Asymptotic theory of the nonresonant charge-transfer process

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In the framework of an asymptotic theory, analytic expressions are found for the probability and cross section for nonresonant charge-transfer processes as functions of the parameters describing the states of the colliding particles before and after collision. There is good agreement between the analytic and numerical calculations of the charge-transfer probability in the range of impact parameters ρ that makes the main contribution to the cross section for these processes and for which the use of the asymptotic theory is justified, i. e., the range in which $\gamma\rho \gg 1$.

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1. One of the possible reaction channels when ions and atoms collide is the charge-transfer reaction, i.e., the transition of an electron from one atom core to another:

$$A^+ + B \to A + B^+ + \Delta E. \tag{1}$$

Atoms in excited states can be produced as a result of the transfer of charge from one atom to another, and this makes possible the efficient production of beams of neutral atoms in excited states. A particularly interesting case is that of so-called quasiresonance charge transfer, in which the electronic energy of the system is almost unchanged in the collision, i.e., when $\Delta E \ll 1$. [Here and throughout the atomic system of units (a.u.) with $e = \hbar = m - 1$ is used.] The large cross sections corresponding to these processes distinguish them from a number of other physical phenomena that go on among atoms and positive and negative ions in gas discharges, in the upper layers of the atmosphere, and in low-temperature plasmas. Therefore there has been a great deal of theoretical and experimental research on these processes.[1]

Since these processes correspond to almost resonant conditions of charge transfer, we shall assume that there is interaction only between two states of the system such that transitions between them leaves the electronic energy of the system practically unchanged before and after the collision transitions to other states involve a more considerable energy consumption, so that their probabilities are adiabatically improbable and they can be neglected. In this case the nonstationary wave function that describes the behavior in time of the system $(AB)^*$ can be written in the form

$$\Psi(t) = C_1(t)\varphi_1(r_a)e^{-iE_1t} - iC_2(t)\varphi_2(r_b)e^{-iE_2t}, \tag{2}$$

where $\varphi_1(r_a)$ and $\varphi_2(r_b)$ are the atomic wave functions which determine the behavior of the electron on the atoms A and B, respectively; E_1 and E_2 are the binding energies of an outer electron on atoms A and B; and $C_{1,2}(t)$ are the probability amplitudes describing transitions of the electron between the atomic cores A and B.

The coefficients C_1 and C_2 satisfy the system of equations

$$\begin{aligned} &\dot{C}_1 = -fC_2, \quad \dot{C}_2 = f^*C_1, \\ &f = \frac{1}{2}\Delta \exp\left(-i\int_{-\infty}^{t} \varkappa dt'\right); \\ &\Delta = 2H_{12}, \quad \varkappa = H_{11} - H_{22}, \quad H_{ik} = \langle \varphi_i | \hat{H} | \varphi_k \rangle. \end{aligned} \tag{3}$$

Here $\hat{H}$ is the Hamiltonian which describes the system of colliding atoms (1), and the case is considered in which the relative velocity of the collision of the atomic particles is much smaller than the speed of the electron in orbit on atom A or atom B:

$$v < (2E_1)^{1/2} \approx (2E_2)^{1/2}. \tag{4}$$

The most general time dependences of the matrix elements $\Delta(t)$ and $\kappa(t)$ for which the system of equations (3) can be solved exactly are well known.[2-4] These model solutions are widely used in the interpretation of nonresonance processes, including the nonresonant charge-transfer processes (1) considered here. In this procedure there is no attention given to the fact that the model solutions[2] do not agree in the limiting case with the results obtained in the framework of perturbation theory. This is because the representation of the nondiagonal matrix element $H_{12} = \frac{1}{2}\Delta(t)$ by an exponential time dependence

$$\Delta = Ae^{-\alpha t}$$

is not justified in the case of large impact parameters ρ, which give the main contribution to the charge-transfer cross section for small collision velocities[1)]

$$\sigma = 2\pi \int_0^\infty W(\rho)\rho d\rho, \tag{5}$$

where $W(\rho) = |C_2(t = \infty)|^2$ is the probability of nonresonant charge transfer.

