Term intersection in multiparticle interactions

V. S. Lisitsa

I. V. Kurchatov Institute of Atomic Energy
(Submitted February 22, 1973)
Zh. Eksp. Teor. Fiz. **65**, 879–885 (September 1973)

The transition probability in a two-level system ("atom") in the presence of a term intersection point (Landau case) is considered when the intersection is due to interaction between the atom and ensemble of many particles. An expression for the transition probability is obtained and extends the Landau result to the case of multiparticle interaction. Concrete calculations are carried out for monopole-dipole and dipole-dipole interactions when the transition is induced by rotation of the perturbing field. In both cases the transition probability can be expressed in terms of functions describing fluctuations of the perturbing particle field and is essentially nonbinary. For low densities the result is identical to that of the binary calculations, and for high densities it tends to a constant which in general is independent of the density and corresponds to the case of complete "mixing" of the atomic terms.

The concept of term crossing is usually used to compute the transition probability during the collision of two slow particles, which we shall, for brevity, call "atoms"[1-3]. This probability is further used to compute the scattering cross section, obtained by either summing over the momenta of the colliding atoms, or by simply integrating over the impact parameter $2\pi\rho d\rho$, since the motion of the atoms is quasiclassical[2,3]. Implicit in such a procedure is the assumption that the collisions are two-body (binary) collisions, and it is thereby assumed (although often without explicitly saying so) that a sphere of radius equal to the effective interaction range R_{eff} contains a small number of particles, i.e., the condition

$$NR_{eff}^3 \equiv g \ll 1 \tag{1}$$

(N is the particle density) is satisfied.

An attempt is made in this paper to take into account the nonbinary (many-particle) nature of the collision between slow atoms. This formulation should obviously correspond to any value of the parameter g in (1). Such a situation can be realized in a sufficiently dense gas, or in a plasma when R_{eff} significantly exceeds the atomic radius a_0. The latter indicates that we are interested in the cases of small (compared to the energy of the atom) energy transfer, e.g., in transitions between adjacent levels[1] (see[2,3]). As to the value of R_{eff}, we shall assume that it is determined by the point of crossing of the corresponding terms.

It is a priori clear that the concept of (binary) collision cross section is inapplicable when the condition (1) is violated, and it makes sense to speak of only a transition probability averaged over an ensemble of perturbing particles.

Let us consider the transition between two electron terms of amplitudes a_1 and a_2 induced by the perturbation $\hat{V}(t)$. The Schrödinger equation has the form[1,2]

$$\begin{aligned} i\hbar da_1/dt &= U_1(t)a_1 + V(t)a_2, \\ i\hbar da_2/dt &= (\hbar\omega_0 + U_2(t))a_2 + V(t)a_1. \end{aligned} \tag{2}$$

Here ω_0 is the term spacing in the absence of interaction, $U_{1,2}$ is the effective potential energy (including the diagonal matrix elements V_{11} and V_{22}), and V(t) is the nondiagonal matrix element of the perturbation inducing the transition.

Since we shall, in what follows, be interested mainly in the nonbinary aspect of the interaction, in solving the system (2), we shall restrict ourselves to the case of sufficiently small V(t) (the Landau case: see[1]). Then the transition probability w (obtainable from (2) under the initial conditions $a_1(-\infty) = 1$ and $a_2(-\infty) = 0$) has the form

$$w = |a_2(+\infty)|^2 = \frac{1}{\hbar^2}\left| \int_{-\infty}^{\infty} dt\, V(t) \times \exp\left\{ i\omega_0 t - i/\hbar \int_{-\infty}^{t} [U_1(t') - U_2(t')]\, dt' \right\} \right|^2. \tag{3}$$

The nature of the interactions $U_{1,2}(t)$ and V(t) has thus far not been specified. In the conventional binary approach, $U_{1,2}$ and V are assumed to be parametrically dependent on the distance R(t) between the atoms. In our case $U_{1,2}$ and V are functions of the coordinates $\mathbf{R}_i(t)$ of all the $\mathcal{N}$ perturbing particles, which we shall assume to be enclosed in a sphere of volume Δ. Thus, the potentials $U_{1,2}$ and V should, in the case being considered, be determined by a point in the $6\mathcal{N}$-dimensional phase space.

