Charge exchange in slow collisions of multiply charged ions with atoms

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Single-electron charge exchange between ions having a charge $Z > 6$ and atoms is considered at relative velocities $v < Z^{1/2}$. An analytic method is developed for the solution of a multilevel problem that is a generalization of the decay model and of the approximation of nonadiabatic coupling between two states. Expressions are obtained for the reaction-product distributions in the principal and angular quantum numbers. The calculated total cross sections agree well with the experimental data on charge exchange of hydrogen atoms and molecules with nuclei. The theory describes the oscillations of the total cross section against the background of a monotonic growth as the charge is increased.

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INTRODUCTION

In slow collisions of a multiply charged ion with an atom the dominant process is single-electron charge exchange with capture of one of the outer electrons of the atom by highly excited states of the atom. From among the methods developed by now to analyze this process, notice should be taken of two approaches that make it possible to establish the general dependences of the transition probabilities and of the cross sections on the physical parameters of the problem. The first is based on the Landau-Zener theory,[1,2] which singles out the quantum transitions in an isolated region where the adiabatic terms of the atom + ion system intersect. The second takes into account the quasistationary character of the state of the atomic electron in the slowly varying field of the ion, and leads to the decay model[4,5] of the charge-exchange process. The various existing models and practical calculations (see, e.g., the review[6]) take one of the two indicated charge-exchange models into account. This leads, even for purely Coulomb system (H atom + nucleus with charge Z), to contradictions in the dependences of the cross sections on the relative velocity. In the low-velocity limit, the theory of nonadiabatic transitions in isolated regions of term quasicrossings leads to an exponential decrease of the cross sections,[7] whereas the decay model calls for them to increase logarithmically.[5,8] It is important that this difference is realized in the ion kinetic-energy region that is of interest for astrophysical and laboratory applications.

It is useful to develop for the study of the charge-exchange process a more general approach that combines the rational elements of the two foregoing ones and establishes the relation between them. This problem is solved in the present paper for the charge exchange of multiply charged ($Z \geqslant 10$) ions with atoms at relative velocities $v < Z^{1/2}$; we use the general properties of the quasiclassical motion of a highly excited electron in a finite reaction channel. The solution obtained (§§ 1,2) reflects, in the low-velocity limit, the dominant influence of quantum transitions in isolated level-crossing terms with allowance for the proximity of the turning point to the crossing point, and yields a natural generalization of the decay model with increasing velocity.

The departure from the framework of pure Coulomb system leads, on account of the change of symmetry, to the presence of a larger number of quasicrossings, so that the applicability of the generalized decay model proposed in the present paper is extended to lower velocities (§ 3). The question of the distribution of the reaction products among the orbital quantum numbers is also connected with the symmetry properties, and the answer to it leads to a difference between the results for systems with and without Coulomb symmetry (§ 1).

Other characteristics of the charge exchange process, determined mainly by the binding energy of the initial and final states and by the relative velocity, are common to all systems. These include the distribution of the reaction products in the principal quantum numbers, as well as the nature of the oscillations of the total charge-exchange cross sections against the background of their growth with increasing ion charge, recently investigated experimentally[9] at low velocities. The solution of the oscillation problem (§ 3), by confirming the accuracy (within a factor of 2) of our earlier calculation,[10] shows that their behavior is closely connencted with the discrete character of the multiply charged ions.

§1. FORMULATION OF PROBLEM AND DERIVATION OF THE BASIC EQUATIONS

When analyzing the charge exchange

$$A + B^{+z} \to A^{+} + B_{n,q}^{+(z-1)}, \tag{1}$$

where n is the principal quantum number and q is the set of angular (and spin) quantum numbers of the produced ion, we shall consider the interaction of the initial state of the system (i) with a group of final states (nq) corresponding to excited states of the ion ($n \gg 1$) in the internuclear distance range $R < (2Z)^{1/2}$. In this region we can use a diabatic basis,[7,8] which leads to the following system of equations for the probability amplitudes:

$$i\frac{da_i}{dt} = \sum_{n,q} V_{in^q}(R) \exp\left[-i\int^t \omega_{in^q}(t')\,dt'\right] b_{nq}, \tag{2}$$

$$i\frac{db_{nq}}{dt} = V_{ni^q}(R) \exp\left[i\int^t \omega_{in^q}(t')\,dt'\right] a_i, \tag{3}$$

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$$|a_i(-\infty)|=1, \quad b_{nq}(-\infty)=0, \tag{4}$$

where $V^q_{in}(R)$ is the exchange interaction of the initial state with the final state, and ω^q_{in} is the energy distance between these states. It is assumed here that the main contribution to the solution of the dynamic problem (2) and (3) is made by the vicinities of the crossing points of the terms $\omega^q_{in}(R^q_n)=0$. In these regions the exchange-interaction coefficients V^q_{in} are determined uniquely in the nultilevel problem [8,11,12] at relative velocities $v \ll Z^{1/2}$. At the crossing points themselves they are equal to half the exchange spliting of the two-center (adiabatic) electronic terms, and the electronic wave functions used for their calculation are orthogonal to within exponentially small corrections.

