Excitation transfer in slow collisions in a dense gas

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Resonant and nonresonant excitation exchange in slow collisions in a dense gas are considered. Asymptotic formulae are derived for the dependence of the excitation lifetime in a given atom on the gas density. It is shown that excitation deactivation at intermediate densities is due to triple collisions by the Landau-Zener mechanism. At high densities the problem reduces to an interaction between the local level and the exciton band, and the process is in effect resonant even in the presence of primary levels difference.

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The question of calculating the probabilities of inelastic processes that develop in collisions in a gas of finite density is of considerable interest for plasma physics, astrophysics, and quantum electronics. In particular, the recent advent of gas lasers operating at high pressures (~ 10 atm)[1] raises the question of the mechanisms that produce inversion and lasing in such systems.

We consider in this paper the problem of exchange of excitation, and pay principal attention to the case of inexact resonance. In the case of inelastic collisions in a dense gas, a distinction can be made between two fundamentally different situations. In the first, quantum transitions occur in a two-particle system (quasi-molecule) and the influence of the gas environment reduces to the action of a random potential field that shifts the terms of the quasi-molecule and depends on the configuration of the gas particles. This case is realized in charge-exchange processes.[2,3] For these problems there exists a region of gas density n in which the pairing criterion1) $n\sigma_0^{3/2} \ll 1$ is still satisfied, where σ_0 is the cross section for the charge exchange in vacuum, but the effective cross section of the process depends already on the gas density. The second situation arises in the case of excitation exchange. Furthermore, the non-additivity of the van der Waals forces makes the problem essentially collective in the quantum-mechanical sense. Strictly speaking, the concept of the cross section becomes meaningless in this case and the process must be characterized by the lifetime of the excitation for a selected atom.

Resonant exchange of excitation in dense gases was considered by Vlasov, Furtsev, and Kazantsev.[4,5] The resonant-exchange cross section in boundary collisions is of the order of d^2/v, where d is the dipole matrix element of the transition and v is the relative velocity. Since the probability of the resonant transition is of the order of unity, the distances ρ_0 that characterize the collisions are of the order of $d/\sqrt{v}$. It follows therefore that there exists in the problem a characteristic density value at which the relation $nd^3v^{-3/2} \sim 1$ is satisfied, i.e., when the number of particles in the interaction sphere is of the order of unity. This parameter has also another meaning, namely, it is equal to the ratio of the energy of the dipole-dipole interaction of the particles over an average distance nd^2 to the transit width v/ρ_0, i.e., to the reciprocal time of interaction during the collision. It is therefore obvious that if the characteristic energy of the interaction is much lower than the transit width ($nd^2 \ll v^{3/2}/d$), then the process remains practically paired. The reciprocal lifetime of the excitation is determined in this case by the formula

$$\gamma = n\sigma_{\mathrm{res}}v \sim nd^2. \tag{1}$$

The opposite limiting case was investigated by Kazantsev.[5] If the condition $nd^2 \gg v^{3/2}/d$ is satisfied, an exciton band appears in the gas (an exciton in a system of randomly disposed atoms), and the thermal motion of the atoms leads to damping of the excitons. A rigorous analysis of this problem is extremely complicated. Kazantsev[5] has considered a simplified model in which it is assumed that all the atomic dipoles are equal in magnitude and parallel to one another. The dispersion distribution for the density of states in the exciton band $f(E)$ is then given by

$$f(E) = \frac{1}{\pi}\frac{E_0}{E^2 + E_0^2}, \quad E_0 = \frac{8\pi^2}{9\sqrt{3}}nd^2. \tag{2}$$

The frequency of relaxation due to thermal motion of the atoms is

$$\gamma = \frac{27\sqrt{3}}{4(2\pi)^{2/3}}n^{1/3}v. \tag{3}$$

The last result means that the effective excitation-transfer cross section is of the order of $n^{-2/3}$, i.e., of the order of the square of the average distance between particles. It is probable that a rigorous analysis will result in a different numerical coefficient in (3), but since the problem contains only one parameter $nd^3v^{-3/2}$, the formulas

$$\gamma = n\sigma_{\mathrm{res}}v, \quad \gamma = cn^{1/3}v, \quad c \sim 1$$

yield the sought solution in two extremal density cases at exact resonance. We note that in contrast to charge-exchange, there is no region here in which the criterion for the paired character of the collisions is still satisfied, but the medium already shifts significantly the terms of the colliding particles. In fact, in order for cross section to change noticeably, the term shift, which is of the order of nd^2, must become comparable with the transit width. But in this case $nd^3v^{-3/2} \sim 1$, i.e., an exciton band is already formed.

