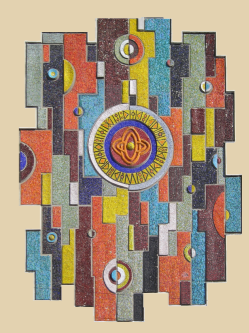


# Resonance in a two-level system caused by time-dependent coupling with the phonon bath

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## SUMMARY

This work shows how a kinetic process is formed in a dynamic system that is in a non-stationary coupling with the environment. It is assumed that the environment has a large number of degrees of freedom and therefore transitions in a dynamic system do not change the state of the environment. However, due to the openness of a dynamic system, the environment is capable of modifying both the states of the system and its energy levels. We are considering a quantum dynamic system, where the exchange of energy between the system and the environment is carried out through vibrational quanta (phonons). Using the method of nonequilibrium statistical mechanics, kinetic equations are obtained that describe the time evolution of the density matrix of a dynamic system under conditions of strong (polaron) coupling with vibrational modes of both the environment and the system. The difference from a similar type of research is that the coupling between the electronic states of the system and its vibration states is assumed to be time-dependent. We proposed a unitary-transformation, which made it possible to take into account this non-stationary coupling directly in the operator responsible for transitions between states of the system. This opened up the possibility of using the perturbation method to derive the master equation for the probabilities of occupying system states. As an example of the application of non-stationary polaron transformation, the kinetics of establishing the probabilities of occupation of electronic states of an open TLS is considered.

E.G. Petrov, Ye.V. Shevchenko, V.O. Leonov, V.I. Teslenko "Kinetics in the two-level system with strong time-dependent coupling of its states to the phonon bath: spin-boson description". Ukr. J. Phys. **69**, 552 (2024).

## MODEL AND BASIC EQUATIONS

We will consider an open dynamic quantum system S, in which the nuclear equilibrium position  $q_{0n}$ , associated with motion along the normal coordinate  $q$ , depends on the  $n$ th electronic state of the system. System S interacts with environment E, which does not change its electronic state, so each  $j$ th equilibrium position of the nuclei  $Q_{0j}$  corresponds to the  $j$ th normal coordinate of motion in a fixed electronic state of the environment. It is assumed that the nuclei in systems S and E have small deviations  $\Delta q_n$  and  $\Delta Q_j$  from their equilibrium positions, so that in the harmonic approximation the noted deviations are characterized by the corresponding frequencies  $\omega_n$  and  $\omega_j$ .

The main features of the temporal behavior of an open quantum dynamical system are determined by the relations between the matrix elements  $V_{nr}$  of transitions between the electronic states of the system and the couplings  $\kappa_n$  of each  $n$ th state to vibrational states of the environment. The influence of external  $dc$  and  $ac$  fields is taken into account, as a rule, in the energies  $E_n = E_n(t)$  of the system and quantities  $V_{nr} = V_{nr}(t)$ . In this work we focus on the situation when the kinetics in an open system is controlled by the couplings  $\kappa_n(t)$  (caused, for example, by external forces). Having expanded the energy into small deviations  $\Delta q_n$  and  $\Delta Q_j$ , after introducing the Bose operators of creation ( $b_j^+$ ) and annihilation ( $b_j$ ) of the phonon mode  $j$  for the environment and similar operators ( $b^+$  and  $b$ ) for a single mode of a dynamical system, we arrive at the following form of the Hamiltonian for the entire system S + E:

$$H_{SE}(t) = \sum_{n,n'} \{ [E_n(t) + \kappa_n(t)(b^+ + b) + \hbar\omega_n(b^+b + 1/2)] \delta_{n,n'} + \sum_j \kappa_{nj}(b_j^+ + b_j) \delta_{n,n'} + (1 - \delta_{n,n'}) V_{nr}(t) |n\rangle \langle n'| + \sum_j \hbar\omega_j(b_j^+ b_j + 1/2) \}.$$

## CHARACTERISTIC TIMES

Let  $\tau_r$  be the characteristic time of a kinetic process responsible for the establishment of a stationary regime in S, and  $\tau_{rel}$  is the characteristic time at which the Boltzmann distribution within the vibrational levels of electronic terms is maintained in both systems E and S. Besides, there exists also the characteristic time  $\tau_{field} \sim \omega^{-1}$  related to the oscillations of an external  $ac$  field of frequency  $\omega$ .

