RELAXATION IN NON-ADIABATIC TRANSITIONS

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We consider non-adiabatic transitions in a system of two parabolic terms coupled by a constant interaction while the magnitude of the interaction of the system under consideration and the medium is arbitrary. Localized thermal transitions of electrons in condensed media correspond to such a model. We find a solution in the semi-classical approximation for the case of a sufficiently weak coupling between the terms. The non-trivial factor multiplying the exponential in the expression for the transition probability has a Lorentzian form with a half-width depending on the activation energy, on the coupling between the system and the medium, on the temperature, and on the correlation time in the medium.

WHEN studying certain localized atomic processes in condensed systems, the problem arises of non-adiabatic transitions such as predissociation,[1] and this problem is nevertheless appreciably different from the corresponding process in collisions in gases because of the presence of bound states of the system at the beginning and end of the process. The system is concentrated periodically in possible states, but a definitive separation of these does not occur at any time. Such a problem has already been discussed in the literature (see, e.g., [2,3]) in connection with the problem of thermal transitions of electrons in impurity centers in crystals. The result of these papers can be reduced to the proof of the fact that at high temperatures the transition has an activation character, while at low temperatures its character is that of a tunnel effect. The magnitude itself of the transition speed cannot be found exactly as the application of a stationary treatment of the problem, used in [2,3] is incorrect in the case considered. This is, in particular, reflected in the fact that the applicability of the final expression for the transition speed turns out to be undetermined.

A rigorous statement of the problem of a localized transition in a medium is to treat it as a relaxation process: the system is given in one of two possible states (we assume the corresponding terms to be parabolic) and we must determine the time sequence of the relaxation to a statistical equilibrium in the two states.

To find a solution we shall use a semiclassical description of the motion of the nuclei and therefore use the Schrödinger equation in the following form[1] ($\hbar = 1$)

$$i\begin{pmatrix}\dot{\psi}_1\\ \dot{\psi}_2\end{pmatrix}=\begin{pmatrix}u_1+\alpha_1 xq, & \beta\\ \beta, & u_2+\alpha_2 xq\end{pmatrix}\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix}. \qquad (1)$$

Here ψ_1 and ψ_2 are the semiclassical functions of the nuclei in the first and in the second electronic states which correspond to the terms u_1 and u_2; β is a constant interaction between the terms, assumed to be real; α_1 and α_2 are the parameters of the interaction of the system with the medium; x and q are the coordinates of the system and of the medium;

$$u_1=\frac{\omega^2x^2}{2}-\frac{\Delta E}{2},\quad u_2=\frac{\omega^2x^2}{2}-Fx+\frac{\Delta E}{2}. \qquad (2)$$

The distance between the equilibrium positions of the oscillators (2) must be sufficiently small so that we can introduce an average trajectory of the motion (corresponding to $\bar{u}$ in the figure)

$$x=x_0\cos\omega t. \qquad (3)$$

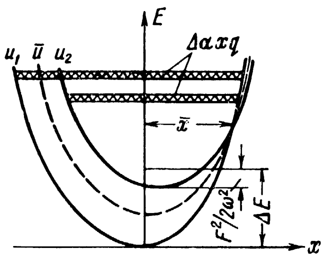
The appropriate inequality looks like[4]

$$F^2/\omega^2\Delta E\ll 1. \qquad (4)$$

The natural condition for the applicability of the semiclassical approximation, the inequality $\omega^2\bar{u}^2\gg\Delta E$, where $\bar{x}$ is the quasi-intersection point of the terms, is satisfied by virtue of (4).

