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Resonant charge exchange involving electronically excited states of nitrogen atoms and ions

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Within the framework of the asymptotic theory the matrices for the exchange interaction potentials of the nitrogen ion, with electron shell p^2, and nitrogen atom, with electron shell p^3, are constructed. The hierarchy of interactions in the nitrogen molecular ion at large internuclear distances is constructed for different electronic states. On the basis of these interaction potentials, the cross sections of resonant charge exchange in slow collisions are evaluated for different values of electron momentum projections and then averaged over these momentum projections. The mobilities of nitrogen ions in atomic nitrogen are also derived.

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I. INTRODUCTION

Transport coefficients of equilibrium and nonequilibrium plasmas have been widely studied in these years due to their importance in determining the properties of high enthalpy flows. The relevant properties (thermal and electrical conductivity, viscosity) are usually determined by using higher order approximations of the Chapman-Enskog method applied to the mixture of electrons, ions, and neutral species. To apply the method one must insert in the relevant equations the composition of the plasma which can be calculated by using the Saha equation for thermal plasmas and kinetic methods for nonequilibrium conditions. In both cases electronically excited states determine the plasma composition through the partition function in the equilibrium case and through the collisional radiative models in the nonequilibrium conditions. On the other hand electronically excited states disappear in the equations for the transport coefficients of plasmas essentially for two reasons. The first one is their low concentration and the second one is the poor knowledge of the transport cross sections of electronically excited states. These two assumptions are a little contradictory considering that the transport cross sections of electronically excited states should present values strongly exceeding the corresponding ones for the ground state so that small concentrations of electronically excited states with their enormous cross sections can play an important role in affecting the transport coefficients of plasmas. These considerations pushed us to consider the role of electronically excited states characterized by principal quantum numbers different from the ground state in affecting the transport coefficients of partially ionized hydrogen mixture [1,2]. Extension of these ideas to air plasmas generates a complication due to the presence in these media of metastable states for both O and N atoms and ions belonging to the same principal quantum number of the ground states. Metastable states are in any case strongly populated under equilibrium and nonequilibrium conditions so that an effort has been made in the past to calculate their transport cross sections. In particular, diffusion cross sections, those controlled by charge transfer cross sections, were calculated for both N and O systems by one of us [3,4] by using the Firsov approximation in combination with the gerade-ungerade splitting of the relevant potential curves [5]. The accuracy of these potentials, obtained by a quantum mechanical configuration interaction method, can be considered unsatisfactory taking into account that these calculations were performed at small internuclear distances. Recently the charge transfer cross sections involving N and O atoms and ions [6–8] were evaluated in the framework of the asymptotic theory by using various models. In particular the calculations in Ref. [6] do consider the *s*-*s* electron transfer without taking into account the coupling of angular and spin momenta. Resonant charge exchange cross sections involving nitrogen atoms and ions, in the ground and first excited states, are calculated in the present work [9–11], allowing the fine structure of nitrogen atoms. The asymptotic theory uses a small parameter according to which electron transitions have a tunnel character and proceed at large impact parameters. Therefore for the cross-section calculation it is necessary first to determine the behavior of the electron terms of an interacting ion and atom going beyond the standard Hund method [12,13], as is done for the halogen [14,15] and oxygen [7] molecular ions.

II. PARAMETERS OF VALENCE ELECTRONS FOR NITROGEN ATOM

We represent the wave function of valence electrons within the framework of the parentage scheme [16–18], dividing the atom into one valence electron and an atomic core. The valence electron is described by the quantum num-

TABLE I. The parentage coefficients for the nitrogen atom.

	Atom state		
Ion state	^4S	^2D	^2P
^3P	1	$\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$
^1D	0	$-\frac{1}{\sqrt{2}}$	$-\sqrt{\frac{5}{18}}$
^1S	0	0	$\frac{\sqrt{2}}{3}$

TABLE II. The values of the parameter γ for the nitrogen atom with the electron shell p^3 depending on the atom and core states.

	Atom state		
Ion state	^4S	^2D	^2P
^3P	1.034	0.945	0.897
^1D		1.016	0.972
^1S			1.050

bers $l_e=1,\mu,1/2,\sigma$, the orbital momentum, its projection on a given axis, the electron spin, and its projection on the quantization axis; the corresponding quantum numbers are l,m_l,s,m_s for the atomic core and L,M_L,S,M_S for the atom. We can write the atom wave function as [16–18]

$$\Phi_{LSM_LM_S}(1,2,\ldots,n)=\frac{1}{\sqrt{n}}\hat{P}\sum_{lm_lsm_s\mu\sigma}G_{ls}^{LS}(l_e,n)\begin{bmatrix} l_e & l & L\\ \mu & m_l & M_L\end{bmatrix}\times\begin{bmatrix} \frac{1}{2} & s & S\\ \sigma & m_s & M_S\end{bmatrix}\times\varphi_{l_e1/2\mu\sigma}(1)\psi_{lsm_lm_s}(2,\ldots,n), \qquad (1)$$

where Φ, ψ, and φ are the wave functions of the atom, ion, and valence electron with indicated quantum numbers, respectively, the operator $\hat{P}$ permutes n valence electrons of the atom, and the parentage coefficient $G_{ls}^{LS}(l_e,n)$ is responsible for the addition of a valence electron to an ion for construction of an atom for given quantum numbers of these atomic particles. This representation of the atom wave function corresponds to the *LS*-coupling scheme and is valid for light atoms. Corresponding parentage coefficients for the nitrogen atom are given in Table I [19].

In analyzing the asymptotic properties of the atom, we remove one electron from the p^2 core taking into account the fine structure. The asymptotic form of the radial electron wave function has the standard form [20,21]

$$\psi(r)=Ar^{1/\gamma-1}e^{-r\gamma},\quad r\gamma\gg 1, \qquad (2)$$

where r is the distance of the jumping electron from the nucleus, A is the asymptotic coefficient, and $-\gamma^2/2$ is the binding energy of the valence electron. Tables II and III give the parameters of this formula for the valence electron of the nitrogen atom depending on the state of core valence electrons. The values of the asymptotic coefficient A are evaluated by the standard method [9,10], matching the asymptotic wave functions (2) with the numerical evaluations of the wave functions [22] in the range of large distances between nuclei, where the asymptotic expressions (2) are valid.

