ЖЭТФ, 2005, том 128, вып. 4 (10), стр. 714–731

ELECTRON TERMS AND RESONANT CHARGE EXCHANGE INVOLVING OXYGEN ATOMS AND IONS

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Submitted 17 May 2005

The electron terms are constructed for oxygen dimer ions at large ion–atom distances with accounting for a certain scheme of summation of electron moments on the basis of a hierarchy of various ion–atom interactions. Because the number of interaction types exceeds that in the Hund scheme, the realistic hierarchy of interactions and corresponding quantum numbers of the diatomic ion are outside the Hund coupling scheme. Electron terms are evaluated for the oxygen dimer ion in the case where the ground and first excited states of an atom and an ion belong to the respective valence electron shells p^4 and p^3 and correspond to the range of separations that determine the cross sections of resonant charge exchange in plasma. These electron terms allow us to calculate the partial and average cross sections for resonant charge exchange involving an oxygen ion and atom in the ground and first excited states in the range of collision energies that is of interest for oxygen plasma. Peculiarities of electron terms of the oxygen ion dimer and the cross section of electron transfer are analyzed.

PACS: 31.25.-v, 34.20.Mq, 34.70.+e

1. INTRODUCTION

In slow collision processes, electrons follow changes of atomic fields, and therefore the cross section of a slow collision process is determined by the behavior of electron terms for the quasimolecule consisting of the colliding atomic particles. Below, we consider the resonant charge exchange processes

$$\begin{aligned} &\mathrm{O}^+(2p^3)(^4S,^2D,^2P) + \mathrm{O}(2p^4)(^3P,^1D,^1S) \to \\ &\to \mathrm{O}(2p^4)(^3P,^1D,^1S) + \mathrm{O}^+(2p^3)(^4S,^2D,^2P) \quad (1) \end{aligned}$$

at low collision velocities compared to those of valence electrons. Because the cross section of resonant charge exchange is large in comparison with a typical atomic cross section, i.e., the electron transfer proceeds at large distances between colliding particles, the analysis of electron terms is required at large ion–atom distances, where various types of interactions may be separated.

The character of coupling of electron moments may be constructed on the basis of the Hund coupling scheme [1–3] that consists in analyzing the hierarchy of interactions in the quasimolecule, which also allows one to determine the quasimolecule quantum numbers. Because the potentials of different interactions depend on distances between atomic particles, the coupling scheme and quantum numbers of the quasimolecule can vary with a change of distances between atomic particles. Therefore, for the analysis of collision processes, the relative trajectory of particle motion can be conveniently divided into several parts such that a certain type of coupling of electron moments is realized in each part [4–7]. The transition between different coupling schemes leads to a change of quantum numbers of colliding particles.

The processes under consideration are of importance for a nonequilibrium dissociating oxygen plasma, in particular, for the atmospheric plasma at altitudes above 100 km. Indeed, oxygen is atomic partially at these altitudes due to the oxygen dissociation under the action of Sun's radiation. Because the cross section of resonant charge exchange significantly exceeds the cross sections of other processes, including elastic collisions of atoms and molecules, the resonant charge exchange process determines the mobility of ions in this plasma and the parameters of other transport processes involving ions. Oxygen atoms and ions are in the ground and lowest excited electron states, and the cross sections of resonant charge exchange depends on these states.

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Because the distribution over these states at a given point of space depends on external conditions, measurement of the mobility for oxygen ions in different electron states at this point allows us to determine the atom distribution over the lowest electron states at the specified point. Hence, determination of the cross sections of resonant electron transfer for oxygen atoms and ions in different states has an applied interest.

The first stage of determination of the cross sections is the construction of electron terms of the quasimolecule, which can be done on the basis of the standard Mulliken scheme of moment summation [1]. This scheme includes three types of interactions in the quasimolecule: V_e, the electrostatic interaction, which is responsible for the energy splitting at different angular momentum projections on the molecule axis; δ_f, which corresponds to the spin–orbit interaction and other relativistic interactions; and V_{rot}, the rotational energy or Coriolis interaction, which accounts for the interaction between the orbital and spin electron momenta with the rotation of the molecular axis. Depending on the ratio between these interaction energies, one can construct six cases of Hund coupling [1–3], each of which corresponds to a certain scheme of moment summation and is characterized by certain quantum numbers of the diatomic molecule. These cases can be used as model ones for the analysis of some transitions in atomic collisions [6–8].

This general scheme may be used for the analysis of the resonant charge exchange process involving an ion and an atom with nonfilled electron shells when different schemes are possible for coupling of electron moments and, correspondingly, the resonant charge exchange process is entangled with other processes (rotation of electron moments, transitions between fine structure states) in different ways. Nevertheless, the electron exchange and other transition processes usually correspond to different trajectory segments, which allows separating the exchange process from other processes. It is therefore necessary to use the correct scheme of angular momentum coupling in the quasimolecule consisting of the colliding ion and atom. The analysis of the resonant charge exchange for halogens [9, 10] shows that the real character of angular momentum coupling corresponds to none of the Hund cases because the number of different interactions is greater than that used in the standard scheme. Nevertheless, a general concept of constructing electron terms of a quasimolecule on the basis of the interaction hierarchy remains valid and underlies the analysis.

Thus, the goal of this paper is to find the character of coupling for the oxygen diatomic ion O_2^+ at large distances between the nuclei on the basis of construction of an interaction hierarchy in this quasimolecule. This allows us to evaluate the partial and average cross sections of resonant charge exchange in the case of oxygen for the lowest state of the electron shells. Solution of this problem also gives a general scheme for determination of the cross section of resonant charge exchange for ion and atom with nonfilled electron shells.

2. HIERARCHY OF ION–ATOM INTERACTIONS FOR OXYGEN

We determine the cross sections of processes (1) on the basis of the asymptotic theory [11–13], i.e., as a result of expansion of the cross section with respect to a small parameter, the ratio of the typical atomic size to the typical distance of electron transfer. This theory uses a large electron transfer cross section compared to the typical atomic cross section at low velocities, and its first stage is the evaluation of the electron terms for the quasimolecule consisting of colliding particles. We find a hierarchy of interactions at large distances between $O^+(2p^3)$ and $O(2p^4)$ and then the electron terms of this system and quantum numbers for the description of the molecular ion states.

Based on the experience for the halogen case [9, 10], as the basis ion–atom interactions at large distances R, we use the fine spin–orbit interaction for $O^+(2p^3)$ and $O(2p^4)$ and the quadrupole interaction of the ion charge with the atom quadrupole moment. In this approximation, the Hamiltonian of the molecular ion at large distances between the nuclei is given by

$$\hat{H} = -a\hat{\mathbf{L}}\cdot\hat{\mathbf{S}} - b\hat{\mathbf{l}}\cdot\hat{\mathbf{s}} - \frac{e\hat{Q}}{R^3}. \qquad (2)$$

This is valid for light atoms in the case of the LS coupling scheme for atoms and ions; here, $\hat{\mathbf{L}}$ is the operator of the angular atom momentum, $\hat{\mathbf{S}}$ is the atom spin operator, $\hat{\mathbf{l}}$ is the operator of the angular ion momentum, $\hat{\mathbf{s}}$ is the ion spin operator, and $\hat{Q}$ is the quadrupole moment operator for the atom, and we take the interaction of a positively charged ion with the quadrupole moment of valence electrons into account.

The parameters of the spin–orbit interaction of an oxygen atom and its ion are given by $a = 77 \pm 2$ cm^{-1} for the atom state ^3P, $b = 8.4$ cm^{-1} for the oxygen ion state ^2D, and $b = 0.7$ cm^{-1} for the ion state ^2P [14, 15]. Because a typical value of the ion–atom exchange interaction potential is several cm^{-1}, we can ignore the fine splitting of levels in the last case. Correspondingly, the matrix elements for the spin–orbit interaction are equal to [3, 16, 17]

$$\begin{gathered}\langle M_L, M_S|\hat{\mathbf{L}}\cdot\hat{\mathbf{S}}|M_L, M_S\rangle = M_L M_S,\\ \langle M_L, M_S|\hat{\mathbf{L}}\cdot\hat{\mathbf{S}}|M_L+1, M_S-1\rangle = \langle M_L+1, M_S-1|\hat{\mathbf{L}}\cdot\hat{\mathbf{S}}|M_L, M_S\rangle = \\ = \frac{1}{2}\sqrt{(L+|M_L|+1)(L-|M_L|)(S+|M_S|)(S-|M_S|+1)},\\ \langle M_L, M_S|\hat{\mathbf{L}}\cdot\hat{\mathbf{S}}|M_L-1, M_S+1\rangle = \langle M_L-1, M_S+1|\hat{\mathbf{L}}\cdot\hat{\mathbf{S}}|M_L, M_S\rangle = \\ = \sqrt{(L+|M_L|)(L-|M_L|+1)(S+|M_S|+1)(S-|M_S|)},\end{gathered} \tag{3}$$

where L and M_L are the atom orbital momentum and its projection onto the molecular axis, S and M_S are the atom spin and its projection on the molecular axis. For the matrix elements of the ion spin–orbit interaction, we have identical expressions.

We consider the quadrupole interaction between an ion and an oxygen atom, which in this case corresponds to the second expansion term of the ion charge–valence electron interaction

$$\frac{e^2}{R} - \left\langle \frac{e^2}{|\mathbf{R}-\mathbf{r}|}\right\rangle.$$

This respects to the small parameter r/R, where $\mathbf{r}$ is the valence electron coordinate in its atom, $\mathbf{R}$ is the distance between the ion of charge e and the atom nucleus, and an average is taken over the wave function of the valence electron. The quadrupole moment of an individual electron is then given by [18]

$$q = 2\left\langle r^2 P_2\cos\theta\right\rangle = 2\frac{l_e(l_e+1)-3m^2}{(2l_e-1)(2l_e+3)}\overline{r^2}, \tag{4}$$

where r, θ are spherical coordinates of the valence electron and l_e, m are the orbital momentum of this electron and its projection on the molecular axis.