We proceed now to nonresonant exchange of excitation and consider the reaction $B^*+A\to B+A^*$. In this problem we encounter a new parameter—the resonance defect Δ—and the number of different limiting cases increases correspondingly. The ratio of the transit width to $|\Delta|$ coincides with the Massey criterion and is a measure of the adiabaticity of the process. If this ratio is large, i.e., $|\Delta|\ll v^{3/2}/d$, then, in accord with the Stückelberg formula,[6] the cross section of the paired process is close to resonance. Thus, in this case all the arguments advanced above concerning the exact resonance are applicable.

We shall consider the opposite limiting case of strong adiabaticity $|\Delta|\gg v^{3/2}/d$. Depending on the value of nd^2, we can separate here three regions:

$$|\Delta|\gg v^{3/2}/d\gg nd^2, \tag{4a}$$

$$|\Delta|\gg nd^2\gg v^{3/2}/d, \tag{4b}$$

$$nd^2\gg|\Delta|\gg v^{3/2}/d. \tag{4c}$$

Conditions (4a) cover the region of the smallest densities in which, obviously, the Stückelberg formula[6] for the binary nonresonant exchange cross section σ_{St} should be applicable, therefore $\gamma=n\sigma_{St}v$. In the adiabatic limit considered by us, σ_{St} is equal to

$$\sigma_{St}=\frac{\pi^2}{8}\frac{2^{2/3}}{[\Gamma(1/8)]^2}\frac{d_1d}{v}\left[\frac{(d_1d)^{1/3}\Delta^{2/3}}{v}\right]\exp\left\{-\frac{(d_1d)^{1/3}\Delta^{2/3}}{v}\right\}, \tag{5}$$

where d_1 is the dipole matrix element of the atom B, while d is the same for the atoms of the gas A.

The region (4b) is characterized by the fact that in the gas of the atoms A there exists an exciton band. Consequently, the deactivation of the atom B corresponds to interaction of a local level with an exciton-state band. The local level is located in that part of the band where the distance to the center of the band is much larger than its width $|\Delta|\gg nd^2$. The density of states in this region is given by the asymptotic form of formula (2): $f(E=\Delta)=E_0/\pi\Delta^2$, and the exciton levels themselves are formed on account of the fluctuation approach of the atoms to distances much shorter than $n^{-1/3}$. The number of levels in the resonant-interaction spheres that fall in the transit width is equal to

$$nd^3v^{-3/2}f(E=\Delta)v^{3/2}/d\sim(nd^2/\Delta)^2\ll 1.$$

Therefore, in the principal order in the density it suffices to consider the interaction of the atom B with a pair of fluctuationally approaching atoms A. The distance r to which the atoms A must approach each other to produce an exciton level located a distance Δ from the center of the band[2)] is estimated from the relation $d^2/r^3\sim|\Delta|$. By virtue of the conditions (4b), the value of r is much less than the resonance radius ρ_0, so that it becomes necessary to consider the interaction of the atom B with the quasi molecule AA.

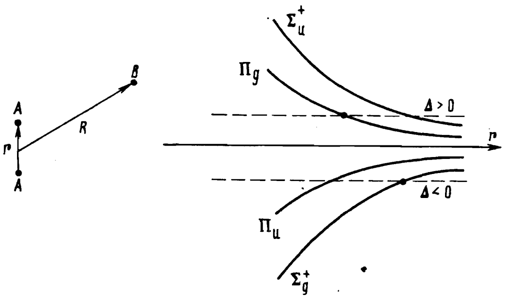

FIG. 1.

Let us find approximate expressions for the electronic terms and the wave functions of this quasi molecule. We assume that the detuning is much less than the Bohr energy, and therefore the distance r between the atoms A is much larger than the dimensions of the latter. Assume for the sake of argument that the ground state of the atom A corresponds to an ^1S term, and the excited state to a ^1P term. Then, obviously, the normal term of the AA system is $^1\Sigma_g^+$, and the corresponding wave function is $\varphi_s(1)\varphi_s(2)$, where φ_s is the wave function of the ground state of the atom A; the numbers 1 and 2 denote the aggregates of the electronic coordinates of the first and second atom of the quasi molecule. The state of the excited system AA^* as $r\to\infty$ is sixfold degenerate, and the dipole-dipole interactions splits it into four terms, two doubly degenerate terms $^1\Pi_g$ and $^1\Pi_u$ and two nondegenerate terms $^1\Sigma_g^+$ and $^1\Sigma_u^+$. We have obtained the signs of the Σ terms by assuming that the excited P state of the atom A is obtained from the normal S state by changing the orbital number of one electron by unity. Then the parity of the atom is reversed, the quantity $(-1)^L$ reverses sign, and consequently the sign of the Σ term of the system AA^* coincides with the sign of the Σ term of the unexcited quasi molecule. Simple calculations lead to formulas for the terms at finite but large r:

