide a strict asymptotic expression as derived from LCAO. The substitution of antisymmetrized asymptotic wave functions $\tilde{\Psi}_{i,f}$ [similarly Eqs. (2.2) and (2.3)] into Eq. (4.1) leads to asymptotic exchange interaction for processes of charge exchange with ion excitation, that is, in a two-electron transition approximation,

$$\begin{aligned}\Delta=C\Bigg[&\int d\mathbf{r}_2\int_{\Sigma_1} d\Sigma_1[\tilde{\Phi}_i(\mathbf{r}_1,\mathbf{r}_2)\nabla_1\tilde{\Phi}_f(\mathbf{r}_1,\mathbf{r}_2)-\tilde{\Phi}_f(\mathbf{r}_1,\mathbf{r}_2)\nabla_1\tilde{\Phi}_i(\mathbf{r}_1,\mathbf{r}_2)]\\&+\int d\mathbf{r}_1\int_{\Sigma_2} d\Sigma_2[\tilde{\Phi}_i(\mathbf{r}_1,\mathbf{r}_2)\nabla_2\tilde{\Phi}_f(\mathbf{r}_1,\mathbf{r}_2)-\tilde{\Phi}_f(\mathbf{r}_1,\mathbf{r}_2)\nabla_2\tilde{\Phi}_i(\mathbf{r}_1,\mathbf{r}_2)]\Bigg]\;,\end{aligned} \tag{4.2}$$

where C is the same coefficient as in Eq. (2.4), $\tilde{\Phi}_{i,f}(\mathbf{r}_1,\mathbf{r}_2)$ are nonantisymmetrized asymptotic two-electron coordinate wave functions, Σ_2 is the same as Σ_1 but for an excited electron. In Refs. [8,12] only the first term in Eq. (4.2) has been taken into account. The last equation can be written as

$$\Delta=C\{\tilde{S}_2\Delta_1+\tilde{S}_1\Delta_2\}\;, \tag{4.3}$$

where $\tilde{S}_{1,2}$ and $\Delta_{1,2}$ are single-electron overlap integrals and exchange interactions of asymptotic wave functions for exchanged and excited electrons, respectively.

Thus, Eqs. (4.2) and (4.3) are a natural asymptotic generalization of Eq. (2.9) and have an asymptotic accuracy. In case (a) the second term in Eqs. (4.2) and (4.3) is vanished in comparison with the first one.

The purpose of this paper has been to propose the theoretical model describing the process of charge exchange with ion excitation at thermal collisions and to apply this model to collisions of helium ions with mercury atoms. The important part of the model is the determination of exchange couplings. The derived approach picks out the dominant terms in the exchange couplings and extracts a mechanism for the process. In the examined process the dominant terms correspond to interaction of valence electrons with a helium ion. The effective potentials are used for these interactions instead of the Coulombic ones. The model yields sufficiently reliable results for the exchange couplings and for the partial rate constant.

ACKNOWLEDGMENTS

The author acknowledges Professor William H. Miller for fruitful discussions and hospitality at the University of California at Berkeley. The author is also grateful to Professor Alexander Dalgarno, Dr. George A. Victor, and Dr. J. Norman Bardsley for stimulating discussions. This work was partially supported by the University of California through EAP and the National Science Foundation through a grand for the Institute for Theoretical Atomic and Molecular Physics at Harvard University and Smithsonian Astrophysical Observatory.

---

*Present address: Department of Theoretical Physics and Astronomy, Russian Pedagogical University, St. Petersburg 191186, Russia.

[1] J. H. Manley and O. S. Duffendack, Phys. Rev. **47**, 56 (1935).
[2] V. I. Bylkin, Opt. Spectrosk. **29**, 1036 (1970) [Opt. Spectrosc. (USSR) **29**, 552 (1970)].
[3] G. J. Collins, J. Appl. Phys. **44**, 4633 (1973).

[4] A. R. Turner-Smith, J. M. Green, and C. E. Webb, J. Phys. B **6**, 114 (1973).

[5] Yu. A. Tolmachev, in *Physics of Electronic and Atomic Collisions,* Proceedings of the 7th All-Union Conference on Physics of Electronic and Atomic Collisions, edited by A. L. Orbeli (Physical-Technical Institute, Leningrad, 1978), p. 53.