For oxygen, it is more convenient to consider a valence electron shell as two p-holes in addition to a completed p-electron shell. The hole quadrupole moment differs from that of the electron by sign only. The total wave function of these holes that corresponds to the total orbital momentum of holes L and its projection M onto a given direction is given by

$$\Psi_{LM} = \sum_m \begin{bmatrix} 1 & 1 & L\\ m & M-m & M\end{bmatrix} \times \psi_{1m}(1)\psi_{1,M-m}(2), \tag{5}$$

where $\psi_{1m}(i)$ is the wave function of ith p-hole with the angular momentum projection m, and the Clebsch–Gordan coefficient

$$\begin{bmatrix} 1 & 1 & L\\ m & M-m & M\end{bmatrix}$$

is responsible for summation of the moments of individual holes into the moment of the entire system. Correspondingly, the electron shell is characterized by quantum numbers $L, -M$ in this case, and because atom quadrupole moment is conserved under $M \to -M$, we ignore the difference between a hole and an electron below.

We use that the sum of quadrupole moments of an electron shell and a hole shell is zero, and therefore, expressing the quadrupole moment of an electron shell through the quadrupole moments of a hole shell, it is necessary to change the sign of the quadrupole moment. In other manner, the sign of the electron quadrupole moment is reciprocal to that of a hole, and therefore, constructing the quadrupole moment of an electron shell through those of individual holes, we must change sign. Hence, the quadrupole moment of an oxygen atom is given by

$$\langle M|\hat{Q}|M'\rangle = -\delta_{MM'}\sum_m \begin{bmatrix} 1 & 1 & L\\ m & M-m & M\end{bmatrix}^2 \times (q_m + q_{M-m}), \tag{6}$$

where q_m is the quadrupole moment of an individual electron with the moment projection m on the molecular axis, and according to formula (3), we have

$$q_0 = \frac{4e\overline{r^2}}{5}, \quad q_1 = q_{-1} = -\frac{2e\overline{r^2}}{5}, \tag{7}$$

where $\overline{r^2}$ is the mean square of a valence electron orbit. For an oxygen atom in the ground state, we have $\overline{r^2} \approx 2a_0^2$ [15], where a_0 is the Bohr radius. For excited oxygen atom states, we take

$$\overline{r^2} \sim 1/\gamma^2, \quad \gamma^2 = J/J_H,$$

J is the ionization potential for this state, and J_H is the ionization potential for a hydrogen atom in the ground state. In particular, it follows that $\overline{r^2} = 2.33a_0^2$ for the ${}^1D$-state of an oxygen atom. Table 1 contains values of the quadrupole moments for an oxygen atom, and we use these values for determination of electron terms of a diatomic oxygen ion.

Table 1. Diagonal matrix elements of the quadrupole moment Q_{MM} expressed in ea_0^2 for an oxygen atom with the electron shell $2p^4$

State	^3P, $M=0$	^3P, $M=\pm1$	^1D, $M=0$	^1D, $M=\pm1$	^1D, $M=\pm2$
Q_{MM}	1.6	−0.8	−1.87	−0.93	1.87

In addition, Table 2 contains the values of γ for the oxygen atom and ion states. The atom ionization potential with transition to a given ion state is

$$J = J^0 - \Delta E_a + \Delta E_i, \tag{8}$$

where J^0 is the oxygen ionization potential with the electron transition from the ground atom state to the ion ground state, ΔE_a is the atom excitation energy, and ΔE_i is the ion excitation energy. Because a given ion state results from a one-electron transition from an indicated atom state, we ignore the cases of ion–atom interactions if a given ion state cannot be formed from the indicated atom state as the result of a one-electron transition.

In considering the electron terms of the quasimolecule O_2^+, we start from large distances R between the nuclei, where the electron energy is equal to

$$\varepsilon = \varepsilon_0 + \Delta E_a + \Delta E_i + \frac{aJ(J+1)}{2} - \\ - \frac{aJ_0(J_0+1)}{2} + \frac{bj(j+1)}{2} - \frac{bj_0(j_0+1)}{2}, \tag{9}$$

where ε_0 corresponds to the atom and ion ground state, such that ΔE_a and ΔE_i account for electron excitation of the quasimolecule; J_0 and j_0 are the total electron moments of the atom and ion in the ground fine state, and the last terms in formula (9) take fine states of the atom and ion into account. Therefore, in evaluating the quasimolecule electron terms, we count the quasimolecule energy from the value $\varepsilon_0 + \Delta E_a + \Delta E_i$ at large separations, adding Hamiltonian (2) to this at finite separations. Because the ion and atom parts of this Hamiltonian commute, we can add the ion and atom parts to the electron energy independently. Quantum numbers due to the ion part — the total ion angular momentum j and its projection on the molecular axis m_j — are conserved at any ion–atom distances, whereas the atom quantum numbers J and M_J are valid at large separations, or quantum numbers M_L and M_S are accurate quantum numbers only if we neglect the spin–orbit interaction. Therefore, finding electron terms accurately, we use the notation M_L, M_S or J, M_J for them only to label the quasimolecule states.

In addition, because the quadrupole interaction is symmetric under the transformation $M_L \to -M_L$ and the spin–orbit interaction is symmetric under the transformation $M_L + M_S \to -M_L - M_S$, we find that the electron terms of a quasimolecule described by Hamiltonian (2) are degenerate with respect to the simultaneous transformations

$$M_L, M_S \to -M_L, -M_S. \tag{10}$$

We can therefore restrict ourselves to a part of the electron terms for the diatomic ion O_2^+ at large separations with

$$|M_L + M_S| \geq 0.$$

In particular, if the oxygen atom is in the ground state $O(^3P)$, the number of nondegenerate electron terms is 6 with respect to atom states.

In constructing the electron terms for the atom part, we construct the Hamiltonian matrix elements

$$\langle M_L, M_S|\hat{H}|M_L', M_S'\rangle.$$

Next, by diagonalization of this matrix, we find the energy positions at a fixed distance R between the nuclei by solving the secular equation for the Hamiltonian matrix elements [3]. This is given by the vanishing condition for the determinant,

$$|E\delta_{M_L M_L'}\delta_{M_S M_S'} - \langle M_L, M_S|\hat{H}|M_L', M_S'\rangle| = 0. \tag{11}$$

Solutions $E(R)$ of Eq. (10) give positions of the electron terms at a given separation R.

Table 3 gives the Hamiltonian matrix $\hat{H}_{ik}$ for the interaction of $O^+(^4S) + O(^3P)$ as an example. We here use the Hamiltonian (2), and the electron energies of an oxygen diatomic ion at a given separation follow from solution of Eq. (10). We can see that this matrix can be divided into five independent blocks, such that one block contains three diagonal elements, two identical blocks contain two diagonal elements, and two identical blocks contain one diagonal element. These identical matrix blocks can be converted into each other by transformations (10), and we include only one of the two identical matrices in Table 2.

Table 2. The parameter $\gamma = \sqrt{J/J_H}$ for various atom and ion oxygen states

Atom state / Ion state	^3P	^1D	^1S
^4S	1.000	–	–
^2D	1.116	1.049	–
^2P	1.170	1.107	1.030

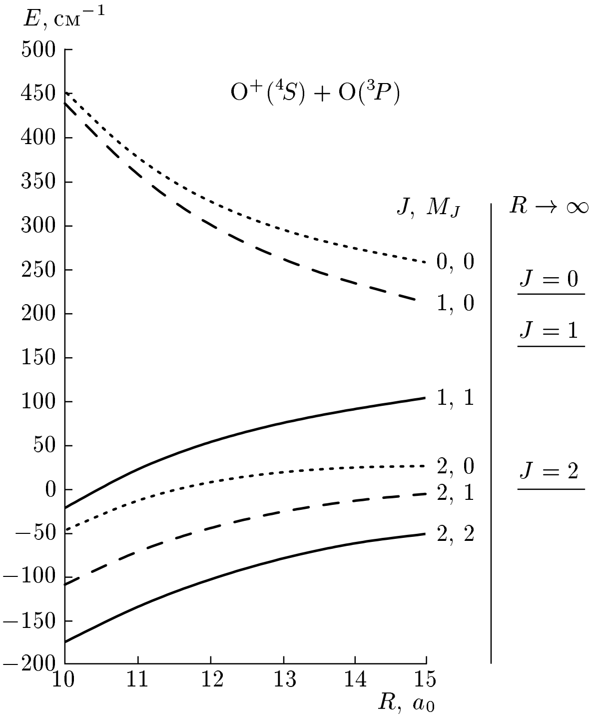

Fig. 1.

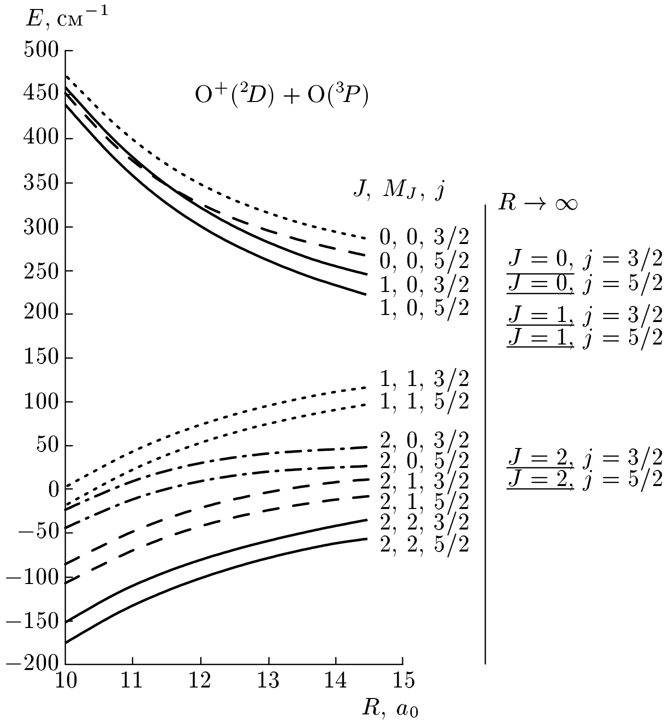

Fig. 2.