TABLE III. The values of the asymptotic coefficients A for the nitrogen atom with the electron shell p^3 depending on the atom and core states.

	Atom states		
Ion states	^4S	^2D	^2P
^3P	2	1.4	1.1
^1D		1.9	1.7
^1S			2.3

TABLE IV. Diagonal matrix elements of the quadrupole moment, expressed in $e a_0^2\overline{r^2}$ units, for a nitrogen atom core with the electron shell $2p^2$ ($\overline{r^2}$ is the average square for the electron orbit of a valence electron).

State of atom rest	^3P $m=0$	^3P $m=\pm 1$	^1D $m=0$	^1D $m=\pm 1$	^1D $m=\pm 2$
$\langle lm\vert\Sigma_{i=1}^{n-1}\hat{q}_i\vert lm\rangle$	$-\frac{4}{5}$	$\frac{2}{5}$	$\frac{4}{5}$	$\frac{2}{5}$	$-\frac{4}{5}$

The asymptotic wave function allows us to find the exchange interaction potential that is determined by transition of one electron. The one-electron exchange interaction potential, the difference of the gerade and ungerade energies of this electron, is given by [10,23]

$$\Delta(R)=2\langle\psi_1|\hat{H}|\psi_2\rangle-2\langle\psi_1|\hat{H}|\psi_1\rangle\langle\psi_1|1|\psi_2\rangle. \qquad (3)$$

Here ψ_1 is the wave function of the valence electron located near the first core, and ψ_2 corresponds to electron location near the second nucleus, $\hat{H}$ is the one-electron Hamiltonian. An accurate evaluation of this interaction requires the accurate wave functions of this electron when its interaction with both cores is comparable [20]. Accounting for this fact, we obtain the following expression for one-electron exchange interaction potential [10,23–25]:

$$\Delta_{l_e\mu}(R)=A^2R^{2/\gamma-1-|\mu|}e^{-R\gamma-1/\gamma}\frac{(2l_e+1)(l_e+|\mu|)!}{(l_e-|\mu|)!|\mu|!(\gamma)^{|\mu|}}. \qquad (4)$$

Here R is the distance between nuclei. In the case under consideration, if one p-electron is located in the field of structureless cores, this exchange interaction potential de-

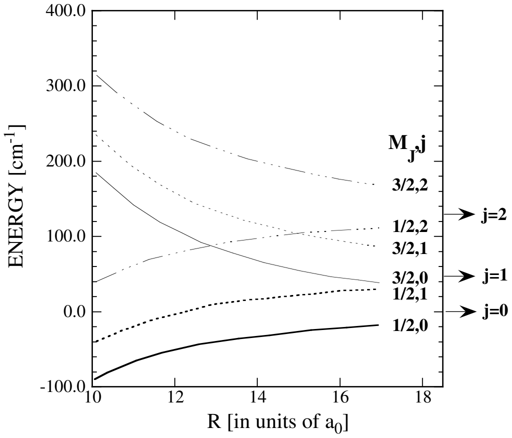

FIG. 1. Electronic terms of N_2^+ correlating with $N(^2P)+N^+(^3P)$ at large distances, which determine the resonant charge exchange cross section for these species.

TABLE V. Diagonal matrix elements of the quadrupole moment Q_{MM}, expressed in ea_0^2 units, for a nitrogen atom core with the electron shell $2p^3$.

State	^2D, $M=0$	^2D, $M=\pm1$	^2D, $M=\pm2$	^2P, $M=0$	^2P, $M=\pm1$	^4S
Q_{MM}	0	0	0	–0.53	1.066	0

pends on the electron momentum projection onto the molecular axis [10,23–25], and can be written

$$\Delta_{10}(R) = 3A^2 R^{2/\gamma-1} e^{-R\gamma-1/\gamma}; \quad \Delta_{1,\pm1}(R) = \frac{2}{R\gamma}\Delta_{10}(R). \quad (5)$$

III. QUADRUPOLE MOMENT OF NITROGEN ATOM

The main part of ion-atom interaction in the case of the molecular nitrogen ion at large distances between nuclei relates to the interaction of the ion charge and atom quadrupole moment, so that one should determine the quadrupole moment of the nitrogen atom in lowest excited states. The operator of atom quadrupole momentum $\hat{Q}$ can be expressed as the sum of quadrupole momenta operators of individual electrons $\hat{q}_i$

$$\hat{Q} = \sum_{i=1}^{n} \hat{q}_i. \quad (6)$$

Hence on the basis of the wave function of valence electrons (1) of the nitrogen atom, we obtain for its quadrupole momentum

$$Q_{LM_L} = \langle LM_L | \sum_i \hat{q}_i | LM_L \rangle = \langle LM_L | \sum_{i=1}^{n-1} \hat{q}_i + \hat{q}_n | LM_L \rangle, \quad (7)$$

where the atom quadrupole momentum is divided into two parts, for an atom core and a valence electron. Using the wave function (1) and the normalization condition for spin wave functions, we obtain

$$Q_{LM_L} = \sum_{ls} (G_{ls}^{LS})^2 \sum_{m_l,\mu} \begin{bmatrix} l_e & l & L \\ \mu & m_l & M_L \end{bmatrix}^2 \times \left(\langle lm_l | \sum_{i=1}^{n-1} \hat{q}_i | lm_l \rangle + \langle l_e\mu | \hat{q}_n | l_e\mu \rangle \right). \quad (8)$$

TABLE VI. Character of the hierarchy of interactions between the nitrogen atom with the electron shell p^3 and nitrogen ion p^2 at large separations.

