

Asymptotic theory of $s \rightarrow p$ charge exchange: Extended Demkov model

V.N. Ostrovsky

Institute of Physics, The University of St. Petersburg, 198904 St. Petersburg, Russia

(Received 14 May 1993)

The asymptotic theory is developed for the calculation of the charge-exchange amplitudes for large impact parameters ρ . The case of the small energy defect is considered which corresponds to the Demkov model (nonadiabatic transitions induced by the switching of the wave functions from the atomic states to the molecular-orbital regime). The effect of electron momentum transfer is included. The initial and final states with nonzero orbital momentum are considered with a special emphasis on the simplest case of $s \rightarrow p$ charge exchange. The large- ρ asymptote of the charge-exchange amplitude is calculated both for the transitions induced by radial and rotational couplings. One-center depolarization transitions (changing the projection of the angular momentum) are also incorporated in the general theory. The orientation and alignment parameters characterizing the asymmetry created in the $s \rightarrow p$ process are obtained in a simple analytical form for large ρ (or small scattering angles). They include contributions both from the one-center depolarization and from the competition of the charge exchange induced by radial and rotational coupling. The relative role of both mechanisms is analyzed and a strong dependence of the asymmetry parameters on the sign of the process energy defect is predicted. The theory is applied to the process $\text{Na}(3p) + \text{H}^+ \rightarrow \text{Na}^+ + \text{H}(n=2)$.

PACS number(s): 34.70.+e

I. INTRODUCTION

For the process of charge exchange with the small defect of resonance the qualitative understanding and the quantitative estimates are greatly facilitated by the well known Demkov [1] model. It describes the nonadiabatic transitions between the quasimolecular states due to the rearrangement of the quasimolecule wave functions from the separated atoms regime to the molecular orbitals as the internuclear separation R varies. Assuming a purely exponential R dependence of the coupling matrix element in the diabatic basis and constant diagonal matrix elements, Demkov [1] obtained an exact solution of the two-state problem. The expressions for the total charge-exchange cross sections within the Demkov model are given in Ref. [2].

As a two-state model, the Demkov model is directly applicable to the $s \rightarrow s'$ charge exchange. For the exchange between the states with nonzero orbital momenta $l_a \rightarrow l_b$ the resonance one-center transitions changing the momenta projections m_a, m_b are very efficient and influence the charge exchange. The final m_b substates are populated coherently with various relative phases and amplitudes. This implies creation of the orbital asymmetry in the charge-exchange process, which is a subject of intensive studies nowadays (for a general review of the asymmetry effects see Refs. [3,4]). Clearly, the two-state model is unable to describe it.

Within the quasimolecular approach the $s \rightarrow s'$ charge exchange is described as the transition induced by the radial motion. In the general case ($l_a \rightarrow l_b$) the charge-exchange transitions induced by the rotation of the internuclear axis are also operative. When the relative collision velocity v increases, the role of the rotation-induced

charge exchange becomes more important.

Even in the simplest case of the $s \rightarrow p$ charge exchange the minimal basis allowing for these effects includes three states (Sec. V). An exact solution of the realistic three-state model can hardly be achieved.

In the present paper we develop *asymptotic* theory for the dynamics of the transitions in the case of large impact parameters ρ . This approach allows us to put under consideration the effects discussed above and also the momentum transfer by the electron which is expressed by the well-known electron translation factors (ETF's). This is particularly important since the modern experiments (for the references see below) are often performed in the medium velocity region where inclusion of ETF's in the theory is necessary.

The general mathematical framework of the present asymptotic approach was developed by the author [5] and applied to the inclusion of the ETF's in the Landau-Zener model. In particular it was employed [6] for the interpretation of the orientation effects in the charge exchange $\text{B}^{3+} + \text{He} \rightarrow \text{B}^{2+}(2p) + \text{He}^+$ where strong circular polarization of the radiation emitted by $\text{B}^{2+}(2p)$ ion was observed [7].

We do not try to generalize the Demkov model in its full extent. Our treatment retains the most important features of the Hamiltonian (as they were stated above). We consider only the limit of large impact parameters ρ where the transition probabilities are small, whereas the exact solution of two-state problem (obtained by Demkov [1]) is applicable both in the cases of small and large transition probabilities. In the other terms we study the threshold behavior of the transition probabilities as ρ decreases. Generally it is related to the small-angle scattering.

In some respects our approach is broader than the Demkov model. We do not need assume purely exponential behavior of the coupling. It is well known [8] that the asymptotic (large- R) behavior of the coupling (in the diabatic basis) is represented by the exponent multiplied by some power of R . Inclusion of the latter factor in the conventional Demkov model requires additional efforts [9] whereas in our approach it is done naturally.

Comparing the present approach with the previous works, we note that Burns and Crothers [10] and Hughes and Crothers [11] introduced ETF's in the Demkov-type Hamiltonian but also did not pursue exact solution of the problem. The Hamiltonian matrix elements in these papers did not satisfy the Hermiticity condition $H_{ij} = H_{ji}^*$, and the authors replaced them by the pragmatic average $\frac{1}{2}(H_{ij} + H_{ji}^*)$. After that the low-velocity case was analyzed. The concept of the effective (velocity-dependent) resonance introduced in this paper has some analogy with our form of the Massey parameter (Sec. III).

The conceptual difficulties due to the non-Hermiticity were met also by Pfeifer and Garcia [12], who attempted to reiterate Demkov's exact solution with inclusion of ETF's. Nevertheless this author demonstrated the importance of the effect in the calculation of the vacancy sharing ratio. Note that the cited authors [10–12] considered only the $s \rightarrow s'$ charge exchange.

As for the rotation-induced transitions, presently the two-state models exist which describe their dynamics in various situations (see, e.g., Refs. [13–15] and the bibliographies therein). They employ some parametrizations of the two-state Hamiltonian. The large- R asymptotic theory for the direct calculations of the Hamiltonian matrix elements [8] was developed previously only for the radial-induced transitions. It was never applied to the transitions induced by the rotational coupling of the quasimolecular states. The only exception seems to be the paper by the present author [5] where the situation corresponding to the Landau-Zener model was considered. Below we start from first principles and do not introduce any parametric Hamiltonian. Both radial- and rotation-induced transitions are treated on equal footing.

Organizing the paper we separate the theoretical construction of the asymptotic theory (Secs. II and IV and the Appendix) from the physical discussion (Secs. III, V, and VI) and applications (Sec. VII). Section II exposes the asymptotic theory of the $s \rightarrow s'$ charge exchange with the small defect of resonance. Its generalization to the $l_a \rightarrow l_b$ process is carried out in Sec. IV. In Sec. III the importance of ETF's is discussed in terms of the Massey parameter.

Section IV contains a qualitative discussion and could be read autonomously. First we reiterate a few basic conclusions of the asymptotic treatment in application to the simplest case of the $s \rightarrow p$ charge exchange. They allow us to calculate the orientation and alignment parameters which characterize the orbital asymmetry created in the charge exchange (Sec. V). The underlying physical mechanisms are analyzed in Sec. VI.

In Sec. VII the theory is applied to the charge-exchange process $\text{Na}(3p) + \text{H}^+ \rightarrow \text{Na}^+ + \text{H}(n=2)$, where quite satisfactory agreement is obtained for the orientation pa-

rameter with the experimental measurements at small scattering angles. Section VIII summarizes the principle conclusions.

II. CHARGE-EXCHANGE AMPLITUDE IN THE LIMIT OF LARGE IMPACT PARAMETERS

We assume the classical description for the colliding atom nuclei which move along some trajectories. The amplitude of charge transfer can be presented *exactly* [5, 16] as an integral over the surface S dividing the colliding atoms and over the time t :

$$F = \frac{i}{2} \int_{-\infty}^{\infty} dt \int_S dS [\Psi_2(\vec{r}, -t) \vec{\nu} \cdot \vec{\nabla} \Psi_1(\vec{r}, t) - \Psi_1(\vec{r}, t) \vec{\nu} \cdot \vec{\nabla} \Psi_2(\vec{r}, -t)], \quad (2.1)$$

where $\vec{\nu}$ is the unit vector normal to S . The wave function $\Psi_1(\vec{r}, t)$ is the *exact* solution of the nonstationary Schrödinger equation for the active electron, and $\Psi_2(\vec{r}, t)$ is the solution of the same equation with the Hamiltonian *inverted in time* t [this is the reason why the expressions (2.2) and (2.3) contain the same ETF $\exp(\frac{i}{2}\vec{\nu} \cdot \vec{r})$]. The formula (2.1) is discussed in detail in Ref. [5]. Below we reiterate briefly some points of the subsequent development in order to introduce the consistent notations and at the same time rearrange the expressions to the form suitable for the present study. Atomic units are used everywhere.

