PHYSICAL REVIEW A **69**, 042718 (2004)

Resonant charge exchange and relevant transport cross sections for excited states of oxygen and nitrogen atoms

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(Received 1 August 2002; published 30 April 2004)

Resonant charge-exchange cross sections and the relevant transport (diffusion) cross sections for excited states of nitrogen and oxygen atoms have been calculated. The calculation is performed using the asymptotic approach, based on the single-electron asymptotic representation of the electron wave function. The ground-state cross sections are in a good agreement with those calculated via comprehensive quantum chemical approach. The results of calculations demonstrate a reasonable accuracy and a high convenience of this approach in determination of cross sections for the manifold of excited states of atoms.

DOI: 10.1103/PhysRevA.69.042718 PACS number(s): 34.70.+e, 52.20.Hv

I. INTRODUCTION

Transport properties of thermal plasmas including the presence of low- and high-lying electronically excited states have been the subject of several investigations [1–5]. In particular, high-lying excited states, i.e., states with principal quantum number different from the ground state, despite their small concentration in a thermal plasma, can strongly affect the transport properties due to the dramatic increase of the corresponding cross sections as a function of principal quantum number [5].

The main difficulty of such calculations relates to the evaluation of collision cross section for excited species. The comprehensive approach to this problem has been demonstrated in Refs. [5–12] for the case of hydrogen atom. The cited authors have performed calculations of the resonant excitation transfer [5–7] and resonant charge-exchange [8–12] cross sections for excited states of hydrogen atom. The cross section of resonant processes is expressed through the exchange interaction potential, which is the difference between the energies of a gerade and ungerade states of a quasimolecule, formed in approaching the atomic particles under consideration.

This approach, which manifested itself quite well in the case of hydrogen atom and ion, becomes much more complicated in the case of many-electron atoms, for example, nitrogen and oxygen, which are of the great practical importance, being the main components of the atmosphere. The difficulties relate mainly to a large variety of possible states of a quasimolecule, which are formed when two atomic particles with not fully filled electron shells start interacting. For example, in the case of ground-state atom N $({}^4S_{3/2})$ and ion N^+ $({}^3P)$ one can select six pairs of quasimolecular states $({}^{2,4,6}\Sigma_{g,u}$ and ${}^{2,4,6}\Pi_{g,u})$, differed from each other in the total spin and the projection of the electron orbital angular momentum. The same situation occurs in collision of ground-state atom O $({}^3P)$ and ion O^+ $({}^4S_{3/2})$. Generally speaking, these pairs of states differ from each other in the magnitude of the exchange interaction potential and therefore in the resonant charge-exchange cross section. The real magnitude of the cross section, which has to be compared with experiment, is the result of averaging the relevant partial magnitudes, related to specific states of a quasimolecule.

The technical difficulties in a comprehensive calculation of the exchange interaction potential for the specific excited many-electron atom and a large variety of excited states of atoms, making a considerable contribution into the transport coefficients of plasma, can be overcome (quite easily) in the frame of the asymptotic approach. This theory is based on the use of a single-electron asymptotic representation for the wave function of the valence electron. In accordance with this approach, which was applied first by Firsov [13] and developed subsequently in detail by Smirnov [14,15], the transition probability is determined mainly by the behavior of the atomic wave function at large internuclear distances, exceeding the characteristic atomic size. The asymptotic approach permits the evaluation of the resonant charge-exchange cross section for all the atoms of the periodic table with the accuracy of about 10%, which is virtually within the accuracy of the modern experiment and only slightly decreases with the complexity of an atom [14,15]. In this work the asymptotic approach is used for evaluation of the resonant charge-exchange cross section for some excited states of nitrogen and oxygen atoms.

The outline of the present paper is as follows. In Sec. II we report the asymptotic method used to calculate the relevant exchange interaction potentials for excited atomic nitrogen and oxygen colliding with their parent ions. In Sec. III we report the method of calculation of resonant charge-transfer cross sections involving excited states and the relevant results for N-N^+ and O-O^+ pairs. Section IV discusses the limits of used approximations and possible scaling laws. Section V is dedicated to the conclusions.

II. METHOD OF CALCULATION

The resonant charge-exchange cross section can be expressed as [13–15]

$$\sigma_t = \int_0^\infty 2\pi P_{12}(\rho)\rho d\rho = \int_0^\infty 2\pi\rho d\rho \sin^2 \int_{-\infty}^\infty \frac{\Delta(R)}{2} dt. \quad (1)$$

Here R is internuclear distance, ρ is the impact parameter, $\Delta(R)$ is the exchange interaction potential, which is the difference between gerade, ε_g, and ungerade, ε_u, potential energy of the quasimolecule, consisted of an ion and the parent atom, $P_{12}(\rho)$ is the probability of the electron transfer from one center to another as a result of the ion-atom collision with the impact parameter ρ.