Let us now state the main assumption about the existence of term intersection, to wit: we shall assume that the dominant contribution to the integral (3) is made by that region $\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_{\mathcal{N}}$, of phase space where the phase of the exponent in (3) is stationary:

$$U_1[\mathbf{R}_1(t_k), \ldots, \mathbf{R}_{\mathcal{N}}(t_k)] - U_2[\mathbf{R}_1(t_k), \ldots, \mathbf{R}_{\mathcal{N}}(t_k)] = \hbar\omega_0. \tag{4}$$

The condition (4) is essentially an expression of the Franck-Condon principle for a "molecule" with $\mathcal{N}$ nuclei, to which is equivalent, in the present case, a gas of interacting particles.

In the binary case the subsequent calculation of (3) usually consists in the expansion of the exponent in a series around the stationary-phase point t_k defined by (4). Such a procedure leads to the Landau formula[1,2]:

$$w = \frac{4\pi |V(t_k)|^2}{|dU_1/dt - dU_2/dt|_{t=t_k}}. \tag{5}$$

To obtain the total transition probability, we should sum (5) over all the points t_k, taking into account the stochastic nature of the perturbation. In the binary case there is a simple connection between t_k and the impact parameter ρ, and this allows us to reduce the summation over t_k to integration over ρ and comparatively simply obtain the transition cross section. In the case of the many-particle interaction t_k is an extremely complicated function in the phase space $\mathbf{R}_1, \ldots \mathbf{R}_{\mathcal{N}}$, and therefore to avoid a direct summation over t_k, we must average over the corresponding ensemble, using the assumption that a random process is a stationary process.

The transition to averaging over the ensemble is accomplished in (3) with the aid of the general formulas of correlation theory (see, for example,[4], Sec. 36). As a result, we obtain for the transition probability per unit time W the expression

$$W=\int_{-\infty}^{\infty} d\tau\, e^{i\omega_0\tau}\Phi(\tau), \tag{6}$$

where $\Phi(\tau)$ is the correlation function (the symbol $\langle\ldots\rangle$ denotes averaging over the ensemble):

$$\Phi(\tau)=\frac{1}{\hbar^2}\left\langle V(0)V(\tau)\exp\left\{-\frac{i}{\hbar}\int_0^{\tau}[U_1(t)-U_2(t)]dt\right\}\right\rangle. \tag{7}$$

The quantity W is the analog of the collision rate which figures in the conventional binary theory.

In essence, (6) and (7) contain information about the evolution of the system for an arbitrary rate of change of the perturbation[2]. The extraction of any explicit analytic results in the general case is however made difficult by the presence in (7) of the ensemble averaging, which is feasible only in certain particular cases. One of such cases is the slow-collision case of interest to us.

In fact, if $U_{1,2}(t)$ and $V(\tau)$ vary sufficiently slowly, then the correlation function $\Phi(\tau)$, (7), can be expanded in a series in τ, which after substitution into (6) yields (in the first nonvanishing order):

$$W=\frac{2\pi}{\hbar}\langle V^2(0)\,\delta\{\hbar\omega_0-U_1[\mathbf{R}_1(0),\ldots,\mathbf{R}_{\mathcal{N}}(0)]+U_2[\mathbf{R}_1(0),\ldots,\mathbf{R}_{\mathcal{N}}(0)]\}\rangle. \tag{8}$$

The result (8) solves the formulated problem in general form. Those regions of the coordinate space $\mathbf{R}_1(0),\ldots,\mathbf{R}_{\mathcal{N}}(0)$ which correspond to the term-crossing condition (4) are automatically separated out when (8) is averaged over this space. It is also not difficult to connect the result (8) with the Landau formula (5). Indeed, by replacing in (8) the ensemble average by the time average, we can verify that the presence of the δ-function leads to the appearance of the stationary-phase points t_k defined in (4). Then, using the relation $\delta[f(t)]=|df/dt|^{-1}_{t=t_k}\delta(t-t_k)$, we arrive at (5)[3]. Thus, the formula (8) is a natural generalization of (5) to the case of many-particle interactions.

Let us now consider concrete examples of the application of the result (8).