In this work, we consider kinetics on a time scale of the order of  $\Delta t \sim \tau_r$ , satisfying the inequalities

$$\tau_{tr} \gg \tau_{field} \gg \tau_{rel}.$$

## POLARON TRANSFORM AT TIME-DEPENDENT COUPLING TO PHONONS

Since  $\tau_r \rightarrow \infty$  for  $V_{nr}(t) \rightarrow 0$ , we can conclude that the absolute value of  $V_{nr}(t)$  is significantly less than the absolute value of  $\kappa_n(t)$ . Consequently, the electronic states of a dynamic system can participate in the transition process as polaron states. To see the role of these states in kinetics, we use the transform operation

$$\tilde{H}_{SE}(t) = \hat{R}(t) H_{SE}(t) \hat{R}^{-1}(t) - i\hbar \hat{R}(t) \frac{d}{dt} \hat{R}^{-1}(t),$$

In our case, we propose a unitary transformation matrix in the following form

$$\hat{R}(t) = \sum_n \hat{S}_n(t) |n\rangle \langle n|,$$

$$\hat{S}_n(t) = \exp[\xi_n(t)b^+ - \xi_n(t)b] \exp\left[\sum_j (\kappa_{nj}/\hbar\omega_j)(b_j^+ - b_j)\right].$$

Unlike the well-known standard unitary polaron transform, the proposed transform is specified by a time-dependent matrix. This dependence is concentrated in the quantities  $\xi_n(t)$  satisfying the equation which follows from the fact that the Hamiltonian  $\tilde{H}_{SE}(t)$  should not contain linear terms proportional to the operators  $b^+$  or  $b$ .

$$i \frac{d\xi_n(t)}{dt} = \omega_n \xi_n(t) - \kappa_n(t).$$

We obtain

$$\tilde{H}_{SE}(t) = \tilde{H}_b(t) + H_{int}(t) + H_B,$$

where

$$\begin{aligned} \tilde{H}_b(t) &= \sum_n \tilde{E}_n(t) |n\rangle \langle n|, \\ H_{int}(t) &= \sum_{n,n'} (1 - \delta_{n,n'}) \tilde{V}_{nr}(t) |n\rangle \langle n'|, \\ H_B &= \sum_\lambda \hbar\omega_\lambda (b_\lambda^+ b_\lambda + 1/2). \end{aligned}$$

The energy of an open system

$$\tilde{E}_n(t) = E_n(t) + E_n^{(env)} + \Delta E_n(t).$$

receives an addition in the form of reorganization energy

$$E_r = \sum_j (\kappa_j^2/\hbar\omega_j)$$

due to the coupling to environmental vibrations, as well as a time-dependent addition

$$\begin{aligned} \Delta E_n(t) &= \hbar\omega_n |\xi_n(t)|^2 - \kappa_n(t) (\xi_n(t) + \xi_n^*(t)) \\ &+ \frac{i\hbar}{2} \left[ \xi_n(t) \frac{d\xi_n^*(t)}{dt} - \frac{d\xi_n(t)}{dt} \xi_n^*(t) \right]. \end{aligned}$$

Phonon creation and annihilation operators included directly in the "dressed" operator

$$\hat{V}_{nr}(t) = \hat{S}_n(t) V_{nr}(t) \hat{S}_n^{-1}(t),$$

which is responsible for phonon accompanying transitions in a dynamic system. Due to the polaron effect, in which the "phonon coat" weakens transitions between electronic states of an open quantum system S, mean values of  $\hat{V}_{nr}(t)$  are much smaller than those of  $V_{nr}(t)$ , so they can be considered as a perturbation, which allows us to use the Born approximation.