The magnitude of the resonant charge-exchange cross section is determined by the internuclear distance dependence of the exchange interaction potential. Therewith the main contribution into the cross section is due to the region of comparatively large internuclear distances $R \gg a_0$ (a_0 is the Bohr radius). This permits the use of the asymptotic approach to the determination of the exchange interaction potential [14–18], which is based on an asymptotic representation of the wave function of the valence electron. This approach seems to be more justified in the case of excited atomic states, because the valence electron is bound with the atomic core to a lesser degree, and can be considered independently.

In accordance with the asymptotic approach the exchange interaction potential is expressed through the single-electron wave function of a valence electron of an atom, having the quantum numbers ℓ, m, $1/2$, σ. This latter is represented as the product

$$\psi_{\ell m 1/2 \sigma} = \mathfrak{R}_\ell(r) Y_{\ell m}(\vartheta, \varphi)\chi_\sigma, \quad (2)$$

where $\mathfrak{R}_\ell(r)$ is the radial part of the wave function, $Y_{\ell m}(\vartheta, \varphi)$ and χ_σ are the angular and the spin part, respectively, and r, ϑ, φ are the spherical coordinates of the electron. The asymptotic behavior of the radial part of the electron wave function at large distance from the nucleus ($r\gamma \gg 1$) has the following form:

$$\mathfrak{R}(r) = A r^{(1/\gamma - 1)} e^{-\gamma r}. \quad (3)$$

Here $-\gamma^2/2$ is the binding energy of the valence electron (in atomic units), and A is the normalization factor.

The most accurate way to evaluate the A parameter is tailoring the long-range asymptotic representation of the electron wave function with that calculated by the Hartree-Fock method, describing the behavior of the electron in the vicinity of the parent nucleus.

We further simplify the problem by calculating the A parameter according to the following formula, basically valid for s states of hydrogenic species and useful in determining an upper limit for the parameter value in p-electron case [18]:

$$A = \frac{\gamma^{3/2}(2\gamma)^{1/\gamma}}{\Gamma\left(\frac{1}{\gamma}\right)}. \quad (4)$$

This assumption, which can be justified by the small sensitivity of charge-transfer cross sections on the absolute value of the A parameter, gives, however, A values close to the corresponding ones calculated by the Hartree-Fock procedure. This point can be appreciated by comparing the A values calculated by Eq. (4) and the "exact" ones calculated by using the Hartree-Fock wave functions (Table I). The magnitudes of the coefficient A for alkali-metal atoms and for the low-lying excited states of nitrogen atom [i.e., for states $(^2D), (^2P)$] were taken from the handbook [16]. An additional calculation, at Hartree-Fock level, has been performed in the case of the first quintet state of oxygen atom (^5S), using a basis set of Gaussian functions $(9s, 5p)$ contracted to $[4s, 2p]$ [19], augmented by a diffuse d (exponential parameter $\zeta = 0.85$) function, and enriched by Rydberg-like $s(\zeta = 0.032, 0.0066)$ and p $(\zeta = 0.028, 0.0054)$ functions. Joining the calculated wave function to its asymptotic expression in the region outside the limits of the atomic core, a value of the parameter A can be determined, which depends on the selected electron-nucleus distance r. The value reported in Table I has been obtained as a mean of the calculated quantity $A(r)$ over the interval $4.0a_0 - 8.0a_0$. Inspection of Table I shows that for alkali-metal atoms the deviation from the exact A value do not overcome 10%; a quite similar situation was found for the ^5S state of oxygen, while the difference increases up to 40% for low-lying excited states of nitrogen. However, these differences do not propagate proportionally in the charge-transfer cross sections. As an example a 40% difference in the A value [case N(^2P)] propagates in 15%, 18%, and 22% errors in the corresponding averaged cross sections, respectively, for 0.1 eV, 1.0 eV, and 10.0 eV energies.

TABLE I. The magnitudes of parameter A, calculated for alkali-metal atoms and for first excited states of atomic nitrogen by the rigorous approach [16] and using the approximation formula (4).