$$U(^1\Sigma_{g,u}^+)=\mp\frac{2}{3}\frac{\langle d\rangle^2}{r^3},\quad U(^1\Pi_{g,u})=\pm\frac{1}{3}\frac{\langle d\rangle^2}{r^3}, \tag{6}$$

where $\langle d\rangle^2$ is the square of the modulus of the reduced dipole matrix element. The relative arrangement of the terms is shown in Fig. 1. The wave functions corresponding to the terms (6) will be written out in a representation in which the z axis coincides with the axis of the quasi molecule AA, while the angular part of the wave function of the atom in the P state is chosen to consist of the real combinations of Y_{1x} and Y_{1y} (instead of $Y_{1,+1}$, $Y_{1,-1}$):

$$\Psi(^1\Sigma_{g,u}^+)=[\varphi_s(1)\varphi_{pz}(2)\pm\varphi_{pz}(1)\varphi_s(2)]/\sqrt{2}, \tag{7a}$$

$$\Psi(^1\Pi_{g,u};\ x,\ y)=[\varphi_s(1)\varphi_{px,y}(2)\pm\varphi_{px,y}(1)\varphi_s(2)]/\sqrt{2}. \tag{7b}$$

As seen from the figure, at definite values of r (of the order of $d^{2/3}|\Delta|^{-1/3}$) resonances take place between the level of the atom B^* and the terms of the quasi molecule AA^*. The calculation of the matrix elements of the dipole-dipole interaction between the molecular states (7a) and (7b) on the one hand, and the state of the atom B, on the other, shows that the only nonzero elements are those corresponding to resonances with the g terms (marked by points in the figure). In the calculations we use the additivity of the dipole moment of the molecule: $\mathbf{d}_{\mathrm{mol}}=\mathbf{d}(1)+\mathbf{d}(2)$, and we obtain

$$\begin{aligned}V_z(i,\ ^1\Sigma_g^+\to f,\ ^1\Sigma_g^+)&=\sqrt{2/3}\langle d\rangle\langle d_{1\alpha}\rangle_{if}T_{\alpha z},\\ V_x(i,\ ^1\Sigma_g^+\to f,\ ^1\Pi_{g;\,x})&=\sqrt{2/3}\langle d\rangle\langle d_{1\alpha}\rangle_{if}T_{\alpha x},\\ V_y(i,\ ^1\Sigma_g^+\to f,\ ^1\Pi_{g;\,y})&=\sqrt{2/3}\langle d\rangle\langle d_{1\alpha}\rangle_{if}T_{\alpha y},\end{aligned} \tag{8}$$

where the indices i and f stand for the initial and final states of the atom B, respectively $d_{1\alpha}$ is the α-component of the dipole-moment vector of this atom ($\alpha, \beta = x, y, z$)

$$T_{\alpha\beta}=(-\delta_{\alpha\beta}+3R_\alpha R_\beta/R^2)R^{-3},$$

R is the radius vector of the atom B relative to the central point on the axis of the molecule AA, and summation over α in (8) is implied. Thus, at each value of Δ there is only one resonant distance r_c:

$$r_c^- = \left(\frac{2}{3}\frac{\langle d\rangle^2}{|\Delta|}\right)^{1/3} \quad \text{if} \quad \Delta<0, \qquad r_c^+ = \left(\frac{1}{3}\frac{\langle d\rangle^2}{\Delta}\right)^{1/3} \quad \text{if} \quad \Delta>0.$$

It is now necessary again to separate two cases. If the velocity of the atom B is much larger than the thermal velocities in the gas A, then we can regard the pair AA as being at rest during the course of the collision. The probabilitiy of excitation transfer is described in this case by a formula of the Stückelberg type, averaged over the distribution of the resonance defects (or, equivalently, over the distances r). It is interesting to note that the probability of encountering a pair at a distance r_c^- at $\Delta<0$, which is double the probability for the distance r_c^+ at $\Delta>0$, is exactly canceled out by the statistical weight of the doubly degenerate ${}^1\Pi_g$ term. There is therefore no asymmetry with respect to the sign of Δ.

