Asymptotic theory of charge transfer at arbitrary velocities

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(Submitted May 6, 1975)
Zh. Eksp. Teor. Fiz. **69**, 1582–1593 (November 1975)

An asymptotic (with respect to large impact parameters) theory of charge transfer at arbitrary collision velocities is constructed. The dominant term in the asymptotic form of the amplitude in the general nonresonance case is computed for transitions between the *s* states of atoms. The result is compared with the findings of different approximation methods. Specific examples of resonance $(p+H \rightarrow H+p)$ and nonresonance $(Li^+ + Na \rightarrow Li + Na^+)$ charge transfer are considered.

1. INTRODUCTION

The object of the asymptotic theory of atomic collisions is to seek the asymptotic form of the probability $W(\rho)$ of the process in question for large impact parameters ρ, i.e., for distant encounters, when the distance between the colliding particles is always much greater than their dimensions. The large values of the impact parameter are connected with small-angle scattering. The exact asymptotic form is of considerable interest in itself, and can serve as a check on the various approximate computational methods. In the case when the probability of the process at some ρ becomes comparable to unity (the so-called dense-target case), knowledge of the asymptotic form allows us to find the total cross section of the process (see[1,2], as well as Sec. 5 of the present paper).

The main attention in the asymptotic theory is given to the processes most interesting and most complex to compute, namely electron exchange between colliding atomic particles. A one-electron exchange occurs in a charge-exchange reaction, while a two-electron exchange occurs in a double charge-exchange reaction, in a spin exchange, as well as in an excitation transfer.

Since the interaction is weak in distant encounters, it is natural to use perturbation theory. It turns out, however, that the latter gives an incorrect result (usually an incorrect value for the preexponential function in the asymptotic form of $W(\rho)$). Such a situation arises quite often in the theory of subbarrier (exponentially small) effects. Of importance in our case is the presence of a long-range Coulomb interaction between the particles; thus, for short-range potentials perturbation theory gives an asymptotically exact result.

So far the development of the asymptotic theory has been tied with the additional assumption that the process is adiabatic in nature, i.e., that the relative collision velocity v is low. In the adiabatic case the search for the asymptotic form of $W(\rho)$ for resonance processes reduces to the determination of the asymptotic form of the splitting, $\Delta E(R)$, of the corresponding terms of the quasi-molecule for large internuclear distances R. A review of these investigations, as well as of their applications is contained in the monograph[1] by Smirnov,

The purpose of the present paper is to construct an asymptotic theory for the general case of arbitrary collision velocity v. We consider the dynamical nonstationary quantum problem, which allows the direct determination of the asymptotic form of $W(\rho)$.

Analysis of the stationary asymptotic theory reveals in it three basic features[3]:

1. The use (usually in the implicit form) of the stationary-phase method to compute the necessary multidimensional integrals. In the latter, the exponential function with the large (linearly increasing with R) phase is separated out. In the asymptotic limit the dominant contribution to the integral is given by the phase-stationarity region in the configurational space of the problem, i.e., by the set on which the derivatives of the phase with respect to the integration variables vanish.

2. The representation of the sought quantity $\Delta E(R)$ in the form of an integral over some hypersurface S in configurational space, the process under consideration being characterized by passage across this surface. The intersection of the surface S with the phase-stationarity region is some region C of lower dimensionality, which simplifies the integration. Furthermore, it is in the region C, which determines the asymptotic form of the integral, that we can most exactly calculate the wave functions of the system (see Item 3).

3. The refinement of the wave functions (in comparison with the case in which there is no interaction). The correction to a wave function is determined by the solution to a first-order partial differential equation.

All the three indicated points are carried over in a changed and generalized form into the nonstationary theory (Secs. 2—4), where integrals involving integration over the coordinates, as well as over time, arise. In Sec. 5 the final results are discussed, compared with the findings of various approximations, and illustrated with specific processes.

In the paper we consider the simple process of one-electron charge transfer from an atom to a positive ion: $A + B^+ \rightarrow A^+ + B$. It is assumed that the atoms A and B are hydrogen-like and are in their *s* states.