A number of the properties of the solutions of the system (2), (3) can be obtained under rather general assumptions concerning its coefficients. Since the motion of the highly excited electron is quasiclassical, the dependence on the angular quantum numbers q in the exchange interaction V^q_{in} can be separated as a factor, so that

$$V_{in}{}^q(R)=f(q,n)\,V_{in}(R). \tag{5}$$

The actual choice of the quantum number q and the form of the coefficients f are determined by the symmetry of the system, including the spin symmetry. In particular, for LS coupling of the angular momenta this problem was solved in Refs. 11 and 12. In most cases the dependence of ω^q_{in} on the angular quantum numbers can be neglected, and we can put

$$\omega_{in}{}^q(R)=\omega_{in}(R). \tag{6}$$

In the approximation (5) and (6), a simple algebraic transformation reduces the system (2), (3) to the form

$$i\frac{da_i}{dt}=\sum_n V_n(R)\exp\left[-i\int^t \omega_{in}(\tau)\,d\tau\right]b_n, \tag{7}$$

$$i\frac{db_n}{dt}=V_n(R)\exp\left[i\int^t \omega_{in}(\tau)\,d\tau\right]a_i, \tag{8}$$

where

$$V_n(R)=\left[\sum_q f^2(q,n)\right]^{1/2}V_{in}(R). \tag{9}$$

$$b_{nq}=f(q,n)\left[\sum_{q'} f^2(q',n)\right]^{-1/2}b_n, \tag{10}$$

and the amplitudes b_n are independent of q.

Equation (10) allows us to express the partial cross sections with respect to the angular quantum numbers in term of the total cross section for populating a level with a given n:

$$\sigma_{nq}=f^2(q,n)\sigma_n\Big/\sum_q f^2(q',n). \tag{11}$$

It is important that (22) does not depend on the method of solving the dynamic problem.

For pure Coulomb systems (e.g., H(1s) + Z), the conditions (5) and (6) are elementary. Owing to the symmetry, the initial term interacts only with the terms corresponding to the Stark states with $n_2 = n - 1$, and the transformations (9) and (19) correspond to a transition from a spherical to a parabolic basis. In this case Eq. (11) yields the Coulomb distribution of the products of the reaction (1) in the orbital quantum numbers:

$$\sigma_{nl}=\sigma_n(2l+1)\frac{[(n-1)!]^2}{[(n+l)!\,(n-l-1)!]}\approx\sigma_n\left(\frac{2l+1}{n}\right)\times\exp\left[-\frac{l(l+1)}{n}\right]. \tag{12}$$

When the Coulomb symmetry is violated, e.g., for the interaction between a hydrogen atom in the ground state and an ion that has no electrons outside the closed shells, we can use for the coefficient $f(q, n)$ an approximate result[11] obtained in the l representation:

$$f(q,n)=f(l)=(2l+1)^{1/2}\exp\left[-l(l+1)/2Z\right]. \tag{13}$$

As a result we obtain from (11)

$$\sigma_{nl}=\left[(2l+1)/Z\right]\exp\left[-l(l+1)/Z\right]\sigma_n, \tag{14}$$

which confirms the l-distribution of the partial cross sections obtained in first-order perturbation theory.[11] Equations (12) and (14) were obtained under different physical assumptions, but lead to numerically close values of the cross sections in the vicinity of the maximum of the distribution in l.

Transformation from Eqs. (2) and (3) to the system (7) and (8) greatly simplifies the solution of the problem. The principal approximation in this transition is the equality (6), violation of which requires an additional investigation for non-Coulomb systems in the low-velocity region.

We consider now the multilevel system (7) and (8) in the internuclear-distance interval $(2Z)^{1/2} < R < 2Z$, using the general properties that follow for its coefficients from the quasiclassical character of the motion of the highly excited electrons. In this region, the main dependence of the exchange matrix elements on the principal quantum number is of the form[11-13]

$$V_n(R)=n^{-3/2}U(R,Z). \tag{15}$$

For a group of highly excited ionic levels with principal quantum numbers $n \sim n_0 \gg 1$, where n_0 is the center of this group, it follows that

$$V_n(R)=n_0^{-3/2}U(R,Z)\left[1+O(\Delta n/n_0)\right]\approx n_0^{-3/2}U(R,Z), \tag{16}$$

$$\omega_{in}(R)\approx(Z-1)/R+I_A-Z^2/2n^2$$

$$\approx(Z-1)/R+I_A-Z^2/2n_0{}^2+\varepsilon\Delta n=\omega_{in_0}(R)+\varepsilon\Delta n;$$

$$\Delta n=n-n_0, \quad \varepsilon=Z^2/n_0{}^3, \tag{17}$$

where I_A is the ionization potential of the atom.