More interesting for the interpretation of processes in gas lasers is the case of thermal equilibrium between the atoms A and B, when their velocities do not differ too greatly. Then the relative motion of the pair of atoms A takes the system out of resonance before the atom B manages to move significantly in space.$^{3)}$ We can therefore assume the matrix elements V in (8) to be constant, and represent the difference $\Delta - U({}^1\Sigma_g^+)$ or $\Delta - U({}^1\Pi_g)$ by a linear function of the time in the vicinity of the resonance point r_c. This situation is typical of the Landau-Zener problem: The difference between the diagonal elements vanishes linearly at the transition point, while the off-diagonal matrix element is constant in the vicinity of this point.

Thus, the mechanism of the deactivation of the atom B reduces in our case to the following. The terms of the three-particle complex $B+AA$ intersect when the distance between the atoms A changes. The excitation transfer $B^*+AA \to B+AA^*$ is described by the Landau-Zener formula, in which the off-diagonal element V depends on the distance R between B and AA. In the vicinity of the atom B, binary collisions of the atoms A take place, and those atoms which are characterized by an impact parameter ρ smaller than r_c cause the atom B, to be de-excited, the Landau-Zener probability of this process being $W(\rho, \mathbf{R}, \mathbf{v})$. Therefore the relaxation frequency sought by us is equal to the number of pair collisions described above, occurring in a unit time in the entire space around the atom B, i.e.,

$$\gamma=\frac{n^2}{2}v\int W(\rho,\mathbf{R},\mathbf{v})\,d^2\rho\, d^3\mathbf{R}. \tag{9}$$

In expression (9), $\mathbf{v}$ is the relative velocity of the atoms A. The parameters in the Landau-Zener formula (for the notation see[7], Sec. 90), are equal in our case to

$$|F_2-F_1| = \left|\frac{\partial}{\partial r}(\Delta-U)\right|_{r_c} = \frac{3^{4/3}|\Delta|^{4/3}}{2^{1/3}\langle d\rangle^{2/3}}, \quad \Delta<0,$$
$$|F_2-F_1| = \frac{3^{4/3}\Delta^{4/3}}{\langle d\rangle^{2/3}}, \quad \Delta>0, \tag{10}$$
$$V_{x,y,z}^2=\langle d\rangle^2\langle d_1\rangle^2\Phi_{x,y,z}^2R^{-6},$$

where $\Phi_{x,y,z}$ are the dimensionless functions of angles of the order of unity, and depend on the relative orientations of the vectors $\mathbf{r}$, $\mathbf{R}$ and $\langle d_1\rangle_{if}$ (see (8)). In contrast to the usual Landau-Zener formula, we must take into account the difference between the values of V pertaining to two passages through the point r_c (when the atoms A approach each other and move apart). This difference is the result of the difference in the orientation of the vectors $\mathbf{r}$ and $\mathbf{R}$ at these two points. It is necessary next to average over the angle between ρ and $\mathbf{R}$, over the velocity directions, and finally over the initial projections of the angular momentum of the atom B and sum over the final projections. It is easy to see, however, that all these cumbersome calculations lead only to the appearance in γ of a numerical coefficient of the order of unity, and the dependence of γ on the parameters is obtained immediately:

$$\gamma=\frac{n^2}{2}v\int\langle(e^{-\delta_1}+e^{-\delta_2}-2e^{-\delta_1-\delta_2})\rangle\, d\rho\, d\mathbf{R},$$
$$\delta_{1,2}=\frac{2\pi\langle d\rangle^2\langle d_1\rangle^2(\Phi_z^2)_{1,2}}{v(1-\rho^2/r_c^2)^{1/2}|F_2-F_1|R^6}. \tag{11}$$

The subscripts 1 and 2 label here the first and second passage of the point r_c, the angle brackets denote the averagings described above. Integrating in (11) over the moduli of the vectors ρ and $\mathbf{R}$, we obtain ultimately

$$\gamma=\text{const}\,\frac{n^2\langle d\rangle^2}{|\Delta|}\langle d_1\rangle\langle d\rangle\frac{\sqrt{v}}{\Delta^{1/3}d^{1/3}}, \quad \text{const}\sim 1. \tag{12}$$

Formula (11) pertains to the case of the transition to the ${}^1\Sigma_g^+$ term. The interaction with the doubly degenerate $({}^1\Pi_g)_{x,y}$ term does not lead to additional difficulties in the Landau-Zener problem. This case was investigated in[8], where it is shown that the situation reduces to replacement of V_z^2 by the sum $V_x^2+V_y^2$. Formula (12) consequently remains in force.

