NONADIABATIC TRANSITIONS BETWEEN INTERSECTING TERMS IN RANDOM MOTION

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The probability for nonadiabatic transitions between linear intersecting terms are calculated for the case of random motion along these terms. The interaction matrix element is considered small and this permits us to apply perturbation theory. Diffusive motion and the Poisson process are considered in the one-dimensional case. The three-dimensional problem is solved for not too rapid diffusive motion. Formulas are obtained which express the probability for a nonadiabatic transition in terms of the parameters of the problem for the homogeneous and quasi-homogeneous (diffusion of unstable particles with a source) stationary random motion.

THE so-called Landau-Zener problem[1,2] is well known in collision theory. This is the problem of the computation of the probabilities of transitions between two intersecting terms U_1 and U_2 separated by the distance

$$U_1(x) - U_2(x) = \Delta U(x) = \hbar\omega(x) = \hbar\gamma x, \tag{1}$$

where x is the coordinate and $\hbar\gamma = F_2 - F_1 = \Delta F$ is the difference between the forces at the point of intersection. The Landau-Zener problem amounts to solving the time-dependent Schrödinger equation with the Hamiltonian:

$$H = {}^1/_2\hbar\omega(x)\sigma_z + \hbar\omega_1\sigma_x, \tag{2}$$

where σ_Z and σ_X are Pauli matrices, and the quantity $\hbar\omega_1 = V_{12}$ represents the interaction matrix element for the states 1 and 2. In the expression (2), the coordinate x is considered as a function of t; x = vt so that uniform motion along the x axis is assumed. The exact solution of the equation $i\hbar\partial\psi/\partial t = H\psi$ allows us to determine the probability of transition from the state $\sigma_Z = 1$ to the state $\sigma_Z = -1$ as x varies from $-\infty$ to ∞ in accordance with the law x = vt. When the condition

$$\omega_1^2 \ll \gamma v \tag{3}$$

is fulfilled, the problem may be solved by perturbation theory, the role of perturbation being played by the quantity $\hbar\omega_1\sigma_X$ in the expression (2). The results of[1,2], representing the transition probability per collision, are widely used in investigations of nonadiabatic processes in the gaseous phase[3]. In the condensed phase, the model of dynamical motion along a special trajectory should be replaced by a statistical analysis of all the possible forms of functional dependence x = x(t). Finally, the concept of collision is itself not defined in the condensed phase and the computation of the transition probability per passage of the point of intersection of the terms is meaningless here.

In the present paper we consider the behavior in time of the system with the Hamiltonian (2), considering the function x(t) as a random function of time, the probability characteristics of which correspond to diffusive or uneven random motion along the x axis. With this aim in mind, we shall express the quantities of interest to us in the form of functionals of the arbitrary function x(t), and then average these functionals over all possible realizations of x(t). This program is feasible only for not too large values of ω_1, when perturbation theory is applicable. A concrete condition of applicability of our analysis, which is similar to (3), will be obtained below.

So let us consider the equation

$$i\frac{\partial\psi}{\partial t} = \frac{1}{2}\omega(x(t))\sigma_z\psi + \omega_1\sigma_x\psi, \quad \psi = \begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix}, \tag{4}$$

the solution of which we seek in the form

$$\psi_1 = \varphi_1\exp\left[-\frac{i}{2}\int_{t_0}^{t}\omega(t')\,dt'\right], \quad \psi_2 = \varphi_2\exp\left[\frac{i}{2}\int_{t_0}^{t}\omega(t')\,dt'\right]. \tag{5}$$

For φ_1 and φ_2 we obtain from (4) and (5) the system of equations

$$\begin{aligned} i\dot{\varphi}_1 &= \omega_1\varphi_2\exp\left[i\int_{t_0}^{t}\omega(t')\,dt'\right],\\ i\dot{\varphi}_2 &= \omega_1\varphi_1\exp\left[-i\int_{t_0}^{t}\omega(t')\,dt'\right]. \end{aligned} \tag{6}$$

