

# Charge Exchange of a Polar Molecule at Its Cation

E. Yu. Buslov<sup>a</sup> and B. A. Zon<sup>a,b</sup>

<sup>a</sup> Voronezh State University, Voronezh, 394006 Russia

<sup>b</sup> Belgorod State University, Belgorod, 308015 Russia

*e-mail: buslov@phys.vsu.ru, zon@niif.vsu.ru*

**Abstract**—The Landau–Herring method is used to derive an analytic expression for the one-electron exchange interaction of a polar molecule with its positively charged ion, induced by a  $\sigma$ -electron. Analogously to the classical Van der Pole method, the exchange interaction potential is averaged over the rotational states of colliding particles. The resonant charge-transfer cross section is calculated, and the effect of the dipole moments of the core on the cross section is analyzed. It is shown that allowance for the dependence of the exchange potential on the orientation of the dipole moments relative to the molecular axis may change the dependence of the cross section on the velocity of colliding particles, which is typical of the resonant charge exchange, from the resonance to the quasi-resonance dependence.

## 1. INTRODUCTION

The charge-exchange process involves the charge transfer upon a collision of an ion with a neutral particle. It is well known [1, 2] that an electron transition during charge exchange is accounted for by the exchange interaction potential of colliding particles. If an electron performs a transition between identical particles or between particles with close energies of electron bound states, we have a resonant or quasi-resonant charge exchange. These reactions are characterized by large cross sections [1, 2], and large (as compared to the characteristic size of particles) interatomic distances play the major role in the description of their dynamics. For this reason, the application of asymptotic methods for calculating the exchange interaction potential of colliding particles at large interatomic distances  $R$  is of special interest. An asymptotically exact (in the powers of  $1/R$ ) description of the one-electron exchange interaction in the range of large internuclear distances was proposed for the first time by Landau [3] and Herring [4, 5]. The Landau–Herring method has found large applications for calculating the one- and two-electron exchange interaction potentials in ion–atom and atom–atom systems. The Landau–Herring method and its applications are reviewed in [6]. However, the application of the asymptotic Landau–Herring method for describing inelastic collisions of molecules with atoms and molecules with molecules has been developed to a much smaller extent. In [7], the Landau–Herring method was used for calculating one-electron exchange interaction of a diatomic homonuclear molecule with an atomic ion. By way of example of application of the expression derived for the exchange interaction potential, the electron capture cross sec-

tion was calculated in [7] for a slow collision  $H_2^+ + He_2^{++}$ ; the results were found to be in good agreement with experiment. In [8, 9], the application of the semiclassical method for describing one-electron capture in collisions of neutral polar molecules with multiply charged ions was considered. The semiclassical approach used in [8, 9] was proposed for the first time in [10] (see also Section 3.4.2 in [6]) and is in fact a generalization of the Landau–Herring method to the case of collision of particles with strongly differing charges (e.g., atoms and multiply charged ions). This method is not used for describing collisions of identical particles. Finally, in a recent publication [11], the method proposed in [7] was generalized to the description of two-electron exchange in collisions of diatomic homonuclear molecules with atomic ions.

This study aims at evaluation of the one-electron exchange interaction potential of a neutral polar molecule with its own positive ion located at a large distance from the molecule. We consider polar diatomic molecules as well as polyatomic molecules of the type of a symmetric top with an excited outer electron. Although the latter assumption limits the applicability of our results, it makes it possible to study the problem analytically.

The expression derived for the exchange interaction potential is used for analyzing the charge exchange during the collision of a polar molecule with its own ion. This reaction is interesting due to the fact that it has features of a purely resonant and quasi-resonant process at the same time. On the one hand, the electron transition occurs between identical molecular cores. On the other hand, due to rotation of the molecule, various mutual orientations of the dipole

moments of molecular cores are possible, leading to a difference in the binding energies of electrons localized at different cores. Thus, a defect of resonance appears, which is not, however, a constant quantity, but depends on the intermolecular distance and on the mutual orientation of the cores. It is natural to refer to this resonance defect as geometrical.

Although the results of this work are quite general, the main emphasis is placed on analysis of the most physically substantiated case of the transition of the outer  $\sigma$ -electron of the molecule. Unless the opposite is stipulated, we will use atomic units.

## 2. ASYMPTOTIC FORM OF THE ELECTRON WAVEFUNCTION IN THE FIELD OF THE MOLECULAR CORE

Let us consider the motion of an electron at large distances  $r \gg 1$  from the charged molecular core possessing a constant dipole moment  $\mathbf{d}$ . The long-range part of the potential of interaction of the outer electron with the core has the form

$$V(\mathbf{r}) \approx -\frac{1}{r} - \frac{\mathbf{d} \cdot \mathbf{r}}{r^3} \quad \text{at } r \gg 1. \quad (1)$$

Choosing the polar axis of the spherical system of coordinates along dipole moment  $\mathbf{d}$ , we can write the Schrödinger equation for the electron moving in field (1) for  $r \gg 1$ :

$$\begin{aligned} & \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \Psi}{\partial r} \right) + \frac{1}{r^2} \\ & \times \left[ \frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left( \sin \vartheta \frac{\partial \Psi}{\partial \vartheta} \right) + \frac{1}{\sin^2 \vartheta} \frac{\partial^2 \Psi}{\partial \varphi^2} \right] \\ & + 2 \left[ E + \frac{1}{r} + \frac{d \cos \vartheta}{r^2} \right] \Psi = 0. \end{aligned} \quad (2)$$

This equation permits the separation of angular and radial variables

$$\Psi(\mathbf{r}) = R(r) \mathcal{L}(\vartheta, \varphi), \quad (3)$$

where dipole-spherical functions  $\mathcal{L}$  satisfy the equation

$$\begin{aligned} & - \left[ \frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left( \sin \vartheta \frac{\partial \mathcal{L}}{\partial \vartheta} \right) + \frac{1}{\sin^2 \vartheta} \frac{\partial^2 \mathcal{L}}{\partial \varphi^2} \right] \\ & - 2d \cos \vartheta \mathcal{L} = \eta \mathcal{L}. \end{aligned} \quad (4)$$

In axially symmetric potential (1), projection  $m$  of the orbital angular momentum of the electron onto the dipole axis is conserved; therefore,  $\mathcal{L} = \mathcal{L}_{Lm}$ , where  $L \geq |m|$  is the integer labeling eigenvalues  $\eta_{Lm}$  of Eq. (4) in their increasing order for a fixed  $m$ . For  $d \rightarrow 0$ , the relation  $\eta_{Lm} \rightarrow L(L+1)$  holds so that  $L$  acquires the meaning of the conventional orbital angular momentum. The properties of the  $\mathcal{L}$  function are described in detail in [12–14].