We note that if the level B^* lies below the level $A^*(\Delta<0)$, then the deactivation of the atom B^* can be accompanied by formation of a bound state of the pair of atoms AA^*, i.e., to formation of an excited molecule A_2. For the inverse reaction $A^*A+B \to AA+B^*$ it is necessary to replace $n^2/2$ in (9) where nn^*, where n^* is the concentration of the excited atoms A^*. In addition, the radio velocity at the point r_c, which enters in (11), is now equal to $v(1-\rho^2/r_c^2-\Delta/\varepsilon)^{1/2}$, where ε is the kinetic energy of the relative motion of the atoms A. This leads to the appearance of an additional factor $(1-\Delta/\varepsilon)^{3/4}$ in formula (12) for γ. Naturally, the reaction is possible only if $\Delta<\varepsilon$.

As seen from (10) and (11), the distances R significant for the described excitation-transfer mechanism are those for which $\delta_{1,2}\sim 1$, i.e.,

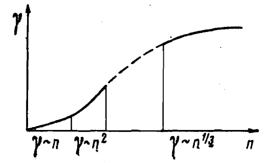

FIG. 2.

$$R^3 \sim \frac{d^{4/3} d_1}{|\Delta|^{2/3} v^{1/2}} \sim \frac{d^2}{|\Delta|} \frac{d_1 |\Delta|^{1/3}}{d^{2/3} v^{1/2}} \sim r_c^3 \left(\frac{|\Delta| d}{v^{3/2}}\right)^{1/3} \gg r_c^3.$$

This justifies the assumption made above, that the essential distances to the atom B are much larger than the dimension of the quasi molecule AA.

Estimates of the effective cross section by means of formula (12) ($\sigma_{\text{eff}} = \gamma/nv$) show that it can reach a rather appreciable value even at a large resonance defect and a low collision velocity. For example, for $\Delta \sim 1$ eV, $v \sim 10^4$ cm/sec, $d \sim d_1 \sim 1\,D$, and $n \sim 10^{20}$ cm^{-3} we obtain $\sigma_{\text{eff}} \sim 10^{-17}$ cm^2. We emphasize that the vacuum excitation-exchange cross section calculated by formula (5), leads for the indicated values of the parameters to a quite negligible value $\sigma_{\text{St}} \sim \exp(-10^3)$ at. un. Therefore formula (12) is valid also in an appreciable part of the region (4a), so long as $\sigma_{\text{eff}} > \sigma_{\text{St}}$. A justification for this statement is the fact that regardless of the satisfaction of the criterion $nd^3 v^{-3/2} \gg 1$ for the formation of the exciton band (it is this which distinguishes (4a) from (4b)), the excitation-transfer process proceeds via two competing channels: transfer in pair collisions with cross section σ_{St}, and collision with the fluctuationally approaching pair of atoms A via the mechanism that leads to formula (12).

We consider now the last region (4c). The local level is located in this case in the central part of the exciton band, where the density of states is $1/\pi E_0$. The number of levels filling in the transit width is estimated at

$$\frac{1}{nd^2} \frac{v^{1/2}}{d} nd^3 v^{-1/2} \sim 1.$$

Thus, the resonance condition is always satisfied in the region (4c), so that Kazantsev's results[5] are applicable. The reciprocal exciton lifetime is given by formula (3). As already mentioned, the effective cross section is in this case $\sigma_{\text{eff}} \sim n^{-2/3}$, i.e., in fact the difference between the atoms B and A becomes inessential. A qualitative plot of γ against the density in the the different regions is shown in Fig. 2.

We have considered here an actual example with definite multipolarities, angular momenta, and other characteristics of the atomic and molecular terms. It is clear, however, that the discussed transfer mechanism can be quite general. Indeed, if a dipole transition in the atom is allowed, then the corresponding dipole matrix element $\mathbf{d}_{\text{mol}}$ of the molecule containing this atom is also different from zero. At interatomic distances that are large in comparison with the Bohr radius, $\langle \mathbf{d}_{\text{mol}} \rangle_{\text{if}}$ is linear in the components of the atomic matrix element. Resonant interaction between A and A^* always leads to a doubling of the number of molecular states and to a splitting, proportional to r^{-3}, of the terms g and u. Therefore in any case of excitation exchange connected with dipole transitions in the colliding atoms, at not too large values of $|\Delta|$, the terms of the three-particle system intersect and the Landau-Zener approximation is valid, as is consequently formula (12).

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(1) It is implied that the probability of the transition is of the order of unity in the essential range of the impact parameters.

(2) The center of the exciton band is, obviously, the energy of the isolated excited atom A^*.

(3) This will be the case even if the atom masses are of the same order. Obviously, the conditions for the applicability of the approximation constructed here become more favorable if the atom B is much heavier than the atom A.

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