	Atom state		
Ion state	^4S	^2D	^2P
^3P	"c"-Hund case	"c"-Hund case	Quadrupole and spin-orbit
^1D		"a"-Hund case	"a"-Hund case
^1S			"a"-Hund case

Table IV gives the quadrupole moments of a nitrogen atom core with the electron shell p^2. We consider the quadrupole interaction between an ion and a nitrogen atom according to the second expansion term of ion charge-valence electron interaction $e^2/R - \langle e^2/|\mathbf{R}-\mathbf{r}|\rangle$ over a small parameter r/R, where $\mathbf{r}$ is a valence electron coordinate in its atom, and $\mathbf{R}$ is a distance between an ion of charge e and atom nucleus, an average is made over the wave function of a valence electron. We have for the quadrupole moment of an individual electron [26]

$$q = 2\langle r^2 P_2 \cos\theta \rangle = 2\frac{l_e(l_e+1)-3\mu^2}{(2l_e-1)(2l_e+3)}\overline{r^2}, \quad (9)$$

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

Therefore for one valence p-electron the quadrupole moment is [26]

$$\langle 10|\hat{q}|10\rangle = \frac{4}{5}ea_0^2\overline{r^2}, \quad \langle 11|\hat{q}|11\rangle = \langle 1,-1|\hat{q}|1,-1\rangle = -\frac{2}{5}ea_0^2\overline{r^2}, \quad (10)$$

where an average over a distance r of a valence electron from the atom nucleus is made with the wave function of the valence electron. Thus the quadrupole moment of the nitrogen atom with the electron valence shell p^3 is given by the formula

$$Q_{LM_L} = \sum_{ls} (G_{ls}^{LS})^2 \sum_{m_l} \begin{bmatrix} l_e & l & L \\ M_L - m_l & m & M_L \end{bmatrix}^2 q_{lm_l}^{(2)} + \sum_{ls} (G_{ls}^{LS})^2 \sum_{\mu} \begin{bmatrix} l_e & l & L \\ \mu & M_L-\mu & M_L \end{bmatrix}^2 q_{1\mu}, \quad (11)$$

where we extract in formula (11) the quadrupole moment of a two-electron system $q_{lsm_l}^{(2)}$ and one electron $q_{1\mu}$, so that values of quadrupole momenta for the two-electron system are given in Table IV, and for one valence electron they are given in formula (9).

IV. HIERARCHY OF INTERACTIONS BETWEEN NITROGEN ATOMIC IONS AND NITROGEN ATOMS AT LARGE SEPARATIONS

The experience for halogen [14,15] and oxygen [7] molecular ions shows that after exchange interaction, that chooses the quantum numbers L,S,l,s, the main interactions are the quadrupole interaction of the ion charge with the quadrupole atom moment and the spin-orbit interaction. The latter interactions mix the fine states or states with the orbital

TABLE VII. Exchange interaction potential for the ground state of the quasimolecule $N^+(^3P)+N(^4S)$ at given quantum numbers J, M_J of the atom and j, m_j of the ion.

$\frac{jm_j}{JM_J}$	2,2	2,1	2,0	1,1	1,0	0,0
$\frac{3}{2},\frac{3}{2}$	Δ_{11}	$\frac{1}{2}\Delta_{10}$	$\frac{\sqrt{2}}{3}\Delta_{10}$	$\frac{1}{2}\Delta_{10}$	$\frac{1}{2}\Delta_{11}$	$\frac{1}{3}\Delta_{11}$
$\frac{3}{2},\frac{1}{2}$	$\left(\frac{1}{3}+\frac{1}{\sqrt{3}}\right)\Delta_{11}$	$\left(\frac{1}{6}+\frac{\sqrt{2}}{3}\right)\Delta_{10}$	$\left(\frac{4}{9}+\frac{\sqrt{\frac{2}{3}}}{3}\right)\Delta_{10}$	$\frac{1}{6}\Delta_{10}$	$\left(\frac{1}{6}+\frac{1}{3\sqrt{2}}+\frac{1}{\sqrt{6}}\right)\Delta_{11}$	$\frac{2}{9}\Delta_{10}$
$\frac{3}{2},-\frac{1}{2}$	$\left(\frac{1}{3}+\frac{1}{3\sqrt{2}}\right)\Delta_{11}$	$\left(\frac{\sqrt{\frac{2}{3}}}{3}+\frac{1}{2\sqrt{3}}\right)\Delta_{10}$	$\left(\frac{4}{9}+\frac{\sqrt{\frac{2}{3}}}{3}\right)\Delta_{10}$	$\frac{-1}{2\sqrt{3}}\Delta_{10}$	$\left(\frac{1}{6}+\frac{1}{3\sqrt{2}}+\frac{1}{\sqrt{6}}\right)\Delta_{11}$	$\frac{2}{9}\Delta_{10}$
$\frac{3}{2},-\frac{3}{2}$	$\frac{1}{3\sqrt{2}}\Delta_{11}$	$\frac{1}{2\sqrt{3}}\Delta_{10}$	$\frac{\sqrt{2}}{3}\Delta_{10}$	$\frac{-1}{2\sqrt{3}}\Delta_{10}$	$\frac{1}{2}\Delta_{11}$	$\frac{1}{3}\Delta_{11}$

momentum projection onto the molecular axis, and this case becomes more complicated than standard Hund cases. However, the quadrupole momentum is zero for many states of the nitrogen atom with the electron shell p^3 (see Table V) so that the hierarchy of interactions becomes more simple.

Table VI gives the character of interactions inside the molecular nitrogen ion, at large distances between nuclei, for states when one-electron transition from the field of one core to another one is considered. In the $N^+(^3P)-N(^2P)$ case the interaction between the ion charge and atom quadrupole moment is comparable to the fine splitting of ion levels. Therefore the quantum numbers of the molecular ion are LSM_Llsj, where the quantum number j, the total angular momentum of the ion, accounts for the spin-orbit interaction. For $N^+(^3P)$

TABLE VIII. Exchange interaction potential for the quasimolecule $N^+(^3P)+N(^2D)$ at given quantum numbers J, M_J of the atom and j, m_j of the ion.