The dipole-spherical functions can be expanded into a series in spherical harmonics:

$$\mathcal{L}_{Lm}(\vartheta, \varphi) = \sum_{l \geq |m|} a_{Ll}^m(d) Y_{lm}(\vartheta, \varphi). \quad (5)$$

Substituting expansion (5) into Eq. (4), we obtain the recurrence relation for coefficients  $a_{Ll}^m$ :

$$\begin{aligned} & -2d \left[ \frac{l^2 - m^2}{4l^2 - 1} \right]^{1/2} a_{Ll-1}^m + [l(l+1) - \eta_{Lm}] a_{Ll}^m \\ & - 2d \left[ \frac{(l+1)^2 - m^2}{(2l+1)(2l+3)} \right]^{1/2} a_{Ll+1}^m = 0. \end{aligned}$$

Radial functions  $R(r)$  satisfy the equation

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) - \frac{\eta}{r^2} R + 2 \left( E + \frac{1}{r} \right) R = 0 \quad (6)$$

coinciding in form with the radial Schrödinger equation in a Coulomb field. This equation leads to the asymptotic form of radial functions  $R(r)$  of electron bound states for  $r \gg 1$ :

$$R(r \gg 1) \approx N r^{1/\kappa-1} e^{-\kappa r}, \quad (7)$$

where  $\kappa = \sqrt{-2E}$  and  $N$  is the normalization factor.

Normalization factor  $N$  of electron wavefunction  $\Psi$  for  $r \gg 1$  can be determined from the condition of joining with the electron wavefunction for  $r \geq 1$ , calculated, for example, by the methods of quantum chemistry. In our numerical calculations, we will use normalization factor  $N$  and energy levels  $E$  of electron bound states from the analytic solution [12] to the Schrödinger equation for an electron in potential (1):

$$N = \frac{(-1)^{n_r} 2^{\nu}}{v^{\nu+1} \sqrt{n_r!} \Gamma(\rho_{Lm} + \nu + 1/2)}, \quad E = -\frac{1}{2\nu^2}, \quad (8)$$

where  $n_r = 0, 1, 2, \dots$  is the radial quantum number,  $\rho_{Lm} = (\eta_{Lm} + 1/4)^{1/2}$ , and  $\nu = n_r + \rho_{Lm} + 1/2$ . Nonintegral number  $\nu$  is analogous to the principal quantum number for the hydrogen atom.

## 3. EXCHANGE INTERACTION POTENTIAL

In the Born–Oppenheimer approximation, the Hamiltonian of an outer electron moving in the field of two identical molecular cores with different orientations in space (Fig. 1) has the form

$$\hat{H} = -\frac{1}{2} \nabla^2 + V_1(\mathbf{r}_1) + V_2(\mathbf{r}_2), \quad (9)$$

where the potential of the cores has asymptotic form (1):

$$V_{1,2}(\mathbf{r}) \approx -\frac{1}{r} - \frac{\mathbf{d}_{1,2} \cdot \mathbf{r}}{r^3} \quad \text{for } r \gg 1,$$

$\mathbf{r}_1 = \mathbf{R} + \mathbf{r}_2$ ,  $\mathbf{R}$  being the vector of the intermolecular axis, and  $|\mathbf{d}_1| = |\mathbf{d}_2| = d$ .

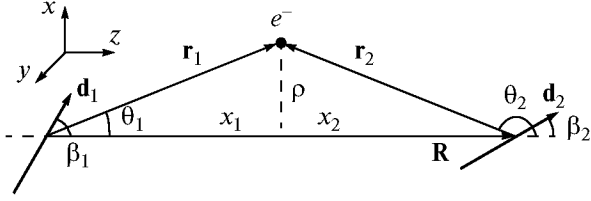


Fig. 1. Geometry of the "outer electron in the field of molecular cores" system.

Solution  $\psi_1$  to the Schrödinger equation with Hamiltonian (9), which corresponds to the localization of the electron on the first molecular core, satisfies the boundary condition

$$\psi_1 \rightarrow \Psi_1 \text{ for } r_1 \ll R, \quad (10)$$

where  $\Psi_1$  is the solution to the unperturbed Schrödinger equation

$$\left[ -\frac{1}{2}\nabla^2 + V_1(\mathbf{r}_1) - E_1 \right] \Psi_1 = 0. \quad (11)$$

In region  $r_1 \ll R$ ,  $r_2 \approx R$ , potential energy  $V_2(\mathbf{r}_2)$  in expression (9) can be treated as a perturbation. In this case, the unperturbed equation has the form (11). We denote the perturbed energy as  $E_I$ . Setting  $1/r_2 \approx 1/R + \mathbf{R} \cdot \mathbf{r}_1/R^3$ , we obtain the following relation correct to the terms on the order of  $R^{-2}$ :

$$E_I = E_1 - \frac{1}{R} - \frac{d \cos \epsilon_2}{R^2} + \frac{d_e \cos \epsilon_1}{R^2} + O\left(\frac{1}{R^3}\right), \quad (12)$$

where  $d_e$  is the projection of the electron dipole moment  $\mathbf{d}_e = -\langle \Psi_1 | \mathbf{r}_1 | \Psi_1 \rangle$  in state  $\Psi_1$  onto the direction of dipole moment  $\mathbf{d}_1$  of the core (obviously, vector  $\mathbf{d}_e$  is directed along  $\mathbf{d}_1$ ; therefore,  $d_e = \pm |\mathbf{d}_e|$ ), and  $\epsilon_{1,2}$  are the angles between vectors  $\mathbf{d}_{1,2}$  and the intermolecular axis. It can be seen from expression (12) that no exact resonance is observed between the energies of the electrons localized at different cores because the term on the order of  $R^{-2}$  depends on the mutual orientation of the molecular cores. This leads to the above-mentioned geometrical defect of resonance.