	Li	Na	K	Rb	Cs	O(^5S)	N(^2D)	N(^2P)
γ	0.63	0.615	0.565	0.554	0.535	0.573	0.945	0.898
A Eq. (4)	0.8	0.75	0.56	0.53	0.46	0.59	1.86	1.73
A exact	0.82	0.74	0.52	0.48	0.41	0.52	1.36	1.23

Values of the parameter A and γ for the different atomic states have been reported in Tables II and III (note that also for the ground state of oxygen (^3P) and nitrogen (^4S) the

TABLE II. The magnitudes of the parameter A, calculated on the basis of the rigorous approach (states $2p^3$) and the approximate expression (4) (states ns) for some levels of nitrogen atom.

State	Energy (eV)	γ (a.u.)	A (a.u.)
N($^4S_{3/2}$)	0	1.034	1.5
N(^2D)	2.384	0.945	1.36
N(^2P)	3.576	0.898	1.23
N($2p^2 3s$ ^2P)	10.687	0.53	0.46
N($2p^2 4s$ ^2P)	12.919	0.344	0.037
N($2p^2 5s$ ^2P)	13.65	0.25	0.0013
N($2p^2 3s$ ^4P)	10.33	0.556	0.54
N($2p^2 4s$ ^4P)	12.857	0.35	0.043
N($2p^2 5s$ ^4P)	13.624	0.26	0.0022

TABLE III. The magnitudes of the parameter A calculated on the basis of the rigorous approach (state $2p^4$) and of the approximate expression (4) (states ns) for some levels of oxygen atom.

State	Energy (eV)	γ (a.u.)	A (a.u.)
$O(2p^4\ {}^3P)$	0	1	1.3
$O(2p^3 3s\ {}^5S)$	9.146	0.573	0.59
$O(2p^3 4s\ {}^5S)$	11.838	0.34	0.034
$O(2p^3 5s\ {}^5S)$	12.661	0.26	0.0022
$O(2p^3 3s\ {}^3S)$	9.521	0.549	0.515
$O(2p^3 4s\ {}^3S)$	11.93	0.352	0.043
$O(2p^3 5s\ {}^3S)$	12.7	0.26	0.0022

exact values were taken from Ref. [16]**)**.

The exchange interaction potential, which is the difference between the gerade and ungerade electronic terms of a quasimolecule, formed by an ion and the parent atom, is derived from the above-given expression for the electron wave function. The general expression for that depends on the scheme of orbital and spin angular-momentum summation in atom and ion core. The most proper scheme for light atoms is LS coupling: in this frame the fine-structure splitting for an ion and the parent atom is negligible in comparison to the energy difference for various angular-momentum projections of the valence electron onto the molecular axis. This allows the separate consideration of states with different total spin of a quasimolecule. Then the quantum numbers of the molecular ion are the atomic quantum numbers L, S, M_L, M_S and the relevant quantum numbers of the ion core are ℓ, s, m, m_s. In such a scheme the orbital and spin angular momenta of the valence electron ℓ_e and $1/2$ are summed up with the corresponding angular momenta of the ion core ℓ and s into the atomic angular momenta L and S, thereafter the atomic spin S and the spin of the ion core s are summed into the total spin of the molecular ion I. Due to the neglect of the spin-orbit interaction the exchange interaction potential does not depend on the total spin of a quasimolecule I. In the frame of this scheme the general expression for the exchange interaction potential has the following form [14,15]:

$$\Delta(\ell_e\mu,\ell m s,L M_L S) = N(G^{LS}_{\ell s})^2 \frac{I+1/2}{2s+1}\begin{bmatrix}\ell_e & \ell & L\\ \mu & m & m+\mu\end{bmatrix} \times \begin{bmatrix}\ell_e & \ell & L\\ \mu & M_L-\mu & M_L\end{bmatrix}\Delta_{\ell_e\mu}. \qquad (5)$$

Here N is the number of valence electrons, $G^{LS}_{\ell s}(\ell_e,N)$ is the genealogical or Racah coefficient, which is responsible for formation of the atom from the parent ion and electron, the expression in the squared brackets is the Clebsch-Gordan coefficient, which is responsible for summation of electron and ion angular momenta into the atom orbital angular momentum, μ is the projection of the orbital angular momentum of the valence electron on the axis of the quasimolecule, $\Delta_{\ell_e\mu}$ is the partial single-electron exchange interaction potential, determined by the following relation:

$$\Delta_{\ell_e\mu} = A^2 R^{(2/\gamma-1)}\ e^{(-R\gamma-1/\gamma)}\frac{(2\ell_e+1)(\ell_e+|\mu|)!}{(\ell_e-|\mu|)!\,|\mu|!\,(R\gamma)^{|\mu|}}, \qquad (6)$$

where ℓ_e is the orbital angular momentum of the valence electron, subjected to the transition, μ is its projection on the axis connecting the nuclei.

