Charge exchange involving ion excitation

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The charge exchange $A^+ + B \rightarrow A + B^{+*}$ with excitation, proceeding via the Landau-Zener pseudocrossing of the quasimolecular terms, is considered. A theory that is asymptotic with respect to a large internuclear distance is proposed for the computation of the term splitting at the pseudocrossing point. The final expression contains two factors, one of which is equal to the splitting for the process of charge exchange without excitation, $A^+ + B \rightarrow A + B^+$ and can be computed from the well-known formulas of the asymptotic theory. The second factor describes a transition in the B^+ ion. The results of the cross-section calculation for the process $He^+ + Hg(6s^2) \rightarrow He + Hg^+(7p)$ are compared with the experimental data.

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§1. INTRODUCTION

The charge exchange $A^+ + B \rightarrow A + B^{+*}$ with ion excitation[1)] proceeds with considerable efficiency in slow collisions in the cases when the Landau-Zener pseudocrossing of the quasimolecular terms corresponding to the initial and final states occurs. It determines, in particular, the population of the excited state in He–Zn, He–Cd, and He–Se lasers (see the bibliography in Ref. 1). In experimental investigations[1–3] only the relative probabilities of excitation of the various B^{+*} states are measured in the majority of cases, while the theoretical cross-section estimates are made as if the excitation of the B^+ ion does not occur, which, of course, is not justified. In those cases in which the absolute cross sections can be measured, they are found to differ from such estimates by several orders of magnitude.[4]

The Landau–Zener pseudocrossing of the quasimolecular terms, which is responsible for the process in question, occurs in many cases encountered in practice at large internuclear distances.[1–3] This allows us to use in the computation of the term splitting Δ at the pseudocrossing point a theory that is asymptotic in the internuclear separation R and has the advantage that it is simple and its results are universally applicable. The formulas of the asymptotic theory (see, for example, Smirnov's monograph[4]) have been successfully used in term-splitting and cross-section calculations in the cases of single-electron transfer (ordinary charge transfer), simultaneous transfer of two electrons from one atomic particle to another (two-electron charge transfer), and collisional interchange of two electrons by particles (spin exchange, etc.).

But there has thus far not been a theoretical study of charge exchange with excitation, a process which is a two-electron transition in which one of the electrons goes over from one atomic particle to another, while the second, remaining at the original center, gets excited.[2)] An asymptotic theory of such a process is developed in the present paper and shown to possess some fundamental distinctive features as compared with previously considered cases.

§2. ASYMPTOTIC THEORY

Let us compute the exchange interaction that determines the process

$$A^{Z_a}+B^{Z_b}\rightarrow A^{(Z_a-1)}+B^{(Z_b+1)*}, \tag{1}$$

where Z_a and Z_b are the charges of the colliding atomic particles. Let us introduce the quasimolecule's electronic wave functions $\Psi_{\rm I}$ and $\Psi_{\rm II}$, which go over, as the nuclei are separated (i.e., as $R \rightarrow \infty$), respectively into the initial- and final-state wave functions of the separate atoms. It is sufficient to consider the dependence of $\Psi_{\rm I}$ and $\Psi_{\rm II}$ only on the coordinates of the active electrons undergoing the transitions.

In the case of the single-electron transfer

$$A^{Z_a}+B^{Z_b}\rightarrow A^{(Z_a-1)}+B^{(Z_b+1)} \tag{2}$$

an approximate representation is derived in the asymptotic theory (see, for example, Ref. 5) for the exchange-interaction strength $H_{12}(R)\equiv\Delta(R)/2$ in terms of an integral over the surface S separating the regions where the electron resides when it is in the initial and final states:

$$\Delta=\oint_S dS[\Psi_{\rm I}(\mathbf{r})\mathbf{n}_S\nabla\Psi_{\rm II}(\mathbf{r})-\Psi_{\rm II}(\mathbf{r})\mathbf{n}_S\nabla\Psi_{\rm I}(\mathbf{r})], \tag{3}$$

where $\mathbf{n}_S$ is the unit vector normal to S (we are using atomic units). The functions $\Psi_{\rm I}$ and $\Psi_{\rm II}$ depend in this case only on the coordinates of the single active electron. As S we can choose the plane perpendicular to, and passing through the middle, of the line joining the nuclei of the quasimolecule.