This approximation for the nondiagonal matrix element is unsuitable in the region of nonadiabatic transition, and leads in the final analysis to errors in the cross section for nonresonant charge transfer, especially for small collision velocities. This was first pointed out by Olson,[5] who solved the system of equations (3) by numerical methods, assuming that in the region of nonadiabatic transition the matrix elements have the behavior

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$\varkappa=\text{const}, \quad \Delta=Ae^{-\gamma R}.$

This conclusion is confirmed by other numerical calculations.[6]

In the present paper simple analytic expressions for the probability and cross section of quasiresonant charge-transfer processes (1) are derived in the framework of the asymptotic theory ($\gamma_\rho \gg 1$); the results are rather different from the well known model solutions,[2-4] but are free from the contradictions that have been mentioned.

2. We solve the system of equations (3) in the framework of the asymptotic method, assuming that the quasiresonant transitions (1) occur at distances between the colliding particles that are large compared with their diameters. In this case we can use for the matrix elements in Eqs. (3) the asymptotic values of the energy difference of the adiabatic terms, $\Delta E = E_1 - E_2$, and the energy $\Delta(R)$ of the exchange interaction[7]:

$$\varkappa = E_2 - E_1 - \frac{\alpha_1 - \alpha_2}{2R^4}, \tag{6}$$

$$\Delta = AR^\beta e^{-\gamma R}, \tag{7}$$

where α_i are the polarizabilities of the atoms A and B, $\gamma = (2E_1)^{1/2} \approx (2E_2)^{1/2}$, E_i are the ionization energies of the atoms A and B, $\beta = 2/\gamma - 1$, $A = A_1 A_2 e^{-1/\gamma}$. amd A_1 are the well known asymptotic coefficients which describe the behavior of outer electrons on atoms A and B.

Since the nondiagonal matrix element Δ which gives the nonadiabatic coupling between the initial and final states depends exponentially on the change of the running parameter with respect to which one integrates the system (3), it can be expected that the transition between the initial and final states occurs in a narrow range of variation of this parameter. Furthermore the position of the transition region is determined by the distance R_0 at which the function $f^*(R_0)$ in Eq. (3) takes its maximum value.

To find the position R_0 of the region of transition and its width we simplify the expressions for the matrix elements $\varkappa$ and Δ:

$$\varkappa = E_1 - E_2 = \text{const}, \quad \Delta = A\rho^\beta e^{-\gamma R}, \tag{8}$$

where ρ is the impact parameter and R is the distance between the colliding particles. The approximation (8) is justified if the transition occurs at large distances between the particles ($\gamma R \gg 1$).

We introduce new symbols

$$R = \rho \operatorname{ch}\xi, \quad t = v^{-1}\rho \operatorname{sh}\xi; \quad -\infty \leqslant \xi \leqslant \infty, \tag{9}$$

and write the system of equations in the form

$$\frac{d}{d\xi}C_1 = -f_1 C_2, \quad C_1|_{\xi=-\infty} = 1,$$
$$\frac{d}{d\xi}C_2 = f_2 C_1, \quad C_2|_{\xi=-\infty} = 0; \tag{10}$$

$$f_1 = f_2^* = \frac{A\rho^{\beta+1}}{2v} \operatorname{ch}\xi \exp\left[-\frac{\gamma\rho}{\cos\alpha}\operatorname{ch}(\xi + i\alpha)\right], \quad \operatorname{tg}\alpha = \frac{\varkappa}{\gamma v}. \tag{11}$$

It is obvious that the main contribution to the solution of Eqs. (10) will come from the range of variation of ξ where f_2 takes its maximum value, i.e., near the point $\xi_0 = i\alpha$. Since the quantities f_1 and f_2 go to zero exponentially as $\xi \to \pm\infty$, the integration over ξ from $-\infty$ to $+\infty$ is equivalent to integration over the ray z that goes through the point $\xi_0 = i\alpha$ parallel to the real axis:

$$\xi = z + i\alpha, \quad -\infty \leqslant z \leqslant +\infty.$$

Furthermore, in the range of the variable z, $|z| \leqslant z_0 \ll 1$, which gives the main contribution to the solution of the system (10), the hyperbolic cosine in the coefficient of the exponential function in Eq. (11) is slowly varying and can be treated as a constant,

$$\operatorname{ch}\xi \approx \cos\alpha = (1 + \varkappa^2/\gamma^2 v^2)^{-1/2}.$$