Using expressions (3), (5), and (7), we can write the electron wavefunction in the unperturbed potential of molecular core 1 in the coordinate system  $\{x'_1, y'_1, z'_1\}$  rigidly fixed to the core, in which the  $z'_1$  axis is directed along vector  $\mathbf{d}_1$ , for  $1 \ll r_1 \ll R$ :

$$\Psi_1 \approx N r_1^{1/\kappa - 1} e^{-\kappa r_1} \sum_{l \geq |m|} a_{Ll}^m Y_{lm}(\vartheta_1, \varphi_1), \quad (13)$$

where  $\kappa = \sqrt{-2E_1}$  and  $\vartheta_1$  and  $\varphi_1$  are the angular coordinates of vector  $\mathbf{r}_1$  in the system  $\{x'_1, y'_1, z'_1\}$ .

Passing to coordinate system  $\{x, y, z\}$  associated with the intermolecular axis, in which the  $z$  axis is

directed along vector  $\mathbf{R}$ , we can write expression (13) for wavefunction  $\Psi_1$  in the form [15]

$$\Psi_1 \approx N r_1^{1/\kappa - 1} e^{-\kappa r_1} \sum_{l \geq |m|} a_{Ll}^m \times \sum_{k=-l}^l D_{km}^l(\alpha_1, \beta_1, \gamma_1) Y_{lk}(\theta_1, \phi_1). \quad (14)$$

Here,  $D_{km}^l(\alpha, \beta, \gamma)$  is the Wigner  $D$  function;  $\alpha_1, \beta_1, \gamma_1$  are the Euler angles for the transformation from the coordinate system  $\{x, y, z\}$  to  $\{x'_1, y'_1, z'_1\}$ ; and  $\theta_1$  and  $\phi_1$  are the angular coordinates of vector  $\mathbf{r}_1$  in system  $\{x, y, z\}$ .

To evaluate the exchange interaction potential, we must know wavefunction  $\psi_I$  in region  $r_1 \sim r_2 \sim R/2$ . In this region, potential energies  $V_1(\mathbf{r}_1)$  and  $V_2(\mathbf{r}_2)$  are of the same order of magnitude; therefore, we cannot treat  $V_2$  as a perturbation relative to  $V_1$  any longer. Accurate to terms on the order of  $R^{-1}$  in Hamiltonian (9) and in expression (12) for  $E_I$ , we can write the Schrödinger equation for wavefunction  $\psi_I$  in region  $r_1 \sim r_2 \sim R/2$ :

$$\left[ -\frac{1}{2}\nabla^2 - \frac{1}{r_1} - \frac{1}{|\mathbf{r}_1 - \mathbf{R}|} - E_1 + \frac{1}{R} \right] \psi_I = 0. \quad (15)$$

In accordance with the Landau–Herring method, we seek the solution to Eq. (15) in the form

$$\psi_I = \Psi_1(\mathbf{r}_1) \chi_1(\mathbf{r}_1). \quad (16)$$

Substituting this expression into Eq. (15) and omitting all terms on the order of  $r_1^{-2}$  (in particular, in the expressions for  $\nabla^2 \chi_1$  and  $\nabla \Psi_1 \nabla \chi_1$ ), we obtain the following equation for  $\chi_1(\mathbf{r}_1)$ :

$$-\frac{1}{2} \frac{\partial^2 \chi_1}{\partial r_1^2} - \left( \frac{1}{\Psi_1} \frac{\partial \Psi_1}{\partial r_1} + \frac{1}{r_1} \right) \frac{\partial \chi_1}{\partial r_1} + W_1 \chi_1 = 0, \quad (17)$$

where

$$W_1 = \frac{1}{R} - \frac{1}{|\mathbf{r}_1 - \mathbf{R}|}.$$

Relation (10) leads to the boundary condition

$$\chi_1(r_1) \rightarrow 1 \text{ for } r_1 \rightarrow 0. \quad (18)$$

Using the fact that

$$\frac{1}{\Psi_1} \frac{\partial \Psi_1}{\partial r_1} = -\kappa + O\left(\frac{1}{R}\right)$$

for  $r_1 \sim R/2$  and disregarding second derivative  $\chi_1''$ , we can reduce Eq. (17) to the form

$$\kappa \frac{d\chi_1}{dr_1} + W_1 \chi_1 = 0. \quad (19)$$

The second derivative in Eq. (17) can be disregarded for  $\kappa R \gg 1$ . This condition follows from the estimates of  $\chi_1'$  in Eq. (19) and of  $\chi_1''$  in Eq. (19) dif-

ferentiated with respect to  $r_1$ . The solution to Eq. (19) satisfying boundary condition (18) has the form

$$\chi_1(\mathbf{r}_1) = \left[ \frac{r_1 + r_2 - R \cos \theta_1}{R(1 - \cos \theta_1)} \right]^{1/\kappa} \exp\left(-\frac{r_1}{\kappa R}\right). \quad (20)$$

The expression for wavefunction  $\psi_{II}$  for an electron localized at the second core in the state with unperturbed energy  $E_2 = E_1$  in coordinate system  $\{x, y, z\}$  can be obtained by the transposition of indices  $1 \leftrightarrow 2$  in expressions (14), (16), and (20) for  $\psi_I$  and by the sign reversal of the cosine in formula (20) because the argument of the cosine in Eq. (20) is in fact the angle between the radius vector of the electron and the intermolecular axis (i.e., for  $\chi_2$ , this angle is  $\pi - \theta_2$ ). To avoid the difficulties associated with the degeneracy of energy levels with  $\pm|m|$  in an axially symmetric field, we confine our analysis to the states with  $m = 0$ . This case appears as most interesting because the effect of the nonspherical dipole potential is most pronounced precisely in these states. For  $m = 0$ , only two states ( $\psi_I$  and  $\psi_{II}$ ) are in resonance.