We change now from the multilevel system of differential equations (7) and (8) to a two-level system that describes the interaction of the initial state with the final state b_{n_0} with allowance for the influence of all the remaining final states. Substituting (8) with $n \neq n_0$ in (7) we obtain

$$i\frac{da_i}{dt}=-in_0^{-3}\int_{-\infty}^{t}U(t)\,U(t')\exp\left[i\int_t^{t'}\omega_{in}(\tau)\,d\tau\right]$$

$$\times K(t-t')\,a_i(t')\,dt'+V_{n_0}(t)\exp\left[-i\int^t\omega_{in_0}(\tau)\,d\tau\right]b_{n_0}, \tag{18}$$

$$K(t-t')=\sum_{\Delta n\neq 0}\exp[i\varepsilon\Delta n(t-t')]\approx 2\pi\delta[\varepsilon(t-t')]. \quad (19)$$

The approximation (19) corresponds to the condition $n\gg|n-n_0|$, i.e., it is valid for the analysis of quantum transitions to a group of highly excited levels with $n_0\sim Z^{3/4}$ in multicharged ($Z\gg 1$) ions (see the Appendix).

The system of two equations obtained with the aid of (19) ($a\equiv a_i$, $b_n\equiv b_{n_0}$, $\omega_n\equiv\omega_{in_0}$)

$$\frac{da}{dt}=-\Gamma(t)a-iV_n(t)\exp\left[-i\int^t\omega_n(\tau)\,d\tau\right]b_n,$$
$$\frac{db_n}{dt}=-iV_n(t)\exp\left[i\int\omega_n(\tau)\,d\tau\right]a, \quad (20)$$

where

$$\Gamma(t)=\pi U^2(t)/Z^2, \quad a(-\infty)=1, \quad b(-\infty)=0,$$

has a simple physical meaning: the transition to this final state takes into account the attenuation of the initial one on account of the interaction with all the remaining final states. In the case $\Gamma\ll|V_n|$ an interaction between two stationary states is realized with predominant (at low velocities) transitions in the vicinity of the term crossing points $\omega_n(R_n)=0$. The opposite limiting case $|V_n|\ll\Gamma$ at all n reflects predominance of the decay mechanism.[4,5,14]

In the zeroth approximation, substituting in the right-hand side of the equation for $a(t)$ the initial conditions, we obtain for the initial-state amplitude and for the total (in all states) charge-exchange probability

$$a^{(0)}(t)=\exp\left[-\int_{-\infty}^{t}\Gamma(t')\,dt'\right], \quad W^{(0)}=1-\exp\left[-2\int_{-\infty}^{+\infty}\Gamma(t)\,dt\right], \quad (21)$$

which is the final result of the decay model.[4,5,14]

The solutions obtained in first-order perturbation theory without damping ($\Gamma=0$) were artificially reduced to the form (21) under the assumption that the function $\omega(t)$ is independent of time.[11] In all the listed cases one finds in the population of the excited levels, as expected, a broad distribution in n as a result of charge exchange, and a logarithmic divergence of the total cross section in the low-velocity limit. These singularities are due to neglect of the strong coupling of the states in the vicinity of the term-crossing points, since the influence of the coupling restricts significantly the region of applicability of the approximation (21) on the low-velocity side.

§2. INFLUENCE OF THE TURNING POINT AND OF THE DAMPING ON THE CHARGE-EXCHANGE PROBABILITY AND CROSS SECTION

To solve the system (20) with allowance for the damping and of term-crossing points located at a distance R_n, i.e.,

$$\omega_n(R_n)=0, \quad R_n\approx 2(Z-1)/(Z^2/n^2-2I_A), \quad (22)$$

we must take into account those trajectories with impact parameter $\rho\sim R_n$ which correspond to proximity of the turning point (along the radial coordinate) to the quasicrossing region. This leads to a splitting, quadratic in time, of the diabatic terms $\omega_n(t)$ (Refs. 7, 15, 16):

$$\omega_n(t)=\frac{Z-1}{2R_n^3}[R_n^2-\rho^2-v^2t^2]. \quad (23)$$

It is known[7] that the proximity of the spinode to the crossing point leads to substantial differences of the solutions from those obtained in the framework of the linear models, where $\omega\sim(t-t_0)$. The limiting cases were investigated without allowance for damping,[15] but the range of parameters where the probabilities (and cross sections) reach the maximum value does not have an exact analytic description.