A remarkable feature of the exchange interaction potential, which follows from the expression (6), relates to the additional selection rules, governing single-electron transitions. Accordingly the transition of a single p electron is possible when

$$|L-\ell| \leqslant 1, \quad |S-s| \leqslant 1/2. \qquad (7)$$

In particular, these conditions are violated for the resonant single-electron transitions,

$$O^+({}^4S) + O({}^1D_2) \rightarrow O({}^1D_2) + O^+({}^4S), \qquad (8)$$

$$O^+({}^4S) + O({}^1S_0) \rightarrow O({}^1S_0) + O^+({}^4S), \qquad (9)$$

so that the resonant charge-exchange cross section for these transitions is zero in the single-electron approximation. For these transitions the process is possible only in the case of simultaneous transition of two electrons, which is of relatively low probability. This is indeed confirmed by the semiclassical calculations reported in Ref. [2].

The specific magnitudes of the genealogical coefficients and Clebsch-Gordan coefficients depend on the specific system under investigation. Let us start from the system

$$N({}^2D_{3/2,5/2}) + N^+({}^3P) \rightarrow N^+({}^3P) + N({}^2D_{3/2,5/2}), \qquad (10)$$

for which $\ell=1$, $\ell_e=1$, and $L=2$. There is a set of states which are differed from each other in projection of the electron angular momenta ℓ, ℓ_e, and L (m, μ, and M_L) onto the quasimolecular axis. Since the total spin of the quasimolecule is a result of summation of total spins of atom and ion (1/2 and 1, correspondingly), one can select from the whole set of states subsets of doublets and quartets, with total spins 3/2 and 1/2, correspondingly. The degeneracy of the first subset is as large as twice of the second one, which is similar to the first one in all the rest features. Each of these subsets is divided in its turn into the groups of Σ and Π terms, differed from each other in the projection of the orbital angular momentum $\mu=0$, ∓ 1 of the valence electron onto the quasimolecular axis. For example, the Clebsch-Gordan coefficients for the system $N^+({}^3P)+e(p)\rightarrow N({}^2D_{3/2,5/2})$ are given in Table IV.

III. CALCULATION AND RESULTS

The resonant charge-exchange cross section for the excited states of oxygen and nitrogen, listed in Tables II and III, were calculated on the basis of the asymptotic approach [13–15,18,20,21].

The probability of charge transfer, P_{12}, can be written as [13]

TABLE IV. Clebsch-Gordan coefficients for the system $N^{+}(^{3}P)+e(p)\rightarrow N(^{2}D_{3/2,5/2})$ [17].

μ	m			M_L		
		2	1	0	-1	-2
1	1	1				
1	0		$2^{-1/2}$			
1	-1			$6^{-1/2}$		
0	1		$2^{-1/2}$			
0	0			$(2/3)^{-1/2}$		
0	-1				$2^{-1/2}$	
-1	1			$6^{-1/2}$		
-1	0				$2^{-1/2}$	
-1	-1					1

$$P_{12}(\rho)=\sin^2\int_{-\infty}^{\infty}dt\frac{\Delta(\rho)}{2}=\sin^2\int_{\rho}^{\infty}RdR\frac{|\varepsilon_u(R)-\varepsilon_g(R)|}{v\sqrt{(R^2-\rho^2)}}, \tag{11}$$

where $R^2=\rho^2+v^2t^2$ is valid for free motion of nuclei.

Due to the fact that the interaction potential has a decreasing exponential character [see Eq. (6)] at large distances, the integral in Eq. (1) can be divided in two parts, in the region of small ρ, $P_{12}(\rho)$ oscillates rapidly between 0 and 1 and may be replaced by its average value $\frac{1}{2}$, and in the second region an exponential approximation can be used:

$$\sigma_{\Lambda}^{I}=\frac{1}{2}\pi\rho^{*2}+2\pi\int_{\rho^*}^{\infty}P_{12}(\rho)\rho d\rho\sim\frac{1}{2}\pi\rho^{*2}. \tag{12}$$

The problem of calculating σ_{Λ}^{I} is then reduced to the estimation of $R_0=\rho^*$ and in the asymptotic approach this quantity can be obtained requiring that the terms linear in R_0 in the cross section, coming from the integration in the second region, must vanish [15]. As a result R_0 can be calculated by solving the following transcendental equation:

$$\int_{-\infty}^{\infty}\frac{\Delta_{\Lambda}^{I}(R)}{2}dt=\frac{e^{-C}}{2}=0.28, \tag{13}$$

$\Delta_{\Lambda}^{I}(R)$ is the partial exchange interaction potential, related to the specified state of a quasimolecule with the total spin I and the projection Λ of the electron orbital angular momentum on the axis of the quasimolecule, and $C=0.577$ is the Euler constant.

