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RESONANT CHARGE EXCHANGE WITH THE p-ELECTRON TRANSITION

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The asymptotic resonant charge exchange theory is developed for slow collisions of atoms and ions with valent p-electrons. Because of a small rotation angle of the molecular axis in the course of the p-electron transition, the resonant charge exchange cross-section is not sensitive to the rotational energy of colliding particles, and the cross-sections are nearly equal for cases «a», «b», and «d» of the Hund coupling, and also for cases «c» and «e» of the Hund coupling. The cross-sections of the resonant charge exchange process are evaluated under various conditions and for various elements of the periodical table with p-electron shells of atoms and ions.

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1. INTRODUCTION

The resonant charge exchange process corresponds to the tunnel transition of a valent electron from the field of one atomic core to another one in the course of a collision of an ion with the parent atom. Under real conditions, one can consider nuclei to move along classical trajectories [1–3]; at small collision velocities compared to a typical atomic velocity, the rate of this process can be expressed through the parameters of the molecular ion consisting of the colliding atom and its ion [4, 5]. In particular, for the transiting s-electron and structureless cores, with only two electron terms of the molecular ion involved in this process, the probability P_{res} of the electron transition from one core to another after the collision is given by [4]

$$P_{res} = \sin^2\zeta(\rho), \quad \zeta(\rho) = \int_{-\infty}^{\infty} \frac{\Delta(R)}{2} dt, \tag{1}$$

where $R(t)$ is the distance between the nuclei, t is time, ρ is the impact parameter of the collision, $\zeta(\rho)$ is the exchange phase, and the ion–atom exchange interaction potential is defined as

$$\Delta(R) = \varepsilon_g(R) - \varepsilon_u(R) \tag{2}$$

where $\varepsilon_g(R)$ and $\varepsilon_u(R)$ are the energies of the even and odd states of the molecular ion. These states are characterized by different symmetries of the electron reflection with respect to the symmetry plane that is perpendicular to the line joining the nuclei and bisects it.

In reality, the resonant charge exchange cross-section is large compared to a typical atomic value of this dimensionality. This implies that transitions at large separations give the leading contribution to the cross-section. This fact is the basis of the asymptotic theory of the resonant charge exchange [6, 7], where the cross-section is expanded with respect to a small parameter that is inversely proportional to the typical separation for the electron transition. Within the framework of the asymptotic theory, the cross-section of this process is expressed through the collision parameters and the radial wave function parameters of the transiting valent electron in the atom when the electron is located far from the core. In particular, for the s-electron transition between structureless cores, the cross-section of the resonant charge exchange is [7]

$$\begin{aligned} \sigma_s &= \int_0^{\infty} 2\pi\rho d\rho \sin^2\zeta(\rho) = \frac{\pi R_0^2}{2}, \\ \zeta(R_0) &= \frac{e^{-C}}{2} = 0.28, \end{aligned} \tag{3}$$

where $C = 0.577$ is the Euler constant and the exchange phase for the free motion of the nuclei $R = \sqrt{v^2t^2 + \rho^2}$ is given by [7]

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$$\zeta(\rho) = \int\limits_{-\infty}^{\infty} \frac{\Delta(R)}{2} dt = \frac{1}{v}\sqrt{\frac{\pi\rho}{2\gamma}}\Delta(\rho) = $$
$$= \frac{1}{v}\sqrt{\frac{\pi}{2\gamma}} A^2 e^{-1/\gamma} \rho^{2/\gamma - 1/2} \exp(-\rho\gamma). \quad (4)$$

Here, v is the collision velocity, $\gamma^2/2$ is the atom ionization potential or the electron binding energy, and A is the asymptotic coefficient of the electron wave function in this atom; we use the atomic units where $\hbar = m_e = e = 1$. The asymptotic parameters of the atom are contained in the normalized radial wave function of the electron at large distances r from the core,

$$\psi(r \to \infty) = A r^{1/\gamma - 1} e^{-r\gamma}. \quad (5)$$

In particular, $A = 2$ for the hydrogen atom [8].

We note that the small asymptotic theory parameter is $1/R_0\gamma$, and because the asymptotic theory involves the information about the electron location far from the core, we can keep only two expansion terms in the expression for the cross-section, as we did in Eq. (3). This corresponds to the asymptotic theory accuracy for the transition of a valent s-electron in the range 1–5% [9] for the eV-collision energies.

For a transiting p-electron, the asymptotic theory of the resonant charge exchange process becomes cumbersome [10, 11] because on the one hand, the electron transfer process is entangled with the rotation of the molecular axis, and on the other hand, the fine splitting of the ion and atom levels can be important in this process. Therefore, the above formulas for the s-electron transition are used in some recent calculations [12–14] as model ones for the evaluation of the cross-section of this process for the transiting p-electron. This leads to an uncontrolled error that is absent in the asymptotic theory. We note that the contemporary computer technique allows us to formulate the asymptotic theory in a simple way and to exhibit various aspects of the process under consideration. In this paper, we present the asymptotic theory for the resonant charge exchange process with the transiting p-electron. We are guided mostly by the ground states of the colliding ion and atom and focus on the cross-section averaging over the directions of the initial momenta.