It is not difficult to verify that the general scheme for deriving the formula (3) is the same for the process (3) and leads to the following natural generalization of the formula:

$$\Delta=\oint_{S_1} dS_1\int d\mathbf{r}_2[\Psi_{\rm I}(\mathbf{r}_1,\mathbf{r}_2)\mathbf{n}_{S_1}\nabla_{\mathbf{r}_1}\Psi_{\rm II}(\mathbf{r}_1,\mathbf{r}_2) -\Psi_{\rm II}(\mathbf{r}_1,\mathbf{r}_2)\mathbf{n}_{S_1}\nabla_{\mathbf{r}_1}\Psi_{\rm I}(\mathbf{r}_1,\mathbf{r}_2)]. \tag{4}$$

For simplicity of notation, we shall first assume the electrons to be different. Then S_1 and $\mathbf{n}_{S_1}$ have the above-

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indicated meaning for the coordinate $\mathbf{r}_1$ of the first electron, i.e., the electron that goes over from one particle to the other, and the integration with respect to $\mathbf{r}_2$ is performed over the entire volume.

As is well known, if in the single-electron case (2) the quasimolecular wave functions Ψ_{I} and Ψ_{II} for large R are approximately replaced by the functions of the corresponding separate atoms, the value of the numerical factor in the exponentially decreasing function Δ (R) turns out to be incorrect. But if we use a similar approximation for the two-electron process (1), and, furthermore, represent the two-electron wave functions in the form of a product of single-electron wave functions, then, according to (4), the splitting generally vanishes because of the orthogonality of the second electron's orbitals.[3)] Thus, allowance for the deviation of the quasimolecular wave functions from the wave functions of the separate atoms is of decisive importance here. The indicated difference in the asymptotic theory is described with the aid of correction functions, which are approximately calculated for large R.

Let us introduce the correction functions χ_{I} and χ_{II} defined by the

$$\Psi_{\text{I}}(\mathbf{r}_1,\ \mathbf{r}_2)=\varphi_b(\mathbf{r}_{1b},\ \mathbf{r}_{2b})\chi_{\text{I}}(\mathbf{r}_1,\ \mathbf{r}_2), \tag{5}$$

$$\Psi_{\text{II}}(\mathbf{r}_1,\ \mathbf{r}_2)=\varphi_a(\mathbf{r}_{1a})\Phi_f(\mathbf{r}_{2b})\chi_{\text{II}}(\mathbf{r}_1,\ \mathbf{r}_2). \tag{6}$$

Here the $\mathbf{r}_{ja,\,b}$ are radius vectors of the j-th electron relative to the nuclei A and B respectively and $\varphi_b(\mathbf{r}_1,\mathbf{r}_2)$ is the wave function, of the active electrons in the atomic particle B^{Z_b} and, generally speaking, takes the interelectron correlations into account. In the spirit of the strong-coupling method in collision theory, it is convenient for what follows to represent this function in the form of an expansion in terms of the complete set of wave functions Φ_ν of the ion $\text{B}^{(Z_b+1)}$:

$$\varphi_b(\mathbf{r}_{1b},\mathbf{r}_{2b})=\sum_\nu F_\nu(\mathbf{r}_{1b})\Phi_\nu(\mathbf{r}_{2b}). \tag{7}$$