Function  $\Delta E \equiv 2\langle \psi_{II} | \hat{H} | \psi_I \rangle = 2H_{II, I}$  is the potential of the one-electron exchange interaction. In the Landau–Herring method, this function can be expressed as the surface integral [3–6]

$$\Delta E(R) = \int_S (\psi_I^* \nabla \psi_{II} - \psi_{II}^* \nabla \psi_I) d\mathbf{S}, \quad (21)$$

where  $S$  is the plane perpendicular to vector  $\mathbf{R}$  and intersecting it at the point for which  $x_{1,2} \sim R/2$  (it should be recalled that  $x_1 + x_2 = R$ ; see Fig. 1). The outward normal vector  $\mathbf{n}$  to plane  $S$  is assumed to be directed from the first core to the second:  $\mathbf{n} = \mathbf{R}/R$ .

For  $\kappa R \gg 1$ , wavefunctions  $\psi_{I, II} \sim \exp(-\kappa r_{1,2})$  in the region where  $r_{1,2} \sim R/2$ , as follows directly from Eqs. (14) and (20). Therefore,  $|\nabla \psi_I| \sim \exp(-\kappa r_1)$ . Introducing polar coordinates  $\{\rho, \phi\}$  (angle  $\phi$  is measured from the positive direction of the  $x$  axis of system  $\{x, y, z\}$ ) on the  $S$  plane with the origin at the point of its intersection with  $\mathbf{R}$ , we obtain the following estimate for one of the integrals in Eq. (21):

$$\int_S \psi_{II}^* \nabla \psi_I d\mathbf{S} \sim \int_0^\infty e^{-\kappa(r_1 + r_2)} \rho d\rho. \quad (22)$$

For small  $\rho$ , we have

$$r_{1,2} \approx x_{1,2} + \frac{\rho^2}{2x_{1,2}}$$

and  $r_1 + r_2 \sim R + \rho^2/R$ ; therefore, we can write relation (22) in the form

$$\int_S \psi_{II}^* \nabla \psi_I d\mathbf{S} \sim e^{-\kappa R} \int_0^\infty e^{-\kappa \rho^2/R} d\rho^2 = \frac{R}{\kappa} e^{-\kappa R}. \quad (23)$$

It can be seen from this relation that the structure of the integrand in Eq. (21) is such that the main con-

tribution to integral (21) for  $\kappa R \gg 1$  comes only from the narrow region on the  $S$  plane near the  $\mathbf{R}$  axis, in which  $\rho \ll R$ . In this region,  $\theta_1 \approx x_1/R \sim \rho/R \ll 1$ ; therefore, for spherical functions  $Y_{lm}(\theta_1, \phi_1)$  in relation (14), we can use the asymptotic expansion [15]

$$Y_{lm}(\theta, \phi)|_{\theta \ll 1} \approx \frac{l^{m+|m|}}{|m|! 2^{|m|}} \times \sqrt{\frac{(2l+1)(l+|m|)!}{4\pi(l-|m|)!}} \theta^{|m|} e^{im\phi}.$$

Using now the approximate expressions for  $\chi_{1,2}$ , which are valid near the  $\mathbf{R}$  axis, where  $\theta_1$  and  $\pi - \theta_2 \ll 1$ ,

$$\chi_1(r_1) \approx \left(\frac{R}{x_2}\right)^{1/\kappa} \exp\left(-\frac{x_1}{\kappa R}\right),$$

$$\chi_2(r_2) \approx \left(\frac{R}{x_1}\right)^{1/\kappa} \exp\left(-\frac{x_2}{\kappa R}\right),$$

as well as the fact that the relations  $\nabla \psi_I \approx -\kappa \psi_I \mathbf{n}$  and  $\nabla \psi_{II} \approx \kappa \psi_{II} \mathbf{n}$  hold to within the terms on the order of  $R^{-1}$ , we obtain the following expression for the exchange interaction potential for  $m = 0$  and  $\kappa R \gg 1$ :

$$\Delta E = \Delta_0(R) \sum_{l_1, l_2 \geq 0} a_{Ll_1}^0 a_{Ll_2}^0 \sum_{|k| \leq l_2} \frac{(-1)^{l_2+k}}{|k|! 2^{|k|} (\kappa R)^{|k|}} \times D_{k0}^{l_1}(\alpha_1, \beta_1, \gamma_1) D_{k0}^{l_2}(\alpha_2, \beta_2, \gamma_2) \times \sqrt{\frac{(2l_1+1)(2l_2+1)(l_1+|k|)!(l_2+|k|)!}{(l_1-|k|)!(l_2-|k|)!}}, \quad (24)$$

where the following notation is used:

$$\Delta_0(R) = N^2 e^{-\kappa R} R^{2/\kappa-1} e^{-1/\kappa}.$$

Since calculations are performed in the first nonvanishing order in  $R^{-1}$ , we must retain in the sum over  $k$  in expression (24) only the term with  $k = 0$ . In addition, we take into account the fact that Wigner function  $D_{00}^l$  depends only on argument  $\beta$ . Thus, we can write

$$\Delta E(R, \beta_1, \beta_2) = \Delta_0(R) \sum_{l_1, l_2 \geq 0} (-1)^{l_2} a_{Ll_1}^0 a_{Ll_2}^0 \sqrt{(2l_1+1)(2l_2+1)} \times D_{00}^{l_1}(0, \beta_1, 0) D_{00}^{l_2}(0, \beta_2, 0). \quad (25)$$

In the coordinate system  $\{x', y', z'\}$  with the  $z'$  axis directed along the dipole moment of the molecule, the wavefunction of the outer electron for  $m = 0$  is axisymmetric; therefore, in the first approximation, the value of the wavefunction in the narrow region between the centers of molecular particles can depend only on the polar angle of the intermolecular axis in system  $\{x', y', z'\}$ , which coincides with Euler angle  $\beta$  (or  $\pi - \beta$ ). For this reason, the exchange interaction

potential (25) does not contain the dependence on Euler angle  $\alpha$  and  $\gamma$ . In the general case of  $m \neq 0$ , this is obviously incorrect.