[6] P. Baltayan, J. C. Pebay-Peyroula, and N. Sadeghi, J. Phys. B **18**, 3615 (1985).

[7] P. Baltayan, J. C. Pebay-Peyroula, and N. Sadeghi, J. Phys. B **19**, 2695 (1986).

[8] V. N. Ostrovskii, Zh. Eksp. Teor. Fiz. **84**, 1323 (1983) [Sov. Phys. JETP **57**, 766 (1983)].

[9] E. L. Duman, N. P. Tishchenko, and I. P. Shmatov, Dokl. Akad. Nauk SSSR **271**, 853 (1983) [Sov. Phys. Dokl. **28**, 641 (1984)].

[10] I. A. Ivakin, M. I. Karbovanets, and V. N. Ostrovskii, Opt. Spektrosk. **63**, 494 (1987) [Opt. Spectrosc. (USSR) **63**, 288 (1987)].

[11] A. K. Belyaev and S. I. Tserkovnyi, Opt. Spektrosk. **63**, 968 (1987) [Opt. Spectrosc. (USSR) **63**, 569 (1987)]; **66**, 778 (1989) [**66**, 455 (1989)].

[12] M. Ya. Ovchinnikova and D. V. Shalashilin, Khim. Fiz. **7**, 175 (1988).

[13] O. P. Bochkova *et al.* Opt. Spektrosk. **67**, 510 (1989) [Opt. Spectrosc. (USSR) **67**, 298 (1989)].

[14] O. P. Bochkova *et al.,* Abstracts of Contributed Papers, 17th International Conference on Physics of Electronic and Atomic Collisions (Brisbane), edited by I. E. McCarthy, W. R. MacGillivray, and M. C. Standage (North-Holland, Amsterdam, 1991), p. 404; Opt. Spektrosk. **70**, 19 (1991) [Opt. Spectrosc. (USSR) **70**, 9 (1991)].

[15] A. K. Belyaev, A. L. Zagrebin, and S. I. Tserkovnyi, Opt. Spektrosk. **70**, 779 (1991) [Opt. Spectrosc. (USSR) **70**, 453 (1991)].

[16] A. K. Belyaev, Abstracts of Contributed Papers 16th, International Conference on Physics of Electronic and Atomic Collisions (New York), edited by A. Dalgarno, R. S. Freund, M. S. Lubell, and T. B. Lucatorto (North-Holland, Amsterdam, 1989), p. 545; 17th International Conference on Physics of Electronic and Atomic Collisions (Brisbane), edited by I. E. McCarthy, W. R. MacGillivray, and M. C. Standage (North-Holland, Amsterdam, 1991), p. 446.

[17] C. Herring, Rev. Mod. Phys. **34**, 631 (1962).

[18] E. Clementi and C. Roetti, At. Data Nucl. Data Tables **14**, 177 (1974).

[19] I. I. Sobelman, *Introduction to the Theory of Atomic Spectra* (Pergamon, Oxford, 1973).

[20] The electron-binding energy in He is small, 0.077 eV, see, for example, A. A. Radzig and B. M. Smirnov, *Reference Data on Atoms, Molecules and Ions* (Springer-Verlag, Berlin, 1985).

[21] E. E. Nikitin, *Theory of Elementary Atomic and Molecular Processes in Gases* (Oxford University Press, London, 1974).

[22] A. K. Belyaev, A. L. Zagrebin, and S. I. Tserkovnyi, Khim. Fiz. **8**, 435 (1989).

[23] H.-S. Chou and K.-N. Huang, Phys. Rev. A **45**, 1403 (1992).

[24] A. D. McLean and R. S. McLean, At. Data Nucl. Data Tables **26**, 197 (1981).

[25] A. Salop and R. E. Olson, Phys. Rev. A **13**, 1312 (1976).

[26] Like a survival factor in the theory of Penning ionization, see W. H. Miller, J. Chem. Phys. **52**, 3563 (1970).

[27] O. P. Bochkova *et al.,* Abstracts of Contributed Papers, 16th International Conference on Physics of Electronic and Atomic Collisions (New York), edited by A. Dalgarno, R. S. Freund, M. S. Lubell, and T. B. Lucatorto (North-Holland, Amsterdam, 1989), p. 482.

[28] M. I. Chibisov and R. K. Janev, Phys. Rep. **166**, 1 (1988).