Here ν is the set of quantum numbers determining the state of $\text{B}^{(Z_b+1)}$: the value $\nu=i$ is assigned to the ground state; the value $\nu=f$, to the final state $\text{B}^{(Z_B+1)*}$ whose wave function enters into the formula (6). When the first electron is removed from the atom B^{Z_b}, the term wth $\nu=i$ is the dominant term in the sum (7):

$$\varphi_b(\mathbf{r}_{1b},\ \mathbf{r}_{2b})\,|_{r_{1b}\to\infty}=\Pi_i(\mathbf{r}_{1b})e^{-\beta r_{1b}}\Phi_i(\mathbf{r}_{2b}),\qquad r_{1b}\gg r_{2b}, \tag{8}$$

where the exponential dependence on r_{1b} has been separated out in the function $F_i(\mathbf{r}_{1b})$: the residual dependence on $\mathbf{r}_{1b}$ is contained in the factor $\Pi_i(\mathbf{r}_{1b})$. It is clear that the quantity β is connected with the first ionization potential I_b of the system B^{Z_b} by the relation $\beta^2/2=I_b$. In the formula (6) $\varphi_a(\mathbf{r}_{1a})$ is the wave function of the active electron in the system $\text{A}^{(Z_a-1)}$ for large $\mathbf{r}_{1a}$ we can separate out an exponentially decreasing factor from this function, too:

$$\varphi_a(\mathbf{r}_{1b})=\Pi_a(\mathbf{r}_{1a})e^{-\alpha r_{1a}}, \tag{9}$$

where α is connected wth the ionization potential I_a of the $\text{A}^{(Z_a-1)}$ system by the relation $\alpha^2/2=I_a$.

As is well known,[5] the exponential dependence of the atomic wave functions on the coordinates leads to a situation in which for large R the integration over $\mathbf{r}_1$ in the expression (3) or (4) is localized around the middle of the internuclear axis ($x_{1a}, y_{1a}\sim 1/(\alpha+\beta)$, $Z_{1a}=Z_{1b}=R/2$, the z axis of the coordinate system coincides with the internuclear axis). The integration over $\mathbf{r}_2$ in (4) is, as can easily be seen, localized in the vicinity of the nucleus B, so that $r_{1b}\gg r_{2b}$. It is in the above-described region of configuration space that we must seek the correction functions.

Let us first consider the computation of the correction function χ_{I} for the initial state. The deviation of this function from unity is caused by the A^{Z_a} particle's field, which is described by the potential

$$U_{\text{I}}(\mathbf{r}_1,\ \mathbf{r}_2)=U_A(\mathbf{r}_1)+U_A(\mathbf{r}_2),\ \ U_A(\mathbf{r}_j)=-Z_a/r_{ja}+Z_a/R. \tag{10}$$

In the expression (10), and in (13) below, we have included only a part of the repulsive potential for the nuclei (that part for which the perturbation potential for $R\to\infty$ does not contain an asymptotic Coulomb term); the remaining part need not be considered in the computation of Δ (R). Let us emphasize that the interelectron interaction has already been taken into consideration in the function $\varphi_b(\mathbf{r}_1,\mathbf{r}_2)$. The perturbation (10) breaks up into a sum of terms that depend only on $\mathbf{r}_1$ and $\mathbf{r}_2$. Accordingly, the correction function can be factorized in the region of configuration space of interest to us, i.e., in the region where the approximation (8) is applicable:

$$\chi_{\text{I}}(\mathbf{r}_1,\mathbf{r}_2)=\chi_{\text{I}}^{(1)}(\mathbf{r}_1)\chi_{\text{II}}^{(2)}(\mathbf{r}_2).$$

The function $\chi^{(1)}$ is required in the region of deep subbarrier (classically forbidden) motion of the first electron, where it is computed by well-known methods of the asymptotic theory:

$$\chi_{\text{I}}^{(1)}(\mathbf{r}_1)=\left[\frac{r_{1a}+r_{1b}-\mathbf{R}\mathbf{r}_{1b}/r_{1b}}{R-\mathbf{R}\mathbf{r}_{1b}/r_{1b}}\right]^{Z_a/\beta}\exp\left(-\frac{Z_a}{\beta R}r_{1b}\right). \tag{11}$$

The correction $\chi_{\text{I}}^{(2)}$ should be found in the vicinity of the nucleus B, where the electron motion is classically allowed. Here we can use ordinary perturbation theory, the first order of which corresponds, in our notation, to

$$\chi_{\text{I}}^{(2)}(\mathbf{r}_2)=1+\frac{1}{\Phi_i(\mathbf{r}_{2b})}\sum_{\nu\neq i}\frac{\langle\Phi_\nu|U_A(\mathbf{r}_2)|\Phi_0\rangle}{E_i-E_\nu}\Phi_\nu(\mathbf{r}_{2b}), \tag{12}$$

where E_ν is the energy of the state Φ_ν.