BINARY INTERACTION

Let us begin with the case of the binary (spherically-symmetric) interaction $U_{1,2}(R)$ and $V(R)$, which is realized when the condition (1) is fulfilled. Let the probability for atoms separated by a distance R be given by the distribution function $f(\mathbf{R})d\mathbf{R}=4\pi R^2 f(R)\,dR$. Then, we have from (8):

$$W=\frac{16\pi^2}{\hbar}\frac{V^2(R_0)R_0^2 f(R_0)}{|dU_1/dR-dU_2/dR|_{R=R_0}}, \qquad U_1(R_0)-U_2(R_0)=\hbar\omega_0. \tag{9}$$

If as $f(R)$ we use the nearest-neighbor distribution law ($f(R)=N\exp(-\frac{4}{3}\pi NR^3)$), then for the power interaction law: $U_1(R)-U_2(R)=\hbar C_k/R^k$, $V(R)=\hbar C_m/R^m$, we obtain from (9) that

$$W=8\pi^2 N\frac{C_m^2}{C_k k R_0^{2m-k-3}}, \qquad R_0=\left(\frac{C_k}{\omega_0}\right)^{1/k} \tag{10}$$

(the exponent in $f(T)$ coincides with the parameter (1) and is therefore unimportant in the binary region ($g\ll 1$)). It can be seen from (10) that the contribution to W from the individual particles is additive ($W\propto N$).

MONOPOLE-DIPOLE INTERACTION

Let the potentials $U_{1,2}$ be determined by the interaction of the dipole moment $\mathbf{d}$ of the atom with the electric field $\mathbf{F}$ produced by the surrounding charged particles (e.g., by the ions of a plasma)[4]:

$$U_1(0)-U_2(0)=-\langle 1,2|\mathbf{dF}(0)|1,2\rangle=\hbar\frac{\alpha}{e}|\mathbf{F}(0)| =\hbar\frac{\alpha}{e}\left|\sum_{i=1}^{\mathcal{N}}\frac{e\mathbf{R}_i(0)}{R_i^3(0)}\right|. \tag{11}$$

The transitions to another state are usually induced in the binary case by the effects of the rotation of the internuclear axis[2,3]. Similar effects are produced in the case under consideration by the rotation of the many-particle field $\mathbf{F}(t)$. The angular velocity Ω of such a rotation is given by the expression[6]:

$$\Omega(0)=|\dot{\mathbf{F}}_\perp(0)|/|\mathbf{F}(0)|, \tag{12}$$

where $\dot{\mathbf{F}}_\perp(0)$ is the component of the field derivative vector $\dot{\mathbf{F}}(0)$ in the direction perpendicular to $\mathbf{F}(0)$.

The interaction of the orbital angular momentum $\mathbf{L}$ of the atom with the rotation of the field has the form

$$V(0)=\hbar\langle 1|\mathbf{L}\Omega(0)|2\rangle\equiv\hbar\gamma|\dot{\mathbf{F}}_\perp(0)|/|\mathbf{F}(0)|. \tag{13}$$

After substituting (11) and (13) into (8), we can conveniently carry out the averaging in two stages: we first average $\dot{F}_\perp^2(0)$ at a fixed value of the ionic field $F(0)\equiv|\mathbf{F}|$ and then integrate over all F with the Holtsmark distribution function $\mathcal{H}(F)$. This allows us to use at the first stage of the averaging the Chandrasekhar-von Neumann results[7] for the quantity $\{\dot{\mathbf{F}}_\perp^2\}_{\text{av F}}$ (the symbol $\{\ldots\}_{\text{av F}}$ denotes averaging at fixed F). Then we obtain for the mean square angular velocity $\{\Omega^2(0)\}_{\text{av F}}$ the expression

$$\{\Omega^2(0)\}_{\text{avF}}=\frac{45}{8}\omega_F^2\frac{G(\beta)-I(\beta)}{\beta^{3/2}\mathcal{H}(\beta)}. \tag{14}$$

Here $\omega_F=\sqrt{\lambda}v_0N^{1/3}$ ($\lambda=2\pi(\frac{4}{15})^{2/3}\approx 2.603$ and v_0 is the most probable velocity) is the characteristic scale of the rate of change of the ionic field, $\beta=F/F_0$, where $F_0=\lambda eN^{2/3}$ is the "normal" Holtsmark field, $\mathcal{H}(\beta)$ is the Holtsmark function[8], and $G(\beta)$ and $I(\beta)$ are the Chandrasekhar-von Neumann functions[7].