2. AN IDENTITY FOR THE CHARGE-TRANSFER AMPLITUDE

Let us choose a system of coordinates in which the nuclei of the atoms A and B move in opposite directions with velocities v/2 along the x axis and in which the moment of time t = 0 corresponds to their closest approach to each other (see Fig. 1). Let us denote by r_a and r_b the distance of an electron from the nuclei of A and B respectively; R is the internuclear dis-

tance. Let us introduce the exact solutions, $\Psi_1(\mathbf{r}, t)$ and $\Psi_2(\mathbf{r}, t)$, to the time-dependent Schrödinger equation:

$$\left(\mathscr{H}-i\frac{\partial}{\partial t}\right)\Psi_{1,2}(\mathbf{r},t)=0, \qquad (2.1)$$

$$\mathscr{H}(t)=-\frac{1}{2}\nabla^2-\frac{1}{r_a}-\frac{1}{r_b}+\frac{1}{R}, \qquad (2.2)$$

solutions which are distinguished by the boundary conditions at large $|t|$:

$$\Psi_1(\mathbf{r},t)=\psi^{(a)}(r_a)\exp\left[i\frac{v}{2}x-i\left(E_a+\frac{v^2}{8}\right)t\right] \text{ as } t\to-\infty, \qquad (2.3)$$

$$\Psi_2(\mathbf{r},t)=\psi^{(b)}(r_b)\exp\left[-i\frac{v}{2}x-i\left(E_b+\frac{v^2}{8}\right)t\right] \text{ as } t\to+\infty. \qquad (2.4)$$

where E_a and E_b are the energies of the electron in the A- and B-atom states under consideration and $\psi^{(a)}(r_a)$ and $\psi^{(b)}(r_b)$ are the corresponding wave functions. Thus, the solution Ψ_1 corresponds to a situation in which initially ($t\to-\infty$) the electron is in the state $\psi^{(a)}$, whereas the solution Ψ_2 corresponds to a situation in which at the end of the process ($t\to+\infty$) the electron is concentrated in the state $\psi^{(b)}$. The factors $\exp[\pm ivx/2 - iv^2t/8]$ in the boundary conditions appear as a result of the Galilean transformation of the wave function when we go over from the coordinate system connected with the atom to a stationary system. The physical meaning of the factor $\exp(\pm ivx/2)$ is, as is well known, that it allows for the transport of momentum by the electron when it is transferred from one atom to the other; the factor $\exp(-iv^2t/8)$ takes the change in the kinetic energy into account.

The sought transition (i.e., charge-transfer) amplitude is given by the integral

$$F(\rho)=\int\Psi_1(\mathbf{r},t)\,\Psi_2(\mathbf{r},t)\,d\mathbf{r}, \qquad (2.5)$$

which, as can easily be verified with the aid of (2.1), does not depend on time because of the hermiticity of the operator $\mathscr{H}(t)$ (more often the transition amplitude is defined more directly in terms of the integral (2.5) in which t is allowed to tend to $\pm\infty$).

Dividing the space into the regions V_I and V_{II} as shown in Fig. 1 (where the region V_I is hatched), we obtain

$$F(\rho)=I_1(t)+I_{II}(t), \qquad (2.6)$$

$$I_{I,II}(t)=\int_{V_{I,II}}\Psi_1(\mathbf{r},t)\,\Psi_2^*(\mathbf{r},t)\,d\mathbf{r}. \qquad (2.7)$$

Each of the terms $I_I(t)$ and $I_{II}(t)$ individually depends on time. Now let the surface S delimiting the regions V_I and V_{II} move in time with some velocity $u(x, t)$. Let us define the motion of S such that it coincides at small x with the plane $y = y_S$, while the slightly-bent edges of the surface turn back, as $t\to\pm\infty$, in different directions, as shown in Figs. 1a and 1b. Then it follows from the boundary conditions (2.3) and (2.4) that

$$I_1(t)\to F(\rho), \quad I_{II}(t)\to 0, \quad t\to-\infty; \qquad (2.8)$$

$$I_1(t)\to 0, \quad I_{II}(t)\to F(\rho), \quad t\to+\infty. \qquad (2.9)$$

Computing the derivative dI_I/dt with allowance for (2.1) and transforming, according to the Green theorem, the volume integral into a surface integral, we find

$$\frac{dI_1}{dt}=\frac{i}{2}\int_S dS[\Psi_1(\mathbf{v}\nabla)\Psi_2^*-\Psi_2^*(\mathbf{v}\nabla)\Psi_1]-\int_S dS(\mathbf{v}u)\Psi_1\Psi_2^*, \qquad (2.10)$$

where ν is the inner–with respect to the volume V_I– normal to the surface S. Finally, integrating both sides of this equality with respect to the time with allowance for the conditions (3.8) and (2.9), we obtain the required exact identity for the amplitude. Before writing it out, let us note that the function $u(x, t)$ is, to a large extent, arbitrary. If we move the surface S everywhere towards the plane $y = y_S$, then the velocity u vanishes, and only the first term on the right-hand side of (2.10) remains. Accordingly, the required identity finally assumes the form[1)]

$$F(\rho)=\frac{i}{2}\int_{-\infty}^{\infty}dt\int_S dS[\Psi_2^*(\mathbf{v}\nabla)\Psi_1-\Psi_1(\mathbf{v}\nabla)\Psi_2^*]. \qquad (2.11)$$

Physically, this result means that an expression of the type of the (mixed) density of the current across a surface dividing the regions of initial and final locations of the electron is integrated over this surface and over time.