The range $|z| < z_0$ is easily determined from the condition $\gamma\rho z_0^2/2\cos\alpha \sim 1$, i.e.,

$$z_0 \sim (2\cos\alpha/\gamma\rho)^{1/2} \ll 1 \quad \text{at} \quad \gamma\rho \gg 1.$$

Let us go over from the system of equations (10) to the second-order differential equation for the amplitude C_2:

$$\frac{d^2C_2}{dz^2} - \frac{\dot f_2}{f_2}\frac{dC_2}{dz} + f_1 f_2 C_2 = 0. \tag{12}$$

In the narrow range $|z| \leqslant z_0$ we can write approximately

$$f_1 f_2 \approx B^2 f_2^2,$$

and determine the constant B from the relation

$$B = \int_0^\infty (f_1 f_2)^{1/2} dz \Big/ \int_0^\infty f_2 dz = \exp\left(\frac{\gamma\rho\sin^2\alpha}{2\cos\alpha}\right) \Big/ \cos\alpha. \tag{13}$$

The system of equations

$$\frac{d^2C_2}{dz^2} - \frac{\dot f_2}{f_2}\frac{dC_2}{dz} + Bf_2^2 C_2 = 0 \tag{14}$$

with the initial conditions

$$C_2(z \to -\infty) = 0, \quad \frac{dC_2}{dz}(z \to -\infty) = f_2$$

has the solution

$$C_2 = B^{-1}\sin\left(B\int_{-\infty}^{z} f_2 dz'\right). \tag{15}$$

Accordingly, the result (15) gives for the probability of the nonresonant charge transfer (1) the expression (at $\gamma\rho \gg 1$)

$$W = |C_2(z=\infty)|^2 = \exp\left[-\frac{\varkappa^2\rho}{\gamma v^2(1+\varkappa^2/\gamma^2v^2)^{1/2}}\right]\sin^2\Phi_0 \Big/ \left(1 + \frac{\varkappa^2}{\gamma^2 v^2}\right) \tag{16}$$

$$\Phi_0 = \frac{A}{v}\left(\frac{\pi}{2\gamma}\right)^{1/2}\rho^{\beta+0.5}\exp\left[-\gamma\rho\left(1+\frac{\varkappa^2}{2\gamma^2v^2}\right)\left(1 + \frac{\varkappa^2}{\gamma^2v^2}\right)^{-1/2}\right] \Big/ \left(1+\frac{\varkappa^2}{\gamma^2v^2}\right)^{1/4}. \tag{17}$$

3. Let us analyze the solution (16), (17). If the argument of the sine, i.e., the phase Φ_0, is very small for all values of

$$\Phi_0 \ll 1$$

the parameters ρ, Eq. (16) goes over into an expression which is found in the framework of perturbation theory:

$$W=\left|2\int_0^\infty f_2 dz\right|^2$$
$$=A^2\frac{\pi}{2\gamma}\frac{\rho^{2\beta+1}}{v^2(1+\varkappa^2/\gamma^2v^2)^{\beta/2}}\exp\left(-2\gamma\rho\left(1+\frac{\varkappa^2}{\gamma^2v^2}\right)^{1/2}\right).$$

A characteristic quantity in this problem is the Massey parameter $\mu=\mathcal{H}/\gamma v$. If $\mu=0$, the solution (16) is the same as the resonant charge-transfer cross section given in Ref. 7, when $\varkappa=0$:

$$W=\sin^2\Phi_0'(\rho).$$

For $\mu\ll1$ Eqs. (16) and (17) can be simplified:

$$W=\exp(-\gamma\rho\mu^2)\sin^2\Phi_0',$$

where $\Phi_0'=v^{-1}(\pi\rho/2\gamma)^{1/2}\Delta(\rho)$ is the phase which determines the frequency of resonant charge transfer.