Using (14) in the averaging of (8), we obtain

$$W=\frac{45\pi}{4}\gamma^2\frac{\omega_F^2}{\alpha F_0/e}\frac{G(e\omega_0/\alpha F_0)-I(e\omega_0/\alpha F_0)}{(e\omega_0/\alpha F_0)^{3/2}}. \tag{15}$$

The result (15) has an essentially nonbinary character, which is manifested in the nonlinear dependence of W on the ion density N. Let us investigate the nature of the behavior of W at high and low densities. Using the expansion of the functions $G(x)$ and $I(x)$ for small and large values of the argument[6,7], we have

$$W\approx\begin{cases}\dfrac{15\sqrt{2\pi}}{4}\lambda^{3/2}N\gamma^2\dfrac{\alpha^{1/2}v_0^2}{\omega_0^{3/2}}=4\pi^2N\gamma^2\dfrac{\alpha^{1/2}v_0^2}{\omega_0^{3/2}}, & \dfrac{\alpha}{e}F_0\ll\omega_0,\\ 10\gamma^2v_0^2/\alpha, & \alpha F_0/e\gg\omega_0.\end{cases} \tag{16}$$

For $\alpha F_0/e\ll\omega_0$, (16) coincides, as it should be, with the result of the binary theory (10) (in which we should set $k=2$, $m=1$, $C_k=C_2\equiv\alpha$, and $C_m=C_1\equiv v_0\gamma$). For $\alpha F_0/e\gg\omega_0$, the function W takes on, as follows from (16), a constant value which, in general, does not depend on the density, a result which is explained by the fact that the two terms get highly mixed up, starting from

a certain density $N^* \sim (\omega_0/\alpha)^{3/2}$, and the effect becomes insensitive to further growth of N.

The obtained results can be generalized without difficulty to the case of a more complicated dependence of $U_{1,2}$ on F (e.g., $U_{1,2} \propto F^p$, where p = 2, 3, ...). The basic qualitative laws of the phenomenon are preserved when this is done and we shall therefore not discuss such cases here.

As a simple physical example of the application of the results, let us consider transitions between the Zeeman sublevels of the hydrogen atom during collisions with slow ions in a dense plasma. This effect determines the polarization of the spectral line[3]. The existence of the point of crossing of the terms is easily verified with the aid of the following arguments: consider the magnetic field **B** and the electric field **F**, which separately give rise to Zeeman ($\Delta\omega_Z$) and Stark ($\Delta\omega_S$) splittings; let us, for clarity of argument, consider the level with the principal quantum number n = 2 without allowance for spin and the case of parallel **B** and **F**; then, if $\Delta\omega_Z \gg \Delta\omega_S$, the components with the magnetic quantum numbers m = ±1 are split, while the components with m = 0 are unperturbed; on the contrary, if $\Delta\omega_Z \ll \Delta\omega_S$, then the components with m = 0 are split, while the components with m = ±1 are "mixed;" hence it is clear that as we gradually go from a Zeeman to a Stark term structure (by gradually increasing the field F), a point of intersection of the m = ±1 terms with the m = 0 terms is bound to arise when $\Delta\omega_Z \sim \Delta\omega_S$. It is precisely this sort of situation that can be realized for the example being considered, in which the field F is produced by slow plasma ions. Notice that the transition between the m = ±1 and m = 0 states is induced here by the rotation of the field F.

Let us estimate the order of magnitude of the density N at which the role of the many-particle effects is important. Assuming (see (15))

$$\omega_0 = \Delta\omega_z \sim 10^{-4} \text{ a.u.}, \quad \alpha F_0/e = \Delta\omega_s \propto N^{2/3} (\alpha \sim 1),$$

we have $N^* \sim 10^{-6}$ a.u. $\sim 10^{18}$ cm^{-3}. In fact, the value of N^* can even be considerably smaller if we allow for the fact that the Stark constant α increases with n ($\propto n^2$).