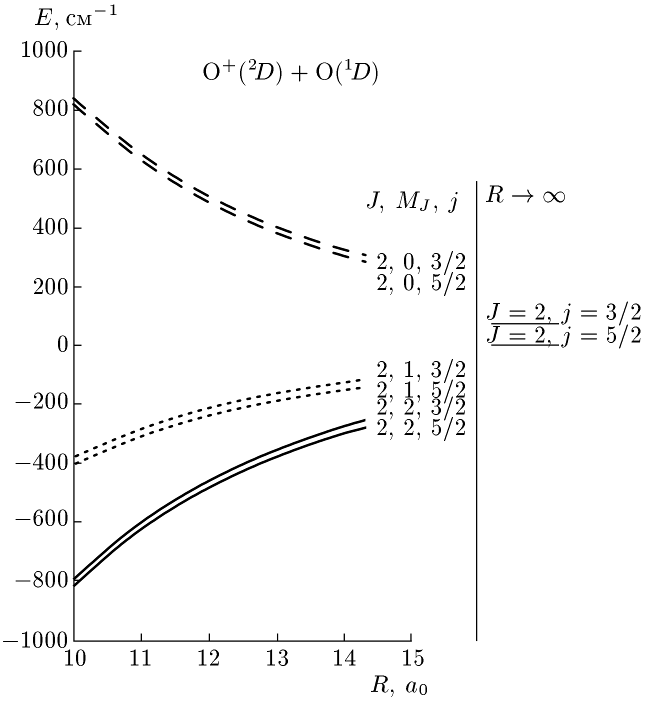

Fig. 3.

In Figs. 1–3, we give the electron terms of the oxygen diatomic ion for the respective atom and ion states

$$O(^3P) + O^+(^4S),$$

$$O(^3P) + O^+(^2D),$$

and

$$O(^1D) + O^+(^2D)$$

with the interactions in Hamiltonian (2) taken into account. The range of separations is such that it gives the main contribution to the cross section of resonant charge exchange at thermal and eV-energies of collision. We characterize the atom state by the quantum numbers J and M_J, the total atom moment and its projection on the molecular axis, which are precise atomic numbers at very large separations and are used as a notation at smaller separations where the ion–quadrupole interaction becomes important. Correspondingly, the electron terms of the oxygen diatomic ion are described by the quantum numbers $J, |M_J|, j$, where j is the total ion angular momentum.

3. ION–ATOM EXCHANGE INTERACTION POTENTIAL

The next step of our program is to determine the ion–atom exchange interaction potential. It is small compared to the interactions in Hamiltonian (2), and therefore each electron term splits into levels with different parities. The ion–atom exchange interaction removes the degeneration with respect to different m_j, the ion moment projection on the molecular axis. The exchange ion–atom interaction allows us to evaluate the partial cross section of resonant charge exchange that proceeds inside a given electron term.

The exchange ion–atom interaction results from the transition of a valence electron from one atomic rest to another one. This interaction divides the quasimolecule states into even (g) and odd (u) according to the property of the corresponding molecular wave function to preserve or change sign as a result of reflection of all the electrons with respect to the symmetry plane perpendicular to the molecular axis. If a valence electron with an orbital momentum l_e and its projection μ on the molecular axis is located in the field of two structureless cores, the exchange interaction potential $\Delta_{l_e\mu}$ is given by the formula [5, 7, 13, 19]

$$\Delta_{l_e\mu}(R) = \\ = A^2 R^{\frac{2}{\gamma}-1-|\mu|} e^{-R\gamma-\frac{1}{\gamma}} \frac{(2l+1)(l_e+|\mu|)!}{(l_e-|\mu|)!\,|\mu|!(\gamma)^{|\mu|}}, \quad (12)$$

where R is the distance between the nuclei, and γ, A are the parameters of the asymptotic wave function of the valence electron; the normalized radial wave function of this electron in the atom at large distances r from its center is given by

$$\psi(r) = A r^{\frac{1}{\gamma}-1} e^{-r\gamma}, \quad r\gamma \gg 1.$$

Formula (12) contains the first term of the asymptotic expansion with respect to the small parameter $1/\gamma R$ for the ion–atom exchange interaction potential at large distances between nuclei. For a valence p-electron, formula (12) becomes

$$\begin{aligned} \Delta_{10}(R) &= 3A^2 R^{\frac{2}{\gamma}-1} e^{-R\gamma-\frac{1}{\gamma}}, \\ \Delta_{1,\pm 1}(R) &= \frac{2}{R\gamma}\Delta_{10}(R). \end{aligned} \quad (13)$$

This one-electron interaction is the basis of the exchange interaction potential in the case where the interacting atom and ion have nonfilled electron shells, and the coupling of electron moments for a transferring electron and the atomic rest is of importance. We use the LS coupling scheme, which is suitable for light atoms. Then the wave function of an atom with n valence electrons of moment l_e is given by [16, 17, 20]

$$\Phi_{LSM_LM_S}(1,2,\ldots,n) = \frac{1}{\sqrt{n}}\hat{P} \times \\ \times \sum_{l,m,s,m_s,\mu,\sigma} G_{ls}^{LS}(l_e,n) \begin{bmatrix} l_e & l & L \\ \mu & m & M_L \end{bmatrix} \times \\ \times \begin{bmatrix} \frac{1}{2} & s & S \\ \sigma & m_s & M_S \end{bmatrix} \times \\ \times \varphi_{l_e\frac{1}{2}\mu\sigma}(1)\psi_{lsmm_s}(2,\ldots,n). \quad (14)$$

Here, Φ, ψ, and φ are the respective wave functions of the atom, ion, and valence electron with the indicated quantum numbers, μ and σ are the projections of the angular momentum and spin of the valence electron, the argument of the wave function indicates electrons involved in each atomic particle, the operator $\widehat{P}$ permutes these electrons, and the parentage coefficient $G_{ls}^{LS}(l_e,n)$ is responsible for addition of a valence electron to the ion for construction of an atom for given quantum numbers of these atomic particles.

The exchange interaction potential is given by the formula [7, 13]

$$\Delta(R) = 2\left\langle \Psi_1 \left| \widehat{H} \right| \Psi_2 \right\rangle - \\ - 2\left\langle \Psi_1 \left| \widehat{H} \right| \Psi_1 \right\rangle \langle \Psi_1 |1| \Psi_2 \rangle, \quad (15)$$

where Ψ_1 is the wave function of the quasimolecule in the case where a valence electron is located near the first core (the electron is connected with the first nucleus), Ψ_2 corresponds to the electron location near the second nucleus, and $\widehat{H}$ is the Hamiltonian of the electrons. We note that an accurate evaluation of this interaction requires using the accurate wave functions of the quasimolecule such that the interaction of a valence electron located between the cores with both cores is taken into account simultaneously. We assume this to be fulfilled within the framework of the asymptotic theory. Using a general method of calculation of the exchange interaction potential $\Delta(R)$ by analogy with that for case «a» of the Hund coupling [13, 21–23] and

Table 3. The Hamiltonian matrix $\hat{H}_{ik}$ for the quasimolecule O$^+(^4S_{3/2})$ + O(^3P) if the exchange ion–atom interaction is neglected and the Hamiltonian is given by formula (2); $a = 77 \pm 2$ cm^{-1}

M_L, M_S	1, 1	1, 0	0, 1	1, −1	0, 0	−1, 1
1, 1	$-a - \dfrac{0.8e^2a_0^2}{R^3}$	0	0	0	0	0
1, 0	0	$-\dfrac{0.8e^2a_0^2}{R^3}$	$-a$	0	0	0
0, 1	0	$-a$	$\dfrac{1.6e^2a_0^2}{R^3}$	0	0	0
1, −1	0	0	0	$a - \dfrac{0.8e^2a_0^2}{R^3}$	$-a$	0
0, 0	0	0	0	$-a$	$\dfrac{1.6e^2a_0^2}{R^3}$	$-a$
−1, 1	0	0	0	0	$-a$	$a - \dfrac{0.8e^2a_0^2}{R^3}$

using the properties of Clebsch – Gordan coefficients, we obtain

$$\Delta_{LSM_LM_Slsmm_s}(R) = n\left(G_{ls}^{LS}\right)^2 \times \sum_{\mu,\sigma,\sigma'} \begin{bmatrix} l_e & l & L \\ \mu & M_L-\mu & M_L \end{bmatrix} \times \begin{bmatrix} \frac{1}{2} & s & S \\ \sigma & M_S-\sigma & M_S \end{bmatrix} \begin{bmatrix} l_e & l & L \\ \mu & m & m+\mu \end{bmatrix} \times \begin{bmatrix} \frac{1}{2} & s & S \\ \sigma' & m_s & m_s+\sigma' \end{bmatrix} \Delta_{l_e\mu}(R). \quad (16)$$

Here, we take the character of the coupling of electron moments in the quasimolecule into account, such that the quantum numbers of an atomic core $ls, M_L-\mu, M_S-\sigma$ and the atomic quantum numbers of a valence electron $l_e\mu\frac{1}{2}\sigma$ are first summed into the atomic quantum numbers LSM_LM_S, and after the electron transition to another atomic rest, the other quantum numbers of the atomic core $lsmm_s$ and electron quantum numbers $l_e\mu\frac{1}{2}\sigma'$ are summed into the atom quantum numbers $LS, m+\mu, m_s+\sigma'$. We note that the electron spin projections are identical, $\sigma = \sigma'$, in the fields of both cores because of normalization of the electron spin wave functions. If we use the atom basis M_LM_S and the ion quantum numbers are $lsjm_j$, formula (16) becomes

$$\Delta_{LSM_LM_Slsjm_j}(R) = n\left(G_{ls}^{LS}\right)^2 \times \sum_{\mu,\,\sigma}\sum_{m,m_s} \begin{bmatrix} l_e & l & L \\ \mu & M_L-\mu & M_L \end{bmatrix} \times \begin{bmatrix} l_e & l & L \\ \mu & m & m+\mu \end{bmatrix} \begin{bmatrix} \frac{1}{2} & s & S \\ \sigma & M_S-\sigma & M_S \end{bmatrix} \times \begin{bmatrix} \frac{1}{2} & s & S \\ \sigma & m_s & m_s+\sigma \end{bmatrix} \begin{bmatrix} l & s & j \\ m & m_s & m_j \end{bmatrix} \times \begin{bmatrix} l & s & j \\ M_L-\mu & M_S-\sigma & M_L-\mu+M_S-\sigma \end{bmatrix} \Delta_{l_e\mu}. \quad (17)$$