Expression (25) for the exchange interaction potential for  $L > 0$  is valid provided that the orbital angular momentum of the outer electron is connected with the axis of dipole  $\mathbf{d}$  and not with the intermolecular axis. The criterion for this (disregarding relativistic interactions) is the requirement that the mean distance between the electron energy level for a fixed  $L$  and for different values of the angular momentum projection  $m = -L, \dots, L$  onto the dipole axis must be much larger than the distance between energy levels with different projections  $m'$  onto the intermolecular axis. This criterion can be violated for  $R \gg 1$  for very small values of dipole moment  $d$  of the core. We will henceforth assume that the values of  $d$  are not too small, so that the conditions for the applicability of formula (25) formulated above hold.

#### 4. RESONANT CHARGE EXCHANGE

The probability of resonant charge exchange as a result of collision of a neutral molecule with a molecular ion for a given impact parameter  $b$  is [2]

$$P = \sin^2 \zeta(b), \quad \zeta(b) = \int_{-\infty}^{\infty} \frac{\Delta}{2} dt, \quad (26)$$

where  $\Delta(R)$  is the exchange interaction potential of a molecule with the molecular ion taking into account the rotation of the cores.

We assume that the ion and the molecule move in rectilinear trajectories  $R^2 = b^2 + v^2 t^2$ , where  $v$  is the relative velocity of the colliding particles. For the above dependence  $R(t)$  and for large impact parameters  $\kappa b \gg 1$ , the expression for  $\zeta(b)$  can be written in the form

$$\zeta(b) = \frac{1}{v} \sqrt{\frac{\pi b}{2\kappa}} \Delta(b). \quad (27)$$

In the expression for the resonant charge-exchange cross section

$$\sigma_r = \int_0^{\infty} 2\pi b \sin^2 \zeta(b) db,$$

quantity  $\sin^2 \zeta$  in the integrand can be replaced by 1/2 for the same impact parameters  $b$  for which the condition  $|\zeta(b)| \gg 1$  is satisfied. The resonant charge-exchange region is bounded by the values of  $b$  for which  $|\zeta(b)| \sim 1$ . A more exact condition for determining the resonant charge-transfer cross section has the form [16]

$$|\zeta(R_0)| = 0.28; \quad (28)$$

here,  $\sigma_r = \pi R_0^2 / 2$ .

To obtain the exchange interaction potential  $\Delta(R)$  taking into account the rotation of the cores, we aver-

age expression (25) for  $\Delta E(R, \beta_1, \beta_2)$  over the rotational states of the molecule and the molecular ion. It will be shown below that this averaging is analogous to the Van der Pole approximation, which is well known in classical mechanics:

$$\Delta(R) = \langle J_1, M_1, K_1, J_2, M_2, K_2 | \times \Delta E(R, \beta_1, \beta_2) | J_1, M_1, K_1, J_2, M_2, K_2 \rangle, \quad (29)$$

where

$$|J_1, M_1, K_1, J_2, M_2, K_2\rangle = \frac{\sqrt{(2J_1+1)(2J_2+1)}}{8\pi^2} \quad (30)$$

$$\times D_{M_1 K_1}^{J_1*}(\alpha_1, \beta_1, \gamma_1) D_{M_2 K_2}^{J_2*}(\alpha_2, \beta_2, \gamma_2)$$

is the product of rotational wavefunctions of molecules, which are assumed for generality to be molecules of the type of a symmetric top. Dipole moment  $\mathbf{d}$  of the core is assumed to be directed along the symmetry axis of the top;  $J, M, K$  are the total angular momentum of a molecular particle, its projection on the intermolecular axis, and on the top axis, respectively.

Performing actual calculation in (29) with the help of the known expression for the integral of the three Wigner  $D$ -functions [15], we obtain

$$\Delta(R) = \Delta_0(R) \sum_{l_1, l_2 \geq 0} (-1)^{l_2} a_{Ll_1}^0 a_{Ll_2}^0 \sqrt{(2l_1+1)(2l_2+1)} \quad (31)$$

$$\times C_{J_1 M_1 l_1 0}^{J_1 M_1} C_{J_1 K_1 l_1 0}^{J_1 K_1} C_{J_2 M_2 l_2 0}^{J_2 M_2} C_{J_2 K_2 l_2 0}^{J_2 K_2}.$$