Nor are there any interpolation formulas for the transition from the adiabatic limit to the perturbation-theory region.[7] Parametrization of the model problem without damping ($\Gamma=0$) and its numerical solution[16] show that in the reaction of the cross-section maximum the Landau-Zener linear model lowers the result by one-half.

The optimal among the approximate methods is the one used in Ref. 17. It gives exact results in the perturbation-theory region, the correct value of the adiabatic exponent in the opposite limit, and a reasonable interpolation in the intermediate region.[18] Under the same assumptions as in Ref. 17, the transition probability obtained from the system (18) is given by the integral

$$W_n=|b_n(+\infty)|^2=\left|\int_{-\infty}^{+\infty}V_n(t)\exp\left[i\Omega(t)-\int_{-\infty}^{t}\Gamma(t')\,dt'\right]dt\right|^2,$$
$$\Omega(t)=\int^t[\omega_n^2(t')+4V_n^2(t')]^{1/2}dt'. \quad (24)$$

In view of the rapid convergence of the integral as a result of the quadratic (in time) splitting of the zeroth-approximation terms (23), we shall carry out the calculations for the case $V_n(t)=V_n(R_n)=V_n$. Carrying out the parametrization

$$\tau=t(v^2\Delta F_n/4V_nR_n)^{1/2}=\mu^{-1}t, \quad \alpha=\Delta F_n(R_n^2-\rho^2)/4V_nR_n,$$
$$\beta=(16V_n^3R_n/v^2\Delta F_n)^{1/2}, \quad \Delta F_n=(Z-1)/R_n^2, \quad (25)$$

we reduce the integral (24) to the form

$$W_n=\left|\int_{-\infty}^{+\infty}\frac{\beta}{2}\exp\left[i\Omega(\tau)-\mu\int_{-\infty}^{\tau}\Gamma(y)\,dy\right]d\tau\right|^2,$$
$$\Omega(\tau)=\beta\int^{\tau}[(y^2-\alpha)^2+1]^{1/4}dy. \quad (26)$$

To compare the results with the known limiting cases,[7,15,16] we shall first carry out the calculations without allowance for the damping. Shifting the integration contour in the upper half-plane on a Stokes line that tends to infinity along the rays $\pi(1/2\pm 1/3)$, and approximating Ω by a third-degree polynomial

$$\Omega(\tau)\approx\beta[\tau^3/3+d(\alpha)\tau^2+g(\alpha)\tau], \quad (27)$$

we obtain

$$W_n=\pi^2\beta^{4/3}\,\mathrm{Ai}^2(\xi)\exp(4/3\,\mathrm{Re}\,\xi^{3/2}-2\,\mathrm{Im}\,S),$$
$$\xi=\beta^{2/3}[g(\alpha)-d^2(\alpha)], \quad (28)$$

where S is the value of Ω at the stationary-phase point:

$$S=\beta\int_0^{(\alpha+i)^{1/2}}[(y^2-\alpha)^2+1]^{1/2}\,dy=\frac{\pi}{4}\beta(\alpha+i)(\alpha-i)^{1/2}\times F\left(-\frac{1}{2},\frac{1}{2};2;\frac{\alpha+i}{\alpha-i}\right),\qquad(29)$$

F is a hypergeometric function, and Ai(x) is an Airy function connected with the function Φ frequently used in Ref. 3 by the relation

$$\mathrm{Ai}\,(x)=\pi^{-1/2}\Phi(x).$$

Since only the positions of the maxima of the oscillations of the probability W_n in (28) depend on g and d, these probabilities were determined by expanding (26) for large α, with the result

$$W_n=\pi^2\beta^{4/3}\,\mathrm{Ai}^2(-\alpha\beta^{2/3})e^{-\nu},\quad \nu=2\,\mathrm{Im}\,S-{}^4/_3\beta\theta(-\alpha)|\alpha|^{3/2},$$
$$\theta(x)=\begin{cases}0, & x<0.\\ 1, & x\geqslant 0.\end{cases}\qquad(30)$$

To calculate the exponent ν we can use directly Eq. (29), from which follow also the limiting cases obtained by various methods.[7] In practical calculations one can use the simple interpolation expression obtained in Ref. 19. The resultant inaccuracies have little effect on the final result.