$\frac{jm_j}{JM_J}$	2,2	2,1	2,0	1,1	1,0	0,0
$\frac{5}{2},\frac{5}{2}$	Δ_{11}	$\frac{3}{2}\left(\frac{1}{6}+\frac{1}{\sqrt{5}}\right)\Delta_{11}$	$\frac{3+\sqrt{2}}{2\sqrt{30}}\Delta_{11}$	$\frac{1}{4}\Delta_{11}$	$\frac{1}{2\sqrt{10}}\Delta_{11}$	0
$\frac{5}{2},\frac{3}{2}$	$\frac{2}{5}\Delta_{10}$	$\frac{3}{2}\left(\frac{1}{15}+\frac{\sqrt{2}}{5}\right)\Delta_{10}$	$\frac{3\sqrt{3}}{10}\Delta_{10}$	$\frac{1}{10}\Delta_{10}$	$\frac{1}{10}\Delta_{10}$	0
$\frac{5}{2},\frac{1}{2}$	$\frac{3}{5\sqrt{2}}\Delta_{10}$	$\frac{3}{2}\left(\frac{3}{10}+\frac{1}{5\sqrt{3}}\right)\Delta_{10}$	$\frac{3(\sqrt{6}+3)}{10\sqrt{6}}\Delta_{10}$	$\frac{3}{20}\Delta_{10}$	$\frac{\sqrt{2}+1}{10\sqrt{2}}\Delta_{10}$	0
$\frac{5}{2},-\frac{1}{2}$	$\frac{3}{5\sqrt{3}}\Delta_{10}$	$\frac{3}{2}\cdot\frac{\sqrt{3}+1}{\sqrt{2}}\Delta_{10}$	$\frac{3(\sqrt{6}+3)}{10\sqrt{6}}\Delta_{10}$	$\frac{\sqrt{2}}{10}\Delta_{10}$	$\frac{\sqrt{2}+1}{10\sqrt{2}}\Delta_{10}$	0
$\frac{5}{2},-\frac{3}{2}$	$\frac{1}{5}\Delta_{10}$	$\frac{3+2\sqrt{2}}{10\sqrt{2}}\Delta_{10}$	$\frac{3\sqrt{3}}{10}\Delta_{10}$	$\frac{1}{10\sqrt{2}}\Delta_{10}$	$\frac{1}{10}\Delta_{10}$	0
$\frac{5}{2},-\frac{5}{2}$	$\frac{1}{2\sqrt{10}}\Delta_{11}$	$\frac{\sqrt{5}}{4\sqrt{2}}\Delta_{11}$	$\frac{3+\sqrt{2}}{2\sqrt{30}}\Delta_{11}$	$\frac{1}{4\sqrt{10}}\Delta_{11}$	$\frac{1}{2\sqrt{10}}\Delta_{11}$	0
$\frac{3}{2},\frac{3}{2}$	$\frac{1}{10}\Delta_{10}$	$\frac{\sqrt{3}+2}{40\sqrt{3}}\Delta_{10}$	$\left(\frac{1}{20\sqrt{2}}+\frac{\sqrt{2}}{30}\right)\Delta_{10}$	$\frac{1}{40}\Delta_{10}$	$\frac{-3}{20\sqrt{6}}\Delta_{10}$	$\frac{1}{3}\Delta_{11}$
$\frac{3}{2},\frac{1}{2}$	$\frac{1}{20\sqrt{3}}\Delta_{10}$	$\frac{2+\sqrt{2}}{120\sqrt{2}}\Delta_{10}$	$\frac{\sqrt{6}-3}{180\sqrt{6}}\Delta_{10}$	$\left(\frac{49}{120}-\frac{3}{20\sqrt{6}}\right)\Delta_{10}$	$\left(\frac{7\sqrt{2}+6}{40}\right)\Delta_{10}$	$\frac{5}{18}\Delta_{10}$
$\frac{3}{2},-\frac{1}{2}$	$\left(\frac{3}{10\sqrt{2}}-\frac{\sqrt{2}}{15}\right)\Delta_{10}$	$\frac{-3\sqrt{2}-10}{120\sqrt{6}}\Delta_{10}$	$\frac{\sqrt{6}-3}{180\sqrt{6}}\Delta_{10}$	$\frac{14\sqrt{3}-7\sqrt{2}}{40\sqrt{6}}\Delta_{10}$	$\left(\frac{7\sqrt{2}+6}{40}\right)\Delta_{10}$	$\frac{5}{18}\Delta_{10}$
$\frac{3}{2},-\frac{3}{2}$	$\frac{-1}{20}\Delta_{10}$	$\frac{-2\sqrt{3}-1}{40\sqrt{3}}\Delta_{10}$	$\left(\frac{1}{20\sqrt{2}}+\frac{\sqrt{2}}{30}\right)\Delta_{10}$	$\frac{-7}{40\sqrt{3}}\Delta_{10}$	$\frac{-3}{20\sqrt{6}}\Delta_{10}$	$\frac{1}{3}\Delta_{11}$

TABLE IX. Exchange interaction potential for the quasimolecule $N^+(^1D)+N(^2D)$ at given quantum numbers JM_J of the atom and jm_j of the ion.

$\frac{jm_j}{JM_J}$	2,2	2,1	2,0
$\frac{5}{2},\frac{5}{2}$	Δ_{10}	$\frac{1}{\sqrt{5}}\Delta_{10}$	$\frac{3\sqrt{2}}{2\sqrt{15}}\Delta_{11}$
$\frac{5}{2},\frac{3}{2}$	$\left(\frac{1}{5}+\frac{1}{\sqrt{5}}\right)\Delta_{10}$	$\left(\frac{1}{5}+\frac{\sqrt{2}}{10}\right)\Delta_{10}$	$\frac{3(2+\sqrt{3})}{10}\Delta_{11}$
$\frac{5}{2},\frac{1}{2}$	$\frac{\sqrt{2}}{10}\Delta_{10}$	$\frac{1}{10}\Delta_{10}$	$\frac{3}{2}\left(\frac{1}{5}+\frac{1}{5}\sqrt{\frac{3}{2}}+\frac{2}{5\sqrt{3}}+\frac{\sqrt{3}}{5}\right)\Delta_{11}$
$\frac{5}{2},-\frac{1}{2}$	$-\frac{1}{2}\sqrt{\frac{2}{5}}\Delta_{10}$	$\frac{-\sqrt{2}}{10}\Delta_{10}$	$\frac{3}{2}\left(\frac{1}{5}+\frac{1}{5}\sqrt{\frac{3}{2}}+\frac{2}{5\sqrt{3}}+\frac{\sqrt{3}}{5}\right)\Delta_{11}$
$\frac{5}{2},-\frac{3}{2}$	$\left(-\frac{1}{5}-\frac{1}{\sqrt{5}}\right)\Delta_{10}$	$\frac{-\sqrt{2}-2}{10}\Delta_{10}$	$\frac{3(2+\sqrt{3})}{10}\Delta_{11}$
$\frac{5}{2},-\frac{5}{2}$	$-\frac{1}{\sqrt{5}}\Delta_{10}$	$-\frac{1}{2}\sqrt{\frac{2}{5}}\Delta_{10}$	$\frac{3\sqrt{2}}{2\sqrt{15}}\Delta_{11}$
$\frac{3}{2},\frac{3}{2}$	$\frac{4}{5}\Delta_{10}$	$\frac{3}{2}\left(\frac{1}{30}+\frac{2}{5\sqrt{3}}\right)\Delta_{10}$	$\frac{3}{2}\left(\frac{1}{10}+\frac{1}{5\sqrt{2}}+\frac{\sqrt{2}}{5}\right)\Delta_{11}$
$\frac{3}{2},\frac{1}{2}$	$\frac{\sqrt{3}}{5}\Delta_{10}$	$\frac{3}{20}\Delta_{10}$	$\frac{3}{2}\left(\frac{3}{10}+\frac{1}{5}\sqrt{\frac{3}{2}}+\frac{\sqrt{2}}{5}\right)\Delta_{11}$
$\frac{3}{2},-\frac{1}{2}$	$\left(\frac{3}{10}+\frac{3}{10\sqrt{2}}\right)\Delta_{11}$	$\frac{-3}{20\sqrt{3}}\Delta_{10}$	$\frac{3}{2}\left(\frac{3}{10}+\frac{1}{5}\sqrt{\frac{3}{2}}+\frac{\sqrt{2}}{5}\right)\Delta_{11}$
$\frac{3}{2},-\frac{3}{2}$	$-\frac{1}{5}\Delta_{10}$	$\frac{3}{2}\left(-\frac{2}{15}-\frac{1}{10\sqrt{3}}\right)\Delta_{10}$	$\frac{3}{2}\left(\frac{1}{10}+\frac{1}{5\sqrt{2}}+\frac{\sqrt{2}}{5}\right)\Delta_{11}$