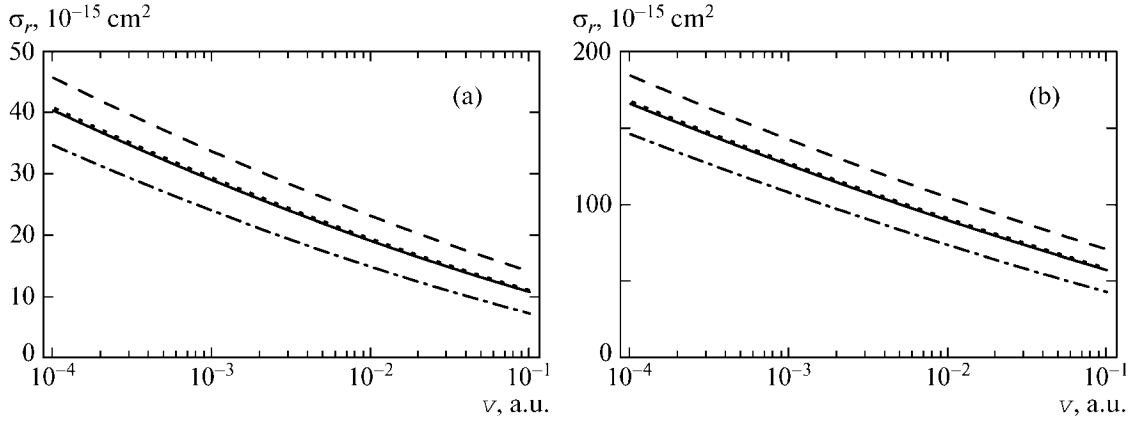
The averaging performed in this expression is justified if the rotational frequency of molecules  $\omega_{\text{rot}} \sim J/I$ , where  $I$  is the moment of inertia of a molecule, is much higher than the frequency of electron tunneling  $\omega_t \sim \Delta E \sim \Delta_0(R)$  through the potential barrier between the cores. In the general case, this means that expression (31) is valid for  $J \gg 1$ . We can obtain a more exact condition for the applicability of formula (31) for calculating the resonant charge-transfer cross section. Relations (27) and (28) lead to the estimate of  $\Delta_0(b)$  at the boundary of the resonant charge-transfer region  $b = R_0$ :

$$\Delta_0(R_0) \sim v \sqrt{\frac{\kappa}{R_0}} \sim v \sqrt{\frac{|E|}{\kappa R_0}},$$

where  $E$  is the binding energy of the outer electron in the molecule. Estimating the molecular moment of inertia  $I \sim \mu a^2$ , where  $\mu$  is the mass and  $a$  is the characteristic size of the molecular core, we can write the condition  $\omega_{\text{rot}} \gg \omega_t$  sufficient for the applicability of formula (31) in the case of resonant charge transfer in the form

$$\sqrt{E_{\text{rot}}} \gg \sqrt{E_k |E|} \frac{a}{\sqrt{\kappa R_0}}, \quad (32)$$

where  $E_{\text{rot}} \sim J^2/I$  is the rotational energy of the core and  $E_k \sim Mv^2$  is the kinetic energy of the translational



**Fig. 2.** Resonant charge-transfer cross section for collision of a polar molecule with a molecular ion for  $d = 0.6$  a.u. The outer electron of the molecule is in state (a)  $2s\sigma$  and (b)  $3s\sigma$ . The rotational numbers of the cores are  $J_1 = J_2 = 10$ ,  $K_1 = K_2 = 10$ . Dashed and dot-and-dash curves correspond to the maximal and minimal values of the resonance charge-transfer cross section, respectively. Solid curves are the cross sections averaged over projections  $M_1, M_2$  of the angular momenta of the cores. Dotted curves correspond to the cross section calculated with exchange interaction potential (34).

motion of the cores. Considering that  $\kappa R_0 \gg 1$  and  $a \sim 1$ , we can write condition (32) in the form

$$E_{\text{rot}} \sim E_k |E|. \quad (33)$$

It follows from this relation that for  $\mu \sim 10$  a.m.u.,  $|E| \sim 1$ ,  $v \sim 10^{-3}$ , the rotational number is  $J \sim 10$ . In addition, condition (31) is applicable for describing the resonant charge transfer in a medium in thermodynamic equilibrium.

Exchange interaction potential (31) averaged over the rotational state of the cores, as well as nonaveraged potential (25), depends on the orientations of the cores relative to the intermolecular axis. For fixed quantum numbers  $J_{1,2}$  and  $K_{1,2}$ , this orientation is specified by the projections  $M_1$  and  $M_2$  of the angular momenta of the cores onto the intermolecular axis. In accordance with conditions (27) and (28), the exchange interaction cross section must also be a function of projections  $M_1$  and  $M_2$ . Such an orientation dependence must obviously be manifested most strongly for  $K_1 = J_1$  and  $K_2 = J_2$ . Figure 2 shows the results of calculation of the resonance charge-transfer cross section with parameters  $N$  and  $E$  of the core potential from formula (8). The state of an electron bound to the core is characterized by quantum numbers  $n, L, m$  of the state of the united atom, where  $n \equiv n_r + L + 1$  and  $n_r$  is the radial quantum number introduced in Section 2. It can be seen from Fig. 2 that this orientation dependence exists indeed. However, it is more interesting for applications to determine the value of the cross section averaged over projections  $M_1$  and  $M_2$  of the angular momenta of the cores. Appropriate calculations show that for  $L = 0$  and for  $d \leq 1.5D \approx 0.6$  a.u., we can disregard the admixture of states with  $l_{1,2} \neq 0$  in the sum over  $l_1, l_2$  in Eq. (31). Then we obtain for  $\Delta(R)$  the following expression

independent of rotational quantum numbers of the cores:

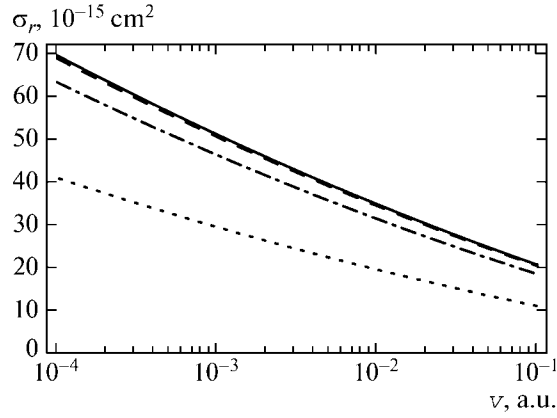
$$\Delta(R) \approx N^2 e^{-\kappa R} R^{2/\kappa-1} e^{-1/\kappa} [a_{00}^0(d)]^2, \quad (34)$$

which leads in accordance with relations (27) and (28) to the resonance charge-transfer cross section independent of the rotational state of the cores. It can be seen from Fig. 2 that the cross section averaged over projections  $M_1$  and  $M_2$  almost coincides with the cross section calculated with the exchange interaction potential (34). If  $L \neq 0$ , the dependence of the exchange interaction potential on projections  $M_1$  and  $M_2$  is preserved if we omit the terms with  $l_{1,2} \neq L$  in relation (31), and averaging over these projections can be carried out only numerically.