In deriving (2.11), we essentially used only the fact that we were considering a charge-transfer type of process in which we can divide space into two parts such that the presence of the electron in the initial or final state uniquely determines its location in one, and total absence in the other, region of space. It is evident that for strict validity of (2.11) the nuclei should recede to infinity as $t\to\pm\infty$, but we need not impose any limitations on their velocities and the shape of their trajectories in a finite region of space. It also follows from the foregoing that the surface S should only be such as to delimit the two indicated regions of space. In all other respects the shape of S is arbitrary (which can easily be verified directly from (2.11) with the aid of (2.1)). In particular, the choice of S made in Fig. 1 with a plane part along the x axis (at $y = y_S$) is, in fact, only for convenience of the subsequent computations.

Comparing the identity (2.11) with the formula expressing $\Delta E(R)$ in the form of a surface integral and used in the stationary theory (the first part of the formula (1.9) in the monograph[1]), we emphasize that, in contrast to (2.11), the latter is an approximate formula, since R was assumed to be large in its derivation. It can be shown that the formula for $\Delta E(R)$ also admits (but to a lesser extent) of some arbitrariness in the choice of the surface S[3].

3. THE STATIONARY-PHASE METHOD

To compute the asymptotic form of the integral (2.11) for large ρ, it is convenient to use the multidimensional stationary-phase method proposed earlier by one of the present authors for the computation of the generalized Massey parameter[2].
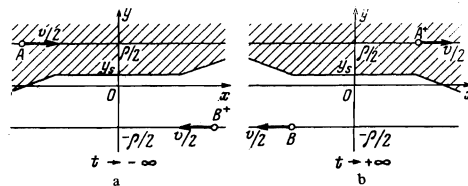

FIG. 1. Schematic representation of the motion of the atomic particles and the integration surface for the computation of the charge-transfer amplitude.

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Let us represent the wave functions Ψ_1 and Ψ_2 in the form

$$\Psi_1(\mathbf{r},t)=\psi^{(a)}(r_a)\exp\left[-S^{(a)}(\mathbf{r},t)+i\frac{v}{2}x-i\left(E_a+\frac{v^2}{8}\right)t\right],\quad(3.1)$$

$$\Psi_2(\mathbf{r},t)=\psi^{(b)}(r_b)\exp\left[-S^{(b)}(\mathbf{r},t)-i\frac{v}{2}x-i\left(E_b+\frac{v^2}{8}\right)t\right],\quad(3.2)$$

where $S^{(a)}(\mathbf{r},t)$ and $S^{(b)}(\mathbf{r},t)$ are some correction functions that take the presence of the second potential center into account. For the present, only the fact that the functions $S^{(a)}$ and $S^{(b)}$ (which are computed approximately in Sec. 4) depend weakly on their arguments and on ρ is of importance to us. A strong dependence is, however, contained in the exponential factors in the formulas (3.1) and (3.2), as well as in the exponential functions contained in the atomic wave functions, which, for s states, have the form

$$\psi^{(a)}(r_a)=\frac{1}{(4\pi)^{1/2}}P^{(a)}(r_a)e^{-\alpha r_a},\quad \psi^{(b)}(r_b)=\frac{1}{(4\pi)^{1/2}}P^{(b)}(r_b)e^{-\beta r_b}.\quad(3.3)$$

Here $P^{(a)}$ and $P^{(b)}$ are some polynomials (for the ground state of the hydrogen atom the polynomial is a constant), while $E_a=-\alpha^2/2$ and $E_b=-\beta^2/2$ are the energies of the electron in the A- and B-atom states under consideration.

Combining under the integral sign in (2.11) the above-computed cofactors with a strong ρ dependence, we obtain an exponential function e^Φ with a phase

$$\Phi=-\alpha r_a-\beta r_b+ivx+i(\alpha^2/2-\beta^2/2)t,\quad(3.4)$$

coinciding with the phase that arises when the charge-transfer process is considered in first-order perturbation theory[2]. We find the region of stationarity of the phase by equating the derivatives $\partial\Phi/\partial x$, $\partial\Phi/\partial z$, and $\partial\Phi/\partial t$ to zero. The simultaneous solution of the equations thus obtained yields

$$x=\frac{i}{2v\varkappa(v)}\left\{y(\alpha^2-\beta^2)+\rho\frac{v^2}{2}\right\},\quad z=0,$$

$$t=\frac{i}{v\varkappa(v)}\left\{yv+\rho\frac{\alpha^2-\beta^2}{2v}\right\},\quad -\frac{\rho}{2}<y<\frac{\rho}{2},\quad(3.5)$$

where $\varkappa(v)=(1/2v)\{[(\alpha+\beta)^2+v^2][(\alpha-\beta)^2+v^2]\}^{1/2}$. Thus, the stationarity region for the phase is the straight-line segment (3.5), the phase being independent of y on this segment and being equal to

$$\Phi_0=-\rho\varkappa(v),\quad(3.6)$$

in this region and larger in absolute value ($\Phi<0$) in the rest of phase space. Let us emphasize that for $v\neq0$ the stationarity region for the phase is complex.