Setting at t = 0, $\varphi_1 = 1$, $\varphi_2 = 0$ (the system is in the state 1), we find in the first approximation

$$\varphi_2(t) = -i\omega_1\int_0^t\exp\left[i\int_{t_0}^{t_1}\omega(t')\,dt'\right]dt_1. \tag{7}$$

Hence the probability of finding the system in the state 2 before the time t is equal to

$$\begin{aligned} W(t) &= \omega_1^2\left|\int_0^t\exp\left[i\int_{t_0}^{t_1}\omega(t')\,dt'\right]dt_1\right|^2\\ &= \omega_1^2\int_0^t d\bar{t}_1\int_0^t dt_2\exp\left[i\int_{t_1}^{t_2}\omega(t')\,dt'\right]. \end{aligned} \tag{8}$$

Averaging over all realizations of the function $\omega(x(t))$, such that $x(t_2) = x$ at $t = t_2$ (we shall denote this incomplete averaging operation by angle brackets with the index x), we find

$$\langle W(t)\rangle_x = \omega_1^2\int_0^t dt_1\int_0^t dt_2\left\langle\exp\left[i\int_{t_1}^{t_2}\omega(t')\,dt'\right]\right\rangle_x, \tag{9a}$$

$$W(t) = \int_{-\infty}^{\infty}P(x)\langle W(t)\rangle_x\,dx, \tag{9b}$$

where P(x) is the one-dimensional distribution function of the random quantity x.

The expression

$$A(x, t_1, t_2) = \left\langle \exp\left[i \int_{t_1}^{t_2} \omega(t')\, dt' \right] \right\rangle_x$$

entering into (9) is easy to find by a method expounded in[4-6]. The essence of the method is as follows. Incomplete averaging for a Markov process is represented by the Wiener integral

$$A(x, t_1, t_2) = \int \dots \int dx_1\, dx_2 \dots dx_p \exp[i\omega(x_1)(t^{(1)} - t_1) + i\omega(x_2)(t^{(2)} - t^{(1)}) + \dots + i\omega(x)(t_2 - t^{(p)})] P(x_1) \times P(x_2, t^{(2)} | x_1, t^{(1)}) \dots P(x_1, t_2 | x_p, t^{(p)}),$$

where $t_1 < t^{(1)} < t^{(2)} < \dots < t^{(p)} < t_2$, $P(x_k, t^{(k)} | x_{k-1}, t^{(k-1)})$ is the conditional probability of the process x(t), while P(x) is the one-dimensional distribution function of this process. It can be seen from this expression that A(x, t, t) = P(x). The variable t_2 enters into the right hand side via the factors $\exp(i\omega(x)t_2)$ and $P(x, t_2 | x_p, t^{(p)})$. For a Markov process the conditional probability obeys the equation

$$\frac{\partial}{\partial t_2} P(x_2, t_2 | x_1, t_1) = L P(x_2, t_2 | x_1, t_1),$$

where L is a linear operator that acts on the variable x_2. Consequently, we obtain for $A(x, t_1, t_2)$ the equation

$$\frac{\partial}{\partial t_2} A(x, t_1, t_2) = i\omega(x) A(x, t_1, t_2) + L A(x, t_1, t_2)$$

with the initial condition A(x, t, t) = P(x). For a homogeneous process, P(x) = const = P_0. Consequently, the initial condition for A may be chosen in the form A(x, t, t) = 1. Then the complete averaging of the quantity

$$\exp\left[i \int_{t_1}^{t_2} \omega\, dt' \right]$$

entails integration of the function $P_0 A(x, t_1, t_2)$ with respect to x.

