# Transitions between sublevels of $^3P$ triplets in slow collisions between atoms and ions

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The cross sections for transitions between the sublevels of $^3P$ triplets in collisions between atoms of a number of elements and their ions are calculated. The relative velocities of the colliding particles are assumed to be small. It is shown that the cross sections for the transitions between sublevels with total electron angular momemta $J=1$ and $J=2$, as well as $J=0$ and $J=2$, are small (of the order of atomic dimensions). The cross sections for transitions between sublevels with $J=0$ and $J=1$ depend significantly on the signs of the charge of the incident ion and of the atomic electric quadrupole moment. For identical signs the cross sections are large in the case of a normal triplet and increase in proportion to the square root of the relative velocity of the colliding particles; for opposite signs the cross sections are of the order of the atomic dimensions. The reverse is true of the inverted triplet.

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## 1. INTRODUCTION

1. For a number of problems in atomic physics, it is of great interest to consider transitions between sublevels of atomic multiplets in collisions of atoms with other atoms or ions. In[1] we considered transitions between sublevels of the multiplets $^2P$ and $^3P$ in collisions between atoms and ions, occurring as a result of charge-quadrupole interaction. The relative velocities of the colliding particles were assumed to be large enough to neglect the energy splitting between the considered sublevels. Interest attaches also to the opposite, adiabatic case, when the frequencies of these transitions are large in comparison with the reciprocal characteristic collision time. It was shown in[1] that the transition cross sections are exponentially small for the $^2P$ doublets but not for the $^3P$ triplets. These latter cross sections are determined in the present paper.

The following two assumptions are made:

1) The motion of the ion nucleus relative to the atom nucleus is classical and along a straight line. The first of these conditions reduces to the inequality (see[1])

$$\lambda\!\!\!^{-}=1/Mv\ll\rho_0 \tag{1}$$

($\lambda\!\!\!^{-}$ is the de Broglie wavelength connected with the relative motion of the nuclei of the atom and of the ion, $M$ is the reduced mass of the ion and the atom, $v$ is their relative velocity, and $\rho_0$ is the characteristic impact distance), while the second condition reduces to the inequality (see[1])

$$\rho_0^3\gg|ZQ|/Mv^2 \tag{2}$$

($Z$ is the charge multiplicity of the ion and $Q$ is the quadrupole moment of the atom).

2) The frequencies of the considered transitions are high in comparison with the characteristic collision time. This condition is the opposite of that assumed in[1], and therefore reduces to an inequality which is the opposite to that given there

$$\rho_0\gg v/|\delta E| \tag{3}$$

($|\delta E|$ is the energy spacing between the considered sublevels). We use the atomic system of units $\hbar=m_e=e=1$ throughout.

The characteristic impact distance $\rho_0$ can be estimated in the following manner: the obtained cross section is of the order of $\pi(|QZ|v)^{1/2}/|\delta E|$ (see (13)). Since $\sigma\sim\pi\rho_0^2$, it follows that

$$\rho_0\sim(|QZ|v/(\delta E)^2)^{1/4}.$$

Taking this condition into account, the requirements (1)–(3) yield respectively

$$v\gg((\delta E)^2/|QZ|M^4)^{1/5}, \tag{4}$$

$$v\gg(|QZ|(\delta E)^6/M^4)^{1/10}, \tag{5}$$

$$v\ll[|QZ|(\delta E)^2]^{1/3}. \tag{6}$$

It must be assumed that $|Q|\sim 1$ and $|Z|=1$. Comparing the conditions (4) and (5) we find that (5) is stronger than (4) (the values of $\delta E$ for the different elements were taken from[2]). In order for the inequalities (5) and (6) to be simultaneously satisfied it is necessary to satisfy the condition

$$(QZ)^2|\delta E|M^3\gg 1.$$

This inequality is satisfied for the resonant $^3P$ term of helium, the metastable term of beryllium,[1)] and the ground state terms of carbon and oxygen. The values of $\delta E$ and the resultant maxima and minima $v_{min}$ and $v_{max}$ of the relative velocities of the atoms and ions and respectively $T_{min}$ and $T_{max}$ of the temperatures are listed for the indicated elements in Table I. It is assumed that the atoms collide with their own ions.