We introduce the following notation for the elements of the density matrix:

$$X_+=\bar{X}_-=\frac{\psi_1\bar{\psi}_2}{\sqrt{2}},\quad X_0=(\psi_1\bar{\psi}_1-\psi_2\bar{\psi}_2)/2 \qquad (5)$$



u_1 and u_2 : electron terms; $\bar{u}$: term corresponding to motion along the average trajectory; $\bar{x}$: coordinate of the quasi-intersection point; $\Delta\alpha xq$: interaction of the system with the medium leading to the relative broadening of the levels.

so that

$$\dot{\mathbf{X}} = i\Omega \mathbf{X}, \tag{6}$$

where

$$\mathbf{X} = \begin{pmatrix} X_+ \\ X_- \\ X_0 \end{pmatrix}, \quad \Omega = \begin{pmatrix} \Delta_\alpha u, & 0, & -\sqrt{2}\beta \\ , & -\Delta_\alpha u, & \sqrt{2}\beta \\ -\sqrt{2}\beta, & \sqrt{2}\beta, & 0 \end{pmatrix}; \tag{7}$$

$$\Delta_\alpha u = \Delta u + \Delta\alpha x q, \ \Delta u = u_1 - u_2,$$

$$\Delta\alpha = \alpha_1 - \alpha_2. \tag{8}$$

We shall assume that $\Delta\alpha/\bar{\alpha} \ll 1$ (where $\bar{\alpha} = (\alpha_1 + \alpha_2)/2$) so that in what follows we need not take into account the process whereby equilibrium is established separately in u_1 and u_2. The matrix equation (6) corresponds to the usual integral equation:

$$X_0(t+\tau) - X_0(t) = -i\sqrt{2}\beta \int_0^\tau \Big\{ X_+(t) \exp\Big[i \int_t^{t+t_1} \Delta_\alpha u(s)\, ds \Big] - X_-(t) \exp\Big[-i \int_t^{t+t_1} \Delta_\alpha u(s)\, ds \Big] \Big\}\, dt_1 - 4\beta^2 \operatorname{Re} \int_0^\tau dt_1 \int_0^{t_1} dt_2 X_0(t+t_2) \exp\Big[i \int_{t+t_2}^{t+t_1} \Delta_\alpha u(s)\, ds \Big]. \tag{9}$$

Denoting the term proportional to β by $L(X_\pm(t)\tau)$, applying perturbation theory with respect to β (the necessary criterion for this will be found in what follows), and averaging Eq. (9) over the coordinates of the medium, we find

$$\langle X_0(t+\tau)\rangle - \langle X_0(t)\rangle = \langle L(X_\pm(t), \tau\rangle - 4\beta^2 \operatorname{Re} \int_0^\tau dt_1 \int_0^{t_1} dt_2 \Big\langle \exp\Big[i \int_{t+t_2}^{t+t_1} \Delta_\alpha u(s)\, ds \Big] \Big\rangle \langle X_0(t)\rangle. \tag{10}$$

The possibility of a separate averaging on the right-hand side of (10) is justified only under the condition (see in this connection[5])

$$\gamma\tau \gg 1;$$

we assume that

$$\langle q(t_1) q(t_2)\rangle = \langle q_0^2\rangle e^{-\gamma|t_1 - t_2|}. \tag{11}$$

This means that the change in the density matrix is considered over a time interval which is much larger than the correlation time $1/\gamma$ in the medium so that we can neglect the influence of the system on the dynamics of the motion of the medium.

Under the condition $\gamma/\omega \ll 1$ and for a Gaussian distribution of q (a random interaction in a liquid or phonons in solids, the dispersion of which we neglect)

$$M(t', \theta) = \Big\langle \exp\Big[i \int_{t+t_2}^{t+t_1} \Delta_\alpha u(s)\, ds \Big] \Big\rangle = \exp\Big[i \int_{(\tilde{\theta} - t')/2}^{(\tilde{\theta} + t')/2} \Delta u(s)\, ds - \varphi(t', \theta) \Big], \tag{12}$$

where

$$\varphi(t', \theta) = \frac{(\Delta\alpha)^2 \langle q_0^2\rangle x_0^2}{\omega^2} [\gamma t' + 1 - \cos\omega t' \cos\theta + e^{-\gamma t'}(\cos\theta - \cos\omega t)],$$

$$t' = t - t_2, \quad \theta = \omega(2t + t_1 + t_2), \quad \tilde{\theta} = \theta/\omega. \tag{13}$$