In the subsequent calculations we employ for the wave functions their large- t asymptotic expressions describing the system before and after the charge exchange, respectively,

$$\Psi_1(\vec{r}, t) = \psi^{(a)}(\vec{r}_a) \exp \left[\frac{i}{2} \vec{\nu} \cdot \vec{r} - i(E_a + \frac{1}{8}v^2t) \right], \quad (2.2)$$

$$\Psi_2(\vec{r}, t) = \psi^{(b)}(\vec{r}_b) \exp \left[\frac{i}{2} \vec{\nu} \cdot \vec{r} - i(E_b + \frac{1}{8}v^2t) \right]. \quad (2.3)$$

These expressions include explicitly the ETF $\exp(\frac{i}{2}\vec{\nu} \cdot \vec{r})$ and gives the exact wave function for the electron bound to the isolated atomic nucleus which moves with the constant velocity $\frac{1}{2}\vec{\nu}$. The electron energy is E_a and E_b and the atomic orbitals $\psi^{(a)}, \psi^{(b)}$ can be presented in the form

$$\psi^{(a)}(\vec{r}_a) = Y_{l_a m_a} \left(\frac{\vec{r}_a}{r_a} \right) P^{(a)}(r_a) \exp(-\alpha r_a), \quad (2.4)$$

$$\psi^{(b)}(\vec{r}_b) = Y_{l_b m_b} \left(\frac{\vec{r}_b}{r_b} \right) P^{(b)}(r_b) \exp(-\beta r_b), \quad (2.5)$$

where $E_a = -\frac{1}{2}\alpha^2$; $E_b = -\frac{1}{2}\beta^2$; l_a, m_a and l_b, m_b are the electron orbital momentum and its projection in the initial and final states, respectively; $Y_{lm}(\vec{n})$ are the spherical harmonics; \vec{r}_a (\vec{r}_b) is the electron radius vector relative to the nucleus a (b). The pre-exponential functions $P^{(a)}(r), P^{(b)}(r)$ are discussed in Refs. [5, 8]. Here we stress that for the present calculations only large- r

asymptotes of these functions are important. They are proportional to $r^{Z_a/\alpha-1}$ and $r^{Z_b/\beta-1}$ respectively, where Z_a (Z_b) is the charge of the atomic core.

The atomic orbital form (2.4) and (2.5) employed in our previous work [5] does not account for the one-center transitions between the degenerate states with different quantum numbers m_a (or m_b). In Sec. IV we generalize these expressions to include such depolarization processes.

The surface integral in (2.1) is calculated for an arbitrary moment of time using the two-dimensional steepest descent (or stationary phase) method. Here we present the results in a more appealing form than before [5]:

$$\int_S dS [\Psi_2(\vec{r}, -t) \vec{\nu} \cdot \vec{\nabla} \Psi_1(\vec{r}, t) - \Psi_1(\vec{r}, t) \vec{\nu} \cdot \vec{\nabla} \Psi_2(\vec{r}, -t)] = V(t) \exp \left(-i \int_0^t [E_1(t') - E_2(t')] dt' \right), \quad (2.6)$$

$$V(t) = [Y_{l_a m_a} Y_{l_b m_b}] A^{(a)} A^{(b)} D \frac{\pi}{\gamma} R(\alpha + \beta) \times \left(\frac{\alpha + \beta}{4\gamma} R \right)^{Z_a/\alpha + Z_b/\beta - 2} \exp(-\gamma R), \quad (2.7)$$

$$\gamma = \frac{1}{2} \sqrt{(\alpha + \beta)^2 + v_x^2}. \quad (2.8)$$

The angular-dependent factor in the square brackets in (2.7) [and below in (2.16) and (4.7)] should be calculated at the stationary phase point:

$$x_0 = i \frac{v_x}{4\gamma} R, \quad y_0 = 0, \quad z_0 = 0, \quad (2.9)$$

in which

$$r_a = r_b = \frac{(\alpha + \beta)R}{4\gamma}. \quad (2.9')$$

The geometry of the collision is shown in Fig. 1. The origin of the coordinate system lies at the center of the internuclear axis. The z axis is directed along this axis, the x axis is perpendicular to z and lies in the collision plane, and the y axis is perpendicular to the collision plane. v_x is the x component (perpendicular to the internuclear axis) of the velocity vector \vec{v} .

The time-dependent exponent in (2.6) was omitted in the related formula (3.9) of Ref. [5]; however, it was included in all subsequent calculations. In the simplest approximation (used later) the energies $E_1(t), E_2(t)$ coincide with the separated atom energies E_a, E_b ; then the time-dependent exponent in (2.6) follows directly from (2.2) and (2.3). More generally, some additional net interaction between the colliding particles can be incorporated in $E_1(t), E_2(t)$. We include in (2.7) the correction factor D . Its calculation is discussed in the Appendix.

The charge-transfer amplitude (2.1) is presented now as the integral over time:

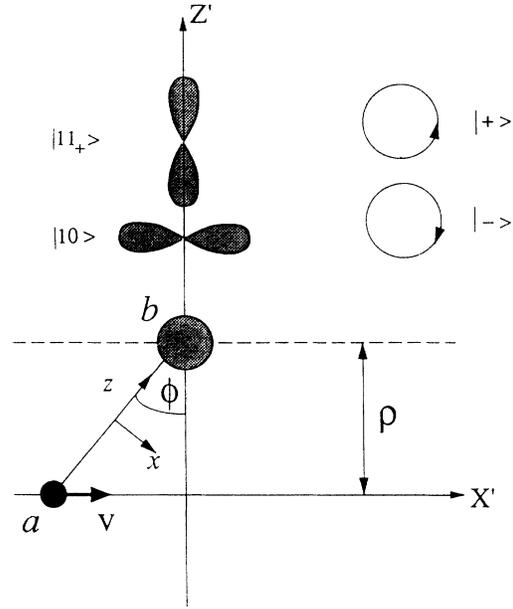


FIG. 1. Charge-exchange collision geometry used in the present calculations (see text).

$$F = \frac{i}{2} \int_{-\infty}^{\infty} dt V(t) \exp \left(-i \int_0^t [E_1(t') - E_2(t')] dt' \right). \quad (2.10)$$

This representation is quite appealing since it has the form of the first-order nonstationary perturbation theory. From this point of view all previous development is intended to provide a proper form of the interaction matrix element $V(t)$ in the case of the charge exchange when the momentum transfer by the electron is taken into account. Note that the well-known problem of non-orthogonality of the electron initial and final states and the non-Hermiticity problem (see the Introduction) do not appear in the present approach.

The specifics of the Demkov model appear when the integral over time in (2.10) is evaluated. In the Landau-Zener model the difference $E_1(t') - E_2(t')$ is zero for some internuclear separation (which corresponds to the crossing of the diabatic potential curves). For the Demkov model we assume that this difference is time independent and equal to the energy defect of the process $E_1(t') - E_2(t') = \Delta E$, $\Delta E \equiv E_a - E_b = \frac{1}{2}(\beta^2 - \alpha^2)$; thus

$$F = \frac{i}{2} \int_{-\infty}^{\infty} dt V(t) \exp(-i\Delta E t). \quad (2.11)$$

The important feature of the integral (2.11) is the exponential dependence of the matrix element V (2.7) on the internuclear separation R . It is taken into account in calculations by the conventional stationary phase method (see, e.g., Ref. [17]) when the exponential factor $\exp(\tilde{\Phi})$ is singled out in the integrand:

$$\tilde{\Phi}(t) = -\gamma_0 R(t) - i\Delta E t. \quad (2.12)$$

For the time dependence of the internuclear separation we assume the straight-line approximation $R = \sqrt{\rho^2 + v^2 t^2}$, where ρ is the impact parameter. The large- ρ asymptote of the transition amplitude is defined by the vicinity of the point of the closest approach on the trajectory of the atomic nuclei ($t = 0$), where the projection v_x [which enters γ (2.8)] is close to v . Therefore for simplicity we use in (2.12) γ_0 instead of γ (2.8):

$$\gamma_0 = \frac{1}{2} \sqrt{(\alpha + \beta)^2 + v^2}. \quad (2.13)$$

The stationary phase point in time t_0 is defined by the equation $d\tilde{\Phi}/dt = 0$. Its solution is

$$t_0 = -i \frac{\rho}{v} \frac{\Delta E}{\kappa}, \quad \kappa = \sqrt{\gamma_0^2 v^2 + \Delta E^2}, \quad (2.14)$$

with the phase at this point

$$\tilde{\Phi}(t_0) = -\frac{\kappa}{v} \rho \quad (2.15)$$

and $R = R_0 = \rho \gamma_0 v / \kappa$. The integral (2.11) is given by

$$F = i2 [Y_{l_a m_a} Y_{l_b m_b}] A^{(a)} A^{(b)} D \pi \gamma_0 g \left(\frac{2\pi \rho v}{\kappa^3} \right)^{\frac{1}{2}} \times \left(\frac{(\alpha + \beta)v}{4\kappa} \frac{\gamma_0}{\gamma} \rho \right)^{Z_a/\alpha + Z_b/\beta - 1} \exp\left(-\frac{\kappa}{v} \rho\right), \quad (2.16)$$

where now

$$\gamma = \frac{1}{2} \sqrt{(\alpha + \beta)^2 + \kappa^2 / \gamma_0^2}. \quad (2.17)$$

The correction factor g

$$g = \exp[-(\gamma - \gamma_0)\gamma_0 v \rho / \kappa] \quad (2.18)$$

appears due to the choice of large phase in the form (2.12) with γ instead of γ_0 . It is discussed in Sec. III.