2. RESONANT CHARGE EXCHANGE WITH THE TRANSITING *p*-ELECTRON FOR LIGHT ATOMS

We first consider the case of a small spin–orbit splitting of atom and ion levels and neglect relativistic interactions. This corresponds to the LS-coupling scheme for the atom. At large separations, the quantum numbers of the molecular ion are the atom quantum numbers LSM_LM_S (the orbital momentum, spin, and their projections on the molecular axis) and the same quantum numbers of the ion $lsmm_s$. The atom orbital and spin momenta L and S are given by the sum of the electron orbital and spin momenta l_e and $1/2$ and of the respective momenta of the atomic core l and s. The atom spin S and the spin of the other atom core s are then summed into the total spin I of the molecular ion. The atomic wave function is then expressed through the parameters of the core and the valent electron by means of the genealogical or Racah coefficients [15, 16]. The ion–atom exchange interaction potential is then given by [10, 17]

$$\Delta(l_e\mu, lms, LM_LS) = \frac{\overline{I} + 1/2}{2s+1} n (G_{ls}^{LS})^2 \times$$
$$\times \left[\begin{array}{ccc} l_e & l & L \\ \mu & m & m{+}\mu \end{array}\right] \left[\begin{array}{ccc} l_e & l & L \\ \mu & M_L{-}\mu & M_L \end{array}\right] \Delta_{l_e\mu}, \quad (6)$$

where n is the number of identical valent electrons of the atom, G_{ls}^{LS} is the genealogical (Racah) coefficient [15, 16], the square brackets are the Clebsch–Gordan coefficients that are responsible for the summation of the electron and ion orbital momenta into the atom orbital momentum, and $\Delta_{l_e\mu}$ is the exchange interaction potential for one valent electron located in the field of structureless cores. We note a weak dependence of the exchange interaction potential on the total spin I of the molecular ion. Indeed, the level splitting corresponding to different total spins of the molecular ion is determined by the exchange of two electrons and varies at large separations R as $\exp(-2\gamma R)$. Therefore, Eq. (6) contains the average spin of the molecular ion. Next, because the exchange interaction potential $\Delta_{l_e\mu}$ decreases as $R^{-\mu}$ with increasing μ, we are restricted by the term with the minimum value of μ in Eq. (6). As a result, for the valent p-electron, we have [10, 17]

$$\Delta_{10}(R) = 3\Delta_0, \quad \Delta_{11}(R) = \frac{6}{R\gamma}\Delta_0, \quad (7)$$

where [7]

$$\Delta_0 = A^2 R^{(2/\gamma)-1} e^{-R\gamma-(1/\gamma)} \quad (8)$$

is the exchange interaction potential for a valent s-electron [7] with the same asymptotic radial wave function (5).

Equation (6) allows one to construct the matrix of the exchange interaction potential of an ion and an atom with valent p-electrons. Below, we represent these matrices in the case where the atom and the ion are in the ground electron states. One can convince oneself in the identity of the transiting electron and the hole. In accordance with Eq. (6) for atoms of group 3 (with one valent p-electron) and atoms of group 8 (with one valent p-hole) in the periodical table of elements, with the ground states of the atom and the ion given by ^1S and ^2P, the exchange interaction potential of the interacting atom and the ion is given by the matrix

$$\Delta(M_L) = \begin{array}{|c|c|c|}\hline M_L=-1 & M_L=0 & M_L=+1 \\ \hline \Delta_{11} & \Delta_{10} & \Delta_{11} \\ \hline \end{array}, \tag{9a}$$

where M_L is the orbital momentum projection for the atom (elements of group 3) or the ion (elements of group 8). For elements of groups 4 and 7 of the periodical table, with the ground electron states of the atom and the ion given by ^3P and ^2P, the matrix of the exchange interaction potential, in accordance with Eq. (6), is

$$\Delta(m, M_L) = \frac{5}{3} \times$$
$$\times \begin{array}{|c|c|c|c|}\hline & M_L=-1 & M_L=0 & M_L=+1 \\ \hline m=-1 & \Delta_{10} & \Delta_{11} & \Delta_{10} \\ \hline m=0 & \Delta_{11} & 2\Delta_{11} & \Delta_{11} \\ \hline m=1 & \Delta_{10} & \Delta_{11} & \Delta_{10} \\ \hline \end{array}, \tag{9b}$$

where m and M_L are the projections of the orbital ion and atom momenta. For elements of groups 5 and 6 of the periodical table with the atom and ion ground states ^4S and ^3P, the matrix of the exchange interaction potential is given by

$$\Delta(m) = \frac{7}{3} \begin{array}{|c|c|c|}\hline m=-1 & m=0 & m=1 \\ \hline \Delta_{11} & \Delta_{10} & \Delta_{11} \\ \hline \end{array}. \tag{9c}$$