We change variables, $t_1 - t_2 \to t'$ in (10):

$$\langle X_0(t+\tau)\rangle - \langle X_0(t)\rangle = \langle L(X_\pm(t), \tau)\rangle - 4\beta^2 \operatorname{Re} \int_0^\tau dt' \int_{t'}^\tau dt_1 M(t', \theta) \langle X_0(t)\rangle,$$

$$\theta = \omega(2t + 2t_1 - t'). \tag{14}$$

If we now consider the expansion

$$M(t', \theta) = A_0(t') + \sum_{n=1}^{\infty} A_n(t') e^{in\theta}, \tag{15}$$

we see easily that its contribution from terms with $n \neq 0$ to the integral in (14) is less than the contribution from $A_0(t')$ at least by a factor $1/\tau\omega n$. Using the conditions imposed earlier upon τ and γ we can restrict ourselves in (15) to the first term and we obtain the result

$$\langle X_0(t+\tau)\rangle - \langle X_0(t)\rangle = \langle L(X_\pm(t), \tau)\rangle - \frac{4\beta^2}{\pi} \operatorname{Re} \int_0^\tau (\tau - t')\, dt' \int_0^\pi d\theta M(t', \theta) \langle X_0(t)\rangle. \tag{16}$$

If now

$$\frac{(\Delta\alpha)^2\langle q_0^2\rangle x_0^2}{\omega^2}\gamma\tau \gg 1$$

we can drop, even for the smallest values of x_0 which are important for the transition, t' in the difference $\tau - t'$ and extend the integral over t' to infinity. If $\beta\tau \gg 1$ we can also drop in (16) the term of first order in β as its ratio to the second order term is $1/\beta\tau$.

Thus

$$\langle X_0(t+\tau)\rangle - \langle X_0(t)\rangle = -W\tau\langle X_0(t)\rangle, \tag{17}$$

where

$$W = \frac{4\beta^2}{\pi}\operatorname{Re}\int_0^\infty dt'\int_0^\pi d\theta M(t',\theta). \tag{18}$$

If $W\tau \ll 1$ we can rewrite Eq. (17) as a differential equation:

$$\frac{d}{dt}\langle X_0(t)\rangle = -W\langle X_0(t)\rangle. \tag{19}$$

To find the observed transition velocity and elucidate the final conditions for the applicability of a possible result we must average W over the equilibrium distribution of x_0 corresponding to the motion along the average trajectory

$$\overline{W} = \left(\frac{2}{\pi\langle x_0^2\rangle}\right)^{1/2}\int_0^\infty \exp\left\{-\frac{x_0^2}{2\langle x_0^2\rangle}\right\}W(x_0)\,dx_0. \tag{20}$$

The result of this averaging has the form

$$\overline{W} = \frac{2\sqrt{2}\beta^2}{\pi}\operatorname{Re}\int_0^\infty dt'\int_0^\pi d\theta\,[1+2\varphi_0(t',\theta)]^{-1/2}\exp[i\Delta Et' - \Phi(t',\theta)]. \tag{21}$$

Here

$$\varphi_0(t',\theta) = \varphi(t',\theta)\,|_{x_0^2=\langle x_0^2\rangle},$$

$$\Phi(t',\theta) = 2\frac{(\Delta A)^2\langle x_0^2\rangle}{1+2\varphi_0(t',\theta)}\sin^2\frac{\omega t'}{2}\cos^2\frac{\theta}{2}. \tag{22}$$

We shall now consider the physically most natural case

$$\omega^{-2}(\Delta\alpha)^2\langle q_0^2\rangle\langle x_0^2\rangle \ll 1. \tag{23}$$