The fact that $\text{Re}t_0 = 0$ shows that the principal contribution to the charge exchange comes from the vicinity of the point of the closest approach on the trajectory. In the next section we discuss the implications of the formula (2.16) for the simplest case of the charge exchange between the atomic s -states, for which the Demkov model was originally suggested.

III. CHARGE EXCHANGE $s\sigma \rightarrow s'\sigma$ AND THE EFFECT OF ETF

Since s states are correlated only with σ molecular states, we denote this transition as $s\sigma \rightarrow s'\sigma$ in order to make the notations uniform with the other cases considered in Secs. IV–VII. The one-center orbital depolarization transitions are absent for s states and the factor in the square brackets in (2.16) is simply $1/(4\pi)$. We rewrite the formula for the charge-exchange amplitude for this important case:

$$F = i f_{s\sigma \rightarrow s'\sigma}, \quad (3.1)$$

$$f_{s\sigma \rightarrow s'\sigma} \equiv A^{(a)} A^{(b)} D \gamma_0 g \left(\frac{\pi \rho v}{2\kappa^3} \right)^{\frac{1}{2}} \times \left(\frac{(\alpha + \beta)v}{4\kappa} \frac{\gamma_0}{\gamma} \rho \right)^{Z_a/\alpha + Z_b/\beta - 1} \times \exp\left(-\frac{\kappa}{v} \rho\right). \quad (3.2)$$

The most important part of this expression (which defines the threshold behavior of the charge-exchange amplitude as the impact parameter ρ decreases) is the exponential factor $\exp(-\rho\kappa/v)$ with the argument

$$\xi \equiv \rho\kappa/v = \frac{\rho}{2v} \sqrt{(\alpha + \beta)^2 v^2 + v^4 + 4\Delta E^2}, \quad (3.3)$$

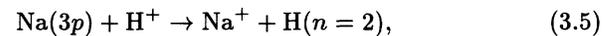
which is essentially the Massey parameter characterizing the transition in the situation considered here. It is somewhat different from the parameter found by Demkov and Ostrovsky [16] for the extremely large impact parameters. In the present formulation the latter regime appears for the impact parameters ρ so large that the exponential behavior of $g(\rho)$ (2.18) becomes essential. Now we analyze the regime of small resonance defect ΔE and moderately large ρ when $g(\rho) \approx 1$. In this region the charge-exchange amplitude F is presented in the appealing form of the integral over time (2.10) whereas for the extremely large ρ the stationary phase integration should be performed simultaneously in the coordinates and time [16].

In the adiabatic limit $v \rightarrow 0$ the Massey parameter is

$$\xi = \frac{\rho}{v} \Delta E. \quad (3.4)$$

The term $(\alpha + \beta)^2 v^2$ under the square root in (3.3) appears due to the specifics of the charge-transfer process described by the Demkov model: the rapid variation of the interaction V with R . It is *not related to ETF's*. The latter effect generates only the term v^4 in Eq. (3.3).

As an example of the situation when v is not small as compared with the typical electron velocity (α or β) we consider the charge-exchange process



extensively studied recently both in experiment [18–21] and theory [22–24] including the differential cross sections for small scattering angles. This process does not belong to the $s\sigma \rightarrow s'\sigma$ type. However, as shown below (Secs. IV and V) the exponential part of the amplitude is the same for all types of the processes. It depends only on the energy parameters α and β and on the collision velocity v . The incident proton energy in the experiments by Houver *et al.* [21] was 1 keV, which corresponds to $v = 0.2$ a.u. The other parameters of the colliding atoms are (in atomic units)

$$\alpha = 0.5, \quad \beta = 0.472, \quad (3.6)$$

$$\Delta E = E_a - E_b = \frac{1}{2}(\beta^2 - \alpha^2) = -0.0134.$$

The first term under the square root in (3.3) prevails and the Massey parameter is recast conveniently as

$$\begin{aligned}\xi &= \rho \frac{\alpha + \beta}{2} \left(1 + \zeta^2 + \frac{4\Delta E^2}{(\alpha + \beta)^2 v^2} \right)^{1/2} \\ &\approx \rho \frac{\alpha + \beta}{2} + \rho \frac{\alpha + \beta}{4} \zeta^2 + \rho \frac{\Delta E^2}{(\alpha + \beta) v^2}.\end{aligned}\quad (3.7)$$

The parameter

$$\zeta = \frac{v}{\alpha + \beta} \quad (3.8)$$

essentially coincides with the similar parameter introduced in Ref. [5]. It is the ratio of the collision velocity and the (doubled) typical velocity of the electron in the bound atomic states and characterizes the importance of ETF's (note that in Ref. [5] the parameter ζ was erroneously named the *square* of the velocities' ratio). In the present example $\zeta^2 = 0.042$ while the third term under the square root in (3.7) is 0.019. For the impact parameter $\rho = 20$ a.u. (which is typical for the small angle scattering observable in experiments) according to (3.7) inclusion of ETF's reduces the charge-exchange amplitude by the factor 0.82. Of course this estimate demonstrates the overall situation and for some scattering characteristics the momentum transfer effects could be more significant. For the electron orbital asymmetry created by the charge exchange the situation is analyzed below.

IV. CHARGE EXCHANGE INDUCED BY RADIAL AND ROTATIONAL COUPLING IN THE DEMKOV MODEL

In order to account for the one-center depolarization transitions (which mix the states with various quantum numbers m_a or m_b) we generalize formulas (2.4) and (2.5) in the following way:

$$\begin{aligned}\psi^{(a)}(\vec{r}_a, t) &= \sum_{m_a} c_{m_a m_{a0}}(t) Y_{l_a m_a} \left(\frac{\vec{r}_a}{r_a} \right) \\ &\quad \times P^{(a)}(r_a) \exp(-\alpha r_a),\end{aligned}\quad (4.1)$$

$$\begin{aligned}\psi^{(b)}(\vec{r}_b, t) &= \sum_{m_b} c_{m_b m_{b0}}(t) Y_{l_b m_b} \left(\frac{\vec{r}_b}{r_b} \right) \\ &\quad \times P^{(b)}(r_b) \exp(-\beta r_b).\end{aligned}\quad (4.2)$$

Here the information about the one-center transitions is contained in the matrix of time-dependent coefficients $c(t)$. The initial conditions are

$$\begin{aligned}c_{m_a m_{a0}}(t) &\rightarrow \delta_{m_a m_{a0}}, \quad c_{m_b m_{b0}}(t) \rightarrow \delta_{m_b m_{b0}} \\ &\text{for } t \rightarrow -\infty.\end{aligned}\quad (4.3)$$

Thus m_{a0} and m_{b0} are the electron azimuthal quantum numbers in the initial and final states, respectively. It is convenient to assume that on the right-hand side of expressions (4.1) and (4.2) the spherical functions are quantized along the internuclear axis. Then the quan-

tum numbers m_{a0}, m_{b0} in (4.1) and (4.2) coincide with the projection λ of the electron orbital momentum on the quasimolecule axis. This implies that we are using the molecular-orbital representation because it is more suitable for the qualitative analysis. Hence the coefficients $c_{mm_0}(t)$ describe the depolarization transitions in the molecular basis (DTMB). Note, however, that in fact our molecular orbits are the atomic states but with the electron orbital momentum coupled rigidly with the internuclear axis.

Consider two important extreme cases. In the adiabatic regime (with respect to DTMB) the electron orbital momentum follows rigidly the internuclear axis; then

$$c_{m_a m_{a0}}(t) = \exp[-i\Xi_{m_a}(t)] \delta_{m_a m_{a0}}, \quad (4.4)$$

$$c_{m_b m_{b0}}(t) = \exp[-i\Xi_{m_b}(t)] \delta_{m_b m_{b0}}$$

for all values of time t . Here $\Xi_{m_a}(t)$ and $\Xi_{m_b}(t)$ are the adiabatic phases gained on the Born-Oppenheimer potential curves $E_\lambda(R)$ correlated with the initial and final states, respectively,

$$\Xi_\lambda(t) = \int_{-\infty}^t \delta E_\lambda(t') dt', \quad \delta E_\lambda(R) \equiv E_\lambda(R) - E_\lambda(\infty). \quad (4.5)$$

The index λ stands for the electron orbital momentum projection on the internuclear axis.

In the opposite regime the electron orbital momentum is completely decoupled from the internuclear axis and retains its orientation in space. This implies that the transitions between the quasimolecule states are operative; they are of purely geometrical origin. The coefficients $c_{m_a m_{a0}}(t), c_{m_b m_{b0}}(t)$ coincide with the matrix elements of the space rotation operator in the basis of the spherical harmonics, i.e., with the well-known Wigner functions (see, e.g., the book by Edmonds [25]);

$$c_{m_a m_{a0}}(t) = d_{m_a m_{a0}}^{(l_a)}(\phi + \pi/2), \quad (4.6)$$

$$c_{m_b m_{b0}}(t) = d_{m_b m_{b0}}^{(l_b)}(\phi + \pi/2).$$

We choose the zero of the internuclear axis rotation angle ϕ corresponding to the position of the closest approach in course of the collision ($t = 0$); then $\sin \phi = vt/R$ (note that in Fig. 1 one has $\phi < 0$). In terms of the locking radius R_L (see, e.g., the review by Hertel *et al.* [26]) the first case considered above corresponds to the relation $\rho \ll R_L$, whereas in the second limit $\rho \gg R_L$.