As the quantization axis, we take the direction on which the projection of the electron momentum is zero. We let θ denote the angle between the quantization and molecular axes. By definition, the exchange interaction potential $\Delta(\theta)$ of the atom and its ion with valent p-electrons is equal to

$$\Delta(\theta) = \frac{1}{3}\sum_M \left|d^1_{M0}(\theta)\right|^2 \Delta_{1M} = \\ = \frac{4\pi}{3}\sum_M \left|Y_{1M}(\theta,\varphi)\right|^2 \Delta_{1M},$$

where $d^1_{M0}(\theta)$ is the Wigner rotation function [20] and $Y_{1M}(\theta)$ is the spherical function; it follows that $4\pi|Y_{1M}(\theta)|^2$ is the probability to find a state with the momentum projection M at the angles θ and φ with respect to the molecular axis. The spherical function satisfies to the normalization condition

$$\int\limits_{-1}^{1} d\cos\theta \, |Y_{1M}(\theta)|^2 = \frac{1}{4\pi}.$$

It follows that for groups 3 and 8 of the periodical table of elements, the exchange interaction potential of an atom and a parent ion is given by

$$\Delta(\theta) = \Delta_{10}\cos^2\theta + \Delta_{11}\sin^2\theta. \tag{10a}$$

Matrix (9b) gives the ion–atom exchange interaction potential as a function of the angles between the quantization and molecular axes for elements of groups 4 and 7 of the periodical system,

$$\Delta(\theta) = \frac{5}{3} \times \\ \times \left[\Delta_{10}\sin^2\theta_1 \sin^2\theta_2 + \Delta_{11}(\cos^2\theta_1 + \cos^2\theta_2)\right], \tag{10b}$$

where θ_1 and θ_2 are the respective angles between the molecular axis and the quantization axes for the atom and the ion, with zero electron momentum projection on the quantization axis. For groups 4 and 7 of the periodical system, the exchange interaction potential is similar to that for atoms of groups 3 and 8 and is given by

$$\Delta(\theta) = \frac{7}{3}\left(\Delta_{10}\cos^2\theta + \Delta_{11}\sin^2\theta\right). \tag{10c}$$

Although we are restricted by the ground states of the ion and the parent atom, this is a general scheme of constructing the ion–atom exchange interaction potential. Being averaged over the total quasimolecule spin I, the exchange interaction potential depends on the ion (m) and the atom (M_L) angular momentum projections on the molecular axis. This corresponds to the LS-coupling scheme for atoms and ions, which means neglecting the spin-orbital interaction. Therefore, the above expressions correspond to the hierarchy of the interaction potentials

$$V_{ex} \gg U(R), \quad \Delta(R), \tag{11}$$

where V_{ex} is the typical exchange interaction potential for valent electrons inside the atom or the ion, $U(R)$ is the long-range interaction potential between the atom and the ion at large separations R, and $\Delta(R)$ is the exchange interaction potential between the atom and the ion. Within the framework of the LS-coupling scheme for atoms and ions, we assume the excitation energies inside the electron shell to be relatively large. This criterion is fulfilled for light atoms and ions. In the same manner, one can construct the exchange interaction potential matrix for excited states within a given electron shell.

Because the exchange interaction potential is determined by the transition of one electron from the valent electron shell and the transiting electron carries a certain momentum and spin, additional selection rules apply for the one-electron interaction. In particular, for the transition of a p-electron, the selection rules are given by

$$|L-l| \le 1, \quad |S-s| \le 1/2. \tag{12}$$

These selection rules follow from the properties of the Clebsch–Gordan coefficients entering Eq. (6). If these conditions are violated, the ion–atom exchange interaction potential is zero at the scale of one-electron interaction potentials. In Table 1, we list the states of atoms and their ions with valent p-electrons for which the ion–atom one-electron exchange interaction potential is zero.

When a valent p-electron transits from one atomic core to the other in the course of collision, the processes of charge exchange and the electron momentum rotation are entangled. One can partially separate these processes because the charge exchange proceeds in a narrow range of separations R where the molecular axis turns at a small angle of the order $1/\sqrt{R_0\gamma}$. Indeed, the range of distances ΔR between the nuclei where the charge exchange phase ζ varies considerably is $\Delta R \sim 1/\gamma$, which corresponds to the rotation angle $\vartheta \sim vt/R \sim 1/\sqrt{R\gamma} \ll 1$. This fact allows us to simplify the derivation of the resonant charge exchange cross-section. In what follows, we find the cross-section averaged over angles between the collision impact parameter and the quantization axis on which the orbital momentum projection is zero.

Proceeding along this way, we orientate the quantization axis with respect to the direction of the collision impact parameter as the motionless axis; the average cross-section of the resonant charge exchange is then given by

$$\overline{\sigma} = \frac{1}{4\pi}\int\limits_{-1}^{1}\int\limits_{0}^{2\pi} \sigma(\vartheta,\varphi)\, d\cos\vartheta d\varphi, \tag{13}$$

where ϑ and φ are the polar angles of the impact parameter direction with respect to the quantization axis direction and $\sigma(\vartheta,\varphi)$ is the charge exchange cross-section at a given direction of the collision impact parameter. We first consider the cases where the momentum projection on the molecular axis conserves in the course of the electron transfer. This corresponds to a small rotational energy, and under condition (11), is determined by the condition

$$\frac{v}{\rho} \ll U(\rho),\ \Delta(\rho), \tag{14}$$

which means that the rotational energy v/ρ at the closest approach distance is small compared to the long-range splitting $U(\rho)$ of molecular levels for states with different projections of the orbital momentum on the molecular axis or the exchange interaction splitting $\Delta(\rho)$. Criterion (14) corresponds to cases «a» and «b» of the Hund coupling [18, 19]. For the free motion of colliding particles, the current angle θ between the molecular and quantization axes and the angle ϑ between these axes at the closest approach distance are related by

$$\cos\theta = \cos\vartheta\cos\alpha + \sin\vartheta\sin\alpha\cos\varphi, \tag{15}$$

where α and φ are the polar angles of the molecular axis with respect to its direction at the closest approach distance; we have $\sin\alpha = vt/R$, where v is the collision velocity, t is time, and R is a current distance between the colliding particles.