Neglecting the nonadiabaticity of the resonant charge-transfer process, the different exit channels, corresponding to different terms of the quasimolecule, can be considered separately and an averaged resonant charge-exchange cross section is evaluated through the following expression:

$$\sigma_t(E)=\frac{1}{g}\sum_{\Lambda,I}(\Lambda+1)(2I+1)\ \sigma_{\Lambda}^{I}(E). \tag{14}$$

Here $g=\Sigma_{\Lambda,I}(\Lambda+1)(2I+1)$ is the total degeneracy for Σ and Π states of the quasimolecule at large internuclear distances. More serious is, probably, the neglect of the coupling to other molecular states. Each *g-u* pair acts independently, so that the present approach is similar to a two-state quantum description. The effect of coupling is therefore neglected. To estimate the dependence of the charge-transfer cross sections on this factor we can use the calculations performed many years ago by Malaviya [11], who compared the two-state approximation (Q_c^2) with the eight-state (Q_c^8) approximation for the process

$$\mathrm{H}(2s,2p)+\mathrm{H}^{+}\rightarrow\mathrm{H}^{+}+\mathrm{H}(2s,2p). \tag{15}$$

Comparison between the two sets of cross sections shows that at 200 eV Q_c^8 is $0.60Q_c^2$, i.e., the two-state approximation (and therefore the present results) can be considered as an upper limit to the true cross sections. For higher excited states one reasonably should expect higher differences due to the enormous increase of molecular states. This point, together with the uncertainty on the A values, limits the accuracy of the present calculations.

The partial magnitudes $\sigma_{\Lambda}^{I}(E)$ and the relevant magnitudes of the averaged resonant charge-exchange cross section, calculated for some excited states of nitrogen and oxygen atoms with the use of expressions (5), (6), and (12)–(14), are given in Tables V and VI. In the case of *s*-electron transfer, the calculation is reduced to the solution of the following transcendent equation:

$$\frac{\pi R_0^2}{2}=\frac{\pi}{2\gamma^2}\ln^2\left(\frac{B}{v}R_0^{(2/\gamma-1/2)}\right), \tag{16}$$

where v is the collision velocity and the parameter B depends on the asymptotic parameter A and on the quantum numbers of the valence electron, the atom and the ion. Since the magnitude of the cross section is determined by the values of parameters A and γ, the cross sections for states $O(ns\ ^3S)$ and $O(ns\ ^5S)$, which are characterized by similar values of these parameters, are close to each other. So the magnitudes of the cross section for the states $O(4s\ ^3S)$ and $O(5s\ ^3S)$ have not been presented.

The above-evaluated velocity dependencies of the resonant charge-exchange cross section for excited states of N and O atoms have been used for calculating the relevant transport cross section $\overline{\sigma^*}(T)$, which is determined by the known expressions

$$\overline{\sigma^*}(T)=\frac{1}{2}\int_0^{\infty}\sigma^*(x)e^{-x}x^2dx,\quad x=\frac{m_rv^2}{2kT}, \tag{17}$$

$$\sigma^*=\int_0^{\rho_0}2\pi(1-\cos\ \theta)\rho d\rho. \tag{18}$$

Here θ is the scattering angle and m_r is the reduced mass of the system. Neglecting the distortion of the rectilinear trajectory of the colliding particles, one obtains $\theta=\pi$ and $\sigma^*=2\sigma_t$.

In the frame of the approximation used, the magnitude σ^* with taking into account the relatively weak velocity dependence of the resonant charge-exchange cross section, is expressed by the following approximate relation [18,20,21],

TABLE V. The partial and averaged magnitudes of the resonant charge-exchange cross section ($10^{-16}\mathrm{cm}^2$) and the relevant transport cross sections, calculated for excited states of nitrogen on the basis of formulas (12) and (13) with the use of expressions (5) and (6).