The polarization interaction can be disregarded in our case. To be able to neglect this interaction, the inequality

TABLE I.

| Element | Term | $\delta E$, cm$^{-1}$ | $v_{min}$, $10^{-5}$ at. un. | $T_{min}$, K | $v_{max}$, $10^{-4}$, at. un. | $T_{max}$, K |
|---|---|---|---|---|---|---|
| He | $2p\,^3P^0$ (res) | −0.355 | 4 | 2 | 1 | 10 |
| Be | $2p\,^3P^0$ (met) | +1.5 | 5 | 7 | 2 | 150 |
| C | $2p^2\,^3P$ (gnd) | +14.5 | 10 | 55 | 10 | $4\cdot10^3$ |
| O | $2p^4\,^3P$ (gnd) | −75.3 | 40 | 900 | 30 | $5\cdot10^4$ |

$$\rho_0 \gg 1/\Delta E$$

must be satisfied ($\Delta E$ is the energy difference between the given level and the nearest level to which the electric dipole transition is allowed. Taking the estimate given above for $\rho_0$ into account, this requirement yields

$$v \gg (\delta E)^2/|QZ|\,(\Delta E)^4.$$

This condition is somewhat weaker than (5), but is of the same order (the values of $\Delta E$ for different elements were also taken from[2]).

## 2. CALCULATION OF CROSS SECTIONS

1. We introduce two coordinate systems: immobile $O_{xyz}$ and rotating $O_{\xi\eta\zeta}$. They have a common origin that coincides with the nucleus of the atom. The $x$ axis lies in the scattering plane and is perpendicular to the velocity vector $\mathbf{v}$ of the incident ion, the $y$ axis is directed along this vector, and the $z$ axis is perpendicular to the scattering plane. The $\xi$ axis is directed along the radius vector $\mathbf{R}$ of the nucleus of the incident ion, the $\eta$ axis also lies in the scattering plane, and the $\zeta$ axis coincides with the $z$ axis.

The states of the atom with definite projection of the total electron angular momentum on the $\xi$ axis are expressed in the form

$$\begin{aligned}\psi_{\pm2} &= Y_{1,\pm1}\chi_{1,\pm1},\\ \psi_{\pm1}^{(i)} &= a_{\pm}^{(i)}Y_{1,\pm1}\chi_{1,0}+b_{\pm}^{(i)}Y_{1,0}\chi_{1,\pm1} \quad (i=1,2),\\ \psi_0^{(j)} &= c^{(j)}Y_{1,+1}\chi_{1,-1}+d^{(j)}Y_{1,0}\chi_{1,0}+e^{(j)}Y_{1,-1}\chi_{1,+1} \quad (j=0,1,2).\end{aligned} \tag{7}$$

Here $Y_{1,M}$ is the angular wave function of the state with orbital quantum number $L=1$ and magnetic quantum number $M=-1,0,+1$; $\chi_{1,S_\xi}$ is the spin state with spin $S=1$ and its projection on the $\xi$ axis $S_\xi=-1,0,+1$ (all the angular momenta are projected on the $\xi$ axis). The real coefficients $a_\pm^{(i)}$, $b_\pm^{(i)}$, $c^{(j)}$, $d^{(j)}$, and $e^{(j)}$ should satisfy the orthonormalization condition.