Using Eqs. (15) and (10), we can represent the exchange phases in the form of an expansion in the small parameter of the theory $1/\rho\gamma$ if criterion (14) is satisfied. For elements of groups 3, 5, 6, and 8 of the periodical system, we have

$$\zeta(\rho,\vartheta,\varphi) = \zeta(\rho,0) \times \\ \times \left[\cos^2\vartheta - \frac{1}{\gamma\rho}\cos^2\vartheta + \frac{1}{\gamma\rho}\sin^2\vartheta(2+\cos^2\varphi)\right]. \tag{16a}$$

This expression applies to large collision impact parameters and $\zeta(\rho,0)$ is the phase of the charge exchange process when the quantization axis has the same direction as the molecular axis at the closest approach distance; $\zeta(\rho,0) = 3\,\zeta_0(\rho)$ for elements of groups 3 and 8 and $\zeta(\rho,0) = 7\,\zeta_0(\rho)$ for elements of groups 5 and 6, where the charge exchange phase ζ_0 is given by Eq. (4) and is related to the s-electron transition with the same asymptotic parameters γ and A. For atoms of groups 4 and 7, the charge exchange phase at large impact parameters of the collision is given by

$$\zeta = 5\zeta_0(\rho)\left\{\sin^2\vartheta_1\sin^2\vartheta_2 + \frac{1}{\gamma\rho} \times \right. \\ \times[2\cos^2\vartheta_1 + 2\cos^2\vartheta_2 + \sin^2\vartheta_1\cos^2\vartheta_2 + \cos^2\vartheta_1\sin^2\vartheta_2 - \\ - \sin^2\vartheta_1\sin^2\vartheta_2(\cos^2\varphi_1 + \cos^2\varphi_2) + \\ \left. + \sin 2\vartheta_1\sin 2\vartheta_2\cos\varphi_1\cos\varphi_2]\right\}, \tag{16b}$$

Table 1. The ion and parent atom states with valent p-electrons. The one-electron transition is forbidden between these states and the exchange interaction potential of the ion and the parent atom is zero

Electron configuration and ion state	Electron configuration and atom state
$p^2(^1D)$	$p^3(^4S)$
$p^2(^1S)$	$p^3(^4S)$
$p^2(^1S)$	$p^3(^2D)$
$p^3(^4S)$	$p^4(^1D)$
$p^3(^4S)$	$p^4(^1S)$
$p^3(^2D)$	$p^4(^1S)$

where ϑ_1, φ_1 and ϑ_2, φ_2 are the respective polar angles of the quantization axes of the atom and the ion relative to the molecular axis at the closest approach distance.

We now determine the average cross-section from Eq. (13) using Eq. (4) for the cross-section at a given angle and the dependence $\zeta \propto \exp(-\gamma\rho)$ for the exchange phase. For elements of groups 3, 5, 6, and 8 of the periodical system, this gives

$$\frac{\overline{\sigma}}{\sigma_s} = \frac{1}{2\pi} \times$$

$$\times \int_0^1 \int_0^{2\pi} \left[1 + \frac{1}{\gamma R_0} \ln \frac{\zeta(R_0, \vartheta, \varphi)}{\zeta_0(R_0)}\right]^2 d\cos\vartheta d\varphi, \qquad (17)$$

where $R_0 = \sqrt{2\sigma_s/\pi}$. The same expression applies to elements of groups 4 and 7 with the integration over 4 angles $\vartheta_1, \varphi_1, \vartheta_2, \varphi_2$; here σ_s is the cross-section in Eq. (3) for the transiting s-electron with the same asymptotic parameters as for the p-electron. Table 2 contains these reduced cross-sections depending on the parameter $R_0\gamma$. The value of Σ_3 in Table 2 gives $\overline{\sigma}/\sigma_s$ for elements of groups 3 and 8 of the periodical table, the value of Σ_4 is $\overline{\sigma}/\sigma_s$ for elements of groups 4 and 7, and the value of Σ_5 gives $\overline{\sigma}/\sigma_s$ for elements of groups 5 and 6. In addition, this table contains the reduced cross-sections Σ_{10} and Σ_{11} corresponding to the respective projections 0 and 1 of the orbital momentum on the impact parameter direction.