As the interaction of the system with the medium is usually relatively weak, (23) is satisfied at all temperatures. Under experimental conditions the following inequalities (in the usual units) are practically always also satisfied:

$$\Delta E \gg \hbar\omega, \quad kT/\hbar\omega \gg 1. \tag{24}$$

In that case

$$\overline{W} = \frac{\Gamma}{\Delta^2+\Gamma^2}\frac{\beta^2}{\hbar\Delta E}e^{-E_0/kT}, \tag{25}$$

where

$$\Gamma = \frac{2E_0(\Delta\alpha)^2\langle q_0^2\rangle\gamma}{\hbar^2\omega^3}, \quad E_0 = \frac{(\Delta E)^2}{2F^2}\omega^2,$$

$$\Delta = \frac{\Delta E}{\hbar\omega} - \mathrm{E}\left(\frac{\Delta E}{\hbar\omega}\right), \tag{26}$$

and E(a) is the integral part of a.

As $\Delta E = F\bar{x}$, Eq. (25) can be changed to

$$\overline{W} = \frac{\omega}{2\pi}W_0 P e^{-E_0/kT}. \tag{27}$$

Here W_0 is probability for a transition near $\bar{x}$ which was evaluated by Landau and Zener, while the physical meaning of the quantity

$$P = \frac{1}{\pi}\frac{\Gamma}{\Delta^2+\Gamma^2} \tag{28}$$

becomes clear, if we write

$$P = \frac{1}{\pi}\int\delta(\tilde{\omega}-\tilde{\omega}_1)\frac{\Gamma}{(\tilde{\omega}-\tilde{\omega}_2)^2+\Gamma^2}d\tilde{\omega}. \tag{29}$$

Here $\tilde{\omega}_1$ and $\tilde{\omega}_2$ are the frequencies, in units of ω of the levels approaching the point $\bar{x}$ in the first and the second state. Because of the equivalence of the levels in u_1 and u_2 we have $\tilde{\omega}_1 - \tilde{\omega}_2 = \Delta$.

When using perturbation theory to evaluate the transition probability the semiclassical wave function of one of the states occurring in the expression for the transition probability is simply a constant while the function of the other state which is linear in β depends on $\Delta_\alpha u$, and the level of the first state is therefore not broadened while that of the second state has a width $\Gamma \sim (\Delta\alpha)^2$ (see the figure). The probability that the packets corresponding to the levels of the two states which we are considering and which are approaching one another and the point $\bar{x}$ overlap, which we need as well as W_0 to find $\overline{W}$, must thus, indeed, have the form (29).

If in one of the terms the motion were free, we must integrate this probability over Δ over the interval $-1/2$, $1/2$, which would give

$$P' = \frac{2}{\pi}\tan^{-1}\frac{1}{2\Gamma}$$

and as $\Gamma \to 0$ Eq. (27) would go over exactly into the Landau-Zener relation.

The region of applicability of (19) and simultaneously the condition that one can use perturbation theory, and thus the condition on $\overline{W}$, has the form

$$\gamma, \Gamma\omega, \beta \gg \frac{\omega}{2\pi} W_0 P. \qquad (30)$$

The range of temperatures for which (27) is correct is limited by conditions (23) and (24), and the factor multiplying the exponential in (27) satisfies by virtue of (30) the natural inequality

$$W_0 P < 1.$$

When the problem is stated as a stationary one, a relation of this type which has a clear physical meaning could not be obtained.

The region which we have found where our result is applicable does not impose strict limitations upon the relative magnitude of Γ and Δ, so that $\overline{W}$ may contain maxima as function of T, E_0, and γ, which can be observed experimentally. Such a dependence on E_0 is obtained in experiments which give simultaneously the depths of traps and the electron capture cross-section (see, for instance, [6]) and in a number of predissociation processes which restrict the thermal decomposition of ionic crystals.

In conclusion we must note that when there is no statistical damping in the medium and when there is only a dynamical decrease of the correlations of the q(t) at different times, we cannot evaluate $\overline{W}$ by the method given here, but, as was shown by Osherov[7] $\langle x(t)x(0)\rangle$ decreases all the same exponentially because of the reaction of the medium on the system and the corresponding $\overline{W}$ has a meaning although the line shape for the transition near the point of the quasi-intersection of the terms is not Lorentzian, as it was in (28).

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