In the final state the difference between the Hamiltonian of the quasimolecule and that of the separated atoms is connected with a potential that can be conveniently divided into two terms as follows:

$$U_{\text{II}}(\mathbf{r}_1,\mathbf{r}_2)=\left(-\frac{Z_b+1}{r_{1b}}+\frac{Z_b+1}{R}\right)+\left(-\frac{Z_a}{\mathbf{r}_{2a}}+\frac{Z_a}{R}+\frac{1}{|\mathbf{r}_{1b}-\mathbf{r}_{2b}|}-\frac{1}{r_{1b}}\right). \tag{13}$$

The correction function can be factorized here, too:

$$\chi_{\text{II}}(\mathbf{r}_1,\mathbf{r}_2)=\chi_{\text{II}}^{(1)}(\mathbf{r}_1)\chi_{\text{II}}^{(2)}(\mathbf{r}_2).$$

The quantity $\chi_{\text{II}}^{(1)}$ is computed similarly to $\chi_{\text{I}}^{(1)}$, with the first term in the expression (13) taken into account as a perturbing potential. The second term in (13) does not have a Coulomb asymptotic form at large r_{1b}, and can therefore be neglected in the determination of $\chi_{\mathrm{II}}^{(1)}$. It should be used as a perturbation in the calculation of $\chi_{\mathrm{II}}^{(2)}$ from a formula similar to (12).

In the evaluation of the integral (4) for the splitting, the dominant contribution in the integration over S_1 is made by the neighborhood of the point $\mathbf{r}_{1b} = \mathbf{R}/2$ (the vector $\mathbf{R}$ is directed from the nucleus B to the nubleus A). This value of $\mathbf{r}_{1b}$ should be used in the formula for $\chi_{\mathrm{II}}^{(2)}$. After this, the integrand can be factorized, and the integrations over $\mathbf{r}_1$ and $\mathbf{r}_2$ performed separately. In the lowest order of the asymptotic theory the result fas the form

$$\Delta=\Delta_1\frac{1}{E_f-E_i}\left\langle \Phi_f\left|\frac{1}{|\mathbf{R}/2-\mathbf{r}_b|}-\frac{2}{R}\right|\Phi_i\right\rangle, \tag{14}$$

where the factor Δ_1 is calculated from the well-known formulas of the asymptotic theory for the single-electron charge transfer, with the excitation of the $\mathrm{B}^{(Z_b+1)}$ particle ignored. The remaining factors contain only the characteristics of the transition in the $\mathrm{B}^{(Z_b+1)}$ ion from the ground state into the excited state in question.

A generalization of the theory, on which we shall not dwell here, shows that the form of the final result remains unchanged when we take account of the indistinguishability of the electrons (i.e., when we symmetrize the wave functions) and also when we allow for the spins of the atomic cores. A refinement of the theory leads to the result that the functions Φ_i and Φ_f in the matrix element in (14) should now be taken to be the many-electron wave functions of the $\mathrm{B}^{(Z_b+1)}$ system.

For the potential in the matrix element in (14) we should use the multipole expansion for large R:

$$\Delta=\Delta_1\frac{1}{E_f-E_i}\sum_{l=1}^{\infty}\left(\frac{2}{R}\right)^{l+1}\langle\Phi_f|r_{2b}{}^{l}P_l(\cos\theta_{2b})|\Phi_i\rangle, \tag{15}$$

where $P_l(z)$ is a Legendre polynomial and the angle θ_{2b} is the spherical coordinate of the second electron in a system with the origin located in the nucleus B and an axis oriented along the internuclear axis. Actually, the sum (15) always contains only one term with $l=\Delta l_2$, where Δl_2 is the change that occurs in the orbital angular momentum of the electron when the transition in question occurs in $\mathrm{B}^{(Z_b+1)}$. In particular, for the transition with $\Delta l_2 = 1$ we arrive at an ordinary dipole matrix element, which is connected with the oscillator strength, and is known in many cases.