We also consider the opposite case to (14), where

$$\frac{v}{\rho} \gg U(\rho), \Delta(\rho). \qquad (18)$$

In this case, the exchange phase for elements of groups 3, 5, 6, and 8 is given by

$$\zeta(\rho, \vartheta, \varphi) = \zeta(\rho, 0)\left(\cos^2\vartheta + \frac{2}{\gamma\rho}\sin^2\vartheta\right) \qquad (19)$$

Table 2. The reduced cross-sections of the resonant charge exchange

$R_0\gamma$	6	8	10	12	14	16
Σ_{10}	1.40	1.29	1.23	1.19	1.16	1.14
Σ_{11}	1.08	0.98	0.94	0.92	0.91	0.91
$\overline{\Sigma}$	1.19	1.08	1.04	1.01	0.99	0.95
Σ_3	1.17	1.09	1.05	1.03	1.02	1.01
Σ_3^d	1.16	1.08	1.04	1.02	1.01	1.00
Σ_4	1.50	1.32	1.23	1.18	1.14	1.12
Σ_5	1.44	1.29	1.22	1.17	1.14	1.11
$\Sigma_{1/2}$	1.18	1.10	1.07	1.05	1.04	1.03
$\Sigma_{3/2}$	1.18	1.10	1.06	1.04	1.03	1.02
$\Sigma_{3/2}^e$	1.16	1.09	1.06	1.04	1.03	1.02

instead of (16a). The corresponding reduced average cross-section is denoted by Σ_3^d in Table 2. This corresponds to cases «b» and «d» of the Hund coupling, and according to the data in Table 2, the results for this case practically coincide with case «a» of the Hund coupling. The value $\overline{\Sigma}$ in Table 2 is

$$\overline{\Sigma} = \Sigma_{10}/3 + 2\Sigma_{11}/3.$$

Comparing it to the average cross-section testifies the sensitivity of the cross-section to different methods of averaging.

Table 3. The Hund coupling cases

Hund coupling case	Relation
a	$V_e \gg \delta_f \gg V_r$
b	$V_e \gg V_r \gg \delta_f$
c	$\delta_f \gg V_e \gg V_r$
d	$V_r \gg V_e \gg \delta_f$
e	$V_r \gg \delta_f \gg V_e$
e'	$\delta_f \gg V_r \gg V_e$

3. RESONANT CHARGE EXCHANGE WITH THE TRANSITING p-ELECTRON FOR HEAVY ATOMS

In considering the resonant charge exchange process, we follow the general scheme of classifying the limiting cases of momentum coupling in diatomic molecules. This scheme is given in Table 3 [18, 19]. The cases of the Hund coupling unify different relations between energetic parameters of colliding particles. An important energetic parameter of the quasimolecule consisting of colliding particles is the interaction potential V_e between the orbital angular momentum of the electrons and the molecular axis. This includes the exchange interaction potential V_{ex} inside the atom and the ion due to the Pauli exclusion principle, the splitting of the molecular ion levels due to the long-range interaction $U(R)$, and the exchange interaction $\Delta(R)$ between the ion and the atom. Within the framework of the Hund schemes, we compare this interaction potential to the relativistic interaction δ_f given by the sum of spin-orbit interactions of the individual electrons and other relativistic interactions and the rotational energy given by $V_r = v\rho/R^2$ for the free motion of colliding particles. For colliding atomic particles, in contrast to a molecule, different types of the Hund coupling can be realized on one classical trajectory of particles. We use the general Nikitin scheme [21–23] that relates the characters of the momentum coupling of colliding atomic particles moving along one trajectory. The problem under consideration is simpler because we are interested in the behavior of colliding particles on the trajectory element where the electron transition occurs. Only one type of the momentum coupling is realized on this part of the trajectory.

Above, we considered the cases where relativistic interactions are negligible and the projection of the orbital electron momentum on the molecular or the motionless axis conserves in the course of the electron transfer, which corresponds to cases «a», «b», and «d» of the Hund coupling and is realized for light atomic particles. In what follows, we are guided by heavy atoms and examine the cases where relativistic interactions are important.

Table 4. The ground states of atoms with p-electron shells in the framework of the LS and jj coupling schemes and the ion–atom exchange interaction potential Δ for the Hund coupling cases «c» and «e»

Shell	J	LS-term	jj-shell	Δ
p	1/2	$^2P_{1/2}$	$[1/2]^1$	$\Delta_{1/2}$
p^2	0	$^3P_0$	$[1/2]^2$	$\Delta_{1/2}$
p^3	3/2	$^4S_{3/2}$	$[1/2]^2[3/2]^1$	$\Delta_{3/2}$
p^4	2	$^3P_2$	$[1/2]^1[3/2]^3$	0
p^5	3/2	$^2P_{3/2}$	$[1/2]^2[3/2]^3$	$\Delta_{1/2}$
p^6	0	$^1S_0$	$[1/2]^2[3/2]^4$	$\Delta_{3/2}$

In the collisions of heavy atomic particles, the relativistic interactions are dominant, and therefore, the jj coupling scheme becomes valid for an individual atomic particle. The quantum numbers of the interacting atom and ion are therefore given by J and M_J, the total atomic electron momentum and its projection on the molecular axis for the atom, and also by the respective ion quantum numbers j and m_j. At large separations, these quantum numbers are related to the molecular ion consisting of the ion and the parent atom. We note that the total momentum J and its projection on a given direction M_J are the quantum numbers of an individual atomic particle in both momentum coupling schemes (LS and jj), which simplifies the analysis in the general case. Next, taking the relativistic effects into account reduces the atom symmetry. For this reason, on the one hand, the ion–atom exchange interaction potential is expressed through the one-electron exchange interaction potential in a simpler way, and on the other hand, the prohibition of some one-electron transitions strengthens in the presence of relativistic interactions because of a weaker mixing of states in this case. Table 4 contains parameters of the electron shells for the ground electron states of atoms and ions with p electron shells. We note that for the jj-coupling, the similarity between the transitions of the p-electron and the p-hole is lost because of different signs of the spin–orbit interaction potential for the electron and the hole.