Let us compare the analytic expression (16) with the numerical calculations of Ref. 6. Figure 1 shows a comparison of the charge-transfer probabilities for $\mu=0.262$, $\varkappa=9.3\cdot10^{-3}$, $v=1/12$, plotted against the impact parameter ρ, as found by numerical methods amd from Eqs. (16) and (17). As was to be expected, in the limit $\gamma\rho\gg1$ the numerical and analytical calculations coincide. For small values of the quantity $\gamma\rho$ the charge-transfer probability oscillates rapidly, and the phases of the numerical and analytic calculations are not the same, because Eq. (17) cannot be used to determine the phase at $\gamma\rho\lesssim1$. It is obvious, however, that this fact cannot have much effect on the value of the cross section (5), since the main contribution to the cross section comes from impact parameters ρ at which the probability oscillates rapidly between 0 and 1, and independently of the actual phase values we can replace the rapidly oscillating function with its average value, $\langle\sin^2\Phi_0\rangle=\frac{1}{2}$.

Accordingly, in this range variation of the impact parameter, the probability of nonresonant charge transfer can be written in the form

$$W\approx\frac{1}{2(1+\mu^2)}\exp\left[-\gamma\rho\frac{\mu^2}{(1+\mu^2)^{1/2}}\right],\quad\rho\leqslant\rho_0. \tag{18}$$

The bounding value of the impact parameter, $\rho=\rho_0$, is to be set just as it is in the case of resonant charge transfer[7]:

$$\Phi_0(\rho_0)=0.28. \tag{19}$$

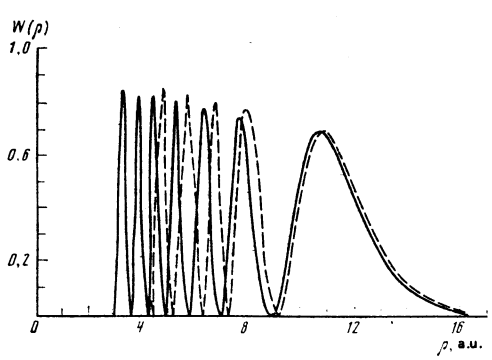

FIG. 1. Comparison of numerical (Ref. 6) and analytic [Eqs. (16) and (17)] calculations of the probability of nonresonant charge transfer, $Li^+ + Na \to Li + Na^+$, with $\varkappa=9.3\cdot10^{-3}$, $v=1/12$, $\mu=\varkappa/\gamma v=0.262$. The solid curve shows the results calculated from Eqs. (16) and (17), and the dashed curve, those of the numerical calculations.

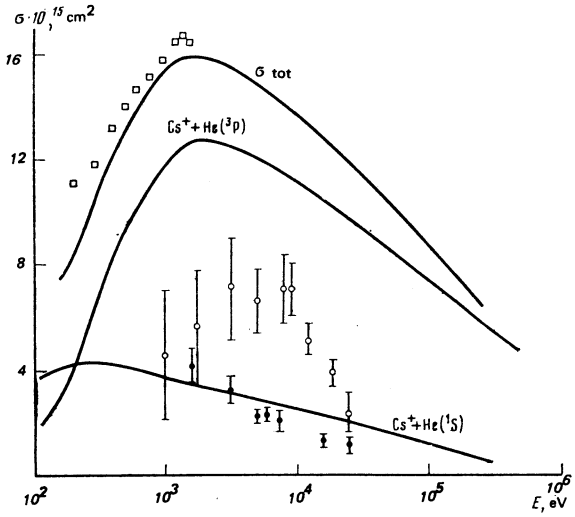

FIG. 2. Cross sections for nonresonant charge transfer $He^+ + Cs \to He(^1S, ^1P, ^3S, ^3P) + Cs^+$. Solid circles show partial cross sections σ_s (Ref. 8), open circles, σ_t (Ref. 8), and squares, total cross sections (Refs. 9, 10); the solid curves are from the theory.