$-N(^4S)$ and $N^+(^3P)-N(^2D)$ interactions the same quantum numbers apply in the whole range of internuclear distances, but a splitting over the quantum number M_L is determined by the ion-atom exchange interaction. In the case of interactions $N^+(^1D)-N(^2D)$, $N^+(^1D)-N(^2P)$, and $N^+(^1S)-N(^2P)$ the selected quantum numbers in the asymptotic region are LSM_Lls.

Thus, neglecting ion-atom exchange interaction, N_2^+ electronic terms at large separations are determined by ion and atom fine states only when the quadrupole atom moment is

TABLE X. Exchange interaction potential for the quasimolecule $N^+(^3P)+N(^2P)$ at given quantum numbers JM_J of the atom and jm_j of the ion.

$\frac{jm_j}{JM_J}$	2,2	2,1	2,0	1,1	1,0	0,0
$\frac{3}{2},\frac{3}{2}$	$\frac{1}{2}\Delta_{10}$	$\left(\frac{1}{8}+\frac{1}{4\sqrt{3}}\right)\Delta_{10}$	$\frac{-1}{12\sqrt{2}}\Delta_{10}$	$\frac{1}{8}\Delta_{10}$	$\frac{1}{4\sqrt{6}}\Delta_{10}$	0
$\frac{3}{2},\frac{1}{2}$	$\frac{1}{4\sqrt{3}}\Delta_{10}$	$\left(\frac{1}{24}+\frac{1}{12\sqrt{2}}\right)\Delta_{10}$	$\left(\frac{1}{36}-\frac{1}{12\sqrt{6}}\right)\Delta_{10}$	$\left(\frac{1}{24}+\frac{1}{4\sqrt{6}}\right)\Delta_{10}$	$\left(\frac{1}{12}+\frac{1}{12\sqrt{2}}\right)\Delta_{10}$	$\frac{1}{18}\Delta_{10}$
$\frac{3}{2},-\frac{1}{2}$	$-\frac{1}{6\sqrt{2}}\Delta_{10}$	$\left(\frac{-1}{8\sqrt{3}}-\frac{1}{12\sqrt{6}}\right)\Delta_{10}$	$\left(\frac{1}{36}-\frac{1}{12\sqrt{6}}\right)\Delta_{10}$	$\left(\frac{1}{12\sqrt{2}}+\frac{1}{8\sqrt{3}}\right)\Delta_{10}$	$\left(\frac{1}{12}+\frac{1}{12\sqrt{2}}\right)\Delta_{10}$	$\frac{1}{18}\Delta_{10}$
$\frac{3}{2},-\frac{3}{2}$	$-\frac{1}{4}\Delta_{10}$	$\left(\frac{-1}{4}-\frac{1}{16\sqrt{3}}\right)\Delta_{10}$	$\frac{-1}{12\sqrt{2}}\Delta_{10}$	$\frac{1}{8\sqrt{3}}\Delta_{10}$	$\frac{1}{4\sqrt{6}}\Delta_{10}$	0
$\frac{1}{2},\frac{1}{2}$	$\frac{1}{12}\Delta_{11}$	$\frac{1}{12}\Delta_{10}$	$\left(\frac{1}{18}+\frac{1}{6\sqrt{6}}\right)\Delta_{10}$	$\frac{1}{12}\Delta_{10}$	$\left(\frac{1}{6}-\frac{1}{6\sqrt{2}}\right)\Delta_{10}$	$\frac{1}{9}\Delta_{10}$
$\frac{1}{2},-\frac{1}{2}$	$\frac{1}{12}\Delta_{11}$	$\frac{1}{6\sqrt{6}}\Delta_{10}$	$\left(\frac{1}{18}+\frac{1}{6\sqrt{6}}\right)\Delta_{10}$	$\frac{-1}{6\sqrt{2}}\Delta_{10}$	$\left(\frac{1}{6}-\frac{1}{6\sqrt{2}}\right)\Delta_{10}$	$\frac{1}{9}\Delta_{10}$

zero. In the case of the $N(^2P)+N^+(^3P)$ system, the atom quadrupole moment is not zero, but spin-orbit interaction for the atom can be neglected, being comparable with the ion-atom exchange interaction potential ($\Delta \sim 10\ \mathrm{cm}^{-1}$). Hence the energy levels $\varepsilon(R)$ can be expressed as

$$\varepsilon(R) = \delta_i + \frac{Q_{MM}}{R^3}, \tag{12}$$

where δ_i is a given fine level of the ion. The second term represents the ion-quadrupole interaction, being Q_{MM} the quadrupole moment of the atom for a given projection M of the electron orbital momentum (see Table V). In Fig. 1 the corresponding electronic terms are reported. It should be noted that quantum numbers of the molecular nitrogen ion at large distances between nuclei differ from those at intermediate distance [27], due to a different hierarchy of interactions.