Since the integral (2.11) to be evaluated is not a volume but a surface integral, only the vicinity of the point C of intersection of the surface S with the stationarity region for the phase (the coordinates of the point C are obtained from (3.5) with $y=y_S$) contributes to its asymptotic form. The stationary-phase method yields for the dominant term of the asymptotic form of $F(\rho)$ the expression:

$$F(\rho)=\frac{i}{v}8\left(\frac{2\pi}{\rho}\right)^{1/2}\alpha\beta\left[\left(\frac{\rho}{2}\right)^2-y_S^2\right]\frac{1}{\varkappa^{5/2}}$$
$$\times\{P^{(a)}P^{(b)}\exp[-S^{(a)}-S^{(b)}]\}ce^{\Phi_0},\quad(3.7)$$

where the expression in the curly brackets should be evaluated at the point C. Thus, to complete the computations, it now remains to find the correction functions $S^{(a)}$ and $S^{(b)}$ (see Sec. 4).

The formula (3.7) has been obtained for an arbitrary value of y_S. It can, however, be verified that for $|y_S|\ll\rho$ the dominant term in the asymptotic form of $F(\rho)$ does not, as was to be expected, depend on y_S, so that we can set $y_S=0$, which will henceforth be implied. The point C then has the coordinates

$$x=i\frac{\rho v}{4\varkappa(v)},\quad y=z=0,\quad t=i\rho\frac{\alpha^2-\beta^2}{2v^2\varkappa(v)}.\quad(3.8)$$

It is evident that it makes sense, in computing the dominant term in the asymptotic form of $F(\rho)$ in (3.7), to take into account only the dominant terms in the asymptotic forms of $P^{(a)}$ and $P^{(b)}$ for large values of the argument:

$$P^{(a)}(r)\approx A^{(a)}r^{1/\alpha-1},\quad P^{(b)}(r)\approx A^{(b)}r^{1/\beta-1},\quad(3.9)$$

where $A^{(a)}$ and $A^{(b)}$ are some numerical coefficients. Let us emphasize that in such a form these expressions are also valid in the case when the potential of the atomic cores A^+ and B^+ acting on the electron is different from the Coulomb potential near the nucleus.

4. THE CORRECTION FUNCTIONS

It is convenient, in computing the correction function $S^{(a)}(\mathbf{r},t)$ ($S^{(b)}$ is found in similar fashion), to go over to a coordinate system connected with the atom A (the quantities pertaining to this system will be distinguished by a prime). Substituting the expression

$$\Psi_1'(\mathbf{r},t)=\psi^{(a)}(r_a)\exp[-S^{(a)}(\mathbf{r},t)-iE_at]\quad(4.1)$$

into the time-dependent Schrödinger equation (2.1), and taking into account the fact that the atomic wave function satisfies the equation

$$\left[-\frac{1}{2}\nabla^2-\frac{1}{r_a}\right]\psi^{(a)}=E_a\psi^{(a)},\quad(4.2)$$

we obtain the exact equation for $S^{(a)}$:

$$\frac{\partial S^{(a)}}{\partial t}=\left(\frac{1}{R}-\frac{1}{r_b}\right)+\frac{1}{\psi^{(a)}}(\nabla\psi^{(a)})(\nabla S^{(a)})+\frac{1}{2}(\nabla S^{(a)})^2-\frac{1}{2}\nabla^2 S^{(a)}.\quad(4.3)$$

Since the correction function varies slowly, the last two terms on the right-hand side of (4.3) can be dropped. We should, in this same approximation, set

$$\frac{1}{\psi^{(a)}}(\nabla\psi^{(a)})=-\frac{\alpha r_a}{r_a},$$

which finally gives the equation

$$i\frac{\partial S^{(a)}}{\partial t}-\alpha\frac{\partial S^{(a)}}{\partial r_a}=\frac{1}{R}-\frac{1}{r_b}.\quad(4.4)$$

Thus, we use for the computation of the correction to the wave function a method similar to the quasi-classical method. The function $S(\mathbf{r},t)$ is then representable in the form of a series in powers of a formal "quasi-classicality" parameter λ:

$$S(\mathbf{r},t)=\sum_{n=0}\lambda^n S_n(\mathbf{r},t).$$

This series, evaluated at the point C, is then a series in inverse powers of ρ, which is necessary for our method. Equation (4.4) determines the lowest-order correction $S_0(\mathbf{r},t)$; only this correction is calculated below. In principle, we can develop a successive method for finding the higher approximations, which will enable us to obtain an asymptotic series for $F(\rho)$. Notice that in the analogous case in the stationary problem the series for $\Delta E(R)$ was calculated with the use of the specific properties of the two-center Coulomb problem (i.e., the possibility of separating the variables; see the

references cited in[1]), whereas the method proposed here is applicable also in the case of potentials of a more general form.