Expression (34) for the exchange interaction potential for  $L = 0$  and  $m = 0$  differs from an analogous expression [6] for an  $s$ -electron in a spherically symmetric potential only in the presence of factor  $[a_{00}^0(d)]^2$ . The limiting case  $d = 0$  in which  $a_{00}^0 = 1$  corresponds to the resonant charge transfer of a hydrogen atom at proton  $H(ns) + H^+$ . In states with  $L = 0$  and  $m = 0$ , the dipole potential produces an additional (as compared to the Coulomb) attraction to the core, which leads to a rapid increase in the electron binding energy  $|E| = \kappa^2/2$  with the core upon an increase in  $d$  and, as a result of an exponential dependence of exchange interaction potential (34) on  $\kappa$ , to a decrease in  $R_0$  in formula (28). Figure 3 shows the effect of dipole moment  $d$  of the core on the resonant charge-transfer cross section.

## 5. QUASI-RESONANT CHARGE TRANSFER FOR GEOMETRICAL RESONANCE DEFECT

We have considered the charge transfer of a polar molecule at its own molecular ion as a resonant pro-



**Fig. 3.** Resonant charge-transfer cross section averaged over projections  $M_1, M_2$  for a collision of a polar molecule for various values of dipole moment  $d$  of the molecular core. The outer electron of the molecule is in state  $2s\sigma$ :  $d = 0.6$  (dotted curve),  $0.3$  (dot-and-dash curve), and  $0.1$  a.u. (dashed curve); the solid curve is the  $H(2s) + H^+$  resonant charge-transfer cross section.

cess. This is true if exchange interaction potential  $\Delta(R)$  is much larger than geometrical resonance defect  $k(R)$ , which is equal to the difference in the energies of states corresponding to the localization of an electron at different cores. Analogously to the calculation of exchange interaction potential  $\Delta(R)$ , we average the difference  $E_1 - E_{11}$  in electron energies (12) over rotational states of the molecule and the molecular ion (30). As a result, we obtain the following expression for  $k(R)$  in the first nonvanishing order in  $R^{-1}$ :

$$k(R) = \frac{\mathcal{D}}{R^2} \left[ \frac{M_1 K_1}{J_1(J_1 + 1)} + \frac{M_2 K_2}{J_2(J_2 + 1)} \right], \quad (35)$$

where  $\mathcal{D} = d + d_e$  is the total dipole moment of the molecule. Each term in expression (35) has the meaning of the Stark shift of the energy level of a neutral polar molecule [15] consisting of the first or second core and the outer electron bound to it in the molecular ion electric field on the order of  $1/R^2$ . This is a natural result because in the absence of electrostatic interaction, the energy of the “molecule + molecular ion” system would not depend on the localization of the electron at one of the molecular particles.

Using the estimates

$$k(R_0) \sim \frac{\mathcal{D}}{R_0^2}, \quad \zeta(R_0) \sim \sqrt{\frac{R_0 \Delta(R_0)}{\kappa v}} \sim 1$$

(see relations (27) and (28)), which imply that  $\Delta(R_0) \sim v \sqrt{\kappa/R_0}$ , we can write the condition  $|\Delta(R_0)| \gg |k(R_0)|$ , under which the charge exchange process can be treated as resonant, in the form

$$v \gg \frac{\mathcal{D}}{\sqrt{\kappa R_0^{3/2}}}. \quad (36)$$

Setting  $\kappa \approx 1$ ,  $R_0 \approx 10$ , and  $\mathcal{D} \approx 1$ , we find that condition (36) is violated in the region of  $v \lesssim 10^{-3}$  to  $10^{-2}$ . Thus, the charge exchange process for molecules of the type of a symmetric top with low relative velocities of collision should be treated as a quasi-resonant process. The characteristic size  $R_c$  for a quasi-resonant process can be determined from the condition

$$|\Delta(R_c)| = |k(R_c)|.$$

Since  $\Delta$  depends on  $R$  exponentially and  $k$  depends on  $R_c$  only as a power function, the resonance defect in the vicinity of  $R = R_c$  can be treated as constant and equal to  $k_c \equiv k(R_c) = \text{const}$ . Then, in accordance with the Rosen–Zener–Demkov formula, the probability of quasi-resonant charge transfer as a result of collision with a given impact parameter  $b$  and relative velocity  $v$  of colliding particles is given by [16]

$$P = \frac{\sin^2 \zeta(b)}{\cosh^2(\alpha/x)}, \quad (37)$$

where quantity  $\zeta(b)$  was introduced in (26),  $\alpha = \pi k_c / 2\kappa v$ , and  $x = \sqrt{1 - b^2/R_c^2}$ .

The quasi-resonant charge-transfer cross section corresponding to probability (37) has the form [16]

$$\sigma_{qr} = \begin{cases} 1/2\pi R_c^2 f(\alpha), & \text{if } R_c < R_0 \\ 1/2\pi R_0^2, & \text{if } R_c > R_0, \end{cases} \quad (38)$$