Let us verify the consistency of the approximations considered. The condition that the effect of the perturbation should be slow implies that the characteristic ionic field frequency $N^{1/3}v_0$ should be small compared to ω_0: $N^{1/3}v_0 \ll \omega_0$. On the other hand, in order for the "many-particle" crossing point to exist, ω_0 should be comparable to the Spark splitting $\alpha N^{2/3}$ (for still higher densities $\omega_0 \ll \alpha N^{2/3}$: see (16)). The consistency of the two conditions requires the fulfilment of the inequality $N^{1/3}\alpha/v_0 \gg 1$. As is well known from the theory of line broadening in a plasma[4-6], this inequality is usually satisfied for ions.

From the experimental point of view, the foregoing example is interesting in at least two respects. First, by measuring in a magnetic field **B** the polarization of the line under investigation, we can, according to (16), observe the disappearance of the density dependence of the effect at $N > N^*$; so that knowing B, we can determine N^*, and vice versa. Secondly, since when $N \gg N^*$, the quantity $W \propto v_0^2 \propto T$, the computed effect can be used to determine the ion temperature.

DIPOLE-DIPOLE INTERACTION

In the case of the dipole-dipole interaction the potential $U_{1,2}$ has the form

$$\frac{U_1 - U_2}{\hbar} = \frac{1}{\hbar}\langle 1,2|\mathbf{d}\mathbf{D}(0)|1,2\rangle = \varepsilon D(0) = \varepsilon \left| \sum_{i=1}^{\mathcal{N}} \frac{(\mathbf{d}_i\mathbf{R}_i)\mathbf{R}_i - \mathbf{d}_i R_i^2}{R_i^5} \right|. \tag{17}$$

As was done above, we shall assume that the interaction V(0) is connected with the angular velocity Ω_D of the rotation of the vector **D**:

$$\Omega_D(0) = |\dot{\mathbf{D}}_\perp(0)| / |\mathbf{D}(0)|, \quad V(0) = \hbar\gamma_D\Omega_D(0). \tag{18}$$

Substituting (17) and (18) into (8) and averaging first over $\dot{\mathbf{D}}_\perp^2(0)$ at a fixed value of $|\mathbf{D}| \equiv D$, we obtain

$$W = 2\pi\gamma_D^2 \left\langle \frac{\{\dot{D}_\perp^2(0)\}_{cpD}}{D^2(0)} \delta[\omega_0 - \varepsilon D(0)] \right\rangle. \tag{19}$$

The remaining averaging over D requires knowledge of the distribution function of the fields produced by the dipole moments $\Lambda(D)$. Such a distribution function was computed by Holtsmark[8] for randomly oriented dipoles d_i of equal magnitude d_0. Let us cite this function, in view of its simplicity (and in view of the fact that it is not well known):

$$\Lambda(D)\,dD = \frac{4}{\pi}\frac{z^2\,dz}{(1+z^2)^2}, \tag{20}$$

where $z = D/D_0$ ($D_0 = 4.54Nd_0$ is the "normal" field of the dipoles).

As to the quantity $\{\dot{\mathbf{D}}_\perp^2(0)\}_{av\,D}$, it has thus far not been computed and we shall therefore restrict ourselves to writing it in dimensionless variables. Performing the necessary integrations, we obtain

$$W \propto \gamma_D^2 \frac{\omega_D^2}{\varepsilon D_0} P\left(\frac{\omega_0}{\varepsilon D_0}\right) \frac{4}{\pi}\left[\frac{\omega_0 \varepsilon D_0}{(\varepsilon D_0)^2 + \omega_0^2}\right]^2. \tag{21}$$

Here $\omega_D \sim v_0 N^{1/3}$ is the characteristic scale of the rate of change of the field D and P(x) is a function characterizing the rate of fluctuations in **D**.

The result (21), like (15), has a fundamentally nonbinary character connected with the presence of the functions P(x) and $\Lambda(x)$ that describe the fluctuations in the collective microfield. Although the explicit form of the function P(x) has thus far not been found, it can be asserted that in the limit of low densities when $\epsilon d_0 N \ll \omega_0$, the result (21) should go over into the binary result (10) (for k = 3 and m = 1, $C_k = C_3 \equiv \epsilon d_0$ and $C_m = C_1 \equiv v_0\gamma_D$); on the other hand, for high densities when $\epsilon d_0 N \gg \omega_0$, the probability (21) should tend to a constant corresponding to complete mixing of the terms. These results, like those obtained above, can easily be generalized to the case $U_1 - U_2 \propto D^p$ (p > 1).