In the new variables

$$\xi=(-it-r_a/\alpha)/2, \quad \eta=(-it+r_a/\alpha)/2 \qquad (4.5)$$

Eq. (4.4) assumes the form

$$\partial S^{(a)}/\partial\xi = 1/r_b - 1/R, \qquad (4.6)$$

after which it can easily be solved with allowance for the natural initial condition

$$S^{(a)}(r_a=0, t=-\infty)=0. \qquad (4.7)$$

The details of the computations and their result are given in the Appendix. It can be seen from them, in particular, that the function $S^{(a)}$, computed in the lowest approximation, does not generally depend on ρ at the point C. This circumstance indicates that, without allowance for the correction to the wave function, it is impossible to compute the correct preexponential coefficient in the asymptotic form of $F(\rho)$. On the other hand, the relation $S_C^{(a)} = O(1)$ justifies the assertion that we did not include the corrections $S^{(a)}$ and $S^{(b)}$ in the phase Φ when finding the stationarity region for the latter (Sec. 3).

5. RESULTS AND DISCUSSION

The expression (3.7) for the asymptotic form of $F(\rho)$ with the use of the correction function found in Sec. 4 assumes the form

$$F(\rho) = -\frac{i}{v}\left(\frac{\pi}{32}\right)^{1/2}\frac{\alpha\beta}{\varkappa^{5/2}}DA^{(a)}A^{(b)}\left(\frac{\alpha\rho}{2\varkappa}\right)^{1/\alpha-1}\left(\frac{\beta\rho}{2\varkappa}\right)^{1/\beta-1}\rho^{1/2}e^{-\varkappa\rho}, \quad (5.1)$$

where

$$D \equiv \{\exp[-S^{(a)}-S^{(b)}]\}_C = 2^{1/\alpha+1/\beta}.$$

$$\cdot\exp\left\{-\frac{1}{v}\left[\arcsin\frac{\alpha^2-\beta^2+v^2}{2v\varkappa}+\arcsin\frac{\beta^2-\alpha^2+v^2}{2v\varkappa}\right]\right\}. \quad (5.2)$$

In particular, in the resonance case, i.e., for $\beta=\alpha$,

$$D=4^{1/\alpha}\exp\left\{-\frac{2}{v}\arcsin\frac{v}{2\varkappa}\right\}, \quad \varkappa(v)=\left(\alpha^2+\frac{v^2}{4}\right)^{1/2}. \quad (5.3)$$

Let us first consider some properties of the found asymptotic form at fixed ρ. In the nonresonance case the factor $e^{-\varkappa\rho}$ guarantees the exponential decrease of the amplitude at low, as well as at high, velocities. The minimum of the function $\varkappa(v)$ corresponds exactly to that velocity ($v^2=|\alpha^2-\beta^2|$) at which the kinetic energy of the electron is equal to the energy defect of the reaction. In the resonance case the amplitude decreases only when $v \to \infty$; for $v \to 0$ we have $e^{-\varkappa\rho} \to e^{-\alpha\rho}$, and the amplitude diverges because of the factor v^{-1} in the preexponential function. The latter corresponds to a logarithmic divergence of the cross section in the dense-target approximation. All the enumerated properties of the generalized Massey parameter $\varkappa\rho$ make it highly visualizable and useful for the class of problems under consideration.

Let us establish the correspondence between our results and those of the adiabatic approximation. In the latter case knowledge of the splitting of the terms, $\Delta E(R)$, allows the computation of the amplitude of the resonance charge-transfer process with the aid of the well-known formula[4]

$$F_{Ad}(\rho)=i\sin\left\{\frac{1}{v}\int_\rho^\infty\frac{\Delta E(R)RdR}{(R^2-\rho^2)^{1/2}}\right\}. \qquad (5.4)$$

Using the exact asymptotic form of $\Delta E(R)$[1], and considering large ρ, when the sine in (5.4) can be replaced by its argument, we obtain for the asymptotic form of the amplitude in the adiabatic approximation, $F_{AAd}(\rho)$, the formula (5.1), in which

$$\varkappa_{Ad}=\alpha, \quad D_{Ad}=(4/e)^{1/\alpha}. \qquad (5.5)$$

This result, like (5.1)—(5.3), thus describes the exponential decrease of the amplitude at large ρ. At the same time, the formula (5.4) allows us to also reproduce the oscillations in the probability at small ρ, although only in the resonance adiabatic case. To estimate the total cross section in the dense-target approximation, we need only to know the exponential asymptotic form. The merit, however, of the formulas (5.1)—(5.3) lies in the fact that they are valid at arbitrary velocities and also provide a unified description of the resonance and nonresonance cases.