In reality, due to the properties of the Clebsch – Gordan coefficients, this formula is simplified. In particular, the exchange interaction potential is conserved under the transformations

$$M_L, M_S, m_j \to -M_L, -M_S, -m_j. \quad (18)$$

4. ION–ATOM EXCHANGE INTERACTION FOR THE DIATOMIC OXYGEN ION

Formula (17) gives the ion–atom exchange interaction potential that determines the cross section of resonant charge exchange at given quantum numbers. This is considered below for different states of an oxygen

Table 4. The exchange interaction potential $\Delta_{LSM_LM_Ssm_s}$ for the ground state of the quasimolecule O$^+(^4S)+$O(^3P) at given quantum numbers M_L, M_S of an atom and quantum numbers s, m_s of an ion on the basis of formula (18)

M_L, M_S s, m_s	1, 1	1, 0	0, 1	1, −1	−1, 1	0, 0
$\frac{3}{2}, \frac{3}{2}$	Δ_{11}	$\sqrt{\frac{2}{3}}\Delta_{11}$	Δ_{10}	$\frac{1}{\sqrt{3}}\Delta_{11}$	Δ_{11}	$\sqrt{\frac{2}{3}}\Delta_{10}$
$\frac{3}{2}, \frac{1}{2}$	$\frac{1+\sqrt{6}}{3}\Delta_{11}$	$\frac{2+\sqrt{2}}{3}\Delta_{11}$	$\frac{1+\sqrt{6}}{3}\Delta_{10}$	$\frac{\sqrt{3}+\sqrt{2}}{3}\Delta_{11}$	$\frac{1+\sqrt{6}}{3}\Delta_{11}$	$\frac{2+\sqrt{2}}{3}\Delta_{10}$
$\frac{3}{2}, -\frac{1}{2}$	$\frac{\sqrt{3}+\sqrt{2}}{3}\Delta_{11}$	$\frac{2+\sqrt{2}}{3}\Delta_{11}$	$\frac{\sqrt{2}+\sqrt{3}}{3}\Delta_{10}$	$\frac{1+\sqrt{6}}{3}\Delta_{11}$	$\frac{\sqrt{2}+\sqrt{3}}{3}\Delta_{11}$	$\frac{2+\sqrt{2}}{3}\Delta_{10}$
$\frac{3}{2}, -\frac{3}{2}$	$\frac{1}{\sqrt{3}}\Delta_{11}$	$\sqrt{\frac{2}{3}}\Delta_{11}$	$\frac{1}{\sqrt{3}}\Delta_{10}$	Δ_{11}	$\frac{1}{\sqrt{3}}\Delta_{11}$	$\sqrt{\frac{2}{3}}\Delta_{10}$

atom and an ion. We start from the ground state of the atom and ion, with the ion–atom exchange interaction potential given by formula (18). The analysis of this case in [9, 10] was based on the limiting coupling cases where the quasimolecule is characterized by the quantum numbers J, M_J or J, M_L depending on the relation between spin–orbit and quadrupole interactions. We now consider the general case numerically by the Hamiltonian diagonalization for an arbitrary relation between these values.

Formula (17) gives the ion–atom exchange interaction potential at large separations for the ion ground state O$^+(^4S_{3/2})$ ($l = 0$, $m = 0$, $s = j = 3/2$). We then have $M_L = \mu$, $m_j = m_s$, and formula (17) is reduced to the form ($l_e = 1$, $n = 4$, $G^{LS}_{ls} = -1/\sqrt{3}$)

$$\Delta_{LSM_LM_Slsm_s}(R) = \frac{4}{3}\Delta_{1M_L}(R) \times \\ \times \sum_\sigma \begin{bmatrix} \frac{1}{2} & s & S \\ \sigma & M_S-\sigma & M_S \end{bmatrix} \times \\ \times \begin{bmatrix} \frac{1}{2} & s & S \\ \sigma & m_s & m_s+\sigma \end{bmatrix}. \qquad (19)$$

Table 4 contains the values of the ion–atom interaction potential obtained on the basis of formula (19). We account for symmetry (18) and the one-electron exchange interaction potentials are given by formulas (13).

We next use the same operation for determination of the exchange interaction potential for excited ion and atom states at large separations. Table 5 contains the exchange interaction potential for the quasimolecule O$^+(^2D)$ + O(^3P) and Table 6 contains the exchange interaction potentials for the quasimolecule O$^+(^2D)$ + O(^1D) for the basis M_L, M_S, j, m_j. Because $\Delta_{11}(R) \ll \Delta_{10}(R)$ at large separations, we ignore $\Delta_{11}(R)$ wherever possible. We also take the symmetry of the exchange interaction potential in (18) into account, and in the atom basis M_L, M_S used, the identical values of the exchange interaction potential correspond to quantum numbers in parentheses.

The electron terms of the quasimolecule with the ion–atom exchange interaction potential taken into account can be found by diagonalization of the corresponding Hamiltonian matrix. Because the splitting of electron terms due to the exchange interaction depends on a fine ion state, the number of electron levels in this case increases in comparison with the case of Hamiltonian (2). Performing this diagonalization for each fine ion state at the distance $12a_0$ between the nuclei (this distance determines the resonant charge exchange cross section in thermal collisions), we assume that the renormalization of the exchange interaction potential in comparison with the basis M_L, M_S, j, m_j is the same in a neighboring range of distances. This allows us to determine the exchange interaction potentials given in Table 5 for the quasimolecule and in Table 7 for the quasimolecule O$^+(^2P)+$O(^3P). As the quantum numbers of the quasimolecule, we now take the total atom moment J and its projection M_J on the molecular axis. Although these are accurate quantum numbers only at very large separations, where the ion–atom quadrupole interaction can be ignored, they can be used for labeling electron states of the quasimolecule.

Table 5. The exchange interaction potential for the quasimolecule $O^+(^2D) + O(^3P)$ at given quantum numbers M_L, M_S of an atom and quantum numbers j, m_j of an ion

M_L, M_S	1, 1	1, 0	0, 1	1, −1	0, 0	−1, 1
j, m_j						
$\frac{5}{2}, \frac{5}{2}$	Δ_{11}	$\frac{\sqrt{10}+2}{2\sqrt{10}}\Delta_{11}$	$\frac{\sqrt{2}}{\sqrt{5}}\Delta_{11}$	$\frac{1}{\sqrt{10}}\Delta_{11}$	$\frac{\sqrt{2}}{\sqrt{5}}\Delta_{11}$	$\frac{1}{\sqrt{10}}\Delta_{11}$
$\frac{5}{2}, \frac{3}{2}$	$\frac{2}{5}\Delta_{10}$	$\frac{2}{5}\Delta_{10}$	$\frac{2}{5}\Delta_{10}$	$\frac{1}{5}\Delta_{10}$	$\frac{\sqrt{2}+1}{5}\Delta_{10}$	$\frac{\sqrt{2}}{5}\Delta_{10}$
$\frac{5}{2}, \frac{1}{2}$	$\frac{3}{5}\Delta_{10}$	$\frac{7}{10}\Delta_{10}$	$\frac{3}{5}\Delta_{10}$	$\frac{2}{5}\Delta_{10}$	$\frac{1}{5}\left(2+\frac{3}{\sqrt{2}}\right)\Delta_{10}$	$\frac{3\sqrt{2}}{10}\Delta_{10}$
$\frac{5}{2}, -\frac{1}{2}$	$\frac{2\sqrt{2}}{5}\Delta_{10}$	$\frac{\sqrt{2}}{2}\Delta_{10}$	$\frac{2\sqrt{2}}{5}\Delta_{10}$	$\frac{3\sqrt{2}}{10}\Delta_{10}$	$\frac{1}{5}\left(2+\frac{3}{\sqrt{2}}\right)\Delta_{10}$	$\frac{2}{5}\Delta_{10}$
$\frac{5}{2}, -\frac{3}{2}$	$\frac{\sqrt{2}}{5}\Delta_{10}$	$\frac{3\sqrt{2}}{10}\Delta_{10}$	$\frac{\sqrt{2}}{5}\Delta_{10}$	$\frac{\sqrt{2}}{5}\Delta_{10}$	$\frac{\sqrt{2}+1}{5}\Delta_{10}$	$\frac{1}{5}\Delta_{10}$
$\frac{5}{2}, -\frac{5}{2}$	$\frac{1}{2\sqrt{5}}\Delta_{11}$	$\frac{10+2\sqrt{5}}{\sqrt{20}}\Delta_{11}$	$\frac{1}{\sqrt{10}}\Delta_{11}$	$\frac{1}{\sqrt{10}}\Delta_{11}$	$\frac{\sqrt{2}}{\sqrt{5}}\Delta_{11}$	$\frac{1}{\sqrt{10}}\Delta_{11}$
$\frac{3}{2}, \frac{3}{2}$	$\frac{1}{10}\Delta_{10}$	$\frac{-\sqrt{6}+1}{20}\Delta_{10}$	$\frac{\sqrt{6}}{15}\Delta_{10}$	$\frac{-\sqrt{6}}{20}\Delta_{10}$	$\frac{\sqrt{6}-2\sqrt{3}}{30}\Delta_{10}$	$\frac{\sqrt{3}}{10}\Delta_{10}$
$\frac{3}{2}, \frac{1}{2}$	$\frac{\sqrt{6}}{60}\Delta_{10}$	$\frac{-3-\sqrt{6}}{60}\Delta_{10}$	$\frac{1}{15}\Delta_{10}$	$\frac{1}{10}\Delta_{10}$	$\frac{-\sqrt{2}-2}{30}\Delta_{10}$	$\frac{\sqrt{2}}{20}\Delta_{10}$
$\frac{3}{2}, -\frac{1}{2}$	$-\frac{\sqrt{3}}{30}\Delta_{10}$	$\frac{-3\sqrt{2}-\sqrt{3}}{60}\Delta_{10}$	$\frac{\sqrt{2}}{15}\Delta_{10}$	$\frac{\sqrt{2}}{20}\Delta_{10}$	$\frac{-\sqrt{2}-2}{30}\Delta_{10}$	$\frac{1}{10}\Delta_{10}$
$\frac{3}{2}, -\frac{3}{2}$	$\frac{-1}{10\sqrt{2}}\Delta_{10}$	$\frac{-\sqrt{3}-\sqrt{2}}{20}\Delta_{10}$	$\frac{-1}{5\sqrt{3}}\Delta_{10}$	$\frac{\sqrt{3}}{10}\Delta_{10}$	$\frac{\sqrt{6}-2\sqrt{3}}{30}\Delta_{10}$	$\frac{-\sqrt{6}}{20}\Delta_{10}$