In the case of an S-S junction the formula (15) leads to a null result. To compute the splitting here, we should seek the correction function for the second electron with allowance for the terms of the second-order perturbation theory, which yields

$$\Delta=\Delta_1\frac{1}{E_f-E_i}\frac{4}{R^2}\sum_{\nu}v_{i\nu}v_{\nu f}\left(\frac{Z_a}{E_i-E_\nu}+\frac{Z_a-4}{E_f-E_\nu}\right), \tag{16}$$

$$v_{\nu\nu'}=\langle\Phi_\nu|r_{2b}\cos\theta_{2b}|\Phi_{\nu'}\rangle,$$

where the summation is extended to include those intermediate states for which $v_{i\nu}\neq 0$.

§3. DISCUSSION AND COMPARISON WITH EXPERIMENT

In the asymptotic theory the term splitting is expressed in terms of the asymptotic form of the wave function of the atom with one electron removed. The latter function is expressed in turn in terms of the wave function of the ground state of the ionic core. Therefore, our expression (15) for the splitting contains a matrix element that connects wave functions of the ion. In an earlier paper by Bylkin[5] there arose matrix elements between single-electron orbitals of the ion and a core electron in the atom. Their nonorthogonality led to the appearance of corresponding (scrambling-type) overlap integrals, which are responsible, in particular, for the s–s transitions that occur when the ion is excited. The scrambling effects (which, generally speaking, are comparable in magnitude to the correlation effects) do not occur in the consistently asymptotic theory. Let us emphasize that no assumptions need be made in the theory developed in the present paper about the role of the correlation and the applicability of the single-electron approximation for the description of the atom B.

Another distinctive feature of the theory expounded above is the use of different methods in the computation of the correction functions for the various regions of the electron motion.

In the region of asymptotically large internuclear distances the splitting given by the formula (15) is significantly smaller than Δ_1, and decreases rapidly with increasing Δl_2.

We have[4] computed the splitting that determines the process:

$$\mathrm{He}^+(1s)+\mathrm{Hg}_0(6s^2)\rightarrow\mathrm{He}(1s^2)+\mathrm{Hg}^+(7p),$$

whose absolute cross section has been measured.[3] The term corresponding to the final state was assumed to be horizontal, and the polarization interaction in the initial state was taken into account. The oscillator strength for the transition in the Hg^+ ion was estimated in the Bates–Damgaard approximation. At room temperature the velocity of the atoms at the pseudocrossing point of the terms ($R_0 = 6.4a_0$) is primarily determined by the acceleration of the atoms on account of the polarization attraction in the initial channel. The computed Landau-Zener transition cross section $\sigma = 1.5\times10^{-16}$ cm^2 is higher than the experimental value[3] $\sigma = (0.9 - 1.3)\times10^{-17}$ cm^2. The latter, as discussed in Ref. 3, is apparently much too low, owing to the indeterminacy of the branching ratio for the radiative decay of the final excited state of Hg^+ (let us note that earlier experimental estimates yielded higher values: according to Ref. 7, $\sigma = 1.6\times10^{-16}$ cm^2, while according to Ref. 2, $\sigma = 8.5\times10^{-15}$ cm^2). On the other hand, the simplest theoretical estimate presented above is an overestimate because it does not take account of the presence of competing excitation channels for the ion. There competing channels may correspond to states with an excited d electron in Hg^+ (the corresponding lines have not been identified in the spectrum of the Hg^+ ion). The lack of data on the energies of these states makes it impossible for us to take them into consideration in the calculation.

[1] In the literature the indicated process is also called charge transfer into an excited state. But the latter term seems to us to be more justified for the reaction $A^+ + B \rightarrow A^* + B^+$.

[2] In Bylkin's paper,[5] which is devoted to the investigation of the process in question, a consistent asymptotic theory is not constructed, and the splitting calculation is not carried through (see the discussion below).

[3] The possible role of the nonorthogonality of the orbitals of the second electron in the B^{Z_b} and $B^{(Z_b+1)}$ systems is discussed below.

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