Let us, to begin with, consider the one-dimensional diffusive motion. The equation for the conditional probability has the form

$$\partial P / \partial t_2 = D \partial^2 P / \partial x^2, \tag{10}$$

where D is the coefficient of diffusion, while for $A(x, t_1, t_2)$ we obtain

$$\frac{\partial A}{\partial t_2} = i\omega(x) A + D \frac{\partial^2 A}{\partial x^2}, \quad A(x, t, t) = 1. \tag{11}$$

For $\omega(x) = \gamma x$, the solution of (11) is

$$A(x, t_1, t_2) = \exp[i\gamma x (t_2 - t_1) - {}^1/_3 \omega_c^3 (t_2 - t_1)^3], \tag{12}$$

where $\omega_c^3 = D\gamma^2$. Setting $t_2 - t_1 = \tau$, we write (12) in the form

$$A(x, t_1, t_2) = A(x, t_2 - t_1) = A(x, \tau) = \exp[i\gamma x\tau - {}^1/_3 \omega_c^3 \tau^3]. \tag{13}$$

The expression (13), as well as the equation (10), is valid for $\tau = t_2 - t_1 > 0$. Proceeding from the definition of the quantity A, it is easy to show that

$$A(-\tau) = A^*(\tau). \tag{14}$$

Therefore, the formula

$$A(x, \tau) = \exp[i\gamma x\tau - {}^1/_3 \omega_c^3 |\tau|^3] \tag{15}$$

determines the quantity $A(x, \tau)$ for all values of τ.

Substituting (15) into (9), we obtain after simple transformations

$$\langle W(t) \rangle_x = 2\omega_1^2 \int_0^t (t - \tau) \operatorname{Re} A(x, \tau)\, d\tau. \tag{16}$$

Since for $\omega_c \tau \gg 1$ the function $A(x, \tau)$ decays very rapidly, it follows that for sufficiently large t, such that

$$\omega_c t \gg 1, \tag{17}$$

we may extend the integral in (16) to infinity and write for $\langle W(t) \rangle_x$

$$\langle W(t) \rangle_x = 2t\omega_1^2 \operatorname{Re} \int_0^\infty A(x, \tau)\, d\tau. \tag{18}$$

As can be seen from (18) and (9b), the transition probability is proportional to the time. Let us introduce the incompletely averaged quantity

$$W(x) = 2\omega_1^2 \operatorname{Re} \int_0^\infty A(x, \tau)\, d\tau. \tag{19}$$

With the aid of (9b) and (19), we find for the transition probability per unit time

$$W = 2\omega_1^2 P_0 \operatorname{Re} \int_{-\infty}^{\infty} dx \int_0^\infty A(x, \tau)\, d\tau. \tag{20}$$

The quantity (19) has a maximum at x = 0 equal to ${}^1/_3 \omega_1^2 / \omega_c$. The width of this maximum is $\Delta x = \omega_c / \gamma$. For $|x| \gg \Delta x$ the value of W(x) tends to zero exponentially. This circumstance clearly illustrates the fact that in our problem, as well as in[1,2], the transitions occur mainly in the vicinity of the point of intersection of the terms.

Let us at any moment of time (including the initial moment) be dealing with a large number N of systems in the state 1, all values of x for each of the systems being equally probable. This means that in a sample of dimension 2L there is maintained a constant concentration, c = N/2L, of particles making transitions. Since P_0 in that case is equal to $(2L)^{-1}$, the transition probability per unit time calculated for one particle is

$$W_1 = (2L)^{-1} \int_{-L}^{L} W(x)\, dx,$$

while the total number of transitions in unit time equals

$$W = \frac{N}{2L} \int_{-L}^{L} W(x)\, dx. \tag{21}$$

Going over in (21) to the limit $L \to \infty$, $N \to \infty$, we obtain

$$W = 2\omega_1^2 c \operatorname{Re} \int_{-\infty}^{\infty} dx \int_0^\infty d\tau \exp\left[i\gamma x\tau - \frac{\omega_c^3 \tau^3}{3} \right].$$

Reversing the order of integration, we finally find for the quantity W

$$W = 2\pi c \omega_1^2 / \gamma. \tag{22}$$

It may seem strange that the value of the diffusion coefficient D does not enter into the final result. This fact, however, has a clear physical meaning. As is well-known from[1,2], the transition probability is inversely proportional to the rate of passage through the point of intersection of the terms, i.e., inversely proportional to D. On the other hand, for a one-dimensional diffusive motion, the rate of "delivery" to the

point of intersection of the terms is directly proportional to D. As a result, the number of transitions per unit time does not depend on D at all.