2. The states (7) are acted upon by the operator $\hat H(t)$:

$$\hat H(t)=\hat H_0+\hat V(t), \tag{8}$$

where $\hat H_0$ is the spin-orbit interaction operator:

$$\hat H_0=\delta E\,\hat{\mathbf{L}}\hat{\mathbf{S}}, \tag{9}$$

and $\hat V(t)$ is the carriage-quadrupole interaction operator

$$\hat V(t)=\mathscr{E}(3\hat L_\xi^2-2). \tag{10}$$

Here $\hat{\mathbf{S}}$, $\hat{\mathbf{L}}$, and $\hat L_\xi$ are respectively the operators of the total spin of the atom, its total orbital angular momentum, and of the projection of the latter on the $\xi$ axis, with $S=1$, $L=1$ and $L_\xi=M=-1,0,+1$;

$$\mathscr{E}=QZ/2R^3.$$

(For the derivation of the form of the operator $V(t)$ see[1].)

The terms $\mathscr{E}_{J_\xi}^{(j)}$ of the states (7) are obtained by solving the secular equations that result from the action of the operator $H(t)$. As a result we get

$$\begin{aligned}&\mathscr{E}_2=\delta E(1+y), \quad \mathscr{E}_1^{(i)}=\delta E\{-{}^1\!/_2\,y+(-1)^i[1+({}^3\!/_2\,y)^2]^{1/2}\} \quad (i=1,2);\\ &\mathscr{E}_0^{(1)}=\delta E(y-1), \quad \mathscr{E}_0^{(2j)}={}^3\!/_2\,\delta E[-1-y-3(-1)^j(1-{}^3\!/_2\,y+y^2)^{1/2}] \quad (j=0,1).\end{aligned} \tag{11}$$

Here $\mathscr{E}_{J_\xi}^{(j)}$ denotes the energy of the state with projection $J_\xi$ of the total electron angular momentum $J$ on the $\xi$ axis, and furthermore such that at $\mathscr{E}=0$ we have $J=i$;

$$y=\mathscr{E}/\delta E.$$

The signs of $J_\xi$ are not marked, since the values of the energy $\mathscr{E}_{J_\xi}^{(i)}$ do not depend on them (it is known that the electric field does not lift completely the degeneracy with respect to the projection of the angular momentum on the direction of this field).

Plots of $\mathscr{E}_{J_\xi}^{(i)}/\delta E$ as functions of $y$ are shown in Fig. 1. The energies are reckoned from the values $E_1+\delta E = E_2-\delta E$, where $E_J$ is the energy of the sublevel with total electronic angular momentum $J$, and $\delta E = E_1 - E_0$.

The equation for $\mathscr{E}_0^{(1)}$ separates from the equation for $\mathscr{E}_0^{(2j)}$. The reason is that the state $\psi_0^{(1)}=|1,0\rangle$ while the states $\psi_0^{(2j)}$ are superpositions of the states $|0,0\rangle$ and $|2,0\rangle$ ($|J,J_\xi\rangle$ is a state with total electron angular momentum $J$ and its projection $J_\xi$ on the $\xi$ axis). No superpositions of the states $|1,0\rangle$ on one hand, and $|0,0\rangle$

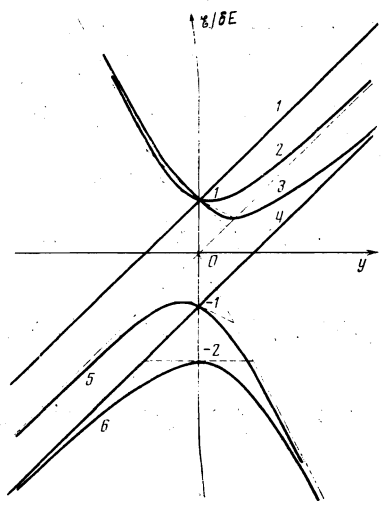


FIG. 1. The terms $\mathscr{E}_j^{(i)}/\delta E$ as functions of $y$: 1) $\mathscr{E}_2/\delta E = 1+y$. 2) $\mathscr{E}_1^{(2)}/\delta E$, 3) $\mathscr{E}_0^{(2)}/\delta E$, 4) $\mathscr{E}_0^{(1)}/\delta E = y-1$, 5) $\mathscr{E}_1^{(1)}/\delta E$, 6) $\mathscr{E}_0^{(0)}/\delta E$. The dashed lines show the tangents to the hyperbolas at $y=0$ and the asymptotes at $\mathscr{E}/\delta E = y$ and $\mathscr{E}/\delta E = -2y$.

and $|2,0\rangle$ on the other, take place, however, because they are of different symmetry. Indeed, reflection in the scattering plane does not change the states $|0,0\rangle$ and $|2,0\rangle$, but the state $|1,0\rangle$ reverses sign; the operator $\hat{H}(t)$, on the other hand, is invariant to such an operation (this is seen from (8)–(10)).