Table 5. The exchange interaction potential for atoms of group 5 of the periodical system of elements whose atomic electron shell is p^3 and their ions have the electron shell p^2

LS		${}^4S_{3/2}$	${}^2D_{3/2}$	${}^2D_{5/2}$	${}^2P_{1/2}$	${}^2P_{3/2}$
	jj	$\left[\left(\frac{1}{2}\right)^2\left(\frac{3}{2}\right)\right]_{3/2}$	$\left[\left(\frac{1}{2}\right)\left(\frac{3}{2}\right)^2\right]_{3/2}$	$\left[\left(\frac{1}{2}\right)\left(\frac{3}{2}\right)^2\right]_{5/2}$	$\left[\left(\frac{1}{2}\right)\left(\frac{3}{2}\right)^2\right]_{1/2}$	$\left[\left(\frac{3}{2}\right)^3\right]_{3/2}$
${}^3P_0$	$\left[\left(\frac{1}{2}\right)^2\right]_0$	$\Delta_{3/2}(+)$	$0(+)$	$0(+)$	$0(+)$	$0(+)$
${}^3P_1$	$\left[\left(\frac{1}{2}\right)\left(\frac{3}{2}\right)\right]_1$	$\Delta_{1/2}(+)$	$\Delta_{3/2}(+)$	$\Delta_{3/2}(+)$	$\Delta_{3/2}(+)$	$0(+)$
${}^3P_2$	$\left[\left(\frac{1}{2}\right)\left(\frac{3}{2}\right)\right]_2$	$\Delta_{1/2}(+)$	$\Delta_{3/2}(+)$	$\Delta_{3/2}(+)$	$\Delta_{3/2}(+)$	$0(+)$
${}^1D_2$	$\left[\left(\frac{3}{2}\right)^2\right]_2$	$0(0)$	$\Delta_{1/2}(+)$	$\Delta_{1/2}(+)$	$\Delta_{1/2}(+)$	$\Delta_{3/2}(+)$
${}^1S_0$	$\left[\left(\frac{3}{2}\right)^2\right]_0$	$0(0)$	$\Delta_{1/2}(0)$	$\Delta_{1/2}(0)$	$\Delta_{1/2}(+)$	$\Delta_{3/2}(+)$

Hence, the ion–atom exchange interaction potential is different in the cases where the p-electron shells of the atom and its ion are replaced by the shells consisting of identical p-holes. Moreover, for group 6 of the periodical system of elements, the one-electron ion–atom exchange interaction potential is zero if the atom and the ion are found in the ground states. We note that for all the groups in the periodic table of elements with valent p-electrons, the ion–atom one-electron exchange interaction potential is not zero for light atoms if atoms and their ions are found in the ground states.

It follows from the data in Table 4 that the ion–atom exchange interaction potential is simpler in the presence of relativistic interactions because of a lower symmetry of atomic particles in this case. For the LS-coupling scheme for individual atomic particles, we were restricted by the ground states of atomic particles because of a cumbersome problem, but the presence of relativistic effects simplifies this problem. As a demonstration of this, Table 5 contains the matrix of the exchange interaction potential for elements of group 5. The notation for the ion and atom electron terms used in Table 5 applies to the LS- and jj-coupling schemes. The values of the exchange interaction potentials are given assuming that the jj momentum coupling scheme applies, and it is indicated in parentheses whether this potential is zero (0) or non zero (+) for the LS-coupling scheme. In particular, for the ground atom and ion states, the exchange interaction potential occupies one cell in Table 5, while within the framework of the LS-coupling scheme, it is given by matrix (9c).

We note that for the jj-coupling scheme, the p-electron shell of an atom or an ion is separated into two independent subshells with $j = 1/2$ and $j = 3/2$. Hence, the difference between the numbers of electrons in these subshells for the interacting ion and the atom cannot exceed one. This is the criterion of the one-electron transition replacing Eq. (12) for the LS-coupling scheme. If this criterion is not satisfied, the one-electron ion–atom exchange interaction potential is zero; otherwise, it is equal to $\Delta_{1/2}$ or $\Delta_{3/2}$ depending on the momentum of the transiting electron (see Tables 4 and 5).