Of particular importance in applications are those stationary processes in which the particle distribution in space cannot be considered homogeneous (we shall henceforth call them processes with a source). Let particles be created at the point $x_0 < 0$ and let these particles decay in all space with the time constant τ_0, so that the stationary distribution of particles in space is given by the function $c(x)$. If the process being considered is diffusion of unstable particles (with a lifetime τ_0) along the half-line $x > x_0$ with a particle source at the point x_0, then for the function $c(x)$, normalized to unity, we have

$$c(x) = \sigma^{-1}\exp[-(x - x_0)/\sigma],\ \sigma^2 = D\tau_0.$$

Such a process, generally speaking, is Markovian only when $\tau_0 \to \infty$. Let us suppose, however, that the particles cross (on the average) the section Δx which is important for nonadiabatic transitions in the time $\Delta\tau \sim \Delta x^2/D$ considerably less than τ_0: $\Delta\tau \ll \tau_0$. Then we may, close to the point of intersection of the terms $x = 0$, approximately replace the inhomogeneous process by a homogeneous diffusion process along the total length of the line, choosing the one-dimensional distribution density $P_0 = \text{const}$ such that it coincides with the distribution $c(x)$ for the inhomogeneous process near the point of intersection of the terms:

$$P_0 = c(0) = \sigma^{-1}\exp\{-|x_0|/\sigma\}. \tag{23}$$

Therefore, we obtain directly from (9b), (19) and (23) the transition probability per unit time for the indicated case:

$$\bar{W}' = \frac{2\pi\omega_1^2}{\gamma\sqrt{D\tau_0}}\exp\left\{-\frac{|x_0|}{\sqrt{D\tau_0}}\right\}. \tag{24}$$

The condition of applicability of formula (19) and, hence, the formulas (22) and (24) may be obtained in the following fashion. It is clear that Eq. (5), generally speaking, cannot be solved with the aid of perturbation theory for an arbitrary function $x(t)$. However, only the most probable of the trajectories make appreciable contributions to the final result, which is averaged over all the trajectories. For such trajectories, the duration of stay of the system in the region $\Delta x = \omega_c/\gamma$, where a transition is most likely, is, by order of magnitude, given by

$$\Delta t \sim \Delta x^2/D \sim \omega_c^2/D\gamma^2 \sim \omega_c^{-1}. \tag{25}$$

Therefore, the velocity with which the overwhelming majority of trajectories go through the point of intersection is, by order of magnitude, equal to

$$\bar{v} \sim \Delta x/\Delta t \sim \omega_c^2/\gamma.$$

Consequently, the condition of applicability of perturbation theory may, on the basis of (3), be written in the form

$$\omega_1^2 \ll \omega_c^2,\quad \omega_1^2 \ll (D\gamma^2)^{2/3}. \tag{26}$$

We have used formula (3) to obtain the condition (26) since (3) is a necessary and sufficient condition of applicability of perturbation theory to the nonadiabatic problem of two intersecting terms. The necessity of (26) may be proved once we require that it be possible to indicate an interval of time t during which the quantity $\langle W(t)\rangle_x$ is considerably less than unity even at the maximum (i.e., at $x = 0$) while at the same time the condition (17) is fulfilled. In other words, two conditions should be fulfilled simultaneously:

$$W(x=0)\ t \ll 1,\ t \gg \omega_c^{-1}. \tag{27a}$$

The first of these conditions may be written as $\omega_1^2 t/\omega_c \ll 1$, or $t \ll \omega_c/\omega_1^2$. Therefore, both relations (27) may be satisfied if $\omega_c/\omega_1^2 \gg 1/\omega_c$, i.e.,

$$\omega_c^2 \gg \omega_1^2. \tag{27b}$$

In other words, we again arrive at the condition (26).