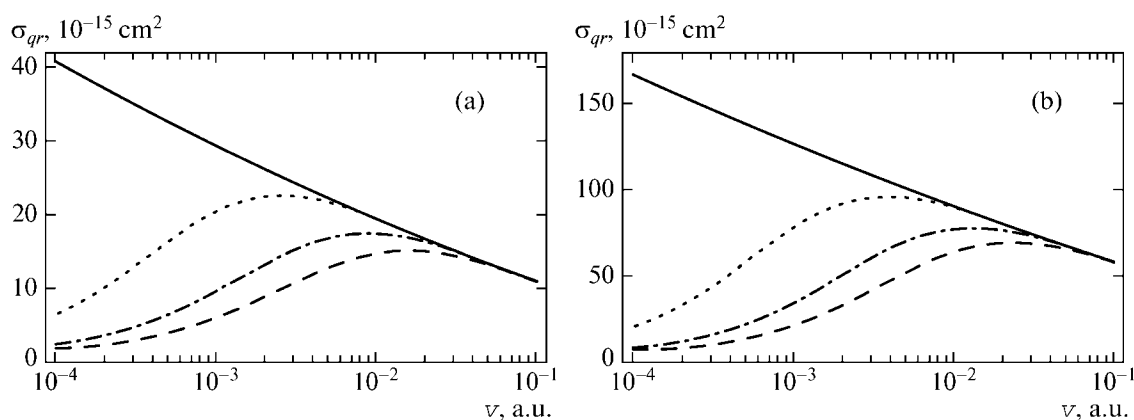
where

$$f(\alpha) = \int_0^1 \frac{2xdx}{\cosh^2(\alpha/x)}.$$

Expression (38) is valid for  $\kappa R_c \gg 1$ .

Figure 4 shows the results of calculation of the quasi-resonant charge-transfer cross section for the same parameters of motion of the outer electron as in Fig. 2. For  $\zeta(b)$ , we used the expression independent of the orientation of the cores, which can be derived using exchange interaction potential (34). In this case, the geometrical resonance defect  $k(R)$  and, hence,  $R_c$  and  $k_c$  in accordance with formula (35) depend considerably on projections  $M_1, M_2$  of the angular momenta of the cores on the intermolecular axis (we assume that  $J_{1,2}$  and  $K_{1,2}$  are fixed). Therefore, cross section  $\sigma_{qr}$  also depends substantially on  $M_1, M_2$ . Figure 4 shows the cross section  $\sigma_{qr}$  averaged over  $M_1, M_2$ . It can be seen that when the relative velocity of colliding particles decreases, the electrostatic interaction between them may change the type of charge transfer from resonant to quasi-resonant. The charge-transfer cross section calculated with allowance for the emerging geometric resonance defect has a peak in the dependence on the velocity of colliding particles, which is typical of nonresonant processes.

The results obtained above for molecules of the type of a symmetric top (in particular, expressions (31)



**Fig. 4.** Resonant charge-transfer cross section averaged over projections  $M_1, M_2$  for a collision of a polar molecule for  $d = 0.6$  a.u. and  $K_1 = K_2 = 5$  (dashed curves), 3 (dot-and-dash curves), and 1 (dotted curves). The outer electron of the molecule is in state (a)  $2s\sigma$  and (b)  $3s\sigma$ . The angular momenta of the cores are  $J_1 = J_2 = 10$ . Solid curves correspond to the resonant charge-transfer cross section calculated with exchange interaction potential (34).

for the exchange interaction potential and (35) for the geometric resonance defect) can be extended to the case of diatomic polar molecules by substituting quantum number  $\Lambda$  (projection of the total orbital angular momentum of electrons of a diatomic molecule on its axis) for the projection of angular momentum  $K$  of the core on the top axis. For  $\Sigma$ -terms ( $\Lambda = 0$ ) of a diatomic molecule, we have  $k(R) \sim 1/R^4$ , and the charge-exchange process can be treated as resonant in the entire admissible interval of collision velocities.

## REFERENCES

1. B. M. Smirnov, *Asymptotical Methods in the Theory of Atomic Collisions* (Nauka, Moscow, 1973) [in Russian].
2. E. E. Nikitin and B. M. Smirnov, *Slow Atomic Collisions* (Energoatomizdat, Moscow, 1990) [in Russian].
3. L. D. Landau and E. M. Lifshitz, *Course of Theoretical Physics*, Vol. 3: *Quantum Mechanics: Non-Relativistic Theory* (Nauka, Moscow, 1989; Butterworth-Heinemann, Oxford, 1991).
4. C. Herring, *Rev. Mod. Phys.* **34**, 631 (1962).
5. C. Herring and M. Flicker, *Phys. Rev. Sect. A* **134**, 362 (1964).
6. M. I. Chibisov and R. K. Janev, *Phys. Rep.* **166**, 1 (1988).
7. V. Yu. Lazur, M. V. Khoma, and R. K. Janev, *Phys. Rev. A: At., Mol., Opt. Phys.* **73**, 032723 (2006).
8. M. V. Khoma, M. Imai, O. M. Karbovanets, Y. Kikuchi, M. Saito, Y. Haruyama, M. I. Karbovanets, I. Yu. Kretinin, A. Itoh, and R. J. Buenker, *Chem. Phys.* **352**, 142 (2008).
9. M. V. Khoma, O. M. Karbovanets, M. I. Karbovanets, and R. J. Buenker, *Phys. Scr.* **78**, 065201 (2008).
10. M. I. Chibisov, *Zh. Eksp. Teor. Fiz.* **76** (6), 1898 (1979) [*Sov. Phys. JETP* **49** (6), 962 (1979)].
11. M. V. Khoma, V. Yu. Lazur, and R. K. Janev, *Phys. Rev. A: At., Mol., Opt. Phys.* **80**, 032706 (2009).
12. B. A. Zon, *Zh. Eksp. Teor. Fiz.* **102** (1), 36 (1992) [*Sov. Phys. JETP* **75** (1), 19 (1992)].
13. P. G. Alcheev, V. E. Chernov, and B. A. Zon, *J. Mol. Spectrosc.* **211**, 71 (2002).
14. V. E. Chernov, I. Yu. Kiyani, H. Helm, and B. A. Zon, *Phys. Rev. A: At., Mol., Opt. Phys.* **71**, 033410 (2005).
15. D. A. Varshalovich, A. N. Moskalev, and V. K. Khersonskii, *Quantum Theory of Angular Momentum* (Nauka, Leningrad, 1975; World Scientific, Singapore, 1988).
16. E. E. Nikitin and B. M. Smirnov, *Atomic-Molecular Processes in Problems with Solutions* (Nauka, Moscow, 1988) [in Russian].

Translated by N. Wadhwa