We now focus on elements of groups 3 or 8 of the pe-

Table 6. Parameters of the resonant charge exchange process for collisions of atoms of group 3 of the periodical system with their ions at the energy 1 eV in the laboratory coordinate system

	B	Al	Ga	In	Tl
$\overline{\sigma}, 10^{-14}$ cm^2	1.1	1.8	2.0	2.2	2.1
γR_0	12	14	14	15	14
$\Delta\sigma/\overline{\sigma}$, %	0.7	0.5	0.4	0.3	0.4
δ_f, cm^{-1}	15	112	826	2213	7793
$U(R_0)$, cm^{-1}	360	350	320	330	390
$\Delta(R_0)$, cm^{-1}	11	5	3	2.5	2

Table 7. Parameters of the resonant charge exchange process for collisions of atoms of group 8 of the periodical system with their ions at the energy 1 eV in the laboratory coordinate system

	Ne	Ar	Kr	Xe
$\overline{\sigma}, 10^{-15}$ cm^2	3.3	5.8	7.5	10
γR_0	11	12	13	14
$\Delta\sigma/\overline{\sigma}$, %	0.8	0.5	0.4	0.3
δ_f, cm^{-1}	780	1432	5370	10537
$U(R_0), 10^{-3}$ cm^{-1}	5	4	2	2
$\Delta(R_0)$, cm^{-1}	13	8	5	3

riodical table, where one transiting p-electron (or p-hole) is located in the field of two structureless cores. If the spin–orbit splitting of the electron levels is large compared to the electrostatic ion–atom interaction, the quantum numbers of the molecular ion are jm_j, the total electron momentum and its projection on the molecular axis. The exchange interaction potential Δ_{jm_j} pertaining to the jj-coupling scheme for atoms and ions and the exchange interaction potentials Δ_{1m} pertaining to the LS-coupling schemes are related by

$$\Delta_{jm_j} = \sum_{\mu} \begin{bmatrix} \frac{1}{2} & 1 & j \\ \sigma & \mu & m_j \end{bmatrix}^2 \Delta_{1\mu}.$$

This follows from the relation between the electron wave functions for the respective states. For the exchange interaction potentials Δ_{jm_j}, where $m_j = \sigma + \mu$ in accordance with the properties of the Clebsch–Gordan coefficients, this gives

$$\begin{aligned} \Delta_{1/2,1/2} &= \frac{1}{3}\Delta_{10} + \frac{2}{3}\Delta_{11}, \\ \Delta_{3/2,1/2} &= \frac{2}{3}\Delta_{10} + \frac{1}{3}\Delta_{11}, \\ \Delta_{3/2,3/2} &= \Delta_{11}, \end{aligned} \tag{20}$$

where Δ_{10} and Δ_{11} are given by Eqs. (7) and (8).

By analogy with the previous operations, if the molecular axis is at the angle θ to the quantization axis on which the angular momentum projection is zero, the exchange interaction potentials are given by

$$\begin{aligned} \Delta_{1/2} &= \frac{1}{3}\Delta_{10} + \frac{2}{3}\Delta_{11}, \\ \Delta_{3/2}(\theta) &= \left(\frac{1}{6} + \frac{1}{2}\cos^2\theta\right)\Delta_{10} + \\ &+ \left(\frac{1}{3} + \frac{1}{2}\sin^2\theta\right)\Delta_{11}. \end{aligned} \tag{21}$$

This corresponds to elements of groups 3 and 8 of the periodical system and gives the exchange phases for case «c» of the Hund coupling,

$$\begin{aligned} \frac{\zeta_{1/2}(\rho,\vartheta)}{\zeta_0(\rho)} &= 1 + \frac{4}{\rho\gamma}, \quad \frac{\zeta_{3/2}(\rho,\vartheta)}{\zeta_0(\rho)} = \frac{1}{2} + \frac{3}{2}\cos^2\vartheta + \\ &+ \frac{1}{\rho\gamma}\left(\frac{1}{2} + \frac{9}{2}\sin^2\vartheta + \frac{3}{2}\sin^2\vartheta\cos^2\varphi\right), \end{aligned} \tag{22}$$

where $\zeta_0(\rho)$ is the charge exchange phase for the transiting s-electron with the same asymptotic parameters A and γ as defined in accordance with Eq. (4) and ϑ, φ are the polar angles of the impact parameter direction with respect to the quantization axis. Table 2 contains the reduced cross-sections $\Sigma_j = \overline{\sigma_j}/\sigma_s$, where the average cross-section $\overline{\sigma_j}$ for a given total momentum is determined by Eq. (13). As can be seen, the difference of the average cross-sections for different total momenta is small compared to the accuracy of determining the cross-sections, and we neglect this difference. One can determine the cross-sections for case «e» of the Hund coupling, where because of a large rotational energy, the momentum projection on the motionless axis conserves for the state with $j = 3/2$. In Table 2, $\Sigma^e_{3/2}$ is the reduced cross-section of the resonant charge exchange for the state with $j = 3/2$ in case «e» of the

Table 8. The parameters of the cross-section of the resonant charge exchange for elements with valent p-electrons of atoms and ions at the collision energy 1 eV

Element	B	C	N	O	F	Ne	Al	Si	P
$\sigma, 10^{-15}$ cm^2	11	8.6	6.2	6.6	4.9	3.3	18	15	11
$\alpha = -d\ln\sigma/d\ln v$	0.16	0.16	0.16	0.16	0.17	0.18	0.15	0.14	0.14
Element	S	Cl	Ar	Ga	Ge	As	Se	Br	Kr
$\sigma, 10^{-15}$ cm^2	10	8.0	5.8	20	18	13	13	10	7.5
$\alpha = -d\ln\sigma/d\ln v$	0.15	0.15	0.16	0.14	0.13	0.14	0.14	0.13	0.15
Element	In	Sn	Sb	Te	I	Xe	Tl	Pb	Bi
$\sigma, 10^{-15}$ cm^2	22	19	17	16	13	10	21	20	22
$\alpha = -d\ln\sigma/d\ln v$	0.14	0.13	0.13	0.13	0.13	0.14	0.14	0.13	0.12

Hund coupling. According to the data in Table 2, the connection between the molecular and motionless axis is not essential for the cross-section of this process.