V. EXCHANGE INTERACTION POTENTIAL INVOLVING NITROGEN ATOMS AND ATOMIC IONS

In constructing the ion-atom exchange interaction potential, we start from "a" Hund case when quantum numbers of atom and ions are, respectively, LSM_LM_S and lsm_lm_s. In this basis the ion-atom exchange interaction potential (3) presents the following form [10,28–30]:

$$\Delta_{LSM_LM_Slsm_lm_s}(R) = n(G_{ls}^{LS})^2 \sum_{\mu,\sigma,\sigma'} \begin{bmatrix} l_e & l & L \\ \mu & M_L-\mu & M_L \end{bmatrix} \times \begin{bmatrix} \frac{1}{2} & s & S \\ \sigma & M_S-\sigma & M_S \end{bmatrix} \times \begin{bmatrix} l_e & l & L \\ \mu & m_l & m_l+\mu \end{bmatrix} \times \begin{bmatrix} \frac{1}{2} & s & S \\ \sigma' & m_s & m_s+\sigma' \end{bmatrix} \Delta_{l_e\mu}(R). \tag{13}$$

TABLE XI. Exchange interaction potential for the quasimolecule $N^+(^1D)+N(^2P)$ and $N^+(^1S)+N(^2P)$ at given quantum numbers JM_J of the atom and jm_j of the ion.

$\frac{jm_j}{JM_J}$	^1D 2,2	^1D 2,1	^1D 2,0	^1S 0,0
$\frac{3}{2},\frac{3}{2}$	$\frac{1}{2}\Delta_{11}$	$\frac{1}{4}\Delta_{10}$	$\frac{1}{3\sqrt{2}}\Delta_{10}$	Δ_{11}
$\frac{3}{2},\frac{1}{2}$	$\left(\frac{1}{6}+\frac{1}{2\sqrt{3}}\right)\Delta_{11}$	$\left(\frac{1}{12}+\frac{1}{3\sqrt{2}}\right)\Delta_{10}$	$\left(\frac{2}{9}+\frac{1}{3\sqrt{6}}\right)\Delta_{10}$	$\frac{2}{3}\Delta_{10}$
$\frac{3}{2},-\frac{1}{2}$	$\left(\frac{1}{6}+\frac{1}{6\sqrt{2}}\right)\Delta_{11}$	$\left(\frac{1}{3\sqrt{6}}+\frac{1}{4\sqrt{3}}\right)\Delta_{10}$	$\left(\frac{2}{9}+\frac{1}{3\sqrt{6}}\right)\Delta_{10}$	$\frac{2}{3}\Delta_{10}$
$\frac{3}{2},-\frac{3}{2}$	$\frac{1}{6\sqrt{2}}\Delta_{11}$	$\frac{1}{4\sqrt{3}}\Delta_{10}$	$\frac{1}{3\sqrt{2}}\Delta_{10}$	Δ_{11}
$\frac{1}{2},\frac{1}{2}$	$\frac{1}{3}\Delta_{11}$	$\frac{1}{6}\Delta_{10}$	$\left(\frac{1}{9}+\frac{1}{3\sqrt{6}}\right)\Delta_{10}$	$\frac{1}{3}\Delta_{10}$
$\frac{1}{2},-\frac{1}{2}$	$\frac{1}{6}\Delta_{11}$	$\frac{1}{3\sqrt{6}}\Delta_{10}$	$\left(\frac{1}{9}+\frac{1}{3\sqrt{6}}\right)\Delta_{10}$	$\frac{1}{3}\Delta_{10}$

It is more convenient to rewrite this exchange interaction potential in the basis $LSJM_Jlsjm_j$, where JM_J are the total atom momentum and its projection onto molecular axis, and jm_j are the corresponding ion quantum numbers. Using the connection between the wave functions in these bases, we obtain the ion-atom exchange interaction potential at large separations in the basis $LSJM_Jlsjm_j$ in the form

$$\Delta_{JM_Jjm_j}(R) = n(G_{ls}^{LS})^2 \sum_{\mu,\sigma,} \sum_{M_L,M_S} \sum_{m_l,m_s} \begin{bmatrix} l_e & l & L \\ \mu & M_L-\mu & M_L \end{bmatrix} \times \begin{bmatrix} l_e & l & L \\ \mu & m_l & m_l+\mu \end{bmatrix} \begin{bmatrix} \frac{1}{2} & s & S \\ \sigma & M_S-\sigma & M_S \end{bmatrix} \times \begin{bmatrix} \frac{1}{2} & s & S \\ \sigma & m_s & m_s+\sigma \end{bmatrix} \begin{bmatrix} l & s & j \\ m_l & m_s & m_j \end{bmatrix} \times \begin{bmatrix} l & s & j \\ M_L-\mu & M_S-\sigma & M_L-\mu+M_S-\sigma \end{bmatrix} \times \begin{bmatrix} L & S & J \\ M_L & M_S & M_J \end{bmatrix} \times \begin{bmatrix} L & S & J \\ m_l+\mu & m_s+\sigma & m_l+\mu+m_s+\sigma \end{bmatrix} \Delta_{l_e\mu}. \tag{14}$$

TABLE XII. Resonant charge exchange cross section $\sigma_{ex}(10^{-16}\mathrm{cm}^2)$ for the process $N^+(^3P)+N(^4S) \rightarrow N(^4S)+N^+(^3P)$ at collision energies of 0.1 and 1 eV in the laboratory frame of reference.

$\frac{jm_j}{JM_J}$	2,2	2,1	2,0	1,1	1,0	0,0
$\frac{3}{2},\frac{3}{2}$	62(50)	75(61)	74(61)	76(62)	55(45)	51(41)
$\frac{3}{2},\frac{1}{2}$	61(49)	78(64)	80(66)	63(50)	60(49)	66(53)
$\frac{3}{2},-\frac{1}{2}$	56(45)	77(63)	80(66)	69(66)	60(49)	66(53)
$\frac{3}{2},-\frac{3}{2}$	48(38)	68(55)	74(61)	69(66)	55(45)	51(41)

TABLE XIII. Resonant charge exchange cross section $\sigma_{ex}(10^{-16}\mathrm{cm}^2)$ for the process $\mathrm{N}^+(^3P)+\mathrm{N}(^2D)\rightarrow\mathrm{N}(^2D)+\mathrm{N}^+(^3P)$ at collision energies of 0.1 and 1 eV in the laboratory frame of reference.