State	Λ	I	Collision energy (eV)		
			0.1	1.0	10.0
			Collision velocity (10^5 cm/s)		
			1.66	5.24	16.6
N($4S$) ($\gamma=1.034$)	0	1/2	65.9	52.7	40.8
		3/2	73.3	60.0	47.8
		5/2	79.5	65.2	52.1
	1	1/2	47.0	36.7	27.9
		3/2	53.8	43.0	33.0
		5/2	57.9	46.6	36.4
		σ_t	61.5	49.5	39.0
		$\overline{\sigma^*}(T)$	108	72.5	65.6
N($2D3/2,5/2$) ($\gamma=0.945$)	0	1/2	62.2	50.8	39.5
		3/2	72.0	56.0	43.8
	1	1/2	36.3	23.3	15.9
		3/2	42.9	28.5	20.0
		σ_t	50.0	36.1	27.2
		$\overline{\sigma^*}(T)$	85.2	60.0	43.9
N($2P1/2,3/2$) ($\gamma=0.898$)	0	1/2	65.7	53.9	38.4
		3/2	75.7	61.9	46.7
	1	1/2	39.0	29.3	18.7
		3/2	44.6	33.4	23.6
		σ_t	52.8	41.2	29.0
		$\overline{\sigma^*}(T)$	90.3	67.4	47.5
N($2p23s$ $2P$) ($\gamma=0.53$)	0	1/2	404	332	265
		3/2	438	374	307
		σ_t	426	361	293
		$\overline{\sigma^*}(T)$	764	647	518
N($2p24s$ $2P$) ($\gamma=0.344$)	0	1/2	2690	2400	2130
		3/2	2870	2580	2270
		σ_t	2800	2520	2220
		$\overline{\sigma^*}(T)$	5280	4720	4160
N($2p25s$ $2P$) ($\gamma=0.25$)	0	1/2	4900	4300	3710
		3/2	5290	4670	4090
		σ_t	5160	4540	3970
		$\overline{\sigma^*}(T)$	9700	8520	7400
N($2p23s$ $4P$) ($\gamma=0.556$)	0	1/2	201	149	100
		3/2	233	179	129
		5/2	274	216	161
		σ_t	249	192	140
		$\overline{\sigma^*}(T)$	390	288	200
N($2p24s$ $4P$) ($\gamma=0.35$)	0	1/2	1770	1520	1300
		3/2	1910	1660	1440
		5/2	2000	1750	1520
		σ_t	1930	1690	1460
		$\overline{\sigma^*}(T)$	3670	3150	2680
N($2p25s$ $4P$) ($\gamma=0.26$)	0	1/2	4310	3780	3260
		3/2	4680	4090	3590
		5/2	4850	4290	3760
		σ_t	4710	4140	3620
		$\overline{\sigma^*}(T)$	8860	7740	6750

which is well justified for the high-energy region, where the elastic scattering is negligible in comparison with the resonant charge-exchange process,

$$\overline{\sigma^*}(T)=2\sigma_t(2.2v_T), \quad v_T=(2kT/m_r)^{1/2}. \tag{19}$$

The magnitudes of the transport cross section, calculated by the relations (17)–(19) for temperatures corresponding to the relevant collision energies, are also presented in the Tables V and VI. An evaluation of the contribution of elastic scattering on the $\mathrm{N}-\mathrm{N}^+$ ground-state interaction based on a polarizability model [22] shows that this contribution is less than 10% for $T \geqslant 10^4$ K, which is within the characteristic accuracy of the asymptotic approach applied. Moreover, recently, a polarizability approach was employed to estimate the dependence of diffusion (momentum-transfer) cross sections for $\mathrm{H}^+ + \mathrm{H}(n)$ on the principal quantum number [23]. The comparison of the corresponding collision integrals, up to $n=5$, with those of Ref. [2], based on charge-transfer cross sections, shows that elastic contribution is still of the order of 10%.

The data for the ground-state systems $\mathrm{N}^+ + \mathrm{N}$ and $\mathrm{O}^+ + \mathrm{O}$ are also compared in Table VII with the calculation data of Refs. [2,24,25], as well as experimental data [26], obtaining in general a satisfactory agreement. The same is also observed between the present calculations and the diffusion cross sections of low-lying excited states calculated in Ref. [2]. Note that in all cases the results of Ref. [2] underestimate the relevant cross sections.