## BALANCE-LIKE KINETIC EQUATIONS FOR AN OPEN SYSTEM AT POLARON COUPLING

Using the unitary operator  $\hat{R}(t)$ , the Liouville equation transforms into the  $\tilde{\rho}_{SE}(t) = -(i/\hbar)[\tilde{H}_{SE}(t), \tilde{\rho}_{SE}(t)]$ , with the Hamiltonian  $\tilde{H}_{SE}$ , and the nonequilibrium density operators are transformed so that  $\rho_{SE}(t) = \hat{R}(t) \tilde{\rho}_{SE}(t) \hat{R}^{-1}(t)$ . In such a way, the occupation probability can be calculated using the expression  $P_n(t) = \text{tr}(\tilde{\rho}_{SE}(t) |n\rangle \langle n|)$ . This value coincides with the diagonal element of the nonequilibrium density matrix  $\tilde{\rho}_{SE}(t)$ , specified by its elements  $\langle n | \tilde{\rho}_{SE}(t) | n' \rangle$ .

We can use the Born approximation in deviations

$$\Delta \hat{V}_{nr}(t) = V_{nr}(t) (\hat{S}_n(t) \hat{S}_n^{-1}(t) - \langle \hat{S}_n(t) \hat{S}_n^{-1}(t) \rangle),$$

Considering also that in Born approximation the decoupling  $\tilde{\rho}_{SE}(t) \approx \rho(t) \rho_B$  is well satisfied, we come to the following integro-differential equation for the density matrix of an open quantum system, "dressed" by bath phonons:

$$\dot{\rho}(t) = -iL_S(t)\rho(t) - \int_0^t dt' \text{Tr}_B(L_V(t)D(t,t')L_V(t')\rho_B\rho(t'))$$

where

$$D(t, t') = \hat{T} \exp[-i \int_{t'}^t d\tau (L_S(\tau) + L_B)]$$

is the evolution unitary matrix ( $\hat{T}$  is the Dayson's time-ordering operator).  $L_S(t) \equiv \hbar^{-1}[H_S(t), \dots]$ ,  $L_B \equiv \hbar^{-1}[H_B, \dots]$ , and  $L_V(t) \equiv \hbar^{-1}[\Delta H_{int}(t), \dots]$  are the Liouville operators related to a modified Hamiltonian of the quantum system

$$H_S(t) = H_0(t) + (H_{int}(t))$$

and the modified interaction

$$\Delta H_{int}(t) = H_{int}(t) - \langle H_{int}(t) \rangle.$$

If the rotational wave approximation is fulfilled, then the mixing of diagonal  $\rho_{nn}(t)$  and non-diagonal  $\rho_{nm}(t)$  elements of the density matrix becomes insignificant, and we arrive at the following balance-like equations for the probabilities of occupation of the states of a dynamic system:

$$\dot{P}_n(t) = -\frac{1}{i\hbar^2} \sum_{n'} \int_0^t \Gamma_{nn,n'n'}(t, t') P_{n'}(t') dt'.$$

$\Gamma_{nn,n'n'}(t, t')$  – the elements of the relaxation supermatrix.

$$\begin{aligned} \Gamma_{nn,n'n'}(t, t') &= \sum_{r,r'} \left[ \langle \Delta V_{nr}(t) \Delta V_{r'n'}^*(t') \rangle U_{rr}(t, t') U_{n'n}^*(t', t) \right. \\ &+ \langle \Delta V_{nr}(t) \Delta V_{r'n'}(t') \rangle U_{rr}(t, t') U_{n'n}^*(t', t) \\ &- \langle \Delta V_{nr}(t) \Delta V_{r'n'}^*(t') \rangle U_{nr}(t, t') U_{n'n}^*(t', t) \\ &\left. - \langle \Delta V_{nr}(t) \Delta V_{nr}(t') \rangle U_{nr}(t, t') U_{n'n}^*(t', t) \right] \end{aligned}$$

are determined through correlation functions of type

$$\begin{aligned} K_{ab,ab'}(t, t') &= \langle \Delta \hat{V}_{ab}(t) \Delta \hat{V}_{ab'}^*(t') \rangle, \\ K_{ab,ab'}(t, t') &= \langle \Delta \hat{V}_{ab}^*(t) \Delta \hat{V}_{ab'}(t') \rangle \end{aligned}$$