The general variation of the probability with changing ρ can be easily tracked where the Airy function assumes its asymptotic values. In the subbarrier region ($\rho>R_n$, $\alpha<0$) the value of W_n attenuates exponentially with increasing impact parameter ρ, and in the opposite cases of above-barrier transitions the probability oscillates with decreasing ρ:

$$W_n=\frac{\pi\beta}{4|\alpha|^{1/2}}\exp\left\{-\beta\left[\frac{4}{3}(0.16-\alpha)^{3/2}+1.15\right]\right\},$$
$$\rho>R_n,\quad \alpha<0;$$
$$W_n=\frac{\pi\beta}{\alpha^{1/2}}\exp\left\{-\frac{\beta\pi}{4}[(1.3+\alpha)^{1/2}-0.5]^{-1}\right\}\times\sin^2\left(\frac{2}{3}\beta\alpha^{3/2}+\frac{\pi}{4}\right),\qquad(31)$$
$$\rho<R_n,\quad \alpha>0.$$

To trace the connection with the known limiting formulas it suffices to consider the case of small and large β. Since the argument of the exponential in (30) depends linearly on β, it follows that at $\beta\ll 1$ the exponential becomes equal to unity and (30) goes over into the result of the perturbation theory. In the second case, $\beta\gg 1$, which corresponds to adiabatically low velocity, Eq. (30) describes the exponential decrease of the probability exactly, but overestimates somewhat the pre-exponential factor. When the charge-exchange cross sections are calculated this does not affect the accuracy adversely, inasmuch as at low velocities ($\beta\gg 1$) the contribution of the rotational transitions, which has not been accounted for, increases the cross sections somewhat. A comparison of the calculations with the experimental results illustrates this circumstance. The cross section determined with the aid of (30) was compared with the exact calculation[16] in the parameter range where the cross sections differ most from the results obtained within the framework of the linear model. At the maximum of the cross section the deviation from Ref. 16 was of the order of 5%; the region where the cross section falls off at high velocities is described exactly.

We turn now to the general case and determine the probability W_n for nonzero $\Gamma(t)$ in Eqs. (20). A similar problem, which arises in the investigation of transitions between quasistationary levels, was considered in Refs. 20–24. It is important that in (20) only the initial state is quasistationary and there is no interaction due to the decay of both states into one continuum.[23] For the Landau-Zener model the transition probability for a single passage through the crossing point of the diabatic terms is independent of Γ (Refs. 22,23). In the more general case the decay of the initial state can influence the dynamics of a nonadiabatic transition only at large values of Γ; the transition probability is then exponentially small as a result of the strong damping of the initial state. Bearing the foregoing in mind, we shall take the decay into account in the form of factors that correspond to the change of the value of a_i in two successive quasicrossing points.[20] The integration interval in (24) breaks up into two parts containing two nonadiabaticity regions as nuclei, which enter with weights γ_1 and γ_2 move towards and away from each other:

$$\gamma_1=\exp\left[-\mu\int_{-\infty}^{\bar{\tau}_n}\Gamma(\tau)\,d\tau\right],\quad \gamma_2=\exp\left[-\mu\int_{-\infty}^{\tau_n}\Gamma(\tau)\,d\tau\right],$$
$$\omega_n(\tau_n)=0,\quad \tau_n>0.\qquad(32)$$

Leaving out the intermediate calculations, which are similar to those used to derive (30), we present the result:

$$W_n=\frac{\pi^2}{4}\beta^{4/3}e^{-\nu}[(\gamma_1+\gamma_2)^2\mathrm{Ai}^2(-\alpha\beta^{2/3})+(\gamma_1-\gamma_2)^2\mathrm{Gi}^2(-\alpha\beta^{2/3})],$$
$$\mathrm{Gi}(x)=\pi^{-1}\int_0^{\infty}\sin(y^3/3+xy)\,dy.\qquad(33)$$

Let us emphasize the main consequences of the effect of the damping $\Gamma(t)$ on the result (33), which distinguish it from (30). In the absence of decay of the initial state, the probability (30) oscillates and takes on zero values at the zeros of the Airy function. The influence of $\Gamma(t)$, besides the general de-

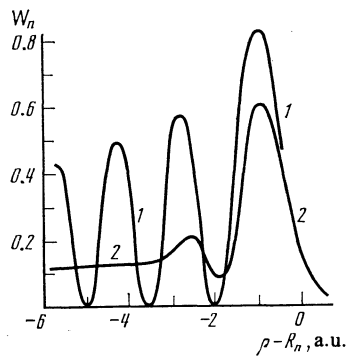

FIG. 1. Transition probability W_n as a function of the impact parameter ρ at the following parameter values: $Z=20$, $n=11$, and $v=0$, 28 a.u. 1) Eq. (30), 2) Eq. (33).

crease of the probability, is that the minimum values reached in the oscillations are not zero. Figure 1 shows by way of example a calculation of the probability (33) as a function of the impact parameter for an ion charge $Z = 20$.

We note that in the limit as $\nu \to 0$ Eq. (33) corresponds to the perturbation theory solution of (20) in first order in the interaction $V_n(t)$. It can be easily seen that in this case the solution is given as before by the integral (24), with $\Omega(t)$ replaced by $\int^t \omega_n(t')dt'$. In a physical sense this limiting case is the simplest generalization of the decay model (21), and yields the partial cross sections σ_n. The total cross sections calculated as the sums of the partial ones, contain information more accurate than (18) on the dependence of the results on the charge of the ion and on the relative velocity. Analysis shows that in this case, in particular, the total cross section becomes nonmonotonically dependent on the ion charge at a given relative velocity. At $\nu > 1$ the decay model is incorrect even in order of magnitude (see Fig. 2).