It may also be noted that the ratio of the factor $e^{-\varkappa(v)\rho}$ to its adiabatic limit $e^{-\alpha\rho}$ for an arbitrarily small, but fixed, velocity can be made to differ from unity by any amount by increasing ρ. This inconsistency in the adiabatic approximation serves as another example of the violation of adiabaticity at large distances, a violation which has been noted before in the problem of electron detachment in atomic collisions[5].

As has been noted above, the correction factor D in the resonance case is, for $v \to 0$, equal to $(4/e)^{1/\alpha}$, i.e., coincides with the result (5.5) obtained in the adiabatic limit. As is well known, for $\alpha=1$, the LCAO MO approximation gives in place of this factor a coefficient equal to $4/3$, which, although incorrect, is numerically close to the exact value of $4/e$[1]. At high velocities the correction factor tends to a constant value equal to $4^{1/\alpha}$. The corresponding limits in the nonresonance case are equal to $2^{(1/\alpha+1/\beta)}$.

Perturbation theory with allowance for only the interaction of the electron with the nuclei, but not the internuclear repulsion (the so-called Brinkman-Kramers (BK) approximation) leads to the following expression for the charge-transfer amplitude (in the case when $\alpha=\beta=1$):

$$F_{BK}(\rho) = \frac{2}{v}\left(\frac{\rho}{\varkappa}\right)^2 K_2(\varkappa\rho), \qquad (5.6)$$

where $K_2(z)$ is the Macdonald function. Thus, there is in the asymptotic expression for the BK amplitude for large ρ,

$$F_{ABK}(\rho)=\sqrt{2\pi}\,v^{-1}\varkappa^{-5/2}\rho^{3/2}e^{-\varkappa\rho}, \quad (\varkappa=\sqrt{1+v^2/4}), \qquad (5.7)$$

a superfluous factor $2i/D$ (here $A=2$). At high velocities this factor tends to the value $i/2$. At the same time, it is well known that the BK approximation gives for the cross section for charge transfer occurring in fast collisions a value that is higher than both the experimental value and the value obtained in the more exact calculations. This seeming contradiction is resolved by the fact that the overestimated total cross section obtained in the BK approximation is accumulated at small ρ in the integration of the probability over the impact parameter. Notice that as $\rho \to 0$ the function (5.1) goes to zero like $\rho^{3/2}$, but the asymptotic theory is no

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longer applicable here (as $\rho \to 0$, the BK amplitude tends to a constant, while the Born approximation leads to a weak (logarithmic) divergence[6]). At high velocities the situation corresponds to the case of nondense (transparent) targets, when knowledge of the exact asymptotic form of $F(\rho)$ for $\rho \to \infty$ is not yet sufficient for the estimation of the cross section.

Let us also give the asymptotic form of the amplitude in the Born approximation for $\alpha = \beta = 1$, computed on the basis of the paper[6]:

$$F_{AB}(\rho) = \frac{\sqrt{2\pi}}{vx^{1/2}}\left\{1 - \frac{1}{v^2} + \frac{4-v^2}{2v^3}\arcsin\frac{v}{2x}\right\}\frac{\rho^{1/2}}{e^{x\rho}}. \qquad (5.8)$$

At high v this expression coincides with the asymptotic form of the BK amplitude, (5.7).

In order to be in a position to make a judgment about the relation between the results of the indicated approximations and the exact asymptotic form at intermediate velocities, we present in Fig. 2 the modulus of the amplitude of the resonance charge-transfer process

$$p+H\to H+p \qquad (5.9)$$

for $v = 1$ a.u. Here the adiabatic approximation (the curve II) highly overestimates the result, and so also does the BK approximation (IV). Notice that for the not-too-large values of ρ shown here the asymptotic form of the BK amplitude (V) differs greatly from the BK amplitude itself. For the velocity in question, the results in best agreement with the exact asymptotic form (I) are those of the Born approximation[6] (VI) (let us recall that, as shown above, this agreement should break down with increasing v), as well as those obtained in the four-Sturmian-state approximation by Gallacher and Wilets in their numerical computation[7] (III).