Now the functions (4.1) and (4.2) should be used instead of (2.4) and (2.5) in the calculation of the surface integral in Eq. (2.1) and the integral over time [see (2.11)]. Clearly this substitution does not change the position of the stationary phase point (2.9) and (2.14) and influences only the ρ -dependent pre-exponential factor which should be calculated at this point. Only this factor incorporates the orbital quantum numbers l_a, m_a, l_b, m_b . Both the exponential factor and the power of ρ in the pre-exponential are universal and hence coincide with these obtained above for the case $l_a = m_a = l_b = m_b = 0$

($s\sigma \rightarrow s'\sigma$ transitions). This is an important property of the asymptotic regime in the large impact parameter ρ . Note, however, that the pre-exponential factors have different v dependence for various types of transition and differ in magnitude substantially (see below).

Formally it is convenient to express the charge-exchange amplitude in terms of the standard expression (3.2) for the amplitude of the $s\sigma \rightarrow s'\sigma$ transition, which incorporates the exponential and power ρ dependence. The factor before this amplitude contains the coefficients $c_{m_a m_{a0}}(t)$, $c_{m_b m_{b0}}(t)$ calculated at the stationary phase point t_0 (2.14):

$$F_{l_a m_a \rightarrow l_b m_b} = i 4\pi \sum_{\lambda, \lambda'} [Y_{l_a m_a} Y_{l_b m_b}] c_{\lambda m_a}(t_0) \times c_{\lambda' -m_b}(-t_0) (-1)^{l_b} f_{s\sigma \rightarrow s'\sigma}. \quad (4.7)$$

For the $s \rightarrow s'$ charge exchange the formula (4.7) reduces to (3.1). Both on the left- and right-hand sides of (4.7) the quantum numbers in the initial (l_a, m_a) and final (l_b, m_b) atomic states correspond to the quantization in the space-fixed frame along the *initial* position of the internuclear axis which coincides with the collision velocity vector \vec{v} . The *final* position of the internuclear axis is *antiparallel* to the vector \vec{v} , which in the straight-line approximation does not change its direction. Transitions to the \vec{v} axis in the final state lead to the appearance of the phase factor $(-1)^{l_b}$ and the subscript $-m_b$ on the right-hand side of Eq. (4.7).

The expression (4.7) describes the amplitude of the charge exchange between the atomic states $l_a, m_a \rightarrow l_b, m_b$ in the space-fixed frame as a sum of the contributions related with various *molecular quantum numbers* λ, λ' . Here λ (λ') refers to the projection of the electron orbital momentum on the internuclear axis. The molecular orbitals are correlated in the separated atom limit with various substates of the atoms a (b). In other words, the same final atomic state can be populated via various paths corresponding to the transitions between the quasimolecular states.

The terms in (4.7) with $\lambda = \lambda'$ correspond to the charge-exchange transitions induced by the radial coupling which do not alter the electron orbital momentum projection on the internuclear axis. It should be noted, however, that below we account only for $\sigma \rightarrow \sigma'$ transitions of this type ($\lambda = \lambda' = 0$). The analysis of $\pi \rightarrow \pi'$ transitions (and more generally, the transitions with $\lambda = \lambda' \neq 0$) in the framework of the present theory contains some peculiarities which need a separate study.

The terms with $\lambda \neq \lambda'$ represent the transitions induced by the rotational (or Coriolis) coupling between the quasimolecular states. Note that the matrix elements of *direct* rotational coupling do not vanish only for $|\lambda - \lambda'| = 1$. However, *indirectly* (i.e., via the intermediate states) the rotation-induced transitions occur also for all $|\lambda - \lambda'| > 1$. It can be shown that the related contributions to the total charge-exchange amplitude (4.7) decrease for the higher $\Delta\lambda \equiv |\lambda - \lambda'|$ as $\eta^{\Delta\lambda}$, where $\eta = \kappa(\alpha + \beta)/\gamma_0$ is small: $\eta \approx v/(\alpha + \beta)$ for $v > 2\Delta E/(\alpha + \beta)$. The account for the transitions with

$\Delta\lambda > 1$ clearly demonstrates that the present approach is broader than the first-order perturbation theory in the molecular basis.

As an independent variable it is convenient to use instead of time t the angle, ϕ which has the simple geometrical meaning (see Fig. 1). Then the value of ϕ_0 corresponding to the *stationary phase point in time* t_0 is defined by the relations

$$\sin \phi_0 = -i \frac{\Delta E}{\gamma_0 v}, \quad \cos \phi_0 = \sqrt{1 + [\Delta E/(\gamma_0 v)]^2}. \quad (4.8)$$

Physically t_0 (or ϕ_0) specifies the moment of time (or the point on the trajectory) when (where) the charge exchange primarily occurs and the related final molecular states are populated. Generally the contributions which come from various moments of time t should be summed coherently as the formula (2.10) [or (2.11)] implies. In the asymptotic region considered here this coherent summation is equivalent to calculating the contribution from the single point of stationary phase t_0 (or ϕ_0). Since $\phi_0 \neq 0$, this point is somewhat shifted from the point of the closest approach $\phi = 0$ and the value of ϕ_0 can be considered as a "geometrical" measure of this "retardation" effect. For subsequent analysis it is essential that the sign of ϕ_0 depends on the sign of the charge-exchange energy defect ΔE and thus bears information on the charge-transfer dynamics. The direct geometrical interpretation is somewhat obscured by the fact that ϕ_0 is imaginary. For the simplification of the formulas below it is convenient to introduce its real counterpart

$$\Phi_0 = \text{Im} \phi_0 = -\sinh^{-1} \frac{\Delta E}{\gamma_0 v}. \quad (4.9)$$

Qualitatively this "quasiangle" characterizes the importance of the DTMB for the charge exchange.

The angular factor in the square brackets in (4.7) should be evaluated at the *stationary phase point in space* (2.9). In practical calculations it is convenient to introduce the other quasiangle Θ_0 by the relations

$$\sinh \Theta_0 = \frac{\kappa}{\gamma_0(\alpha + \beta)}, \quad \cosh \Theta_0 = \frac{\sqrt{(\alpha + \beta)^2 + \kappa^2/\gamma_0^2}}{\alpha + \beta}. \quad (4.10)$$

The charge-exchange process can be interpreted in terms of the electron flux from the atom a to the atom b . Qualitatively it is important to trace how the electron current crosses the surface S dividing the colliding atoms (for the precise definition of S see Ref. [5]). In the case of large R (or ρ) the electron flux crossing S is concentrated at the vicinity of the stationary phase point x_0 (2.9). The geometrical meaning of Θ_0 is clear from the relation $\tan(i\Theta_0) = -x_0/(R/2)$: this (quasi)angle shows how the line of the electron flux deviates from the straight line which joins a and b (for the latter $x_0 = 0$). Thus in contradistinction to Φ_0 the quasiangle Θ_0 characterizes the *dynamics of the electron* in the course of charge exchange.

In the subsequent discussion we use the spectroscopic notations as the indices of the spherical harmonics quantized on the internuclear axis that cannot lead to con-

fusions. Note that the $p\pi_+$ quasimolecular state is symmetric under the reflection in the collision plane.

The following simple arguments applied to the simplest case of the $s \rightarrow p$ charge transfer show the relation between the magnitude of the quasiangle Θ_0 and the rotation-induced charge exchange. In the case $\Theta_0 = 0$ (or $x_0 = 0$) the spherical functions $[Y_{s\sigma}]$ and $[Y_{p\sigma}]$ are nonzero, whereas $[Y_{p\pi_+}]$ is zero ($[Y_{p\pi_-}]$ is always zero due to the symmetry reasons). Thus, due to the factor in the square brackets in (4.7), only $s\sigma \rightarrow p\sigma$ charge-exchange transitions ($\lambda = \lambda' = 0$) are operative in this case and the rotation-induced $s\sigma \rightarrow p\pi$ transitions are absent. This limit corresponds to the low collision velocity regime (Sec. VI). As Θ_0 increases (which occurs for the higher collision velocities), the value of the spherical function $[Y_{p\pi_+}]$ at the point of stationary phase is enhanced and the rotation-induced charge exchange becomes more important. Quantitatively the situation can be interpreted in terms of the Coriolis forces which deflect the electron flux in the charge-transfer process from the straight line, thus enhancing the λ -changing transitions.

In the adiabatic regime with respect to the DTMB the summation in formula (4.7) is lifted due to (4.4). This makes the expression for the charge-exchange amplitudes particularly simple. Note that in this case $m_a = \lambda$ and $m_b = -\lambda'$, but the amplitude (4.7) is nonzero for all λ, λ' including $\lambda \neq \lambda'$. Thus the rotation-induced charge exchange is operative in this limit also. Below we concentrate primarily on the opposite case which seems to be most likely for the distant collisions.