An estimate of the distribution of the reaction products in the quantum numbers can be obtained in analytic form. Integration of the probability (33) with respect to the impact distance with exponential accuracy yields

$$\sigma_n \sim R_n^2 \delta_n \exp\left[-\delta_n - \frac{2}{v}\int_{R_n}^{\infty} \frac{\Gamma(R)}{(R^2-R_n^2)^{1/2}} dR\right], \tag{34}$$

$$\delta_n = 2\pi V_n^2/v\Delta F_n.$$

The use of the exchange interaction in the form[11]

$$V_n(R) = (2Z/\pi n^3)^{1/2} R \exp(-R^2/3Z) \tag{35}$$

leads to the following values:

$$\frac{2}{v}\int_{R_n}^{\infty} \frac{\Gamma(R)}{(R^2-R_n^2)^{1/2}} dR = \left(\frac{6\pi Z}{v^2}\right)^{1/2}\left(\frac{R_n^2}{Z}+\frac{3}{4}\right)\exp\left(-\frac{2R_n^2}{3Z}\right), \tag{36}$$

$$\delta_n = (4R_n^4/n^3 v)\exp(-2R_n^2/3Z).$$

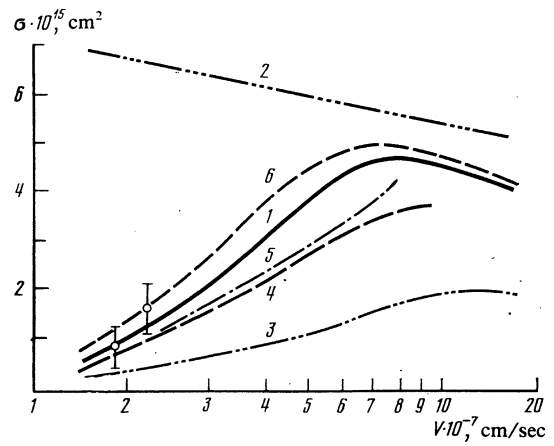

FIG. 2. Total cross section for the charge exchange of carbon C^{+6} nuclei with hydrogen atoms. Points—experiment,[25] 1) calculation from Eq. (21), 3) Landau-Zener model,[32] 4) method of strong coupling of 11 states,[26] 5,6) method of strong coupling of 6 states.[27,28]

It is seen from (34) that the level population depends mainly on the distance R_n to the crossing point of the corresponding diabatic terms. With increasing velocity the number of populated levels increases. Calculations have shown that the maximum population probability takes place at $n \sim Z/2$ (for $Z < 25$ this value of n practically coincides with $Z^{3/4}$).

For ions with charge $Z < 10$ Eq. (30) is not directly applicable, since the factors γ_1 and γ_2 in it were obtained by using model assumptions that require a large number of ion excited states interacting with the initial atomic state. This holds true with sufficient accuracy only for $Z > 10$. In accord with its physical meaning the time integral of the damping $\Gamma(t)$ at $Z < 10$ should be replaced by the sum[8]

$$\int_{-\infty}^{t} \Gamma\, dt = \int_{+\infty}^{n(t)} \Gamma\left(\frac{dn}{dt}\right)^{-1} dn = -\int_{n(t)}^{\infty} \frac{\pi V_n^2[t(n)]}{\Delta F_n\, dR/dt}\, dn$$
$$\approx \sum_{n>n(t)} \frac{\pi V_n^2}{v\Delta F_n (1-\rho^2/R_n^2)^{1/2}}, \tag{37}$$

which leads obviously to a decrease of the influence of the decay in the case of a small number of crossings. At $Z = 6$ (see Fig. 2), the state populated with the overwhelming probability is the one with $n = 4$, and the sum (37) contains only a term with $n = 5$. Comparison with experimental results[25] and with numerical calculations,[26-28] performed using exact Coulomb two-center wave functions by the method of strong coupling of five and more states, offer evidence of the sufficient accuracy of (33).