Let us now consider, as a random process, the discrete Poisson process of jumps of magnitude a, occurring with mean frequency ν in the positive direction of the x axis. The equation for the conditional probability $P(n, t\,|\,n_0, t_0)$ that a particle occupying the position $x_0 = n_0 a$ at the moment t_0 be found at the point $x = na$ at the moment t, has the form[7]

$$\partial P(n, t|n_0, t_0)/\partial t = \nu[P(n-1, t|n_0, t_0) - P(n, t|n_0, t_0)],\ n > n_0,$$
$$\partial P(n, t|n_0, t_0)/\partial t = -\nu P(n_0, t|n_0, t_0).$$

Consequently, we have for the function $A(n, \tau)$

$$\partial A(n,\tau)/\partial\tau = i\gamma a n A(n,\tau) + \nu[A(n-1,\tau) - A(n,\tau)]. \tag{28a}$$

The initial condition may, as before, be written in the form

$$A(n, 0) = 1. \tag{28b}$$

We carry out the normalization of the one-dimensional probability $P(n)$ for the homogeneous Poisson process in the same manner as in the case of the one-dimensional diffusion process:

$$P_0 = ca. \tag{29a}$$

For the process with a source at the point $n = -n_0$, the probability $c(n)$ is given by the stationary, normalized (to unity) solution of the system of equations

$$\frac{\partial c(n)}{\partial t} = -\frac{c(n)}{\tau_0} \mp \nu[c(n-1) - c(n)],\quad \sum_{n=-n_0}^{\infty} c(n) = 1.$$

The required solution is

$$c(n) = \frac{1}{(1+\nu\tau_0)}\left(1 + \frac{1}{\nu\tau_0}\right)^{-n-n_0}. \tag{29b}$$

Note that for $\nu \to \infty$, $a \to 0$, $\nu a \to \bar{v} = \text{const}$, we obtain for $c(n)$

$$c(n) = \frac{1}{\nu\tau_0}\exp\left[-\frac{(x - x_0)}{\bar{v}\tau_0}\right],$$

so that in going over (in the limit) to a continuous process, we must put $c(n) = c(x)a$,

$$c(x) = \frac{1}{\bar{v}\tau_0}\exp\left[-\frac{x - x_0}{\bar{v}\tau_0}\right] = \frac{1}{\sigma}\exp\left[-\frac{x - x_0}{\sigma}\right]. \tag{29c}$$

Let us seek the solution of Eq. (28) in the form

$$A(n,\tau) = y(\tau)e^{i\gamma a n\tau},\quad dy/d\tau = \nu(e^{-i\gamma a\tau} - 1)y.$$

Using (28b), we find

$$A(n,\tau) = \exp[-\nu\tau + i\gamma n a\tau - \nu(e^{-i\gamma a\tau} - 1)/i\gamma a]. \tag{30}$$

We compute the transition probability W from formula (20), where integration with respect to x should be

replaced by summation over n:

$$W = 2\omega_1^2 P_0 \operatorname{Re} \int_0^\infty d\tau \sum_{n=-\infty}^{\infty} A(n,\tau) = 4\pi\omega_1^2 P_0 \int_0^\infty \delta(\gamma a\tau)\, d\tau = 2\pi\omega_1^2 P_0/\gamma a. \tag{31}$$

For a stationary process, formula (31) gives

$$W = 2\pi\omega_1^2 c/\gamma,$$

while for a process with a source

$$W' = \frac{2\pi\omega_1^2}{\gamma a \nu\tau_0}\left(1 - \frac{1}{\nu\tau_0}\right)^{-n_0}.$$

As can be seen from (29c), in the limit of small jumps, the last expression goes over into

$$W' = \frac{2\pi\omega_1^2}{\gamma\sigma}\exp\left\{-\frac{|x_0|}{\sigma}\right\}, \quad \sigma = \bar{v}\tau_0.$$

Thus, the expressions obtained for W for the one-dimensional Poisson process coincide with the formulas (22) and (24) which were obtained for the one-dimensional diffusion process.