V. CHARGE EXCHANGE $s \rightarrow p$ AND THE ORBITAL ASYMMETRY EFFECTS

Applying the general theory of the preceding section to the most simple case of the $s \rightarrow p$ charge exchange, we see that three quasimolecular states should be considered: $s\sigma$, $p\sigma$ and $p\pi_+$ (the subscript indicates that the $p\pi$ state is symmetric under the reflection in the collision plane). For the subsequent discussion we need two corollaries of the preceding asymptotic analysis.

The *first* corollary is the relation between the amplitudes of the charge exchange induced by the radial ($s\sigma \rightarrow p\sigma$) and rotational ($s\sigma \rightarrow p\pi_+$) coupling. According to Sec. V the amplitudes for the transitions between the *quasimolecular states* are

$$F_{s\sigma \rightarrow p\sigma} = -i \cosh \Theta_0 \sqrt{3} f_{s\sigma \rightarrow s'\sigma}, \quad (5.1)$$

$$F_{s\sigma \rightarrow p\pi} = -\sinh \Theta_0 \sqrt{3} f_{s\sigma \rightarrow s'\sigma}, \quad (5.2)$$

where the definitions (3.2) and (4.10) should be employed. The quasiangle Θ_0 characterizes the relative importance of the two types of transitions. For the small collision velocities the quasiangle Θ_0 is small (see Sec. VI) and the radial-induced charge exchange prevails. However, for the medium velocities both types of transition should be taken into account. Note also that the phases of the amplitudes (5.1) and (5.2) differ by $\frac{1}{2}\pi$.

The third type of transition is the one-center depolarization mixing $p\sigma \leftrightarrow p\pi_+$. The most natural assumption

for the distant collisions is that the electron orbital momentum in the p state is completely decoupled from the internuclear axis. Hence there is no transition between the atomic p substates in the space-fixed frame. In this frame as an axis of quantization we choose the vector of the initial collision velocity \vec{v} (axis X' in Fig. 1). Then we denote as $|10\rangle$ the atomic p state with zero projection m_b of the orbital momentum on this axis, and as $|11_+\rangle$ the superposition of the states with $m_b = 1$ and $m_b = -1$ symmetrical under the reflection in the collision plane. The definition of the states $|10\rangle$ and $|11_+\rangle$ is elucidated by Fig. 1.

The connection between the space-fixed and the quasimolecular states is given by an obvious relation

$$|10\rangle = \cos(\phi) |p\pi_+\rangle - \sin(\phi) |p\sigma\rangle, \quad (5.3)$$

$$|11_+\rangle = \cos(\phi) |p\sigma\rangle + \sin(\phi) |p\pi_+\rangle, \quad (5.4)$$

where $\phi = \tan^{-1}(vt/\rho)$ (see Fig. 1). Equations (5.3) and (5.4) show in particular that the time (or ϕ) independence of the wave function in the space-fixed basis implies strong depolarizing transitions in the quasimolecular basis.

Now we use the *second corollary* of the asymptotic analysis: for large ρ the charge exchange is effectively concentrated at one moment of time $t = t_0$ [or $\phi = \phi_0$; see Eq. (4.9)], which is, however, complex valued. Combining these results with formulas (5.1)–(5.4) we obtain straightforwardly the final expression for the amplitudes of the charge exchange into the space-fixed p states [this formula is a particular case of the general expression (4.7)]:

$$F_{00 \rightarrow 11_+} = (-i \cosh \Theta_0 \cos \phi_0 - \sinh \Theta_0 \sin \phi_0) \sqrt{3} f_{s\sigma \rightarrow s'\sigma}, \quad (5.5)$$

$$F_{00 \rightarrow 10} = (-\sinh \Theta_0 \cos \phi_0 + i \cosh \Theta_0 \sin \phi_0) \sqrt{3} f_{s\sigma \rightarrow s'\sigma}. \quad (5.6)$$

The amplitudes (5.5) and (5.6) are written in the particular concise form if the real quasiangle Φ_0 (4.9) is employed instead of imaginary ϕ_0 :

$$F_{00 \rightarrow 11_+} = -i \cosh(\Theta_0 + \Phi_0) \sqrt{3} f_{s\sigma \rightarrow s'\sigma}, \quad (5.7)$$

$$F_{00 \rightarrow 10} = -\sinh(\Theta_0 + \Phi_0) \sqrt{3} f_{s\sigma \rightarrow s'\sigma}. \quad (5.8)$$

Thus the substates of the final atomic p states are populated coherently with various amplitudes and phases which generally implies the presence of the orbital asymmetry effects.

The alignment is characterized by the parameter A :

$$A = \frac{|F_{00 \rightarrow 10}|^2 - |F_{00 \rightarrow 11_+}|^2}{|F_{00 \rightarrow 10}|^2 + |F_{00 \rightarrow 11_+}|^2}. \quad (5.9)$$

This definition coincides with that used, for instance, in the experimental papers [20]: the amplitude $F_{00 \rightarrow 10}$ defines population of the p states with the electron orbital parallel to the collision velocity vector \vec{v} , and $F_{00 \rightarrow 11_+}$

corresponds to the p orbital perpendicular to \vec{v} (Fig. 1).

The circular orbital polarization of p state is characterized by the orientation parameter

$$\Pi = \frac{|c_1|^2 - |c_{-1}|^2}{|c_1|^2 + |c_{-1}|^2}, \quad (5.10)$$

where c_1 and c_{-1} are the population amplitudes of the final p substates with the angular momentum projection $m' = 1$ and $m' = -1$ on the axis perpendicular to the collision plane. The signs are chosen so that the relative motion of the colliding particles proceeds in the positive direction. Thus in the states with $m' = 1$ (shown in Fig. 1 as $|+\rangle$) the electron rotates around its nucleus in the same direction as the colliding particles. The population of such states is conventionally referred to as being in agreement with the *velocity matching picture*.

Formulas (5.7) and (5.8) lead to the compact analytical expressions for A and Π :

$$A = -\text{sech}(2\Theta_0 + 2\Phi_0), \quad (5.11)$$

$$\Pi = \tanh(2\Theta_0 + 2\Phi_0). \quad (5.12)$$

Note that the ρ dependence is canceled in this expression, i.e., A and Π are approximately constant for large impact parameters. We discuss the physical implications of this result in more detail in Sec. VI.

We cite also the expressions for A and Π in the situation adiabatic with respect to the DTMB:

$$A = \text{sech}(2\Theta_0), \quad (5.13)$$

$$\Pi = -\tanh(2\Theta_0 + 2\Phi_0) \cos \Delta, \quad \Delta = \Xi_0(t_0) - \Xi_1(t_0). \quad (5.14)$$

Here the adiabatic phases $\Xi_0(t_0)$ and $\Xi_1(t_0)$ are calculated respectively for σ and π quasimolecular potential curves correlated with the p state of the atom b .

VI. MECHANISMS FOR CREATION OF THE ELECTRON ORBITAL ASYMMETRY IN THE CHARGE-EXCHANGE PROCESSES

In this section we analyze the physical implications of the results obtained above.

(i) The influence of the electron momentum transfer is of the order of the square of the parameter ζ (3.8) for various $l_a m_a \rightarrow l_b m_b$ charge-exchange processes. Since the influence is small in the conditions of the existing experiments [18–21], it does not appear as an independent source of the asymmetry effects, although it somewhat modifies the manifestation of the effects generated by the other mechanisms. Therefore we neglect it in the discussion of points (ii) and (iii) below, which correspond to the replacement of γ and γ_0 by $(\alpha + \beta)/2$ in the calculation of the asymmetry parameters A and Π . Note that the electron momentum transfer effect on the exponential part of the charge-exchange amplitude (discussed in Sec. III) is the same for all $l_a m_a \rightarrow l_b m_b$ charge-exchange transitions. Therefore it does not influence the asymmetry parameters.

The definition of the electron momentum transfer effects deserves some clarification. The present calculations employ the electronic wave functions in the form (2.2) or (2.3), which can be considered as the atomic orbitals multiplied by ETF's (the deviation from this form appears in the calculations of the correction factor D). Calculation of the stationary phase point shows that x_0 (or Θ_0) is nonzero only in the presence of ETF's. Then the discussion in Sec. IV implies that the rotation-induced transitions would not appear in the present formalism if ETF's would be omitted.

However, it is well known that the rotation-induced transitions alternatively can be described in the quasimolecular theory without ETF's. Therefore we do not consider the rotation-induced $\sigma \rightarrow \pi$ charge-exchange transition as due to the physical effect of the electron momentum transfer defining as *the electron momentum transfer effects* only those which *cannot be described in the few-state quasimolecular calculations without the ETF's*. Thus in the definition adopted here the physical electron momentum transfer effects do not coincide with the results of ETF inclusion in the formal scheme of the calculations in the atomic basis. With such (actually conventional) definition the effect of the momentum transfer by electron plays a minor role in the medium collision velocity region discussed in Sec. III.

(ii) Coherent population of various p substates results in the orbital asymmetry in the final state. The substates are populated due to the radial- and rotation-induced charge exchange. The relative importance of this transition is governed by the quasiangle Θ_0 . Equation (4.10) shows that for very small velocities the quasiangle Θ_0 has a constant value $2\Delta E/(\alpha + \beta)^2$. However, if

$$v \gg v_0 \equiv 2\Delta E/(\alpha + \beta), \quad (6.1)$$

then the quasiangle Θ_0 becomes a linear function of ζ : $\Theta_0 = \zeta$. This important domain can be named the medium velocity region. Its upper boundary is defined by the condition $\zeta \ll 1$. For the parameters (3.6) one has $v_0 = 0.0276$ a.u. and the condition (6.1) is well satisfied in the current experiments [21] where $v = 0.2$ a.u. and $\zeta = 0.2$.