Thus, one can see that the molecular axis rotation gives a small contribution to the resonant charge exchange cross-section. That is, the difference between cases «a», «b», and «d» of the Hund coupling, as well as between cases «c» and «e», is not essential for this process. Next, according to the data in Table 2, the difference between the cross-sections for cases «a» and «c» of the Hund coupling is not significant for atoms of groups 3 and 8 of the periodical system of elements, and it is essential for atoms of groups 4, 5, 6, and 7. Thus, the transition between these coupling cases results from the competition between the splitting $U(R)$ due to the long-range ion–atom interaction, the splitting $\Delta(R)$ due to the exchange interaction, and the fine level splitting δ_f. Tables 6 and 7 contain these values for atoms of groups 3 and 8 of the periodical system of elements. Next, the long-range splitting of levels depends on the atom and ion states. If atoms and ions are found in the ground states, the long-range splitting $U(R)$ of atomic levels for elements of groups 3, 4, 6, and 7 results from the interaction of the ion charge with the atom quadrupole moment and is given by

$$U(R) = \frac{5\left\langle r^2\right\rangle}{6R^3}, \tag{23a}$$

where R is the distance between the interacting particles and $\left\langle r^2\right\rangle$ is the mean square of the electron orbit radius of the valent electron in the atom. The long-range splitting of ion levels for elements of groups 4 and 7, where the quadrupole momenta of the atom and the ion is not zero, is determined by the interaction of the quadrupole momenta, and the long-range ion–atom interaction potential $V(R)$ is then given by

$$V(R) = \frac{Q_i Q_a}{R^5}, \tag{23b}$$

where Q_a and Q_i are the respective quadrupole momenta of the atom and the ion, which are $\pm 2\left\langle r^2\right\rangle/5$ for states with zero orbital momentum projection and $\mp 4\left\langle r^2\right\rangle/5$ for states for which the orbital momentum projection on the motionless axis is 1. Expression (23b) relates to elements of groups 4 and 7 of the periodical system, where the quadrupole moment of atoms and ions is not zero. Next, the splitting of ion levels for elements of groups 5 and 8, whose atoms have zero quadrupole moment, is given by

$$U(R) = \frac{12\beta(\left\langle r^2\right\rangle)^2}{25R^8}, \tag{23c}$$

where β is the atom polarizability. The value $\Delta\sigma/\overline{\sigma}$ in Tables 6 and 7 characterizes the error in the cross-section arising from using only the exponential dependence of the exchange phase $\zeta(\rho) \propto \exp(-\gamma\rho)$, as we did in Table 2.

The information in Tables 6 and 7 exhibits the role of different interactions for the resonant charge exchange process involving real ions and atoms. In particular, it follows from these tables that the long-range splitting of molecular terms is important for elements of group 3 and is negligibly small compared to the exchange interaction potential for molecular ions of rare gases. In addition, in Table 8 we give the average cross-sections of the resonant charge exchange processes for elements with valent p-electrons. We note that in accordance with Eqs. (3) and (4), the cross-section σ of this process depends on the collision velocity v as [1, 5]

$$\sigma = \frac{\pi}{2\gamma^2} \ln^2 \frac{C}{v}, \tag{24}$$

where C is a constant. The first order of the asymptotic theory allows representing this relation as

$$-\frac{d \ln \sigma}{d \ln v} = \alpha = \frac{1}{2R_0\gamma}, \text{ or } \frac{\sigma(v)}{\sigma(v_0)} = \left(\frac{v_0}{v}\right)^{\alpha}. \tag{25}$$

Table 8 gives the parameters of this formula at the collision energy 1 eV in the laboratory coordinate system.

4. CONCLUSION

We have developed the asymptotic theory for the resonant charge exchange process in slow collisions of an ion and a parent atom with the transiting p-electron. The cross-section of this process is not sensitive to the relation between the rotational interaction and other interactions of the colliding particles and inside them, but can depend on the spin–orbit interaction. We have two limiting cases that correspond to cases «a», «b», and «d» and cases «c» and «e» of the Hund coupling, or to the LS- and jj-coupling schemes for isolated colliding atomic particles. For elements of groups 3 and 8 of the periodical system, the average cross-sections of the resonant charge exchange are nearly equal for these limiting cases of the momentum coupling, while for other groups the difference between the cross-sections for different coupling schemes exceeds the accuracy of the evaluation of these cross-sections. The accuracy of the asymptotic theory of the resonant charge exchange with the transiting p-electron is worse than that in the case of the transiting s-electron (1–5% [9]) and is estimated as $\sim$ 10% at eV energies.

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