$\frac{jm_j}{JM_J}$	2,2	2,1	2,0	1,1	1,0	0,0
$\frac{5}{2},\frac{5}{2}$	71(58)	70(57)	60(48)	55(43)	50(38)	0
$\frac{5}{2},\frac{3}{2}$	84(68)	88(71)	88(71)	64(50)	64(50)	0
$\frac{5}{2},\frac{1}{2}$	85(68)	90(74)	91(75)	70(55)	51(57)	0
$\frac{5}{2},-\frac{1}{2}$	82(66)	110(96)	91(75)	69(54)	51(57)	0
$\frac{5}{2},-\frac{3}{2}$	74(59)	84(68)	88(71)	60(46)	64(50)	0
$\frac{5}{2},-\frac{5}{2}$	50(38)	60(47)	60(48)	43(32)	50(38)	0
$\frac{3}{2},\frac{3}{2}$	64(50)	64(50)	62(48)	47(35)	58(44)	58(46)
$\frac{3}{2},\frac{1}{2}$	49(36)	45(33)	18(9.3)	82(66)	84(67)	78(63)
$\frac{3}{2},-\frac{1}{2}$	67(52)	55(42)	18(9.3)	69(55)	84(67)	78(63)
$\frac{3}{2},-\frac{3}{2}$	56(42)	59(45)	62(48)	65(50)	58(44)	58(46)

TABLE XIV. Resonant charge exchange cross section $\sigma_{ex}(10^{-16}\mathrm{cm}^2)$ for the process $\mathrm{N}^+(^1D)+\mathrm{N}(^2D)\rightarrow\mathrm{N}(^2D)+\mathrm{N}^+(^1D)$ at collision energies of 0.1 and 1 eV in the laboratory frame of reference.

$\frac{jm_j}{JM_J}$	2,2	2,1	2,0
$\frac{5}{2},\frac{5}{2}$	110(90)	95(78)	72(58)
$\frac{5}{2},\frac{3}{2}$	100(84)	98(80)	81(67)
$\frac{5}{2},\frac{1}{2}$	78(63)	73(58)	86(71)
$\frac{5}{2},-\frac{1}{2}$	90(73)	78(63)	86(71)
$\frac{5}{2},-\frac{3}{2}$	100(84)	91(75)	81(67)
$\frac{5}{2},-\frac{5}{2}$	95(78)	90(73)	72(58)
$\frac{3}{2},\frac{3}{2}$	100(87)	96(79)	77(62)
$\frac{3}{2},\frac{1}{2}$	92(75)	79(63)	83(68)
$\frac{3}{2},-\frac{1}{2}$	71(58)	71(56)	83(68)
$\frac{3}{2},-\frac{3}{2}$	83(67)	89(72)	77(62)

TABLE XV. Resonant charge exchange cross section $\sigma_{ex}(10^{-16}\ \mathrm{cm}^2)$ for the process $\mathrm{N}^+(^3P)+\mathrm{N}(^2P)\rightarrow\mathrm{N}(^2P)+\mathrm{N}^+(^3P)$ at collision energies of 0.1 and 1 eV in the laboratory frame of reference.

$\frac{jm_j}{JM_J}$	2,2	2,1	2,0	1,1	1,0	0,0
$\frac{3}{2},\frac{3}{2}$	95(77)	85(68)	62(47)	73(57)	70(54)	0
$\frac{3}{2},\frac{1}{2}$	75(59)	70(54)	34(23)	75(59)	75(59)	62(47)
$\frac{3}{2},-\frac{1}{2}$	72(56)	71(55)	34(23)	74(58)	75(59)	62(47)
$\frac{3}{2},-\frac{3}{2}$	84(67)	86(69)	62(47)	65(50)	70(54)	0
$\frac{1}{2},\frac{1}{2}$	47(35)	67(52)	73(57)	67(52)	86(68)	72(55)
$\frac{1}{2},-\frac{1}{2}$	47(35)	64(49)	73(57)	72(56)	86(68)	72(55)

Tables VII–XI give the values of the matrix elements for these interaction potentials [since $\Delta_{11}(R)\ll\Delta_{10}(R)$ at large separations, we neglect $\Delta_{11}(R)$ when possible]. These values are used below for the evaluation of electron transfer cross sections.

VI. CROSS SECTIONS OF RESONANT CHARGE EXCHANGE FOR NITROGEN

The process of resonant charge exchange is accompanied by processes of transition between states with different values of orbital momenta and spins of the atom and ion, and these processes are entangled with resonant charge exchange. In reality, the situation is simplified because of a sharp change of the exchange interaction potential with the distance between nuclei. This leads to a small rotation of the molecular axis during electron transition, resonant charge that allows us to neglect transition and to consider electron transition at certain values of angular and spin momenta of the atom and ion. Therefore we use the two-state approximation for electron transition from one core to another one, and the cross section of resonant charge exchange is given by the formula [5]

TABLE XVI. Resonant charge exchange cross section $\sigma_{ex}(10^{-16}\ \mathrm{cm}^2)$ for the process $\mathrm{N}^+(^1D)+\mathrm{N}(^2P)\rightarrow\mathrm{N}(^2P)+\mathrm{N}^+(^1D)$ and $\mathrm{N}^+(^1S)+\mathrm{N}(^2P)\rightarrow\mathrm{N}(^2P)+\mathrm{N}^+(^1S)$ at collision energies of 0.1 and 1 eV in the laboratory frame of reference.