From formulas (11) and from the figure we can draw the following conclusions:

a) No terms cross, with the exception of the obvious crossing point at $\mathscr{R}=0$.

b) The terms $\mathscr{E}_0^{(2)}$ and $\mathscr{E}_1^{(2)}$ converge asymptotically as $y\to-\infty$, but this of no interest, since they belong to one and the same sublevel with total electron angular momentum $J=2$, as do also the terms $\mathscr{E}_0^{(0)}$ and $\mathscr{E}_0^{(1)}$; as $y\to+\infty$, the terms $\mathscr{E}_0^{(1)}$ and $\mathscr{E}_0^{(2)}$ as well as $\mathscr{E}_0^{(0)}$ and $\mathscr{E}_1^{(1)}$ converge asymptotically.

It is easy to show that transitions between the states $\psi_0^{(0)}$ and $\psi_0^{(1)}$, on the one hand, and $\psi_0^{(1)}$ and $\psi_0^{(2)}$ on the other, do not exist at all. Indeed, assume that prior to the start of the collision the atom is in the state $\psi_0^{(0)}=|0,0\rangle$. This state, as already noted, does not change upon reflection in the scattered plane. Since the collision process is symmetrical with respect to this plane, it follows that after its completion the atom should be in a state that is invariant relative to such a reflection. On the other hand, this operation reverses the sign of the state $\psi_0^{(1)}=|1,0\rangle$. Consequently, such a transition is impossible. The proof of the impossibility of the inverse transitions, and also transitions between the states $\psi_0^{(1)}$ and $\psi_0^{(2)}$, is analogous.

Thus, the only nonzero and exponentially not small transitions are those between the states $\psi_0^{(0)}$ and $\psi_{\pm1}^{(1)}$, i.e., between sublevels with total angular momentum $J=0$ and $J=1$.

3. The equations from which the sought transitions are calculated are the usual differential equations for the coefficients of the expansion of the wave function of an atom in the eigenstates of a Hamiltonian $\hat{H}(t)$ with explicit time dependence. For a derivation of such equations see, for example, Smirnov's book.[3] In our case the Hamiltonian $H(t)$ is determined by formulas (8)–(10), its eigenstates are $\psi_{J\xi}^{(i)}$ (7), and the coefficients of expansion of the atom wave function in terms of these states are designated by $c_{J\xi}^{(i)}(t)$.

Since the sought transitions occur at $y\to+\infty$, it is necessary to write down the equations also in the asymptotic form as $y\to+\infty$. The equations describing transitions between the states $\psi_0^{(0)}$ and $\psi_{\pm1}^{(1)}$ as $y\to+\infty$ take the form

$$\frac{dc_0}{d\tau}=\frac{c_{+1}^{(1)}+c_{-1}^{(1)}}{\sqrt{2}}\frac{\exp[-iPF(\tau)]}{1+\tau^2}$$

$$\frac{dc_{\pm1}}{d\tau}=-\frac{c_0}{\sqrt{2}}\frac{\exp[iPF(\tau)]}{1+\tau^2}$$

where

$$\tau=vt/\rho,\quad p=(\delta E)^2\rho^3/6|QZ|v,$$

$$F(\tau)=4\int_0^{\tau}[1+(\tau')^2]^{1/2}d\tau'=\tau(^5/_2+\tau^2)(1+\tau^2)^{1/2}+^3/_2\ln[\tau+(1+\tau^2)^{1/2}].$$