4. Substituting Eqs. (16)–(18) in Eq. (5), we get an expression for the cross section for the nonresonant charge transfer (1) as a function of the parameters $\mu=\varkappa/\gamma v$, $\gamma=(\gamma_1+\gamma_2)/2$, and $A=A_1A_2e^{-1/\gamma}$ which determine the initial and final states of the system of colliding atomic particles [cf. Eq. (7)]:

$$\sigma(\mu,\gamma)=\frac{\pi}{\gamma^2\mu^4}\left[1-\exp\left[-\frac{\gamma\rho_0\mu^2}{(1+\mu^2)^{1/2}}\right]\left(1+\frac{\gamma\mu^2\rho_0}{(1+\mu^2)^{1/2}}\right)\right]. \tag{20}$$

$$\Phi_0(\rho_0)=\frac{A}{v}\left(\frac{\pi}{2\gamma}\right)^{1/2}\frac{\rho_0^{2/\gamma-0.5}}{(1+\mu^2)^{1/4}}\exp\left[-\gamma\rho_0\frac{1+{}^1/_2\mu^2}{(1+\mu^2)^{1/2}}\right]=0.28. \tag{21}$$

As $\mu\to0$ the cross section (20) behaves like that for resonant charge transfer:

$$\sigma_{ex}(\mu\to0)=\pi\rho_0^2/2.$$

When $\mu\approx0.5(\gamma\rho_0)^{-1/2}<1$ the cross section takes its maximum value

$$\sigma_{max}=0.43\pi\rho_0^2=0.86\sigma_{rct}.$$

As $\mu\to\infty$ we must take into account the curvature of the trajectories of the colliding particles

$$\frac{dR}{dt}=v\left(1-\frac{\rho^2}{R^2}-\frac{U(R)}{E}\right)^{1/2}.$$

It is easy to show that if the motion of the nuclei occurs in a central potential $U(R)$ which varies according to an exponential law, then as $\mu=\varkappa/\gamma v\to\infty$ the behavior of the cross section for nonresonant charge transfer is given by

$$\sigma\approx\frac{\pi}{\gamma^2\mu^4}\exp\left(-\frac{\text{const}}{v}\right).$$

Let us check our calculations (20) and (21) with a specific example. We consider the process of nonreso-

TABLE I.

States of He	Ionization energy, a.u.	$\varkappa = I_{He} - I_{Cs}$, a.u.	$\gamma = (\gamma_1 + \gamma_2)/2$, a.u.	$A = A_1 A_2$, a.u.
^3S	4.77	0.032	0.564	0.27
^1S	3.97	0.003	0.538	0.18
^3P	3.62	−0.01	0.526	0.27
^1P	3.37	−0.019	0.517	0.18

nant charge transfer from a helium atom to a cesium atom:

$$He^+ + Cs = He^*(^1S, ^1P, ^3S, ^3P) + Cs^+ + \Delta E. \quad (22)$$

The basic parameters needed for the calculation of the cross sections for the charge transfer (22) are shown in the table.

Figure 2 shows a comparison of the cross sections for the nonresonant charge transfer (22) calculated from Eqs. (20) and (21) with experimental values of these cross sections.[8-10] The charge transfer leads to production of helium atoms in excited states (^1P, ^3P) and in metastable states (^1S, ^3S). The total charge-transfer cross section is

$$\sigma_{tot} = {}^1/_4\sigma_s + {}^3/_4\sigma_t;$$
$$\sigma_s = \sigma(^1P) + \sigma(^1S), \quad \sigma_t = \sigma(^3P) + \sigma(^3S).$$

5. Accordingly, in the framework of the asymptotic approximation we have succeeded in finding an analytic solution of a system of two equations which describes the process of nonresonant charge transfer (1). There is good agreement between numerical and analytical calculations of the charge-transfer probability in the range of impact parameters that makes the main contribution to the cross section for these processes and for which the use of the asymptotic method is justified, i.e., for which $\gamma\rho \gg 1$. A virtue of this method is the simple and explicit form of the final results for the nonresonant charge-transfer cross sections. The universal nature of the dependence of the cross sections on the parameters that describe the state of the system before and after the collision makes it possible to determine quickly and reliably the cross section for any specific process of charge transfer with a small resonance defect.

[1)] We note that for heavy particles, even with slow collisions, $v < 1$, the paths of the nuclei can be regarded as rectilinear, i.e., $R = (\rho^2 + v^2t^2)^{1/2}$, where ρ is the impact parameter, v is the relative velocity, and t is the time, $-\infty \leqslant t \leqslant \infty$.

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