Nonadiabatic transitions between randomly fluctuating levels

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The problems of the absorption of intense frequency-modulated light, the absorption of intense light by a paramagnetic solid, and also the nolinear absorption of light by a solvated electron are solved in the Landau-Zener approximation. An expression extending beyond the limits of perturbation theory is obtained for the transition probability per unit time for the electron transfer reaction.

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The problem of transitions in a two-level system, where the energy levels $\epsilon_1(t)$ and $\epsilon_2(t)$ are random functions of the time, is investigated in the present article. Furthermore, it is assumed that the quantity $\delta\epsilon(t) = \epsilon_1 - \epsilon_2$ is differentiable with respect to the time. This problem has several applications. The calculation of the probability for the absorption of intense light having a randomly modulated frequency is related to it. The absorption of intense monochromatic light by a paramagnetic solid also pertains here, where the randomness of the quantity $\delta\epsilon(t)$ is caused by fluctuations of the self-consistent field, exerted on a given spin by all remaining spins of the system. The problem of the absorption of intense monochromatic light by a solvated electron or by a polaron in ionic crystals at high temperatures also reduces to this same formal statement, and also the determination of a formula for the rate of the electron transfer reaction extending beyond the framework of perturbation theory. In these problems the randomness of $\delta\epsilon(t)$ is caused by temperature fluctuations in the polarization of the medium.

Let the fluctuations of the energy levels be sufficiently slow, i.e., the condition $\Delta\tau_c \gg 1$ is fulfilled, where Δ is a parameter characterizing the scale of the fluctuations in the quantity $\delta\epsilon(t)$ and τ_c is the correlation time of this same variable. Under this condition the system behaves adiabatically on the average, since a large phase builds up during the time τ_c. In this connection, if the conditions $V < \Delta$ and $|\omega - \omega_1| > \Delta$ are satisfied, where V is the matrix element of the interaction between the levels, causing the transition, and $\omega - \omega_1 = \langle\delta\epsilon(t)\rangle$ is the average separation between the system's energy levels, then the transitions primarily take place in the neighborhood of the points of intersection of the energy levels. In actual fact the time, during which the transition is being formed, is equal to $\tau \sim V/\dot\epsilon$ in order of magnitude, where $\dot\epsilon$ is the rate of change of the quantity $\delta\epsilon(t)$ at the intersection point. On the other hand, τ should be smaller than τ_c; therefore, assuming that $\dot\epsilon \sim \Delta/\tau_c$, we obtain the condition $V < \Delta$.

For the probability of a transition from the first level to the second during a single intersection, we shall utilize the Landau-Zener formula,[1,2] which is well known in collision theory:

$$W_{12} = 1 - \exp[-2\pi V^2/|\dot\epsilon|]. \tag{1}$$

The probability per unit time of a transition from level 1 to level 2 is then obtained by averaging (1) over the average number of intersections of the levels per unit time $d\nu$. It is obvious that

$$d\nu = |\dot\epsilon| f(\omega - \omega_1, \dot\epsilon)\, d|\dot\epsilon|, \tag{2}$$

where $f(\epsilon, \dot\epsilon)$ is the distribution function for the number of intersections associated with a fluctuation of magnitude ϵ having a rate of change $\dot\epsilon$. Then, by using Eqs. (1) and (2) we obtain the following result for the transition probability per unit time:

$$\overline{W}_{12} = \int_0^\infty \left[1 - \exp\left(-\frac{2\pi V^2}{|\dot\varepsilon|}\right)\right] f(\omega - \omega_1, \dot\varepsilon)\, \dot\varepsilon\, d\dot\varepsilon. \tag{3}$$

One can easily analyze the case of a weak interaction, $V^2\tau_c/\Delta \ll 1$, in the general formula (3). In this case, by expanding the exponent in Eq. (3) in a series in powers of V^2, we obtain

$$\overline{W}_{12} = 2\pi V^2 \varphi(\omega - \omega_1), \quad \varphi(\omega - \omega_1) = \int_0^\infty f(\omega - \omega_1, \dot\varepsilon)\, d\dot\varepsilon, \tag{4}$$

that is, the well known result of perturbation theory. In order to analyze the case of a strong interaction, $V^2\tau_c/\Delta \gg 1$, it is necessary to specify the random process. Let us consider the case which is most typical for applications, when $\delta\epsilon(t) = \omega - \omega_1 - \Delta\epsilon(t)$, where the fluctuation process $\Delta\epsilon(t)$ is a random Gaussian process. The distribution $f(\omega - \omega_1, \dot\epsilon)$ can be easily found for a random Gaussian process. It is also Gaussian and is expressed by the following formula:[3]