5. MIXING OF EXCHANGE INTERACTIONS FOR COUPLED ELECTRON TERMS

Above, we have determined the ion–atom exchange interaction potential in the basis M_L, M_S, j, m_j, which are not quantum numbers of the quasimolecule, and the Hamiltonian matrix H_{ik} is not diagonal in this basis. The electron terms of the quasimolecule follow from diagonalization of the Hamiltonian matrix, and the electron levels $E(R)$ at a given separation are solutions of the secular equation

$$|E\delta_{ik} - H_{ik}| = 0.$$

Above (see Figs. 1–3), we solved this equation for Hamiltonian (2) with the ion–atom exchange interaction ignored. We now solve this equation including the ion–atom exchange interaction potential into consideration and determine the exchange interaction potential for eigenstates of the quasimolecule.

We demonstrate this operation for the interaction of the oxygen ion and atom in the ground states $O(^3P) + O^+(^4S)$. Table 3 then gives the Hamiltonian matrix without the exchange interaction, and the matrix of the ion–atom exchange interaction potential is diagonal in the basis M_L, M_S, j, m_j. We note that the matrix H_{ik} in Table 3 is divided into three blocks consisting of matrices with 1, 2, and 3 diagonal elements. For a block with one element, where $M_L = 1$, $M_S = 1$, the exchange interaction potential is $\Delta_{11}(R)$. For two other blocks, the exchange interaction follows from diagonalization of the Hamiltonian matrix for the gerade and ungerade states of the quasimolecule, and the exchange interaction potential is the difference of the electron energies for the gerade and ungerade quasimolecule states with accounting for the smallness of the exchange interaction potential in comparison with a typical potential of electrostatic interaction.

We perform this operation analytically for the block

Table 6. The exchange interaction potential $\Delta_{LSM_LM_Slsjm_j}(R)$ for the quasimolecule O$^+(^2D)$ + O(^1D) at given quantum numbers M_L, M_S of an atom and quantum numbers j, m_j of an ion

M_L, M_S / j, m_j	2, 0 (−2, 0)	1, 0 (−1, 0)	0, 0
$\frac{5}{2}, \frac{5}{2}$	Δ_{10}	$\frac{1}{\sqrt{5}}\Delta_{10}$	$\frac{\sqrt{3}}{\sqrt{10}}\Delta_{11}$
$\frac{5}{2}, \frac{3}{2}$	$\left(\frac{1}{\sqrt{5}}+\frac{1}{5}\right)\Delta_{10}$	$\frac{2+\sqrt{2}}{10}\Delta_{10}$	$\frac{3(2+\sqrt{3})}{10}\Delta_{11}$
$\frac{5}{2}, \frac{1}{2}$	$\frac{1}{5\sqrt{2}}\Delta_{10}$	$\frac{1}{10}\Delta_{10}$	$\left(\frac{3}{10}+\frac{3}{10}\sqrt{\frac{3}{2}}+\frac{\sqrt{3}}{2}\right)\Delta_{11}$
$\frac{5}{2}, -\frac{1}{2}$	$-\frac{1}{\sqrt{10}}\Delta_{10}$	$\frac{-1}{5\sqrt{2}}\Delta_{10}$	$\left(\frac{3}{10}+\frac{3}{10}\sqrt{\frac{3}{2}}+\frac{\sqrt{3}}{2}\right)\Delta_{11}$
$\frac{5}{2}, -\frac{3}{2}$	$\frac{-\sqrt{5}-1}{\sqrt{5}}\Delta_{10}$	$\frac{-\sqrt{2}-1}{5\sqrt{2}}\Delta_{10}$	$\frac{3(2+\sqrt{3})}{10}\Delta_{11}$
$\frac{5}{2}, -\frac{5}{2}$	$-\frac{1}{\sqrt{5}}\Delta_{10}$	$-\frac{1}{\sqrt{10}}\Delta_{10}$	$\frac{\sqrt{3}}{\sqrt{10}}\Delta_{11}$
$\frac{3}{2}, \frac{3}{2}$	$\frac{4}{5}\Delta_{10}$	$\frac{1+4\sqrt{3}}{20}\Delta_{10}$	$\left(\frac{3}{20}+\frac{9}{10\sqrt{2}}\right)\Delta_{11}$
$\frac{3}{2}, \frac{1}{2}$	$\frac{\sqrt{3}}{5}\Delta_{10}$	$\frac{3}{20}\Delta_{10}$	$\left(\frac{9}{20}+\frac{3}{10}\sqrt{\frac{3}{2}}+\frac{3}{5\sqrt{2}}\right)\Delta_{11}$
$\frac{3}{2}, -\frac{1}{2}$	$\frac{6+3\sqrt{2}}{20}\Delta_{11}$	$\frac{-\sqrt{3}}{20}\Delta_{10}$	$\left(\frac{9}{20}+\frac{3}{10}\sqrt{\frac{3}{2}}+\frac{3}{5\sqrt{2}}\right)\Delta_{11}$
$\frac{3}{2}, -\frac{3}{2}$	$-\frac{1}{5}\Delta_{10}$	$\frac{-\sqrt{3}-4}{20}\Delta_{10}$	$\left(\frac{3}{20}+\frac{9}{10\sqrt{2}}\right)\Delta_{11}$

consisting of two diagonal terms. Diagonalization of the Hamiltonian matrix gives the energy of two levels as [3]

$$E_{I,II} = \frac{H_{11}+H_{22}}{2} \pm \sqrt{\frac{(H_{11}-H_{22})^2}{4} + |H_{12}|^2},$$

where the indices 1, 2 relate to the first and second states in the basis M_L, M_S. We next construct the energy matrix for the interaction of an oxygen ion and an atom with the exchange interaction taken into account in addition to Hamiltonian (2). For the states under consideration, according to the data in Table 3, we have

$$\begin{gathered} H_{11} = -0.8\frac{e^2a_0^2}{R^3} \pm \frac{\Delta_1}{2}, \\ H_{22} = 1.6\frac{e^2a_0^2}{R^3} \pm \frac{\Delta_2}{2}, \\ H_{12} = a, \quad \Delta H = H_{11} - H_{22} = 2.4\frac{e^2a_0^2}{R^3}, \end{gathered} \tag{20a}$$

where the plus sign corresponds to the gerade state and the minus sign corresponds to the ungerade state. From this, we have the energy levels of eigenstates given by

$$\begin{gathered} E_I = E_0 - \varepsilon \pm \frac{1}{2}\Delta_I, \quad E_{II} = E_0 + \varepsilon \pm \frac{1}{2}\Delta_{II}, \\ E_0 = 0.4\frac{e^2a_0^2}{R^3}, \quad \varepsilon = \sqrt{\left(1.2\frac{e^2a_0^2}{R^3}\right)^2 + a^2}. \end{gathered} \tag{20b}$$

Table 7. The exchange interaction potential for the quasimolecule O$^+(^2P)$ + O(^3P) at given quantum numbers j, m_j of an ion obtained in the basis M_L, M_S

M_L, M_S	$1, 1$	$1, 0$	$0, 1$	$1, -1$	$0, 0$	$-1, 1$
j, m_j						
$\frac{3}{2}, \frac{3}{2}$	$\frac{1}{2}\Delta_{10}$	$\frac{3+\sqrt{6}}{12}\Delta_{10}$	$\frac{1}{2}\Delta_{11}$	$\frac{1}{2\sqrt{6}}\Delta_{10}$	$\frac{3+\sqrt{6}}{12}\Delta_{11}$	$\frac{-1}{2\sqrt{3}}\Delta_{10}$
$\frac{3}{2}, \frac{1}{2}$	$\frac{1}{2\sqrt{6}}\Delta_{10}$	$\frac{1+\sqrt{6}}{12}\Delta_{10}$	$\frac{3\sqrt{6}+2\sqrt{3}}{12}\Delta_{11}$	$\frac{1}{6}\Delta_{10}$	$\frac{3+\sqrt{2}+2\sqrt{3}+3\sqrt{6}}{12}\Delta_{11}$	$\frac{-1}{6\sqrt{2}}\Delta_{10}$
$\frac{3}{2}, -\frac{1}{2}$	$-\frac{1}{2\sqrt{3}}\Delta_{10}$	$\frac{-\sqrt{3}-\sqrt{2}}{12}\Delta_{10}$	$\frac{2+\sqrt{3}}{6}\Delta_{11}$	$-\frac{1}{6\sqrt{2}}\Delta_{10}$	$\frac{3+\sqrt{2}+2\sqrt{3}+3\sqrt{6}}{12}\Delta_{11}$	$\frac{1}{6}\Delta_{10}$
$\frac{3}{2}, -\frac{3}{2}$	$-\frac{1}{2\sqrt{2}}\Delta_{10}$	$\frac{-3\sqrt{2}-\sqrt{3}}{12}\Delta_{10}$	$\frac{1}{2\sqrt{6}}\Delta_{11}$	$-\frac{1}{2\sqrt{3}}\Delta_{10}$	$\frac{3+\sqrt{6}}{12}\Delta_{11}$	$\frac{1}{2\sqrt{6}}\Delta_{10}$
$\frac{1}{2}, \frac{1}{2}$	$\frac{1}{6}\Delta_{11}$	$\frac{1}{6}\Delta_{10}$	$\frac{1}{3\sqrt{2}}\Delta_{11}$	$\frac{1}{3}\Delta_{10}$	$\frac{1}{6\sqrt{2}}\Delta_{11}$	$\frac{1}{3\sqrt{2}}\Delta_{10}$
$\frac{1}{2}, -\frac{1}{2}$	$-\frac{1}{6\sqrt{2}}\Delta_{11}$	$\frac{1}{3\sqrt{2}}\Delta_{10}$	$-\frac{1}{6}\Delta_{11}$	$\frac{1}{3\sqrt{2}}\Delta_{10}$	$\frac{1}{6\sqrt{2}}\Delta_{11}$	$\frac{1}{3}\Delta_{10}$