The above-considered example bears a relation to a number of physical effects. For example, as in the previous case, it is possible to observe the effects of the depolarization of the Zeeman sublevels of an atom in a gas of dipole molecules. Another effect of direct interest is the transition between the fine-structure sublevels of an excited atom in its own gas.

The result of the binary theory for such transitions, obtained by the crossing-point method (see[3]), coincides with the binary limit of (21). For high densities (here allowance for resonance transfer of excitation is, strictly speaking, necessary), the formula (21) allows us to estimate the magnitude N^* of the density at which the effects of the nonbinary nature of the collisions become important. Thus, for the $2P_{3/2} - 2P_{1/2}$ transi-

tions in sodium we have: $\omega_0 \sim 10^{-5}$ a.u., $4.5\epsilon d_0 \sim 10$ a.u., and $N^* \sim 10^{-6}$ a.u. $\sim 10^{18}$ cm^{-3}. Naturally, the value strongly depends on the specific transition.

With these examples we end our investigation of specific types of interactions. In the present paper we have considered certain general laws for processes connected with term crossing. It is clear that the search for the crossing points is in each specific case an independent complex problem.

After the dispatch of the present paper to the press, Vitlina and Dykhne's paper[9], in which the interesting question of the effect of a dense medium on resonance charge transfer is considered, appeared. In[9] the influence of the medium is considered as some external (with respect to the system that is being recharged) factor that gives rise to resonance detuning. In the present paper the medium is not an external factor, but performs the role of one of the colliding partners. Therefore the results of the present paper cannot be applied directly to resonance processes, which require special consideration. The main difficulty here is connected with the necessity for taking into account the high multiplicity of the degeneracy of a system of resonating identical particles.

The author is deeply grateful to V. I. Kogan and O. B. Firsov for a discussion of the results of the paper.

[1)] Resonance and charge-transfer processes are not considered below.

[2)] The approximation under consideration corresponds to the distorted-wave method of the binary theory [2,3].

[3)] In doing this, we should take into account the factor 2 that arises as a result of the fact that the point of intersection is passed through twice (see [1]).

[4)] Notice that this case describes, in particular, the effects of the broadening of the hydrogen spectral lines in the framework of the so-called quasi-static theory [4,5].

[1] L. D. Landau and E. M. Lifshitz, Kvantovaya mekhanika (Quantum Mechanics), Fizmatgiz, 1963 (Eng. Transl., Addison-Wesley, Reading Mass., 1958).
[2] N. Mott and H. Massey, The Theory of Atomic Collisions, Oxford, 1965 (Russ. Transl., Mir, 1969).
[3] B. M. Smirnov, Asimptoticheskie metody v teorii atomnykh stolknoveniĭ (Asymptotic Methods in the Theory of Atomic Collisions), Atomizdat, 1973.
[4] I. I. Sobel'man, Vvedenie v teoriyu atomnykh spektrov (Introduction to the Theory of Atomic Spectra), Fizmatgiz, 1963 (Eng. Transl., Pergamon Press, New York, 1972).
[5] V. I. Kogan, in: Fizika plazmy i problema upravlyaemykh termoyadernykh reaktsiĭ (Plasma Physics and the Problem of Controlled Thermonuclear Reactions), Vol. 4, Izd. AN SSSR, 1958, p. 258.
[6] G. V. Sholin, V. S. Lisitsa, and V. I. Kogan, Zh. Eksp. Teor. Fiz. 59, 1390 (1970) [Sov. Phys.-JETP 32, 758 (1971)].
[7] S. Chandrasekhar, "Stochastic Problems in Physics and Astronomy," Rev. Mod. Phys. 15, 1 (1943) (Russ. Transl., IIL, 1947).
[8] J. Holtsmark, Ann der Phys. 58, 577 (1919).
[9] R. Z. Vitlina and A. M. Dykhne, Zh. Eksp. Teor. Fiz. 64, 510 (1973). [Sov. Phys.-JETP 37, No. 2 (1973)].

Translated by A. K. Agyei
91