§3. CHARGE EXCHANGE IN SYSTEMS THAT HAVE NO COULOMB SYMMETRY

For systems that have no Coulomb symmetry the assumption (6) of orbital degeneracy of ionic terms that interact with the atomic does not hold. This increases the number of spatially separated quasicrossings. Each splitting (at a given n) is determined not by the expression (9) summed over all the angle numbers q, but only by that part of (9) which corresponds to the components that remain degenerate. From the formal point of view this means that the strong coupling of the final states with the initial one, which is postulated in the coupled equations (30) by the coefficient $V_n(t)$, is violated. At low velocities this decreases the adiabatic exponent [the parameter ν, in (33)], and consequently expands the region of applicability of perturbation theory, which takes into account the damping of the initial state. On the other hand, the decay width of the initial state $\Gamma(t)$, being an integral characteristic, depends little on the details of the quasicrossing picture. A similar situation is realized in the Demkov-Osherov linear model[29] and in other multilevel problems with term crossing (see, e.g., Ref. 8).

Taking the foregoing into account, we shall solve the initial system (2), (3) by using, in this case approximately, Eq. (18) for the initial state. Retention in its right-hand side of the term proportional to b_{in}^q is for non-Coulomb systems an exaggeration of the accuracy in this approximation. Equations (2) and (3) take the form

$$\frac{da}{dt} = -\Gamma(t)a, \quad i\frac{db_{nq}}{dt} = V_{nt}^q(t)\exp\left[i\int^t \omega_{in}^q(t')dt'\right]a, \tag{38}$$

where n and q run through all the possible values and the function $\Gamma(t)$ is defined in Eqs. (20). The solutions corresponding to the initial conditions (4)

$$a(t)=\exp\left[-\int_{-\infty}^{t}\Gamma(t')\,dt'\right],$$
$$b_{nq}(t)=-i\int_{-\infty}^{t}V_{in}^{q}(t')\exp\left[i\int^{t'}\omega_{in}^{q}(\tau)\,d\tau\right]a(t')\,dt' \tag{39}$$

take into account, for the initial state, all the orders of perturbation theory (in V_{in}^{q}) in the decay approximation.

For the final states b_{nq}, the phases of the integrands, in contrast to (24), do not contain off-diagonal matrix elements. The condition for the applicability of (39) are the inequalities

$$\delta_{nq}=\pi[V_{in}^{q}(R_n^{q})]^2/v^2\Delta F_n\ll 1 \tag{40}$$

for all values of n and q. It is important that in this case the quantity $\delta_n=\Sigma\delta_{nq}$ need not be small. Therefore we can neglect in the equations that follow the small difference between the values of ω_{in}^{q} for different q, which lead in (39) to negligible quantitative effects, and sum over the angle quantum numbers. For the probability of charge exchange on a level with principal quantum number n, we thus obtain

$$p_n=\sum_q p_n^{q}\approx\left|\int_{-\infty}^{\infty}V_n(t)\exp\left[-\int_{-\infty}^{t}\Gamma(t')\,dt'+i\int^{t}\omega_{in}(t')\,dt'\right]dt\right|^2$$
$$p_n^{q}=|b_n^{q}(+\infty)|^2\ll 1, \tag{41}$$

where V_n is given by (9). When the approximation (23) and the parametrization (25) are used, Eq. (41) reduces to Eq. (33) with $\nu=0$. In view of the non-Hermitian character of the system (38), the condition for normalization of the total transition probability may generally speaking be violated. In the same approximation (39)–(41) we can show [6,17,18] that the unitarized probabilities are equal to

$$W_n^{q}=p_n^{q}\Big/\Big(\sum_m p_m+W_i\Big),\quad W_n=\sum_q W_n^{q};$$
$$W_i=1-\exp\left[-2\int_{-\infty}^{\infty}\Gamma(t)\,dt\right]. \tag{42}$$

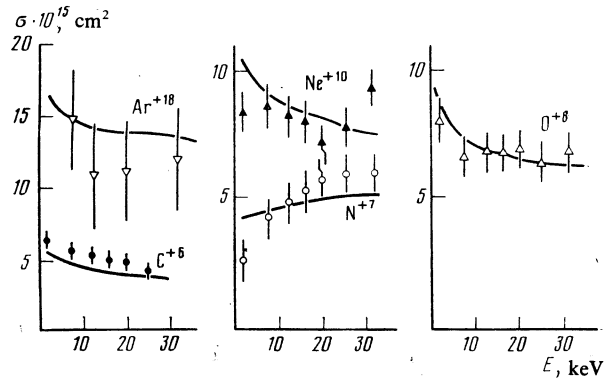

FIG. 3. Total cross section for the charge-exchange reaction $H_2+B^{+z}\to H_2^{+}+B^{+(z+1)}$ as a function of the incident-ion energy divided by the atomic weight. Individual points—experiment,[31] solid curves—calculation.

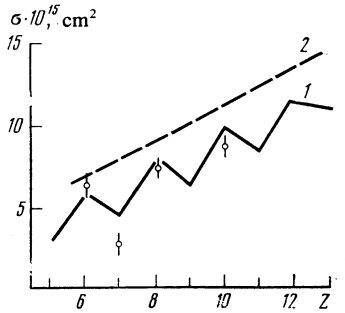

FIG. 4. Total cross section for charge exchange $H_2+B^{+z}\to H_2^{+}+B^{+(z+1)}$ as a function of the nuclear charge Z at a relative velocity $v=0.14$ a.u. Points—experiment[9]; 1) calculation with Eqs. (42) and (43); 2) decay model [Eq. (21)].