As an example of the case of nonresonance charge transfer, we present in Fig. 3 the probability of the process Li + Na$^+$ = Li$^+$ + Na $-$ 0.25 eV (the values of the parameters α and A were taken from Smirnov's book[11]). It can be seen that at $v^{-1} = 6$ a.u., Mellius and Goddard's computation[8], carried out in the two-state approximation, somewhat overestimates the charge-transfer probability in the asymptotic region, whereas at $v^{-1} = 18$ a.u. the situation is already reversed.
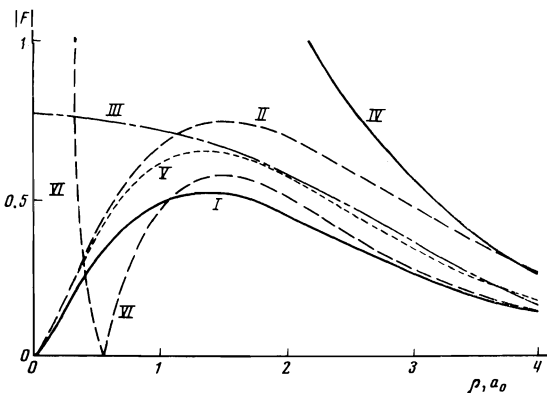
FIG. 3. Probability of the resonance charge-transfer process Li + Na$^+$ $\to$ Li$^+$ + Na $-$ 0.25 eV for different velocities: I) $v^{-1} = 6$ a.u., II) $v^{-1} = 12$ a.u., III) $v^{-1} = 18$ a.u. The solid curves represent the results of Mellius and Goddard's calculation [8], carried out in the two-state approximation; the dashed curves represent the asymptotically exact probability

The application of the asymptotic form of the amplitude to the estimation of the total cross section requires additional assumptions. In the dense-target approximation, it is assumed that in the region where $W(\rho)$ is comparable in magnitude to unity, the probability has an oscillating character with a stochastically varying phase, so that the mean probability in this region $\overline{W} = \frac{1}{2}$. This assumption may be violated even in the adiabatic case because of transitions to other terms or because of the fact that the phase of the oscillations possesses an extremum (the latter circumstance leads to the appearance in the total cross section of oscillations, which are not accounted for by the simple dense-target approximation).

We used the dense-target approximation to estimate the cross section for the process (5.9). There are several, slightly different ways of estimating the cross section. Here we used the variant proposed for the adiabatic case in[1]:

$$\sigma = \pi\rho_0^2/2, \qquad |F(\rho_0)| = 0.28. \qquad (5.10)$$

Comparison of the results of the computation with the aid of the formulas (5.10) and the use of the adiabatic and exact asymptotic forms of $F(\rho)$ shows that for a collision energy $E = 5$ keV the adiabatic approximation overestimates the result by $\sim 10\%$ and that this discrepancy increases with increasing E (Fig. 4). The exact asymptotic form leads to a very good agreement with Gallacher and Wilets' calculations[7] for charge transfer to an atom in the ground state and with McClure's experimental data[9] (these data pertain, however, to the total cross section, including the cross section for charge transfer to all excited states). It is worth noting that the limit of the dense-target region ($E \sim 40$ keV) can clearly be seen in the theoretical[7] and experimental[9] data; at lower energies the cross section almost linearly depends on ln E.

6. CONCLUSION

The merit of the results of the asymptotic theory is the simple and explicit form of the final results as compared to the results of the majority of the other methods (cf., for example,[7,8]). The asymptotic theory is universal, and the specific properties of each atom are re-

FIG. 2. Probability amplitude for the resonance charge-transfer process p + H $\to$ H + p for v = a.u.: I) the asymptotically exact amplitude (5.1), II) adiabatic asymptotic form, III) Gallacher and Wilets' calculation [7] in the four-Sturmian-state approximation, IV) the Brinkman$-$Kramers (BK) approximation (5.4), V) the first term of the asymptotic form of the Brinkman-Kramers amplitude for large ρ, VI) the Born approximation [6].
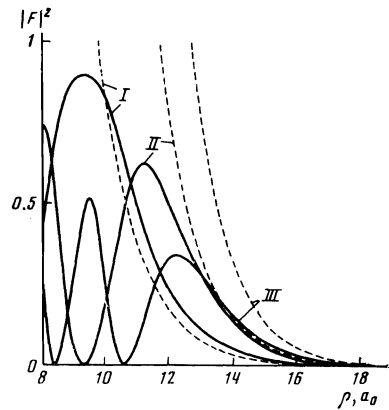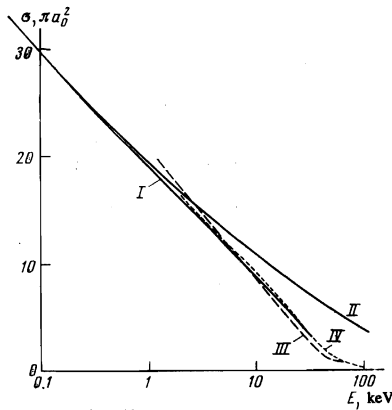
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$$r_b=[\alpha^2(\eta-\xi)^2+2in_{ax}\alpha v(\eta^2-\xi^2)+2n_{ay}\alpha\rho(\eta-\xi)-v^2(\eta+\xi)^2+\rho^2]^{1/2}, \quad \text{(A.3)}$$