It is convenient to make the change of variables

$$u=c_0^{(0)},\quad v=(c_{+1}^{(1)}+c_{-1}^{(1)})/\sqrt{2},\quad w=(c_{+1}^{(1)}-c_{-1}^{(1)})/\sqrt{2}.$$

For the functions $u$, $v$, and $w$ we obtain the system of equations

$$\begin{aligned}\frac{du}{d\tau}&=\frac{v}{1+\tau^2}\exp[-iPF(\tau)],\\ \frac{dv}{d\tau}&=-\frac{u}{1+\tau^2}\exp[iPF(\tau)],\\ dw/d\tau&=0.\end{aligned}\tag{12}$$

In general form (for arbitrary $P$), the system (12) cannot be solved analytically. Certain properties of its solution, however, are obvious:

$$|u|^2+|v|^2=1;$$

if $u(\tau)$, $v(\tau)$ is a solution, then $v(-\tau)$, $u(-\tau)$ and $-v^*(\tau)$, $u^*(\tau)$ are also solutions. Using these properties, we easily find that on going from $\tau=-\infty$ to $\tau=+\infty$ the solutions change in the following manner:

$$\begin{pmatrix}1\\0\end{pmatrix}\to\begin{pmatrix}fe^{i\varphi}\\-g\end{pmatrix};\quad\begin{pmatrix}0\\1\end{pmatrix}\to\begin{pmatrix}g\\fe^{-i\varphi}\end{pmatrix},$$

where $f$, $g$, and $\varphi$ are real functions of the parameter $P$, with $f^2+g^2=1$.

The system (12) can be solved analytically at $P\ll1$ by successive approximations, and at $P\gg1$ by the contour integration method. For these cases, solutions change in the following manner: at $P\ll1$

$$\begin{pmatrix}1\\0\end{pmatrix}\to\begin{pmatrix}-1+i(2\pi P)^{1/2}\\-(1+\sqrt{2})^{1/2}\Gamma(^3/_4)P^{1/4}\end{pmatrix},$$

$$\begin{pmatrix}0\\1\end{pmatrix}\to\begin{pmatrix}(1+\sqrt{2})^{1/2}\Gamma(^3/_4)P^{1/4}\\-1-i(2\pi P)^{1/2}\end{pmatrix}$$

and at $P\gg1$

$$\begin{pmatrix}1\\0\end{pmatrix}\to\begin{pmatrix}1\\-\pi e^{-3\pi P/16}\end{pmatrix},\quad\begin{pmatrix}0\\1\end{pmatrix}\to\begin{pmatrix}\pi e^{-3\pi P/16}\\1\end{pmatrix}.$$

4. Since we are considering a transition between the states $\psi_0^{(0)}$and $\psi_{\pm1}^{(1)}$, and no other states take part in this transition, the state of the atom can be represented in the form of a vector $\Phi$ made up of the coefficients $c_{\pm1}^{(1)}$, $c_0^{(1)}$, and $c_0^{(0)}$. It is necessary to change over from this vector to a vector $\Psi$ made up of the functions $u$, $v$, $w$, and $c_0^{(1)}$. This transition is effected by a unitary matrix $K$:

$$\Psi=K\Phi,\quad KK^+=1.$$

If we choose the vectors $\Phi$ and $\Psi$ in the form

$$\Phi=\begin{pmatrix}c_{+1}^{(1)}\\c_0^{(1)}\\c_{-1}^{(1)}\\c_0^{(0)}\end{pmatrix},\quad\Psi=\begin{pmatrix}u\\v\\w\\c_0^{(1)}\end{pmatrix},$$

then the matrix $K$ takes the form

$$K=\begin{pmatrix} 0 & 0 & 0 & 1 \\ 1/\sqrt{2} & 0 & 1/\sqrt{2} & 0 \\ 1/\sqrt{2} & 0 & -1/\sqrt{2} & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}.$$