Table 8. The values of κ following from diagonalization of the Hamiltonian matrix

M_L, M_S	$1, 1$	$1, 0$	$0, 1$	$1, -1$	$-1, 1$	$0, 0$
s, m_s						
$\frac{3}{2}, \frac{3}{2}$	1	1.35	0.95	1.4	1.36	0.87
$\frac{3}{2}, \frac{1}{2}$	1	1.27	0.96	1.05	1.65	0.88
$\frac{3}{2}, -\frac{1}{2}$	1	1.25	0.96	1.65	1.05	0.88
$\frac{3}{2}, -\frac{3}{2}$	1	1.18	0.95	1.37	1.37	0.88

Correspondingly, the exchange interaction potential for each state is

$$\begin{aligned} \Delta_I &= \frac{\Delta_1+\Delta_2}{2} + \frac{\Delta H}{4\varepsilon}(\Delta_1-\Delta_2), \\ \Delta_{II} &= \frac{\Delta_1+\Delta_2}{2} - \frac{\Delta H}{4\varepsilon}(\Delta_1-\Delta_2). \end{aligned} \tag{21}$$

As can be seen, if $a = 0$ and hence the Hamiltonian matrix is diagonal in the basis M_L, M_S, we have $\Delta_I = \Delta_1$ and $\Delta_{II} = \Delta_2$ in accordance with the expression for the Hamiltonian diagonal elements.

We use the expressions in Table 8 for the exchange interaction potential at the distance $12a_0$ between nuclei for different electron terms; this distance determines the cross section of the resonant charge exchange process in thermal collisions involving the O(^3P) atom and O$^+(^4S_{3/2})$ ion in the ground states. We note that according to formula (13), at this distance, $\Delta_{10} = 6\Delta_{11}$, which is used in Table 8. In Table 8, we give the values of the coefficient

$$\kappa = \frac{\Delta}{\Delta_{M_L M_S}},$$

where $\Delta_{M_L M_S}$ is the exchange interaction potential for the basis $M_L M_S m_s$ according to formula (19) and Δ is its value after diagonalization of the Hamiltonian matrix. As follows from the data in Table 8, the value κ is close to one; below, because of the logarithmic dependence of the cross section on this value, we ignore the variation of the exchange interaction potential due to diagonalization of the Hamiltonian. This simplifies the problem.

6. RESONANT CHARGE EXCHANGE PROCESS FOR OXYGEN

The above values of the ion–atom exchange interaction potentials allow us to determine the partial cross sections of resonant charge exchange on the basis of the asymptotic theory [11, 12]. The asymptotic theory of resonant charge exchange is based on the assumption that the main contribution to the cross section of this process is given by large impact parameters of collisions in comparison with the typical atomic size. Then the inverse value is a small parameter of the asymptotic theory, and the cross section is represented as an expansion over this small parameter. Hence, determination of the exchange ion–atom interaction potential at large separations allows us to determine the cross section of resonant charge exchange. If electron terms are nondegenerate, the relation between the probability and cross section of this process and the exchange interaction potential in the two-level approximation can be used [24]. In particular, this approximation is valid for the transition of an s-electron between two structureless cores (for example, for the processes H^+–H, He^+–He), and then the cross section σ_{ex} of the resonant charge exchange process is given by [11, 12, 24]

$$\sigma_{ex} = \frac{\pi R_0^2}{2}, \tag{22}$$

where

$$\frac{1}{v}\sqrt{\frac{\pi R_0}{2\gamma}}\Delta(R_0) = 0.28.$$

This formula can be used in the cases under consideration for the structureless oxygen ion $O^+(^4S)$ or if the fine ion splitting is small compared to the exchange interaction potential, as for $O^+(^2P)$. We take quantum numbers J, M_J to characterize the atom state at the beginning. Of course, this is valid only at very large distances between the nuclei when the ion–quadrupole interaction can be neglected. Therefore, we use these quantum numbers for labeling the electron terms only. In addition, the cross section of the processes

$$\begin{pmatrix} O^+(^4S) + O(^1D) \to O(^1D) + O^+(^4S) \\ O^+(^4S) + O(^1S) \to O(^1S) + O^+(^4S) \\ O^+(^2D) + O(^1S) \to O(^1S) + O^+(^2D) \end{pmatrix} \tag{23}$$

is zero for the one-electron atom scheme under consideration because the transition of a p-electron cannot lead to these processes.

In Tables 9–13, we give the partial cross sections of other electron transfer processes involving the electron shells $2p^3$ and $2p^4$ for the oxygen ion and atom at energies that are of interest for plasma. The indicated quantum numbers J, M_J of the atom and j, m_j of the ion are accurate only at large separations and are used for labeling the electron states at intermediate separations when the ion–atom quadrupole interaction is important.

Table 9. The cross section of resonant charge exchange σ_{ex} (in 10^{-16} cm^2) for the process $O^+(^4S) + O(^3P) \to O(^3P) + O^+(^4S)$ at the collision energies 0.1 eV and 1 eV (in parentheses) in the laboratory frame of reference

J, M_J	2, 2	2, 1	2, 0	1, 1	1, 0	0, 0
j, m_j						
$\frac{3}{2}, \frac{3}{2}$	60(48)	57(46)	54(43)	82(67)	60(48)	79(64)
$\frac{3}{2}, \frac{1}{2}$	61(49)	61(49)	60(48)	84(69)	61(49)	83(68)
$\frac{3}{2}, -\frac{1}{2}$	60(48)	61(49)	61(49)	82(67)	60(48)	83(68)
$\frac{3}{2}, -\frac{3}{2}$	54(43)	57(46)	60(48)	74(60)	54(43)	79(64)
average	59(47)	59(47)	59(47)	81(66)	59(47)	81(66)

We also note that the small parameter of the asymptotic theory is now

$$\frac{1}{\gamma R_0} \ll 1. \tag{24}$$

In evaluating the cross section of electron transfer, we use the values of the parameter γ in accordance with the data in Table 2. Expanding with respect to this small parameter, we keep two expansion terms in formula (22). For the cases in Tables 8 and 9, the values of γR_0 are between 10 and 14. This means that the accuracy of the asymptotic theory is about 1%. Of course, the real accuracy is worse because of additional factors [26] affecting the accuracy of the cross sections. Nevertheless, we estimate this accuracy as several percent.

If an electron term is degenerate for the quasimolecule consisting of a colliding ion and an atom and the ion–atom exchange interaction removes this degeneracy, the charge exchange process in the course of ion–atom collisions is entangled with other transition processes. In the case under consideration, this degeneracy relates to the projection of the ion total moment on the molecular axis, and hence the exchange process is entangled with rotation of the ion total moment. But because the ion–atom exchange interaction potential decreases exponentially as the separation increases, the region of the exchange process is narrow, and hence the rotation angle of the molecular axis is relatively small [5]. This allows us to separate the process of resonant charge exchange from the processes of moment

Table 10. The cross section of resonant charge exchange σ_{ex} (in 10^{-16} cm^2) for the process $\mathrm{O}^+(^2D) + \mathrm{O}(^3P) \rightarrow \mathrm{O}(^3P) + \mathrm{O}^+(^2D)$ at the collision energies 0.1 eV and 1 eV in the laboratory frame of reference

J, M_J	2, 2	2, 1	2, 0	1, 1	1, 0	0, 0
j, m_j						
$\frac{5}{2}, \frac{5}{2}$	43(34)	41(33)	39(31)	34(26)	34(26)	39(31)
$\frac{5}{2}, \frac{3}{2}$	50(40)	50(40)	50(40)	44(34)	47(37)	52(41)
$\frac{5}{2}, \frac{1}{2}$	54(43)	55(45)	54(43)	50(40)	51(40)	57(46)
$\frac{5}{2}, -\frac{1}{2}$	53(43)	56(45)	53(43)	51(40)	50(40)	57(46)
$\frac{5}{2}, -\frac{3}{2}$	47(37)	51(40)	47(37)	47(37)	44(34)	52(41)
$\frac{5}{2}, -\frac{5}{2}$	32(25)	36(28)	34(26)	34(26)	34(26)	39(31)
$\frac{3}{2}, \frac{3}{2}$	38(29)	35(26)	42(32)	39(30)	42(33)	29(21)
$\frac{3}{2}, \frac{1}{2}$	31(22)	37(28)	34(26)	38(29)	35(26)	39(30)
$\frac{3}{2}, -\frac{1}{2}$	33(25)	38(29)	37(28)	35(26)	38(29)	39(30)
$\frac{3}{2}, -\frac{3}{2}$	35(26)	24(16)	39(30)	42(33)	39(30)	29(21)
average	42(32)	42(33)	41(32)	43(34)	41(32)	43(34)

Table 11. The cross section of resonant charge exchange σ_{ex} (in 10^{-16} cm^2) for the process $\mathrm{O}^+(^2D) + \mathrm{O}(^1D) \rightarrow \mathrm{O}(^1D) + \mathrm{O}^+(^2D)$ at the collision energies 0.1 eV and 1 eV in the laboratory frame of reference

J, M_J	2	1	0
j, m_j			
$\frac{5}{2}, \frac{5}{2}$	71(58)	62(49)	46(36)
$\frac{5}{2}, \frac{3}{2}$	66(53)	59(47)	53(42)
$\frac{5}{2}, \frac{1}{2}$	49(38)	46(35)	47(37)
$\frac{5}{2}, -\frac{1}{2}$	58(46)	49(38)	47(37)
$\frac{5}{2}, -\frac{3}{2}$	75(62)	59(47)	53(42)
$\frac{5}{2}, -\frac{5}{2}$	62(49)	58(46)	46(36)
$\frac{3}{2}, \frac{3}{2}$	68(55)	60(48)	49(39)
$\frac{3}{2}, \frac{1}{2}$	59(47)	50(39)	54(43)
$\frac{3}{2}, -\frac{1}{2}$	45(36)	44(34)	54(43)
$\frac{3}{2}, -\frac{3}{2}$	53(41)	57(45)	49(39)
average	61(48)	54(43)	50(40)

rotation, i.e., to consider the resonant charge process for each angular momentum direction of the ion independently. Therefore, we evaluate the cross section of resonant charge exchange for each ion moment projection on the basis of formula (22).