with  $\Delta \hat{V}_{ab}(t) = e^{-iH_b t/\hbar} \Delta \hat{V}_{ab}(t) e^{iH_b t/\hbar}$ , where  $\tau = t - t'$ . For those open systems where average values  $\langle \hat{V}_{nr}(t) \rangle$  disappear and, therefore,  $\langle H_{int}(t) \rangle = 0$  the Hamiltonian  $H_S(t)$  is diagonal for any  $t$ . This reduces the elements  $U_{ab}(t, t') = \langle a | \hat{U}_S(t, t') | b \rangle$  of unitary matrix to a simple form

$$U_{ab}(t, t') = \delta_{a,b} \exp \left[ -(i/\hbar) \int_{t'}^t \tilde{E}_a(\tau) d\tau \right].$$

## MASTER EQUATION FOR TWO-LEVEL SYSTEM UNDER NONSTATIONARY COUPLING WITH A PHONON BATH

Applying kinetic equations to the open TLS, we must take into account the fact that  $n = 1, 2$ . Thus, transitions in TLS are associated with matrix elements  $V_{12}(t)$  and  $V_{21}(t)$ , as well as couplings  $\kappa_1(t)$  and  $\kappa_2(t)$ . We will assume that the matrix elements do not depend on time and there is no external  $ac$  field. This means that in the considered TLS the time dependence is concentrated only in the couplings  $\kappa_n(t)$ . Below, based on the spin-boson version of TLS, we set  $V_{nr} = \hbar v, \kappa_1(t)/2 = -\kappa_2(t)/2 = \kappa(t)$  and  $\omega_1 = \omega_2 = \omega_0$ .

For simplicity, we assume that the average  $\langle \hat{V}_{nr}(t) \rangle$ , is equal to zero. This means that in the relaxation supermatrix  $\Delta \hat{V}_{ab}(t) = \hat{V}_{ab}(t) = \hbar v \hat{S}_a(t) \hat{S}_b^{-1}(t)$ . Taking this circumstance into account, we arrive at balance equations for the occupation probabilities  $P_1(t)$  and  $P_2(t)$ , where quantities  $\Gamma_{nn,n'n'}(t, t')$  are determined through the correlation functions  $K_{ab,ba}(t, t')$  and  $K_{ab,ba}(t', t)$ . In the spin-boson description, the difference in occupation probabilities

$$\sigma_z(t) = P_1(t) - P_2(t)$$

is usually analyzed. Taking into account the normalization condition  $P_1(t) + P_2(t) = 1$ , we arrive at the equation:

$$\dot{\sigma}_z(t) = - \int_0^t g(t, t-\tau) \sigma_z(t-\tau) d\tau - \int_0^t f(t, t-\tau) d\tau$$

where  $g(t, t') = (1/2\hbar^2)(\Gamma_1(t, t') + \Gamma_2(t, t'))$ ,  $f(t, t') = (1/2\hbar^2)(\Gamma_1(t, t') - \Gamma_2(t, t'))$  and

$$\Gamma_n(t, t') = K_{nr,n'n}(t, t') e^{i\omega_n t} + K_{nr,n'n}(t', t) e^{i\omega_n t'}.$$

The time-independent frequency  $\omega_{nr} = (1/\hbar)(E_n - E_{n'})$  of the  $n \rightarrow n'$  transition reflects the fact that in the spin-boson version of TLS, the reorganization energies and time-dependent additions are the same for  $n = 1$  and  $n = 2$ . Therefore, in the absence of the  $ac$  field according we have  $\tilde{E}_n(t) - \tilde{E}_{n'}(t) = E_n - E_{n'}$ . Correlation functions

$$\begin{aligned} g(t, t-\tau) &= v^2 (\Lambda(t, t-\tau) + \Lambda^*(t, t-\tau)) \cos \omega_s \tau, \\ f(t, t-\tau) &= -iv^2 (\Lambda(t, t-\tau) - \Lambda^*(t, t-\tau)) \sin \omega_s \tau. \end{aligned}$$