$$f(\omega - \omega_1, \dot\varepsilon) = \frac{1}{2\pi\Delta(-K''(0))^{1/2}} \exp\left[-\frac{(\omega - \omega_1)^2}{2\Delta^2} + \frac{\dot\varepsilon^2}{2K''(0)}\right], \tag{5}$$

where $K(\tau) = \langle\Delta\epsilon(\tau)\Delta\epsilon(0)\rangle$ is the correlation function of the energy fluctuations, and $K''(0)$ is the second derivative of $K(\tau)$ evaluated at zero. Then, by substituting (5) into (3) and evaluating the integral by the method of steepest descents, which we apply to (3) in the case of a strong interaction, we obtain

$$\overline{W}_{12} = \left[\frac{(-K''(0))^{1/2}}{2\pi\Delta} - \frac{1}{\pi^{1/6}\Delta}\left(-\frac{V^2K''(0)}{4}\right)^{1/3} \times \exp\left\{-\frac{\pi V^{4/3}}{(-2K''(0))^{1/6}}\right\}\right] \exp\left[-\frac{(\omega - \omega_1)^2}{2\Delta^2}\right] \tag{6}$$

in order of magnitude this gives

$$\overline{W}_{12} \approx \left[\frac{1}{2^{1/2}\pi\tau_c} - \frac{1}{\pi^{1/6}\tau_c}\left(\frac{V^2\tau_c}{4\Delta}\right)^{1/3} \exp\left\{-\frac{\pi V^{4/3}\tau_c^{2/3}}{2\Delta^{2/3}}\right\} \exp\left\{-\frac{(\omega - \omega_1)^2}{2\Delta^2}\right\}. \tag{7}$$

Let us consider the absorption of intense light having a carrier frequency ω; ω_1 denotes the difference between the two levels involved in the transition, $V = |d_{12}|E_0$, where d_{12} denotes the dipole moment of the transition, and E_0 denotes the amplitude of the incident field. The quantity $\Delta\epsilon(t)$ is a Gaussian variable with a Gaussian correlation function, that is,

$$K(\tau) = \Delta^2 \exp(-\tau^2/2\tau_c^2);$$

substituting the expression for $K''(0) = -\Delta^2/\tau_c^2$ into Eq. (6), we obtain formula (7).

As is clear from Eq. (7), the shape of the absorption line for an intense field is Gaussian, just as in the case

of perturbation theory; however, in contrast to the case of perturbation theory the absorption probability is a nonlinear function of the intensity of the incident field.

We note that under the condition $\Delta\tau_c \gg 1$ the shape of the incident light spectrum is Gaussian and does not depend on the frequency correlation time τ_c. At the same time it is clear from Eq. (7) that the probability for absorption of the field significantly depends on τ_c; therefore, the absorption of an intense field may serve as one of several methods for measuring the quantity τ_c.

The energy fluctuation process in paramagnetic solids[4] is also Gaussian with a Gaussian correlation function. Therefore, the same formula (7) is obtained for the nonlinear absorption of light of frequency ω. We call attention to the fact that the absorption of low intensity light, calculated according to perturbation theory, does not depend on the time τ_c. At the same time the nonlinear absorption of an intense field significantly depends on τ_c. Therefore, just as in the preceding case, nonlinear absorption may serve as one of several methods for measuring the energy correlation time τ_c.

One of the most interesting problems in which formula (6) is used is the problem of the absorption of intense light having a frequency ω by a solvated electron or by a polaron in an ionic crystal. This problem was investigated according to perturbation theory in[5,6]. As is shown in[5], the quantity

$$\delta\varepsilon(t) = E_{II} - E_I + E_p - \Delta E(t),$$

where

$$E_p = \frac{c_0}{4\pi}\int [\Delta D(\mathbf{r})]^2\, d\mathbf{r}, \tag{8}$$

$c_0 = 1/\epsilon(\infty) - 1/\epsilon(0)$ is the well known Pekar factor, and $\Delta\mathbf{D}(\mathbf{r}) = \mathbf{D}^{II}(\mathbf{r}) - \mathbf{D}^{I}(\mathbf{r})$ is the difference between the values of the displacement in electron states I and II,

$$\Delta E(t) = -\int \Delta D_j(\mathbf{r})\,\delta P_j(\mathbf{r},t)\,d\mathbf{r},$$