The partial and total charge-exchange cross sections are defined as

$$\sigma_n=2\pi\int_0^{\infty}W_n\rho\,d\rho,\quad \sigma_T=\sum_n\sigma_n. \tag{43}$$

The integrals in (41) were calculated with the aid of Eq. (33) with $\nu=0$, and also numerically without the approximation (23), i.e., with $V_n(t)$ specified by Eq. (35) and

$$\omega_n(t)=(Z-1)/R(t)-Z^2/2n^2+I_A.$$

We note that in both cases the cross sections (43) are differed by not more than 5%. The results were used to calculate the charge-exchange cross sections of the hydrogen molecules with nuclei for which experimental data are available.[9] It follows from Ref. 12 that the matrix elements V_n averaged over the angular quantum numbers must contain $\sqrt{N}$ as a factor, where N is the number of equivalent electrons ($N=2$ in the case of H_2). The results are given in Figs. 3 and 4 and compared there with the experimental data.[9,30]

Greatest interest attaches to the nonmonotonic character of the dependence of the total cross sections on the ion charge. Analysis of Eqs. (33) and (34) shows that the reasons of the oscillations in Z is the discrete character of the spectrum of the produced ion. The minima of the total cross section correspond to the absence, from the discrete spectrum of the ion, of levels with nearly half-integer values of the principal quantum numbers, for which the capture probability would be a maximum under the given conditions. It was indicated earlier (§ 2) that a similar nonmonotonicity is realized also for pure Coulomb systems. The decay model (21) obviously does not take into account the discreteness and assumes[5,14] that the ion spectrum in quasicontinuous. As a result this model yields the maximum estimate of the cross section, as shown in Fig. 4.

With decreasing velocity, the inequalities (40) no longer hold, and an exponential fall-off should be observed in the partial (and total) cross sections. A quantitative analysis of this regions calls, however, for a more accurate picture of the behavior of the terms of the ion + atom (molecule) system, with account taken of the properties of the cores and of the Stark splitting, as well as of the interactions due to the rotation of the internuclear axis, both between the components

of the ionic levels[31] and at the points of their crossing with the atomic levels having the necessary symmetry.

The physical nature of the results of the present paper is based on the damped (decay) character of the initial state of the atom + ion system and on the discreteness of each of the final levels at which the electron transition terminates. The method developed here admits also of generalization to relative velocities $v > Z^{1/2}$. In this case it is necessary to take into account in the exchange-interaction coefficients the velocity dependence due to the momentum transfer to the electron on going from one center to another. Another application of the results is to ionization in ion-atom collisions and the mutual relation between the ionization and charge-exchange channel.

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Appendix

We introduce the variable $x = vt$ and rewrite Eq. (18) with allowance for (8) in the form

$$i\frac{da_i}{dx} = -\frac{i}{vn_0^3}\int_{-\infty}^{x} dx' a_i(x') F(x,x') Q(x-x'), \qquad (A.1)$$

$$F(x,x') = U(x)\,U(x')\exp\left[\frac{i}{v}\int_{x'}^{x}\omega_{in}(y)\,dy\right], \qquad (A.2)$$

$$Q(x-x') = K(x-x')+1 = \sum_{\Delta n=-N}^{N}\exp\left[\frac{i\varepsilon\Delta n}{v}(x-x')\right]. \qquad (A.3)$$

(Here $2N+1$ is the number of levels). For multiply charged ($Z \gg 1$) ions we can use the limiting value of the function Q:

$$\lim_{N\to\infty} Q(x-x') = \sum_{m=-\infty}^{\infty}\frac{2\pi v}{\varepsilon}\delta\left(x-x'-\frac{2\pi v}{\varepsilon}m\right). \qquad (A.4)$$

We note that the terms with $m < 0$ make a zero contribution when substituted in the integral of (A.1), since $x - x' \geqslant 0$ in this integral.

The term of (A.4) with $m = 0$ corresponds to Eq. (19), which is approximate at finite N. The remaining sum can be replaced in the limit as $v \to 0$ by the integral

$$\lim_{v\to 0}\sum_{m=1}^{\infty}\frac{2\pi v}{\varepsilon}\delta\left(x-x'-\frac{2\pi v}{\varepsilon}m\right) = \int_{-\infty}^{x-x'}\delta(y)\,dy, \quad x-x'>0, \qquad (A.5)$$

which yields, together with Eq. (8), the second term of the right-hand side of (18).

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