As the result of the collision, the vector $\Psi_{in}$, which describes the initial state of the atom, goes over into the vector $\Psi_{out}$, which describes its final state. This transition is described by the unitary matrix $S$:

$$\Psi_{out}=S\Psi_{in}, \quad SS^{+}=1.$$

The matrix $S$ is expressed simply in terms of the functions $f$, $g$, and $\varphi$ of the parameter $P$:

$$S=\begin{pmatrix} fe^{i\varphi} & g & 0 & 0 \\ -g & fe^{-i\varphi} & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$

If we express the states of the atom in terms of the vector $\Phi$, then these transitions will be effected by the matrix $S'$:

$$\Phi_{out}=S'\Phi_{in}, \quad S'=K^{+}SK.$$

We consider here a transition from a state with angular momentum $J=0$ prior to the collision into a state with total electron angular momentum $J=1$ after the collision, and the inverse transition, the initial state with $J=1$ being assumed to be completely unpolarized. Summing over the final states or averaging over the initial states, we easily obtain

$$W_{0\to 1}=\sum_{J_z}|S(0,0;1,J_z)|^2=g^2,$$
$$W_{1\to 0}={}^1/_3\sum_{J_z}|S'(1,J_z;0,0)|^2={}^1/_3 g^2,$$

where $S'(J, J_z; J', J_z')$ is the $S'$-matrix element describing the transition from the state $|J, J_z\rangle$ to the state $|J', J_z'\rangle$.

The corresponding cross sections are

$$\sigma_{0\to 1}=2\pi\int_0^\infty \rho\, d\rho\,[g(P)]^2=\frac{\pi}{2}\frac{(6|QZ|v)^{1/2}}{|\delta E|}\int_0^\infty \frac{dP}{\sqrt{P}}[g(P)]^2,$$
$$\sigma_{1\to 0}={}^1/_3\sigma_{0\to 1}.$$

The function $g(P)$ was obtained by solving equations (6) with a computer. The succeeding numerical integration yields the following values of the cross sections (in ordinary units):

$$\sigma_{0\to 1}=0.735\pi(|QeZ|\hbar v)^{1/2}/|\delta E|, \quad \sigma_{1\to 0}={}^1/_3\sigma_{0\to 1}. \qquad (13)$$

## 3. DISCUSSION OF RESULTS

For the ballistics case we have previously obtained the general form of the cross sections $a_{J\to J'}|QeZ|/\hbar v$, where $a_{J\to J'}$ is a certain number of the order of unity and depends on which of the transitions is being considered. The sign of the quadrupole moment and of the ion is of no significance. In the present adiabatic case, however, the situation is entirely different. In fact, for the doublets $^2P$ the cross sections are exponentially small (more accurately speaking, they are of the order of $\pi a_0^2$, where $a_0^2$ is the atom unit of length). The same holds also for the cross sections $\sigma_{0\rightleftarrows 2}$ and $\sigma_{1\rightleftarrows 2}$.

However, only the cross sections $\sigma_{0\rightleftarrows 1}$ are large in comparison with $a_0^2$. Since the transitions occur only at $y>0$, i.e., at $QeZ/\delta E>0$, the sign of $QeZ$ is important. In the case of the normal triplet $^3P$ they take place only at $QeZ>0$, and in the case of the inverted triplet at $QeZ<0$.

At $\hbar v\sim[|QeZ|(\delta E)^2]^{1/3}$ we have a case intermediate between adiabatic and ballistic. For the cross sections $\sigma_{0\rightleftarrows 1}$ and at $QeZ/\delta E>0$, both methods yield the same order of magnitude:

$$\sigma_{0\rightleftarrows 1}\sim\pi(QeZ/\delta E)^{2/3}.$$

Since the cross section depends on the velocity like $v^{1/2}$ in the adiabatic case and like $v^{-1}$ in the ballistic case, this expression gives the maximum order of magnitude of the cross section. For beryllium, for example,

$$\sigma_{0\rightleftarrows 1}\sim 10^3\pi a_0^2.$$

We see that these cross sections are very large.

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[1)]This term is designated as resonant in[1], but this is a mistake.

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