It should be noted that the case (a) of Hund coupling is used throughout. A more careful analysis [18] of the interaction potentials acting, for example, in the case of $\mathrm{O}(^3P) - \mathrm{O}^+(^4S)$ shows that the scheme of angular-momentum coupling can change, depending on the collision energy, up to case (c) of Hund, opening to question the choice of the quantum numbers reported in Tables V and VI. However, the differences in the averaged cross sections do not strongly depend on the orbital and spin angular-momentum coupling selection, while the partial contribution can depend on the choice [27]. The present choice, which is similar to the one used in Refs. [2,24,25], gives results in satisfactory agreement with the experimental and theoretical ones [24–26], thus confirming the small dependence of charge-transfer cross sections on the coupling schemes. Note also that the

TABLE VI. The partial and averaged magnitudes of the resonant charge-exchange cross section (10^{-16} cm^2) and the relevant transport cross sections, calculated for excited states of oxygen on the basis of formulas (12) and (13) with the use of expressions (5) and (6).

State	Λ	I	Collision energy (eV)		
			0.1	1.0	10.0
			Collision velocity (10^5 cm/s)		
			1.55	4.9	15.5
$O(^3P)(\gamma=1.0)$	0	1/2	56.7	44.8	32.6
		3/2	63.8	51.3	39.5
		5/2	69.8	56.1	43.8
	1	1/2	39.0	29.0	21.1
		3/2	45.2	35.3	25.7
		5/2	49.8	38.7	28.8
		σ_t	52.9	41.1	30.8
		$\overline{\sigma}^*(T)$	88.4	67.5	51.5
$O(2p^3 3s\ ^5S)(\gamma=0.573)$	0	1/2	308	255	207
		3/2	344	286	233
		5/2	365	306	254
		7/2	381	320	268
		σ_t	367	312	261
		$\overline{\sigma}^*(T)$	664	558	462
$O(2p^3 4s\ ^5S)(\gamma=0.34)$	0	1/2	1890	1640	1390
		3/2	2060	1800	1530
		5/2	2160	1890	1630
		7/2	2240	1970	1700
		σ_t	2150	1870	1620
		$\overline{\sigma}^*(T)$	4020	3470	2980
$O(2p^3 5s\ ^5S)(\gamma=0.26)$	0	1/2	4240	3710	3200
		3/2	4590	4000	3520
		5/2	4780	4170	3690
		7/2	4940	4290	3840
		σ_t	4750	4150	3660
		$\overline{\sigma}^*(T)$	8950	7790	6890
$O(2p^3 3s\ ^3S)(\gamma=0.549)$	0	1/2	360	300	246
		3/2	400	336	276
		5/2	423	357	298
		σ_t	412	350	291
		$\overline{\sigma}^*(T)$	745	630	516

ratio of partial cross sections for the Σ states of $N(^4S)-N^+(^3P)$ interaction calculated in the present paper agree very well with the same results reported in Ref. [28], obtained by the Firsov approximation with Heitler-London potentials.

IV. DISCUSSION

The above-presented calculations show that this approach is a quite effective tool for solution of the complicated and time-consuming problem of evaluation of the resonant charge-exchange cross section for excited many-electron atoms. The accuracy of this approach is determined by the accuracy of the asymptotic representation of the single-electron wave function (3) and exchange interaction potential (5) and (6). The relative uncertainty of the calculated cross-section data is estimated as $(R_0\gamma)^{-1} \ll 1$, where R_0 is the solution of Eq. (16).

The second important simplification, which is inherent to all approaches to the determination of the resonant charge-exchange cross section, concerns the neglect of the change of the quantum number Λ during the collision. This allows a separate consideration of partial resonant charge-exchange cross sections related to various states of a quasimolecule, resulting in the averaging formula (14). This change can be due to the rotation of the molecular axis during the collision, which can promote the violation of the angular-momentum conservation law and a transition of a quasimolecule from one term to another. Therefore, strictly speaking, the collision processes related to specific quasimolecular state cannot be considered independently, which bears additional technical difficulties in calculating the cross section (see Refs. [18,20,21]).

One more source of a possible uncertainty of the calculation result relates to type of coupling of the valence electron orbital and spin angular momenta with those of ionic core, and also of the variety of possible states of the ion core. These issues are also analyzed in detail in Refs. [18,20,21]. Particularly, there has been stated that in the case of many-electron atoms with not fully filled outer electron shell the exchange interaction potential depends generally on the angle between the quantization axis and the axis of the quasimolecule. The specific form of this dependence is determined by the scheme of angular-momentum addition and therefore by the sort of the element under consideration. In these cases the exchange interaction potential is changing during the collision not only due to change in the internuclear distance, but also due to the rotation of the quasimolecular axis. However, the detailed analysis, presented in Refs. [18,20,21], shows a rather low sensitivity of the calculated resonant charge-exchange cross section to the choice of the electron coupling and to account for the angular dependence of the exchange interaction potential.