and

$$R=[\rho^2-v^2(\eta+\xi)^2]^{1/2}. \quad \text{(A.4)}$$

The Eqs. (A.2) with allowance for (A.3) and (A.4) are soluble in terms of elementary functions up to an additive constant (with respect to ξ) that depends on η and the angular variables and that should be found from the initial condition (4.7). After this the final result assumes the form

$$S^{(1a)}=[\alpha^2-2in_{ax}v-v^2]^{-1/2}$$
$$\times \ln\{[(\alpha^2-2in_{ax}v-v^2)^{1/2}r_b+(\alpha^2-2in_{ax}v-v^2)\xi$$
$$+(-\alpha^2\eta-n_{ay}\alpha\rho-v^2\eta)][(\alpha^2-2in_{ax}v-v^2)^{1/2}$$
$$\times(\rho^2-4v^2\eta^2)^{1/2}-2in_{ax}\alpha v\eta-2v^2\eta-n_{ay}\alpha\rho]^{-1}\}, \quad \text{(A.5)}$$

$$S^{(2a)}=-\frac{1}{v}\left[\arcsin\frac{v(\eta+\xi)}{\rho}-\arcsin\frac{2v\eta}{\rho}\right]. \quad \text{(A.6)}$$

At the point C, for $y_S=0$ (see the formula (3.8)), we obtain after some transformations the solutions

$$S^{(1a)}=\frac{1}{\beta}\ln\frac{1}{2}, \quad \text{(A.7)}$$

$$S^{(2a)}=-\frac{1}{v}\left\{\arcsin\frac{\beta^2-\alpha^2}{2v\varkappa}-\arcsin\frac{\alpha^2-\beta^2+v^2}{2v\varkappa}\right\}. \quad \text{(A.8)}$$

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[1] The nonstationary surface S was required by us only for the derivation of the conditions (2.8) and (2.9); these conditions can be derived in the same way if we use a stationary plane surface, but nonparallel, slightly diverging—at large distances—trajectories; subsequently, the trajectories can be allowed to become straight lines [3].

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FIG. 4. Cross section for the resonance charge-transfer process p + H → H + p: I) the dense-target approximation with the use of the asymptotically exact amplitude, II) same, but with the use of the adiabatic asymptotic form of the amplitude, III) Gallacher and Wilets' calculation [7], IV) McClure's experimental data [9] (total cross section, including the cross section for charge transfer to all excited states).

flected in the theory by the magnitudes of the parameters α and $A^{(a)}$. Another advantage lies in the fact that the asymptotic theory is not connected with any approximations. It should be noted here that for the nonresonance processes the search for the amplitude in the adiabatic theory requires additional assumptions[1]. The nonadiabatic theory constructed in the present paper provides a uniform and universal description of the resonance and nonresonance cases.

The question, however, arises: At what values of ρ is the asymptotic form sufficiently well approximated by the above-computed dominant term? Comparison with other calculations makes us think that this approximation is also admissible at not too large ρ (e.g., those at which the amplitude of the charge-transfer probability is just a few tenths). In order to be able to make a more consistent judgment about the nature of the convergence of the asymptotic series, we must compute its next terms (notice that the first nine terms of the asymptotic expansion of $\Delta E(R)$ have at present been found in the adiabatic approximation for the system H_2^+[1]). The determination of the next terms of the series is quite practicable with the aid of the method described in the present paper, although it does require somewhat more tedious computations.

APPENDIX

Let us integrate the partial differential equation (4.6). Let us note first of all that, as the variables, it is convenient to choose ξ, η, and the angular variables n_{ax}, n_{ay}, n_{az} ($n_a = r_a/r_a$), only two of the latter variables being independent $n_{ax}^2 + n_{ay}^2 + n_{az}^2 = 1$). It is also convenient to set

$$S^{(a)}=S^{(1a)}+S^{(2a)}, \quad \text{(A.1)}$$

where

$$\partial S^{(1a)}/\partial\xi=1/r_b, \quad \partial S^{(2a)}/\partial\xi=-1/R, \quad \text{(A.2)}$$

with