$\frac{jm_j}{JM_J}$	^1D 2,2	^1D 2,1	^1D 2,0	^1S 0,0
$\frac{3}{2},\frac{3}{2}$	80(65)	98(80)	97(79)	99(82)
$\frac{3}{2},\frac{1}{2}$	79(64)	100(83)	76(61)	130(110)
$\frac{3}{2},-\frac{1}{2}$	72(58)	100(81)	76(61)	130(110)
$\frac{3}{2},-\frac{3}{2}$	61(48)	89(71)	97(79)	99(82)
$\frac{1}{2},-\frac{1}{2}$	75(60)	91(73)	71(56)	110(94)
$\frac{1}{2},-\frac{1}{2}$	65(51)	88(70)	71(56)	110(94)

TABLE XVII. Average resonant charge exchange cross section $(10^{-16}\ \mathrm{cm}^2)$ at collision energies of 0.1, 1, 5, and 10 eV in the laboratory frame of reference. Data in parentheses have been calculated averaging the interaction potential $\overline{\Delta(R)}$.

	^4S	^2D	^2P
$^3P, j=2$	68(68),55,47,44	69,55,46,42	69,53,44,40
$^3P, j=1$	66(64),53,45,42	63,50,41,35	73,57,47,42
$^3P, j=0$	59(58),47,40,37	27,22,18,17	44,34,27,25
^1D		87,71,61,57	83,67,56,52
^1S			113,94,81,76

$$\sigma_{ex}=\int_0^\infty 2\pi\rho d\rho \sin^2\int_{-\infty}^{\infty}\frac{\Delta_i}{2}dt, \qquad (15)$$

where the index i refers to fine states of the ion and atom. An average over degenerated states allows us to determine the resonant cross sections for a given fine atom and ion states, and these values are given in Tables XII–XVI. Note that neglecting the rotation of the molecular axis during the electron transfer is justified by a small parameter of the asymptotic theory that is [9] $1/(R_o\gamma)$ (the cross section of this process is $\sigma_{ex}=\pi R_o^2/2$). For the considered collision energies we have $R_o\gamma\sim 10$. The rotational angle θ of the molecular axis during electron transfer is $\theta\sim(\rho\gamma)^{-1/2}$, where ρ is the impact parameter of collision, so that separation of the electron transfer process and rotation of the molecular axis can be open to some criticism. Therefore we also determine the cross sections of electron transfer under the assumption of total mixing of momentum projections during electron transitions. In this case the average exchange interaction potential $\overline{\Delta(R)}$ over momentum projections of given fine states is used, and the cross sections of electron transfer for this assumption are given in Table XVII in parentheses. The new results, obtained by average $\overline{\Delta(R)}$, are within 1% compared with the present calculations.

A comparison of the present results at 10 eV with existing data is reported in Table XVIII. Despite the different methods the present calculations do not differ too much from the previous experimental and theoretical values, the only exception being represented by the old values calculated by one of us [3]. In this last case only exchange forces were taken into account and the corresponding gerade-ungerade splittings were obtained by the behavior of molecular states at distances not too much important for the exchange process. It should be also noted: the strong increase up to a factor of 2 in the exchange cross-section excited(atom)-excited(ion) processes as compared with the excited(atom)-ground(ion) process. On the other hand the differences of the present $\mathrm{N}^+(^3P)-\mathrm{N}(^4S)$, $\mathrm{N}^+(^3P)-\mathrm{N}(^2D)$, $\mathrm{N}^+(^3P)-\mathrm{N}(^2P)$ charge exchange cross sections with corresponding results of Ref. [8] are due to a different choice of the A value and a different adopted coupling scheme. It should be also noted that the differences of 16% between the present results and those of Ref. [6] can be ascribed to the neglect of fine structure in the latter calculations.

On the basis of the resonant charge exchange cross sections one can find the mobilities of nitrogen ions in a gas that contains atomic nitrogen. The mobility, ignoring elastic ion-atom scattering, can be calculated according to [31]

$$K=\frac{131}{\sqrt{Tm\sigma_{ex}}}, \qquad (16)$$

where the ion mobility is given in $\mathrm{cm}^2/(\mathrm{V\ s})$ and is reduced to the atom number density $2.69\times10^{19}\ \mathrm{cm}^{-3}$, the gas temperature T is given in Kelvin, the atom mass, m, is given in atomic mass units, and the cross section σ_{ex} is expressed in

TABLE XVIII. Comparison of average resonant charge exchange cross section $\sigma_{ex}(10^{-16}\ \mathrm{cm}^2)$ at collision energy of 10 eV in the laboratory frame of reference with data in the literature: Eletskii *et al.* [8] (asterisk), Capitelli [3] (in parentheses), Stallcop *et al.* [34,35] (square brackets), beam masurements (double asterisk) [36], and Copeland and Crothers (double square brackets) [6].

	^4S	^2D	^2P
$^3P, j$	41, (21.6), 39^*, [34.0], 34.4^{**}, [[42]]	31.3, (18.2), 27.2^*	35.6, (23.3), 29^*
^1D		57	52
^1S			76

TABLE XIX. Mobility of nitrogen ions in atomic nitrogen at $T=300$ and 800 K (in parentheses) reduced to the number density of nitrogen atoms $N=2.69\times10^{19}$ cm^{-3}.

	^4S	^2D	^2P
^3P	2.6 (1.7)	3.15 (2.1)	2.7 (1.8)
^1D		1.95 (1.3)	2.03 (1.35)
^1S			1.25 (1)

10^{-14} cm^2. The values of the ion mobility in atomic nitrogen in different states are given in Table XIX. In the case when atomic nitrogen is one of the components of a gaseous mixture, the ion mobility is determined by the Blanck formula [32,33]

$$K=\left(\sum_i \frac{c_i}{K_i}\right)^{-1}, \quad (17)$$

where the ith component is molecular nitrogen, oxygen, or atomic oxygen, c_i is the concentration of this component, and K_i is the mobility of ions in a gas consisting of ith component only.

VII. CONCLUSION

We have reported in the present paper detailed calculations of charge transport cross sections involving excited nitrogen atoms and ions. These calculations fully take into account the hierarchy of interactions in the nitrogen molecular ion at large distances. Charge transfer cross sections involving excited atom-excited ion have been calculated in this paper. Their values are up to a factor of 2 higher than the corresponding ones involving excited nitrogen atoms and the ion in the ground state (i.e., ^3P). Comparison of the present fine structure results with other theoretical and experimental values, when existing, shows a satisfactory agreement. The results, also used in deriving the mobility diffusion coefficients, represent a further advancement in the understanding of the role of excited states in affecting the transport properties of thermal plasmas.

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