The influence of the resonant charge-exchange cross section involving excited atomic states on transport properties of an equilibrium low-temperature plasma can be established having the data about the equilibrium composition of the plasma under consideration as well as the scaling law for the dependence of the resonant charge-exchange cross section on the principal quantum number. These types of calculations have been performed recently for hot equilibrium hydrogen plasma [5], in which case the relevant scaling law for $H(n)+H^+$ and $H(n)+H(m)$ resonant electron transfer was determined on the basis of exact wave function. It is interesting to estimate the scaling law for the above-considered systems $N+N^+$ and $O+O^+$ and compare it with that for hydrogen obtained in [5].

As it follows directly from the expression (16) with taking into account the approximate relation (4), the scaling law for the resonant charge-exchange cross section involving highly excited atoms with $n=1/\gamma \gg 1$, is asymptotically close to the following expression:

TABLE VII. Comparison of averaged resonant charge-exchange cross section (10^{-16} cm^2) σ_t and transport cross sections $\overline{\sigma}^*(T)$ with data in the literature: Capitelli [2] (asterisk), Stallcop *et al.* [24,25] (in parentheses), and beam measurements [26] (square brackets).

State		Collision energy (eV)		
		0.1	1.0	10.0
N(^4S)	σ_t	61.5 (58.4)	49.5 (45.0)	39.0 (34.0) [34.4]
	$\overline{\sigma}^*(T)$	108 (106)	72.5 (80.9) 51.3*	65.6 (62.7)
N(^2D)	$\overline{\sigma}^*(T)$		60.0 46.8*	
N(^2P)	$\overline{\sigma}^*(T)$		67.4 55.0*	
O(^3P)	σ_t	52.9 (45.1)	41.1 (36.2)	30.8 (28.3)
	$\overline{\sigma}^*(T)$	88.4 (83.7)	67.5 (65.4) 40.8*	51.5 (51.7)

$$\sigma_t \sim n^\alpha, \quad \alpha \approx 4. \tag{20}$$

This dependence can be derived from the purely classical consideration of the resonant charge exchange process, in accordance with which the electron transfer is seen as an overbarrier transition, but not underbarrier tunneling, as in the case of the quantum consideration. The magnitude of the classical resonant charge-exchange cross section averaged over the quantum numbers ℓ and m is represented by the formula

$$\sigma_{cl} = 8\pi e^4/\varepsilon_H^2 = 32\pi e^4 n^4, \tag{21}$$

where $\varepsilon_H = 1/2n^2$ is the electron binding energy and n is the principal quantum number. The calculation data of Tables V and VI for $n=5$ are of the same order of magnitude as the classical values obtained by Eq. (21). The resonant charge exchange for higher excited atoms should be indeed treated as classical transition.

The fitting parameter α, determined on the basis of calculated cross-section data, ranges in a rather wide interval between 3.0 and 5.0, while the parameter α determined on the basis of $H(n)-H^+$ transport cross sections [5] is about 2.7. Therefore, the use of the scaling law (20) for evaluating the transport characteristics of plasma with taking into account excited atomic states is hardly justified, and state to state calculation is necessary for this purpose.

V. CONCLUSIONS

The present results represent to the best of our knowledge the first calculation on the resonant charge transfer cross sections involving excited atomic states for air components with principal quantum number different from the ground state.

These results have been calculated by using the Firsov approximation for charge-transfer cross section and the asymptotic method for the differences of gerade-ungerade potential energy curves. The method has been tested by comparing the results for ground and low-lying excited states. The results show a dramatic increase of resonant charge-transfer cross section with the principal quantum number of the excited electron, confirming old calculations of resonant charge-transfer cross sections for excited atomic hydrogen.

The obtained charge-transfer cross sections have been used to derive diffusion-type collision integrals (transport cross sections) of the systems $O^* + O^+$ and $N^* + N^+$. Work is now in progress to use these data in determining the contribution of excited states on transport properties (viscosity and thermal conductivity) of nitrogen and oxygen plasmas.

ACKNOWLEDGMENTS

One of the authors (A.V. Eletskii) thanks the CNR-NATO Outreach Program, which supported his stay at the Bari University. The present paper has been partially supported by MIUR (cof.2003 Project No. 2003037912_010).

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