The velocity dependence of the quasiangles Θ_0, Φ_0 for these values of parameters is shown in Fig. 2. The electron momentum transfer effects are responsible for the deviation of γ and γ_0 from their limiting value $\frac{1}{2}(\alpha + \beta)$. The influence of these effects on the quasiangles Θ_0 and Φ_0 is very small in the medium velocity range ($v < 0.6$) and cannot be distinguished in the present scale.

(iii) The other mechanism creating the orbital polarization is connected with the influence of the DTMB on the charge exchange. In the case of the Demkov model this effect is represented by the quasiangle Φ_0 (4.9). More generally, Φ_0 can be considered as an effective parameter which expresses the degree of the adiabaticity in the depolarization process. If the relation (6.1) is satisfied, then Φ_0 (4.9) is small: $\Phi_0 = -2\Delta E/[v(\alpha + \beta)]$. In the opposite case Φ_0 becomes large: $\Phi_0 = \ln[(2(\alpha + \beta)v/|4\Delta E|)]$ ($\Delta E < 0$). Note, however, that for small collision velocity the assumption of the orbital momentum decou-

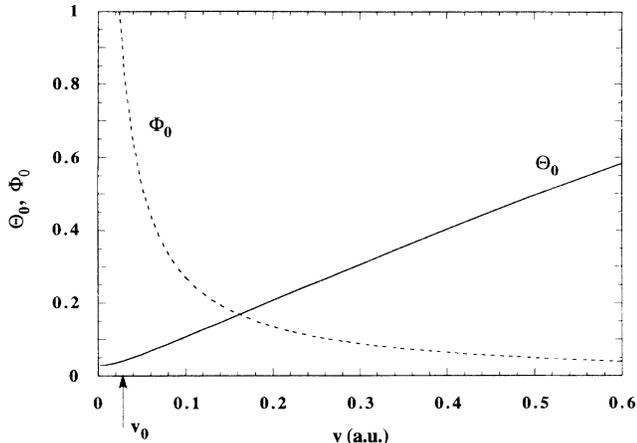


FIG. 2. The collision-velocity dependence of the quasiangles Θ_0 (solid line) and Φ_0 (dashed line) characterizing two principle mechanisms of the orbital asymmetry creation in the $s \rightarrow p$ charge exchange. The system parameters are chosen according to (3.6). The characteristic velocity v_0 (6.1) is indicated.

pling from the internuclear axis holds only for very large impact parameters ρ . In this situation the expressions (5.13) and (5.14) for the asymmetry parameters could be more appropriate than (5.11) and (5.12).

Now we turn to the discussion of the orientation parameter Π . Formula (5.12) shows that nonzero circular orbital polarization in the final p state generally appears provided at least one of the effects (ii) or (iii) is present. In the asymptotic region the contributions of these effects are separated since they are additive under the sign of hyperbolic functions. The important feature of the expression (4.9) is that the quasiangle Φ_0 is an odd function of the energy defect ΔE . If $\Delta E < 0$ (i.e. the binding energy of the s electron exceeds that of the p electron), then $\Phi_0 > 0$ and the contributions of two effects are summed constructively in (5.11) and (5.12) (note that the quasiangle Θ_0 is always positive). The velocity dependence of the orientation parameter is shown in Fig. 3. In the opposite case $\Delta E > 0$ the contributions are summed destructively ($\Phi_0 < 0$), which implies a much smaller value of the orientation parameter in the medium velocity region. This effect has *phase origin*; it is not related to the classical velocity matching arguments. Its counterpart in the Landau-Zener model [6] is the dependence of the Stueckelberg phase Φ on the sign of the energy difference. For $\Delta E = 0$ one has $\Phi_0 = 0$. This situation corresponds to the *accidental* degeneracy between s and p levels of different atoms.

In Fig. 3 we show also the results obtained from (5.12) by setting $\Theta_0 = 0$ or $\Phi_0 = 0$. The contributions of two effects are comparable for $v = 0.2$, although the role of the rotation-induced charge exchange is somewhat larger: $\Theta_0 = 0.206$ and $\Phi_0 = 0.135$. Curiously, the value $v = 0.2$ used in the experiments [21] corresponds to the minimum in the $\Pi(v)$ dependence, which is, however, very shallow.

We show also in Fig. 3 the orientation parameter $\Pi(v)$, which is obtained if one changes the sign of the energy

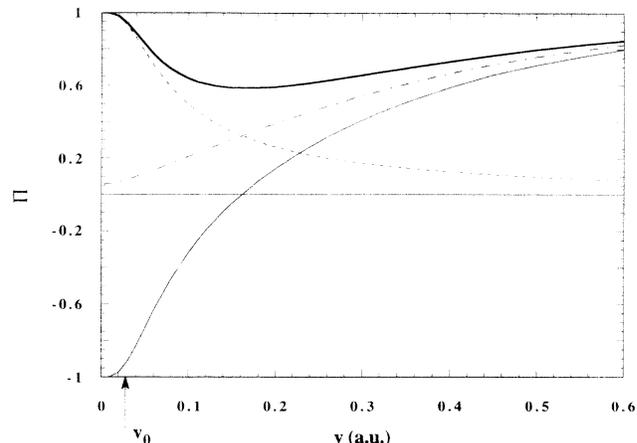


FIG. 3. The orientation parameter $\Pi(v)$ (5.6) (bold solid line) for the final p state calculated according to the formula (5.8) using the quasiangles Θ_0 and Φ_0 shown in Fig. 2. The fine line shows $\Pi(v)$ which is obtained when the sign of Φ_0 is changed, which corresponds to the change of the sign of the process energy defect ΔE (see text). Also shown is the orientation parameter in the absence of the rotation-induced charge exchange ($\Theta_0 = 0$, dashed line) and in the case $\Phi_0 = 0$ (dash-dotted line).

defect ΔE , retaining the absolute values of the parameters according to (3.6). In agreement with the discussion above in this case $\Pi(v)$ turns zero near the value $v = 0.23$ and is negative for the smaller velocities where the contribution of the DTMB prevails. In this region the sign of the parameter $\Pi(v)$ is *opposite that predicted by the conventional velocity matching arguments*. The experimental observation of this effect would be particularly interesting.

The alignment parameter $A(v)$ is equal to -1 in the case $\Theta_0 = \Phi_0 = 0$. This reflects the fact that in the absence of the rotation-induced charge exchange ($\Theta_0 = 0$) only the $p\sigma$ molecular orbital is populated. If $\Phi_0 = 0$ this occurs exactly at the moment of the closest approach when the electron wave function is $|11_+\rangle$. After that the electron cloud retains its orientation in space. If $\Theta_0 + \Phi_0$ is nonzero, then the alignment parameter is smaller in the absolute value but always negative: $0 > A > -1$ (Fig. 4). It is closer to its limiting value -1 when $\Delta E > 0$ and $\Phi_0 < 0$. Note that in a situation diabatic with respect to the DTMB the sign of A is positive as follows from the formula (5.13).

VII. ASYMMETRY IN THE $\text{Na}(3p)+\text{H}^+ \rightarrow \text{Na}^+ + \text{H}(n=2)$ PROCESS

As indicated above, the process (3.5) could be considered as one of the benchmarks for the study of the asymmetry effects in the charge exchange. It was extensively explored in the experiments [18–21] and the coupled-states calculations in the molecular [22, 23] and atomic [24] bases generally demonstrate agreement with the measurements. The object of the present section is complementary to the cited large-scale computer calcula-

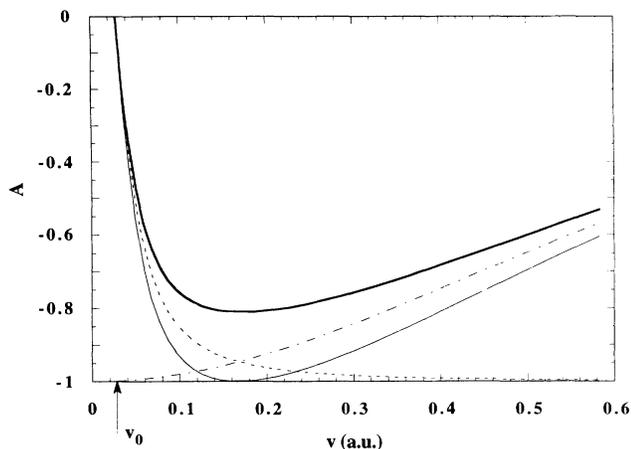


FIG. 4. The same as in Fig. 3 but for the alignment parameter $A(v)$ defined by the expression (5.5) and calculated according to the formula (5.7).

tions. The present asymptotic theory has a more narrow applicability domain and gives less precise numerical results. However, its expressions for the asymmetry parameters are extremely simple and allow a detailed physical interpretation as shown in the preceding sections.