Finally, let us consider the problem of the computation of the probabilities of nonadiabatic transitions for three-dimensional diffusive motion and potential surfaces intersecting on a sphere of radius r_0. In this case, $\omega(r) = \gamma(r - r_0)$ and Eq. (11) takes the form

$$\partial A/\partial\tau = i\gamma(r - r_0)A + D\Delta A, \tag{32}$$

where Δ is the Laplace operator. The substitution $A = A_0 e^{-i\gamma r_0 \tau}$ reduces Eq. (32) to

$$\partial A_0/\partial\tau = i\gamma r A_0 + D\Delta A_0, \tag{33}$$

whereas the expression (20) may be written in the form

$$W = 2\omega_1^2 P_0 \operatorname{Re} \int dV \int_0^\infty A_0 e^{-i\gamma r_0 \tau}\, d\tau. \tag{34}$$

The region near the surface of intersection, which is important for transitions, is determined by the relation $\Delta\omega = \gamma\Delta r \sim \Delta t^{-1} = D/\Delta r^2$, where Δt is the time of diffusive passage through the region Δr. Thus, $\Delta r \sim (D/\gamma)^{1/3}$ and the quantity $\tau^* = \Delta r^2/D = (D\gamma^2)^{-1/3}$ plays the role of correlation time for the function A_0. As can be seen from (34), when the diffusion is slow, i.e., when the condition

$$\gamma r_0 \tau^* \gg 1, \quad \gamma r_0 \gg (D\gamma^2)^{1/3}, \tag{35}$$

is fulfilled, the quantity W is determined by the high-frequency Fourier component of the function A_0. Therefore when the condition (35) is fulfilled, it is important to know only the behavior of the function A_0 for small τ, which is easy to establish by the seven invariants method. Indeed, since $A_0(r, 0) = 1$, then at small τ

$$A_0(r,\tau) \approx 1 + i\gamma r\tau \approx \exp[i\gamma r\tau]. \tag{36}$$

Substituting (36) into (34) and assuming for a stationary process $P_0 = \text{const} = c$, we find for the number of transitions per unit time

$$W = 4\pi\omega_1^2 c \int_0^\infty r^2\, dr \int_{-\infty}^{\infty} e^{i\gamma(r - r_0)\tau}\, d\tau = 8\pi^2\omega_1^2 c r_0^2/\gamma, \tag{37a}$$

where c is the three-dimensional concentration.

In the case of three-dimensional diffusion with a source located at the origin, the quantity c in (37a) should be replaced by $c(r_0) = (4\pi\sigma^2 r_0)^{-1}\exp(-r_0/\sigma)$, where $\sigma^2 = D\tau_0$, so that

$$W' = \frac{2\pi\omega_1^2 r_0}{\gamma D\tau_0}\exp\left\{-\frac{r_0}{\sqrt{D\tau_0}}\right\}. \tag{37b}$$

Like (24), formula (37b) has been obtained under the condition that

$$\sigma = \sqrt{D\tau_0} \gg \Delta r = (D/\gamma)^{1/3}, \text{ т. е. } \tau_0 \gg (D\gamma^2)^{-1/3}.$$

As an example of the application of the formulas obtained here let us consider the following physical problem which arises during the interpretation of experiments on the polarization of nuclear or electron spins. In the presence of a magnetic field, a molecule in a liquid dissociates into two radicals, the electron of one of which enters into contact interaction with one of the nuclei. Before the dissociation, the system of energy levels consists of an electronic singlet degenerate with respect to nuclear spin (nuclear Zeeman interaction may be neglected) and a triplet split by the external magnetic field and the contact interaction, the singlet state lying below all the three triplet levels. After the dissociation, one of the triplet terms lies below the singlet (by an amount that is determined by the Zeeman interaction of the electron spins with the external magnetic field). Therefore, in the process of dissociation the singlet and the triplet terms intersect each other.