On the basis of the partial cross sections of resonant charge exchange in Tables 9–13, we can find the average cross sections (see Table 14) that are convenient for applications. In averaging a cross section, we assume that the population of electron levels of a given group is proportional to statistical weights of the individual states, which is valid at high temperatures. As a result, in Table 12, we give the average cross sections of resonant charge exchange for a given orbital momentum and spin of the colliding ion and atom.

We note that the difference in the cross section for ions in different states is determined mostly by different ionization potentials of the oxygen atom in a given state with ion formation in these states.

The cross sections obtained allow us to determine the mobilities of an oxygen ion in atomic oxygen. In particular, if the atoms are in the ground electron and the fine state $\mathrm{O}(^3P_2)$, the respective mobilities of the oxygen ions $\mathrm{O}^+(^4S)$, $\mathrm{O}^+(^2D)$, and $\mathrm{O}^+(^2P)$ in atomic oxygen are 2.6, 5.1, and 4.6 cm^2/V·s; for the mixture of atoms in the electron states $\mathrm{O}(^3P_2)$ and $\mathrm{O}(^1D_2)$ with equal populations of these states at room temperature, the respective mobilities are 2.6, 3.8, and 4.3 cm^2/V·s at room temperature. These values may be of interest for plasmas of the upper Earth atmosphere and for a nonequilibrium gas-discharge oxygen plasma. We see that measurement of the mobilities of ions in different

Table 12. The cross section of resonant charge exchange σ_{ex} (in 10^{-16} cm^2) for the process $O^+(^2P) + O(^3P) \to O(^3P) + O^+(^2P)$ at given quantum numbers J, M_J of an atom and j, m_j of an ion at the collision energies 0.1 eV and 1 eV in the laboratory frame of reference

J, M_J	2, 2	2, 1	2, 0	1, 1	1, 0	0, 0
j, m_j						
$\frac{3}{2}, \frac{3}{2}$	45(36)	45(35)	33(25)	38(29)	29(22)	45(35)
$\frac{3}{2}, \frac{1}{2}$	38(29)	41(32)	37(29)	36(28)	34(26)	39(31)
$\frac{3}{2}, -\frac{1}{2}$	41(32)	40(31)	34(27)	34(26)	34(28)	39(31)
$\frac{3}{2}, -\frac{3}{2}$	42(33)	45(36)	27(20)	41(32)	36(29)	45(35)
$\frac{1}{2}, \frac{1}{2}$	26(19)	36(28)	28(21)	42(33)	38(30)	24(18)
$\frac{1}{2}, -\frac{1}{2}$	24(18)	39(30)	26(19)	39(30)	39(33)	24(18)
average	36(28)	41(32)	31(24)	38(30)	36(28)	36(28)

Table 13. The cross section of resonant charge exchange σ_{ex} (in 10^{-16} cm^2) for the proceses $O^+(^2D) + O(^1D) \to O(^1D) + O^+(^2D)$ and $O^+(^2P) + O(^1S) \to O(^1S) + O^+(^2P)$ (the last column) at the collision energies 0.1 eV and 1 eV in the laboratory frame of reference

L, M	^1D, $M_L = 2$	^1D, $M_L = 1$	^1D, $M_L = 0$	^1S, $M_L = 0$
j, m_j				
$\frac{3}{2}, \frac{3}{2}$	38(30)	47(37)	46(36)	50(40)
$\frac{3}{2}, \frac{1}{2}$	38(29)	49(39)	50(40)	65(52)
$\frac{3}{2}, -\frac{1}{2}$	34(25)	48(38)	50(40)	65(52)
$\frac{3}{2}, -\frac{3}{2}$	28(21)	42(32)	46(36)	50(40)
$\frac{1}{2}, \frac{1}{2}$	35(27)	43(33)	47(37)	57(45)
$\frac{1}{2}, -\frac{1}{2}$	30(23)	41(31)	47(37)	57(45)
average	34(26)	45(35)	47(38)	58(46)

Table 14. The average cross sections of resonant charge exchange σ_{ex} (in 10^{-16} cm^2) at the collision energies 0.1 eV, 1 eV, and 10 eV (in square brackets) in the laboratory frame of reference

Atom state	$O(^3P)$	$O(^1D)$	$O(^1S)$
Ion state			
$O^+(^4S)$	66(53)[44]	0(0)[0]	0(0)[0]
$O^+(^2D)$	42(33)[25]	56(44)[34]	0(0)[0]
$O^+(^2P)$	37(29)[22]	41(32)[24]	58(46)[35]

states allows analyzing the atom distribution over excited states.

Thus, due to a high symmetry of atoms and ions with nonfilled electron shells, we obtain a large number of electron terms within the framework of the LS coupling scheme for a diatomic ion when the ion and the atom have nonfilled electron shells. Because the exchange interaction is shared between these states, the cross sections of resonant charge exchange are lower. This can be demonstrated by comparison of the cross sections of resonant charge exchange for the LS and $j-j$ types of electron coupling in the oxygen atom and ion. In the case of the $j-j$ coupling, we have a lower symmetry, and therefore a simpler character of this process.

The accuracy of the cross sections of resonant charge exchange is mostly determined by the accuracy of determination of the asymptotic coefficient A and, according to the analysis in [23, 26], is several percent. Comparison for the ground state of a colliding ion and an atom shows [8, 10] that the average cross section differs by about 10 % from that evaluated within the framework of the Hund coupling. As regards the two-level approximation for the electron terms of O_2^+, any coincidence may be occasional, because this scheme of electron term splitting does not take the important peculiarities of this interaction analyzed above into account.

7. COMPARISON WITH OTHER SCHEMES OF ELECTRON COUPLING

We have constructed the lowest electron terms of O_2^+ at large separations, which determine the cross sections of resonant charge exchange. Of course, the character of coupling in this range of distances between the nuclei differs from those at low separations [27]. We next use the LS type of electron coupling in the atom and ion, and the accuracy of using this coupling scheme is about 2 %, which is determined by the coincidence of the level positions for fine states of an oxygen atom located in the ground electron state with formula (9).

Nevertheless, we use the $j-j$ coupling scheme in the case under consideration in order to understand the dependence of the resonant charge exchange cross sections on the coupling type. We consider the collision of an oxygen ion and an atom in the ground electron states, with the resonant charge exchange process occurring according to the scheme

$$\mathrm{O}^+\left[\left(\frac{1}{2}\right)^2\left(\frac{3}{2}\right)\right]_{\frac{3}{2}} + \mathrm{O}\left[\left(\frac{1}{2}\right)^2\left(\frac{3}{2}\right)^2\right]_2 \to \mathrm{O}\left[\left(\frac{1}{2}\right)^2\left(\frac{3}{2}\right)^2\right]_2 + \mathrm{O}^+\left[\left(\frac{1}{2}\right)^2\left(\frac{3}{2}\right)\right]_{\frac{3}{2}} \qquad (25)$$

instead of the process

$$\mathrm{O}^+(^4S_{\frac{3}{2}}) + \mathrm{O}(^3P_2) \to \mathrm{O}(^3P_2) + \mathrm{O}^+(^4S_{\frac{3}{2}}), \qquad (26)$$

that occurs in the case of the LS coupling scheme. As follows from process (25), within the framework of the $j-j$ coupling scheme, the ion–atom exchange interaction and the resonant charge exchange process are determined by the transition of a valence electron with $j = 3/2$ from the field of one core to the other one.

Based on the $j-j$ coupling scheme for valence electrons in the atom and ion for the electron terms of the ion dimer at large separations [23], we note that the character of the exchange splitting is simpler in this case than in the case of the LS coupling scheme. Indeed, we represent the wave function of two valence electrons from a nonfilled electron shell $j = 3/2$ of an oxygen atom as

$$\Phi_{JM_J}(1,2) = \frac{1}{\sqrt{2}}\hat{P}\sum_{m_1,m_2}\begin{bmatrix} 3/2 & 3/2 & J \\ m_1 & m_2 & M_J \end{bmatrix} \times \psi_{\frac{3}{2}m_1}(1)\psi_{\frac{3}{2}m_2}(2). \qquad (27)$$

This wave function is simpler than formula (14) for the LS coupling in an atom. From Eq. (15), we obtain the ion–atom exchange interaction potential

$$\Delta_{JM_Jjm_j}(R) = \sum_m \begin{bmatrix} \frac{3}{2} & \frac{3}{2} & J \\ M_J - m & m & M_J \end{bmatrix} \times \begin{bmatrix} \frac{3}{2} & \frac{3}{2} & J \\ m_j & m & m_j + m \end{bmatrix} \times \Delta_{\frac{3}{2}m}(R), \qquad (28)$$

which is simpler than formula (17) for the LS coupling in an atom and an ion. The one-electron exchange interaction potentials for case «c» of the Hund coupling, which are used in this formula, are given by [22, 26]

$$\begin{aligned} &\Delta_{\frac{3}{2}\frac{3}{2}}(R) = \Delta_{11}(R), \\ &\Delta_{\frac{3}{2}\frac{1}{2}}(R) = \frac{2}{3}\Delta_{10}(R) + \frac{1}{3}\Delta_{11}(R), \end{aligned} \qquad (29)$$

where the one-electron exchange interaction potentials $\Delta_{10}(R)$ and $\Delta_{11}(R)$ for case «a» of the Hund coupling are given by formula (13). Below, we neglect Δ_{11} compared Δ_{10}.