$\delta\mathbf{P}(\mathbf{r}, t)$ denotes the fluctuation of the medium's polarization vector. In a quantum treatment, the quantity $\Delta E(t)$ is an operator. However, at sufficiently high temperatures when kT is much larger than the characteristic frequencies of the medium, the fluctuations of the polarization vector become classical and one can regard the quantity $\Delta E(t)$ as a number. In this connection, as one can easily see from the results of[5,6], the quantity $\Delta E(t)$ is a Gaussian variable with a fluctuating correlation function

$$K(\tau) = \frac{kT}{4\pi^2}\int_{-\infty}^{+\infty}\frac{d\omega}{\omega}\frac{\varepsilon''(\omega)}{|\varepsilon(\omega)|^2}e^{-i\omega\tau}\int d\mathbf{r}[\Delta D(\mathbf{r})]^2. \tag{9}$$

From Eq. (9) we obtain

$$K(0) = \Delta^2 = \frac{kT}{4\pi^2}\int\frac{d\omega}{\omega}\frac{\varepsilon''(\omega)}{|\varepsilon(\omega)|^2}\int d\mathbf{r}[\Delta D(\mathbf{r})]^2, \tag{10}$$

where $\epsilon(\omega) = \epsilon'(\omega) + i\epsilon''(\omega)$ is the complex dielectric constant.

Differentiating (9) two times, we obtain

$$K''(0) = -\int_{-\infty}^{+\infty} d\omega\,\omega\frac{\varepsilon''(\omega)}{|\varepsilon(\omega)|^2}\frac{1}{4\pi^2}\int d\mathbf{r}[\Delta D(\mathbf{r})]^2. \tag{11}$$

For the model of an ionic crystal characterized by a single frequency ω_0 of the longitudinal vibrations, when

$$\frac{\varepsilon''(\omega)}{|\varepsilon(\omega)|^2} = c_0\pi\omega_0[\delta(\omega-\omega_0) - \delta(\omega+\omega_0)], \tag{12}$$

formulas (10), (11), and (4) give the following result for weak intensities and $kT \gg \omega_0$:

$$\overline{W}_{12} = \frac{\pi V^2}{(2\pi)^{1/2}\Delta}\exp\left\{-\frac{[\omega-(E_{II}-E_I+E_p)]^2}{2\Delta^2}\right\}, \tag{13}$$

where $\Delta^2 = 2kTE_p$, in complete agreement with[6].

For high intensities and $kT \gg \omega_0$, it follows from formulas (10), (11), and (7) that

$$\overline{W}_{12} = \left[\frac{\omega_0}{2\pi} - \frac{\omega_0}{\pi^{1/3}(2kT/\omega_0)^{1/3}}\left(\frac{V^2}{4E_p^{1/2}\omega_0^{3/2}}\right)^{1/3} \times \exp\left\{-\frac{\pi V^{4/3}}{\omega_0[4kTE_p/\omega_0]^{1/3}}\right\}\right]\exp\left\{-\frac{[\omega-(E_{II}-E_I+E_p)]^2}{4E_pkT}\right\}. \tag{14}$$

It is evident from formula (14) that the shape of the absorption line for an intense field is exactly the same as for the absorption of a weak field, and is a Gaussian having a width that increases linearly with the temperature. However, in contrast to the absorption of a weak field, the dependence of the absorption on the intensity of a strong field is intrinsically nonlinear, and also a temperature dependence appears.

If the perturbation giving rise to electron transfer is not the interaction with the electromagnetic field but an intrinsic interaction, for example, the operator of nonadiabaticity, and in addition the transfer is resonant, then by setting $\omega = 0$ and $E_{II} = E_I$ in Eq. (14) we obtain the following formula for the probability of electron transfer:

$$\overline{W}_{12} = \left[\frac{\omega_0}{2\pi} - \frac{\omega_0}{(2k\pi T/\omega_0)^{1/3}}\left(\frac{V^2}{4E_p^{1/2}\omega_0^{3/2}}\right)^{1/3} \times \exp\left\{-\frac{\pi V^{4/3}}{\omega_0[4E_pkT/\omega_0]^{1/3}}\right\}\right]\exp\left\{-\frac{E_p}{2kT}\right\}. \tag{15}$$

It is evident from formula (15) that resonant transfer has an activational nature, with the same activation energy as in the case of a weak interaction. This result is very natural and is related to that energy which the polarization fluctuations must acquire in order for an intersection of the energy levels to occur. However, in the case of a strong interaction the dependence of the pre-exponential factor is considerably more complicated, and a temperature dependence of the pre-exponential factor appears.

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