Let the dissociation occur from the singlet state. The question arises as to what will be the population of the lowest triplet term under quasi-stationary conditions. To estimate the order of magnitude of the rate of occupation of the state which is of interest to us, we may apply the model Hamiltonian (2) in which the role of the quantity $\hbar\omega(r)$ is played by exchange and Zeeman interactions, while $\hbar\omega_1$ corresponds to the contact interaction; of all the eight states of the problem we retain only the two states between which transitions take place.

Assuming that the exchange interaction depends exponentially on the distance r, we write for $\omega(r)$

$$\omega(r) = \omega_{ex} e^{-\alpha r} - \omega_0.$$

Expanding this expression near the surface of intersection $r = r_0$ in a series, we obtain

$$\omega(r) \approx \omega_0\alpha(r - r_0) + \ldots, \qquad r_0 = \frac{1}{\alpha}\ln\frac{\omega_{ex}}{\omega_0}, \tag{38}$$

so that $\gamma = \omega_0\alpha$. If $\Delta r = \omega_C/\gamma \ll \alpha^{-1}$, i.e., $\omega_0 \gg \omega_C = (D\omega_0^2\alpha^2)^{1/3}$, then, in the main, transitions occur in the linear region and we may in (38) limit ourselves to the first term. In typical cases $\omega_0 \sim 10^{12}$ sec^{-1}, $D \sim 10^{-5}$ cm^2 sec^{-1}, $\alpha \sim 10^8$ cm^{-1}, so that $\omega_0 \sim 10^{12}$ sec^{-1} $\gg D\alpha^2 \sim 10^{11}$ sec^{-1} and the linear approximation of the terms near the intersection can be considered satisfactory. The condition (27b) can also be considered fulfilled since the quantity ω_1, which is determined by the contact interaction, is, by order of magnitude, equal to 10^8–10^{10} sec^{-1} whereas $\omega_C = (D\gamma^2)^{1/3} \sim 10^{11}$ sec^{-1}. Assuming that the mean life time of the radicals after the dissociation is equal to τ_0, we find for the dispersion σ of the distribution function c(x)

$$\sigma^2 = D\tau_0.$$

The quantity r_0 (the distance which the radicals have to traverse after the dissociation to the intersection of the terms) can be assumed to be considerably smaller

$\sigma(r_0 \sim 10\,\text{Å}, \sigma \sim 10^3\,\text{Å}$, for $\tau_0 \sim 10^{-6}$ sec). Therefore, for W' we find directly from (37b)

$$W' = 2\pi\omega_1^2 r_0 / \alpha\omega_0 D\tau_0 \sim 10^5\ \text{sec}^{-1}.$$

The found value for the rate of occupation of the triplet level is larger than the spin-lattice relaxation rate and, consequently, it is necessary to take the indicated effect into consideration.

In the example given above, the intersection of the terms occurs at large distances between the particles, when their interaction energy is considerably smaller than kT. Therefore, for rough estimates, it is permissible to use, as a model for molecular motion in a liquid, the diffusive motion picture, as is often done in magnetic relaxation problems. In those cases when the intersection of the terms occurs at small distances and it is necessary to take the interaction between the particles into consideration, the method proposed above for the computation of the nonadiabatic transition probabilities may prove effective under the same conditions of validity of the notion of "mean trajectory" (see, for example,[8]), i.e., when the difference between the energy terms ΔU is considerably smaller than the interaction energies U_1 and U_2. In that case, Eq. (10) should be replaced by the equation of diffusion in the external field defined by the potential $\overline{U}(x) = \frac{1}{2}(U_1 + U_2)$.

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