The process (3.5) does not belong to the pure $p \rightarrow s$ type (which is a simple inverse of the $s \rightarrow p$ process). The reason lies in the specific hydrogenic degeneracy of the energy levels which generally lead to the strong one-center $2s \leftrightarrow 2p$ transitions between the final states of H^* . However, the present results can be easily generalized to this case. This possibility stems from the general property of the expression (4.7) for the charge-exchange amplitude in the asymptotic theory: it is factorized in the indices (quantum numbers) of the initial and final states:

$$\begin{aligned}
 & F_{l_a m_a \rightarrow l_b m_b} \\
 &= i 4\pi \left(\sum_{\lambda} [Y_{l_a m_a}] c_{\lambda m_a}(t_0) \right) \\
 & \times \left(\sum_{\lambda'} [Y_{l_b m_b}] (-1)^{l_b} c_{\lambda' -m_b}(-t_0) \right) f_{s\sigma \rightarrow s'\sigma}.
 \end{aligned} \tag{7.1}$$

This expression shows that in the asymptotic region the asymmetry characteristic A or Π calculated for one of the partners (e.g., b) does not depend on the depolarization (m_b -changing) processes in the other partner (a). This property is generalized straightforwardly to the case of the hydrogen-type degeneracy of the energy levels when l_b -changing transitions between the degenerate levels also should be included.

In the experiments [18, 20, 21] the $Na(3p)$ states with various orbital polarization were prepared and the measured cross sections of the charge-exchange process (3.5) do not distinguish the final $H(n=2)$ states. In the

asymptotic region the charge-exchange cross sections can be characterized by the asymmetry parameters calculated according to the formulas from Sec. V; now these parameters refer to the asymmetry of the initial $Na(3p)$ state. The same expressions characterize the asymmetry effects for the experiments [19] where the charge exchange into the final $H(2p)$ states is detected.

The results of the asymptotic theory should be compared with the measurements resolved in the scattering angle since the domain of large impact parameters generally corresponds to the small scattering angles.

For the collision velocity $v = 0.2$ employed in the experiments [20, 21] one obtains with the help of the expressions (5.11) and (5.12), $\Pi = 0.592$ and $A = -0.806$.

The sign of Π is in agreement with the velocity matching picture. Houver *et al.* [21] report the sign of the orientation effect opposite to that expected from the velocity matching picture *assuming a repulsive interaction* between the colliding particles (note that this conditional statement does not imply that the authors really make an assertion about the interaction sign).

However, the asymptotic approach leads to the conclusion about the attractive character of the net interaction between the colliding particles in the process (3.5). Indeed, in the asymptotic theory the probability of the charge exchange is generally proportional to the electron density in the initial and final state at the midpoint between the nuclei in the moment of the closest approach. In the case of hydrogen-type degeneracy the Stark states of H^* are formed in the field of the other collision partner (ion). The charge exchange proceeds primarily into one of the Stark states [27], namely, to that which corresponds to the enhancement of the electron density between the nuclei. The interaction between the atom in this Stark state and the incident ion corresponds to the *attraction* [28].

The absolute value of Π in the experiments by Houver *et al.* [21] varies between 0.4 and 0.3 (with the experimental error bars ± 0.1) when the scattering angle varies in the interval $0.015^\circ < \vartheta < 0.045^\circ$. Our value of Π is somewhat higher (Fig. 5), which is natural if one bears in mind that the quasidegree Φ_0 can be considered as an effective parameter; then formula (4.9) gives its upper limit. Bearing in mind the extreme simplicity of expression (5.12), the relation between theory and experiment could be considered as quite satisfactory.

As for the sign of the alignment parameter A , in the asymptotic theory it corresponds to the more effective charge exchange when initially the electron cloud in $Na(3p)$ is oriented *perpendicularly* to the collision velocity vector \vec{v} (see Fig. 1). In the present picture it retains orientation in space in the course of the collision and in the moment of the closest approach it corresponds to the zero projection of the electron orbital momentum on the internuclear axis. The charge exchange occurs primarily close to this moment of time; for the state under consideration it is induced by the radial coupling, which is more efficient than the rotation-induced charge exchange. Namely, this mechanism is reflected in the sign of A obtained in the present approach.

The measurements [20] give the sign of A opposite

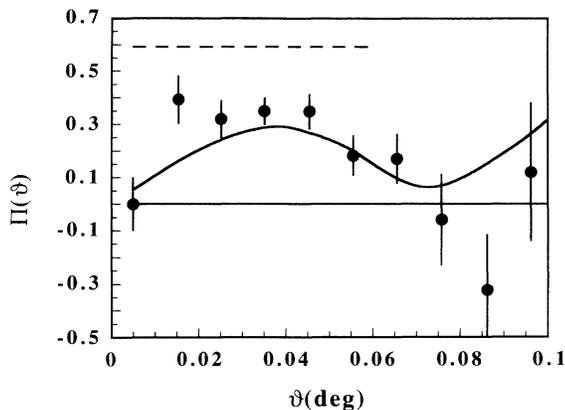


FIG. 5. The orientation parameter Π for the process (3.5) as a function of the scattering angle ϑ for the collision velocity $v = 0.2$ a.u. Closed circles, the experimental data [21]; solid line, large-scale numerical calculations in the atomic basis by Nielsen *et al.* as reported in Ref. [24]. The horizontal dashed line shows the estimate within the present asymptotic theory which is ϑ independent.

this. In contrast to the measurements of Π for the fixed scattering angle [21], these experiments give the integral value of A summed over all scattering angles. The contribution of comparatively small impact parameters incorporated in the experimental value of A could be the tentative reason for the disagreement in sign. Note that for the close collisions the situation adiabatic in the one-center depolarization transitions is more likely. Here the sign of A is positive, as follows from (5.13).

A comparison can also be made with the extensive close coupling calculations in the molecular basis [23]. The charge-exchange probability in this paper is presented as a function of the impact parameter ρ for $v = 0.14$ (Fig. 5 of [23]) and $v = 0.283$ (Fig. 6 of [23]). The $\text{Na}(3p) \Pi^-$ initial state in the notations of this paper corresponds to the state $|11_+\rangle$, which is more effective in the charge exchange in our picture as described above. A comparison between Figs. 5(b) and 5(d) ($v = 0.14$) from Ref. [23] shows that this state is more effective indeed for $\rho > 19$. For $v = 0.283$ [Figs. 6(b) and 6(d) of [23]] the same conclusion is inferred for $\rho > 15$. Thus the sign of A obtained in the numerical calculations [23] for the large impact parameters ρ is the same as in the present approach. The same sign of A was obtained in the recent integral measurements [29] for the charge exchange with the other collision partners: $\text{He}^{2+} + \text{Na}(3p) \rightarrow \text{He}^+(n = 4) + \text{Na}^+$.

VIII. CONCLUSION

The asymptotic approach developed in the present paper combines some features of the calculations in atomic and molecular bases. The introduction of ETF's is most straightforward in the atomic frame. As a result, the applicability region is extended to the higher velocity do-

main as compared with the simple few-state molecular basis treatment. The theory is developed in terms of the molecular orbital picture, which is more convenient for the qualitative interpretation.

The principal results of the present paper are given by formulas (3.2), (5.7), and (5.8). They give simple and general analytic expressions of the asymptotes of the charge-exchange amplitudes. The expressions (5.11) and (5.12) for the asymmetry parameters follow directly from them. Since they are applicable to the large impact parameters (or small scattering angles) they include only characteristics of the separated colliding atoms. The analysis of these formulas allows us to elucidate manifestation of various basic physical effects: momentum transfer by electron, competition between the charge exchange induced by the radial and rotational coupling, and the influence of the DTMB on the charge exchange.

The current understanding of the mechanisms of the asymmetry creation in the charge-exchange process suffers from the absence of the simple physical models. Such models remain important in the age of computers because they contribute much to the understanding of the physical nature of the effects which are sometimes hidden in the large-scale computer calculations. They allow one to trace the role of various parameters of the collision partners. This analysis is difficult in the numerical studies where the parameters are restricted usually to the values specific to the atoms under consideration.

The well known and useful models (Landau-Zener and Demkov models) are the two-state models and apply directly to the $s \rightarrow s'$ transitions. When the $s \rightarrow p$ charge exchange is considered, the description of the direct $s\sigma \rightarrow p\sigma$ transitions proves to be quite similar to $s \rightarrow s'$ process. However, two additional types of transitions appear in the system: the $s\sigma \rightarrow p\pi$ charge exchange induced by the rotational coupling and the one-center $p\sigma \leftrightarrow p\pi$ depolarizing transitions. For the qualitative analysis of the processes involving p states, the concept of the locking radius R_L is often employed. However, it is not useful for the distant collisions ($\rho \sim R_L$ or larger) [26], which are known to play an important role in the charge exchange.

The present paper suggests the simple models, although they are limited to the distant collisions. This is the price which should be paid since the system under consideration is more complicated and actually contains three states: the initial s state and the final $p\sigma$ and $p\pi$ states. The basic results of our analysis are as follows.

(i) The impact-parameter dependence of the charge-exchange amplitudes is factored, which means that the final-state asymmetry characteristics are ρ independent for large ρ .

(ii) For the medium collision velocity (collision velocity is about half of the typical electron velocity) the effects of the momentum transfer by an electron do not play a qualitatively important role.