We note that according to formula (28), the ion–atom exchange interaction potential $\Delta_{JM_Jjm_j}(R)$ for the $j-j$ coupling in the atom and ion is unchanged under the transformations

$$M_J, m_j \to -M_J, -m_j. \qquad (30)$$

Table 15 contains the exchange interaction potentials in the case of oxygen and the $j-j$ coupling scheme. Evidently, this scheme may be valid for heavy atoms of the fourth group of the periodical table of elements.

Table 16 contains the partial cross sections for resonant charge exchange. We see that they are in a restricted range of values. The average cross sections of the resonant charge exchange process (25) at the collision energies 0.1 eV, 1 eV, and 10 eV in the laboratory frame of reference are 10^{-16} cm^2. As follows from Table 16, although the partial cross sections are different, the average cross sections for a given total atom momentum practically coincide.

Above, we have rigorously found the partial cross sections of resonant charge exchange in slow collisions for oxygen. We account for various factors that influence the positions of electron terms of the O_2^+ quasimolecule at large separations within the framework of the LS coupling scheme for valence electrons. This allows us to evaluate the partial cross sections. At the next step, we can find the average cross sections of resonant charge exchange by averaging over states

Table 15. The ion–atom exchange interaction potential $\Delta_{JM_Jjm_j}(R)$ for the $j-j$ coupling scheme for oxygen

M_J	0	1	2
m_j			
$\frac{3}{2}$	$\frac{\sqrt{2}}{3}\Delta_{10}$	$\frac{1}{3}\Delta_{10}$	$\frac{1}{3}\Delta_{10}$
$\frac{1}{2}$	$\frac{1}{6}\Delta_{10}$	$\frac{1}{3\sqrt{2}}\Delta_{10}$	$\frac{1}{2}\Delta_{11}$
$-\frac{1}{2}$	$\frac{1}{6}\Delta_{10}$	$\frac{1}{2}\Delta_{11}$	$\frac{1}{3\sqrt{2}}\Delta_{10}$
$-\frac{3}{2}$	$\frac{\sqrt{2}}{3}\Delta_{10}$	$\frac{1}{3}\Delta_{10}$	$\frac{1}{3}\Delta_{10}$

Table 16. The partial cross sections σ_{ex} (in 10^{-16} cm^2) of resonant charge exchange process (25) at the collision energies 0.1 eV, 1 eV, and 10 eV in the laboratory frame of reference

M_J	0	1	2
m_j			
$\frac{3}{2}$	72(58)[45]	67(54)[42]	67(54)[42]
$\frac{1}{2}$	59(46)[35]	63(50)[38]	52(41)[32]
$-\frac{1}{2}$	59(46)[35]	52(41)[32]	63(50)[38]
$-\frac{3}{2}$	72(58)[45]	67(54)[42]	67(54)[42]
average	65(52)[40]	63(50)[38]	63(50)[38]

using a real distribution over excited states of the quasimolecule. Although this operation is accurate, it is quite cumbersome, and it is therefore interesting to compare the accurate cross sections with those obtained in simplified schemes. We do not consider the two-level approximation [24] that is suitable for transition of an s-electron between two structureless cores. This approximation was also used for oxygen (see, e.g., [28, 29]). This approximation may lead to a relatively large error because it is restricted by one transferring electron, while each valence electron can in fact transfer to the ion core. In the case of oxygen, this gives the factor 7/3 [22, 26] for the exchange interaction potential for case «a» of the Hund coupling. For an ion and an atom in the ground electron state, this leads to an error of approximately 20 % [9] for the cross section of resonant charge exchange and for the range 0.1–10 eV of the collision energies. Rejecting the model of a transferring s-electron and a structureless core, we restrict ourselves to cases «a» and «c» of the Hund coupling for a valence p-electron and assume the ion–atom exchange interaction potential to be independent of the fine ion state.

Reducing the problem of the ion–atom exchange interaction to the standard Hund coupling scheme for the interaction of ion and atom valence electrons, we can consider this for the Hamiltonian if we ignore the spin–orbit interaction for the atom (Hund case «a») or the ion–quadrupole interaction (Hund case «c»). Therefore, averaging the exchange interaction potential in (16) over ion and atom spins, we obtain the ion–atom exchange interaction potential for case «a» of the Hund coupling [5, 8, 13],

$$\Delta_{LSM_Llsm}(R) = n\left(G_{ls}^{LS}\right)^2 \times \\ \times \sum_{\mu}\begin{bmatrix} l_e & l & L \\ \mu & M_L-\mu & M_L \end{bmatrix}\begin{bmatrix} l_e & l & L \\ \mu & m & m+\mu \end{bmatrix} \times \\ \times \Delta_{l_e\mu}(R). \quad (31)$$

In the same manner, in case «a» of the Hund coupling, if we sum the atom orbital L and spin S moments into the total electron moment J and average over ion fine states according to formulas (14) and (17), we obtain

$$\Delta_{LSJM_Jls_j}(R) = n\left(G_{ls}^{LS}\right)^2 \times \\ \times \sum_{\mu,\sigma}\sum_{m,m_s,m_j,M_L,M_S}\begin{bmatrix} l_e & l & L \\ \mu & M_L-\mu & M_L \end{bmatrix} \times \\ \times \begin{bmatrix} l_e & l & L \\ \mu & m & m+\mu \end{bmatrix}\begin{bmatrix} \frac{1}{2} & s & S \\ \sigma & M_S-\sigma & M_S \end{bmatrix} \times \\ \times \begin{bmatrix} \frac{1}{2} & s & S \\ \sigma & m_s & m_s+\sigma \end{bmatrix}\begin{bmatrix} l & s & j \\ m & m_s & m_j \end{bmatrix} \times \\ \times \begin{bmatrix} l & s & j \\ M_L-\mu & M_S-\sigma & M_L-\mu+M_S-\sigma \end{bmatrix} \times \\ \times \begin{bmatrix} L & S & J \\ M_L & M_S & M_J \end{bmatrix} \times \\ \times \begin{bmatrix} L & S & J \\ m+\mu & m_s+\sigma & m+\mu+m_s+\sigma \end{bmatrix}\Delta_{l_e\mu}. \quad (32)$$

In Table 17, cases «a» and «c» of the Hund coupling are compared with a rigorous evaluation for the quasi-

Table 17. The cross section of resonant charge exchange σ_{ex} (in 10^{-16} cm^2) for the process O$^+(^4S)+$O(^3P) at given quantum numbers J, M_J of an atom and j, m_j of an ion at the collision energies 0.1 eV and 1 eV in the laboratory frame of reference. The indicated quantum numbers are accurate only at large separations and are used for labeling the electron states at intermediate separations where the ion–atom quadrupole interaction is important

Quantum numbers M_L, M_s	1, 1	1, 0	1, −1	0, 1	−1, 1	0, 0
Quantum numbers J, M_J	2, 2	2, 1	2, 0	1, 1	1, 0	0, 0
Case «a»	69(56)	84(68)	63(51)	77(62)	51(41)	63(50)
Case «c»	63(51)	77(62)	81(66)	77(62)	56(44)	72(57)
Average for the accurate scheme	59(47)	59(47)	59(47)	81(66)	59(47)	81(66)

molecule under consideration. A general conclusion from this and previous comparisons is that the average cross sections for the precise and approximate methods are close if we account for the transition of any electron from the atom valence electron shell. If we reduce the problem to the electron transfer between two structureless cores, the difference in average cross sections may reach 20 %.

8. CONCLUSIONS

We have constructed the electron terms for the oxygen ion dimer at large separations by the asymptotically accurate method with various interactions in this system taken into account within the framework of the *LS* coupling scheme for the oxygen atom and ion. The hierarchy of interactions in this quasimolecule is such that the exchange electrostatic interaction is stronger for lowest nonfilled electron shells p^3 and p^4 for the ion and atom. As a result, the atom orbital momentum L its spin S, the ion orbital momentum l, and its spin s are the quasimolecule quantum numbers. Weaker interactions are the spin–orbit interaction for an atom and an ion and the interaction of the ion charge and the atom quadrupole moment. Because these interactions are comparable, one can find the electron terms at large separations with these interactions taken into account by diagonalization of the Hamiltonian matrix. The quasimolecule eigenstates are characterized by the total ion angular momentum j and its projection m_j on the molecular axis; atom moments and their projections are mixed in eigenstates of the quasimolecule. The electron term positions for the quasimolecule is determined for each electron term of the diatomic oxygen ion; the exchange interaction potentials for each electron term and for each ion state are also evaluated at large separations. Although this is done for the quasimolecule O_2^+, we thus obtain a general scheme for determination of electron term energies and exchange interaction potentials at large separations for an atom and its ion with nonfilled electron shells within the *LS* scheme of electron coupling.

We note that a general scheme developed for the evaluation of electron terms and the cross sections of resonant charge exchange is asymptotically accurate, but it is simultaneously quite cumbersome. Indeed, in the case of the interaction O$^+(^4S)$ + O(^3P), we have 9 electron terms that are partially degenerate if we neglect the ion–atom exchange interaction; accounting for the ion–atom exchange interaction, we obtain 36 partially degenerate electron terms. In the case of the interaction O$^+(^2D)$ + O(^3P), we have 18 partially degenerate electron terms with the ion–atom exchange interaction ignored and 90 electron terms with the ion–atom exchange interaction taken into account. Because this method is cumbersome, it may be simplified with a partial loss of rigor but with small accuracy loss. Nevertheless, at least one accurate evaluation is needed in the asymptotically accurate scheme in order to know the accuracy of various approximate methods. This procedure is fulfilled in this paper in the case of oxygen.

This paper is supported in part by the RFBR (grant № 04-03-32736) and the grant LSS-1958.2003.2.

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