(iii) Two mechanisms are of comparable importance when the asymmetry is analyzed: the competition between the charge transfer induced by the radial and rotational coupling and the role of the DTMB. These effects can be characterized by the quasiangles Θ_0, Φ_0 which are

defined by the simple analytic expressions. The first becomes predominating for the higher collision velocities whereas the second is more important for slow collisions.

(iv) The sign of the process energy defect ΔE plays an important role: in the medium velocity region the asymmetry is significantly enhanced if the s level lies lower than the p level; it is suppressed in the opposite case. The experimental verification of this effect is highly desirable.

(v) For the charge-exchange process (3.5) the estimated orientation parameter is in satisfactory agreement with the experimental measurements at small scattering angles.

ACKNOWLEDGMENTS

The author is grateful for the hospitality of Laboratoire des Collisions Atomiques et Moléculaires, Université Paris-Sud, Orsay, France where this work was done during a visit under a grant provided by CNRS. It was inspired by the discussion of the experimental results with D. Doweck, N. Andersen, M. Barat, P. Roncin, and C. Adjouri. Discussions with C. Courbin of the results of numerical calculations of the process (3.5) in the molecular basis are especially appreciated.

APPENDIX

The calculation of the correction factor D was discussed previously for the case of the Landau-Zener model.

Here we list the alterations necessary when the Demkov model is considered.

The correction function D is presented as $D = \exp(-S^{(a)} - S^{(b)})$, where the functions $S^{(a)}, S^{(b)}$ are given by formulas (A.1)–(A.3) from Ref. [5]. They express the correction factor as a function of the coordinates ξ and η , which are introduced as

$$\xi = \frac{1}{2} \left(-it - \frac{r_a}{\alpha} \right), \quad \eta = \frac{1}{2} \left(-it + \frac{r_a}{\alpha} \right), \quad (\text{A1})$$

and contain also the components of the unit vector \vec{r}_a/r_a : n_{ax}, n_{ay}, n_{az} .

In the factor D the correction functions $S^{(a)}, S^{(b)}$ should be calculated at the stationary point. As discussed in Sec. II, at this point $r_a = r_{a0} = (\alpha + \beta) R_0/4\gamma$, $R_0 = \rho\gamma_0 v/\kappa$, and $t = t_0$ (2.14). The components n_{ax}, n_{ay}, n_{az} are

$$n_{ax} = i \sinh \Theta_0, \quad n_{ay} = i \cosh \Theta_0, \quad n_{az} = 0. \quad (\text{A2})$$

The final expression for D is not presented here explicitly since it appears to be somewhat cumbersome. It seems that in many cases the adiabatic approximation for D is sufficient where

$$D_{\text{ad}} = (2/\sqrt{\epsilon})^{Z_b/\alpha + Z_a/\beta}. \quad (\text{A3})$$

-
- [1] Yu. N. Demkov, Zh. Eksp. Teor. Fiz. **45**, 195 (1963) [Sov. Phys. JETP **18**, 138 (1964)].
- [2] E.E. Nikitin and S. Ya. Umanskii, *Theory of Slow Atomic Collisions* (Springer, Berlin, 1984).
- [3] E.E.B. Campbell, H. Schmidt, and I.V. Hertel, Adv. Chem. Phys. **72**, 37 (1988).
- [4] N. Andersen, J.W. Gallagher, and I.V. Hertel, Phys. Rep. **165**, 1 (1988).
- [5] V.N. Ostrovsky, J. Phys. B **24**, 4553 (1991); in *Invited Papers of the Seventeenth International Conference on the Physics of Electronic and Atomic Collisions, Brisbane, 1991*, edited by W.R. MacGillivray, I.E. McCarthy, and M.C. Standage (Hilder, Bristol, 1991), pp. 435–450.
- [6] V.N. Ostrovsky, J. Phys. B **24**, L507 (1991); J.P. Hansen, N. Andersen, A. Dubois, S.E. Nielsen, C. Adjouri, M. Barat, M.L. Gaboriaud, V. Ostrovsky, and P. Roncin, in *Correlations and Polarization in Electronic and Atomic Collisions and (e, 2e) Reactions*, edited by P.J.O. Teubner and E. Weigold, IOP Conf. Proc. No. 122 (Institute of Physics and Physical Society, Bristol, 1991), pp. 307–314.
- [7] P. Roncin, C. Adjouri, M.N. Gaboriaud, L. Guillemot, and M. Barat, Phys. Rev. Lett. **65**, 3261 (1990).
- [8] M.I. Chibisov and R.K. Janev, Phys. Rep. **166**, 1 (1988).
- [9] F.F. Karpeshin and V.N. Ostrovsky, J. Phys. B **14**, 4513 (1981).
- [10] W.D. Burns and D.S.F. Crothers, J. Phys. B **9**, 2479 (1976).
- [11] J.G. Hughes and D.S.F. Crothers, J. Phys. B **10**, L605 (1977).
- [12] S.J. Pfeifer and J.D. Garcia, Phys. Rev. A **23**, 2267 (1981).
- [13] Yu. N. Demkov, C.V. Kunacs, and V.N. Ostrovsky, Phys. Rev. A **18**, 2097 (1978).
- [14] D.S.F. Crothers and J.G. Hughes, J. Phys. B **12**, 3063 (1979).
- [15] H. Nakamura, Phys. Rev. A **26**, 3125 (1982); **28**, 486(E) (1982).
- [16] Yu. N. Demkov and V.N. Ostrovsky, Zh. Eksp. Teor. Fiz. **69**, 1582 (1975) [Sov. Phys. JETP **42**, 806 (1975)].
- [17] E.T. Copson, *Asymptotic Expansions* (Cambridge University Press, Cambridge, England, 1965).
- [18] T. Royer, D. Doweck, J.C. Houver, J. Pommier, and N. Andersen, Z. Phys. D **10**, 45 (1988); C. Richter, D. Doweck, J.C. Houver, and N. Andersen, J. Phys. B **23**, 3925 (1990).
- [19] K. Finck, Y. Wang, Z. Roller-Lutz, and H.O. Lutz, Phys. Rev. A **38**, 6115 (1988); Z. Roller-Lutz, K. Finck, Y. Wang, and H.O. Lutz, Phys. Lett. A **169**, 173 (1992).
- [20] D. Doweck, J.C. Houver, J. Pommier, C. Richter, T. Royer, N. Andersen, and B. Palsdottir, Phys. Rev. Lett. **64**, 1713 (1990); D. Doweck, J.C. Houver, and C. Richter,

- in *Invited Papers of the Seventeenth International Conference on the Physics of Electronic and Atomic Collisions* (Ref. [5]), pp. 537–547.
- [21] J.C. Houver, D. Dowek, C. Richter, and N. Andersen, *Phys. Rev. Lett.* **68**, 162 (1992).
- [22] R.J. Allan, R. Shingal, and D.R. Flower, *J. Phys. B* **19**, L521 (1986); R.J. Allan, C. Courbin, P. Salas, and P. Wahnon, *J. Phys. B* **23**, L461 (1990); E. Levartovsky and C. Courbin, *ibid.* **25**, L63 (1992).
- [23] C. Courbin, R.J. Allan, P. Salas, and P. Wahnon, *J. Phys. B* **23**, 3909 (1990).
- [24] S.E. Nielsen, J.P. Hansen and A. Dubois, *J. Phys. B* **23**, 2595 (1990).
- [25] A.R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, 1974).
- [26] I.V. Hertel, H. Schmidt, A. Bahring, and E. Meyer, *Rep. Prog. Phys.* **48**, 375 (1988).
- [27] This observation was originally made by C. Courbin from the analyses of the numerical calculations for the process (3.5) in the basis of the molecular states (private communication).
- [28] The same conclusion (but based on the different arguments) about the interaction sign was communicated to the author by D. Dowek.
- [29] F. Aymar, M. Gieler, J. Schweinzer, H. Winter, and J.P. Hansen, *Phys. Rev. Lett.* **68**, 3277 (1992).

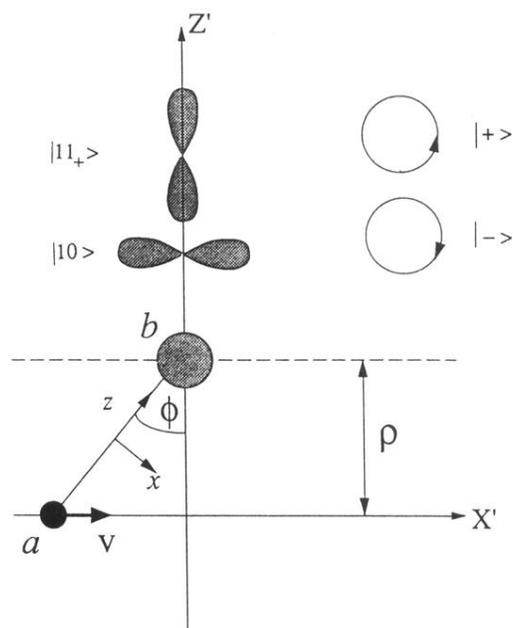


FIG. 1. Charge-exchange collision geometry used in the present calculations (see text).