Here,  $\omega_s = \omega_{12} \geq 0$  is the transition frequency in the open system S and

$$\Lambda(t, t-\tau) = e^{-G_B(\tau)} e^{-G_S(t, t-\tau)}$$

is a factor reflecting the influence of the environment (phonon bath) on transition rates. In this equation the function

$$G_B(\tau) = \sum_j \alpha_j^2 [(2n(\omega_j) + 1)(1 - \cos \omega_j \tau) + i \sin \omega_j \tau],$$

where  $\alpha_j = \kappa_j/\hbar\omega_j$ , is well known in the spin-boson model. As for the function

$$\begin{aligned} G_S(t, t-\tau) &= (1/2) (|\xi(t)|^2 + |\xi(t-\tau)|^2) (2n(\omega_0) + 1) \\ &- [(n(\omega_0) + 1) \xi^*(t) \xi(t-\tau) e^{-i\omega_0 \tau} \\ &+ n(\omega_0) \xi(t) \xi^*(t-\tau) e^{i\omega_0 \tau}], \end{aligned}$$

where  $\xi(t) = (-1)^{n+1} \xi_n(t)/2$ , it characterizes the influence of the phonon bath on electronic transitions in a quantum system through the non-stationary coupling between the electronic states of the system and internal oscillations of frequency  $\omega_0$ . Such a transition is accompanied by the creation or annihilation of one or several intramolecular frequencies  $\omega_0$ , the average number of which is supported by the stationary Bose distribution with  $\lambda = 0$ .

## EXAMPLE: TWO-LEVEL SYSTEM WITH A PERIODIC COUPLING TO THE OHMIC PHONON BATH

Analysis of the master equation for occupation probabilities  $P_1(t) = (1/2)(1 + \sigma_z(t))$  and  $P_2(t) = (1/2)(1 - \sigma_z(t))$  becomes possible if we specify the type of phonon bath and the function  $\kappa = \kappa(t)$ . In this paper we analyze the situation where non-Markovianity is not important, so that  $\sigma_z(t-\tau) \approx \sigma_z(t)$  and thus the integro-differential equation reduce to the differential equation

$$\dot{\sigma}_z(t) = -K(t)\sigma_z(t) + F(t),$$

where

$$K(t) = \int_0^t g(t, t-\tau) d\tau$$

can be thought of as the time-dependent transition rate and

$$F(t) = \int_0^t f(t, t-\tau) d\tau$$

is the time-dependent free term. Note that reducing of master equation is carried out with good accuracy if the Born approximation is used to obtain the relaxation matrix. In this case, the manifestation of non-Markovianity occurs in higher orders with respect to matrix elements of type  $V_{nr}$ .

To have analytical expressions for the  $G_B(\tau)$  in hand, following the spin-boson description let us represent this function in a form

$$G_B(\tau) = \frac{1}{2\pi} \int_0^\infty d\omega \frac{J(\omega)}{\omega^2} \times [(2n(\omega) + 1)(1 - \cos \omega \tau) + i \sin \omega \tau]$$

where  $J(\omega) = (2\pi/\hbar^2) \sum_j \kappa_j^2 \delta(\omega - \omega_j)$  is the bath spectral density. Below we use its Ohmic form

$$J(\omega) = \frac{2\pi E_r}{\hbar\omega_D} \omega \theta(\omega_D - \omega),$$

which guarantees the validity of the condition  $\langle \hat{V}_{nr}(t) \rangle = 0$ . The Ohmic form depends on the value of the reorganization energy  $E_r$  and includes an abrupt cutoff at the Debye frequency  $\omega_D$ .

Assuming  $\chi_n(t) = \chi_n \cos \omega t$  and introducing the notations  $\alpha = \kappa/\hbar\omega_0$  and  $\beta = \chi/\hbar\omega_0$  where  $\kappa_1 = -\kappa_2 \equiv \kappa/2$  and  $\chi_1 = -\chi_2 \equiv \chi/2$  we get the function  $\xi(t) = \xi_1(t) - \xi_2(t)$ :

$$\xi(t) = \alpha + \beta [\phi_a(t) - i\phi_b(t)],$$

$$\phi_a(t) = \frac{1}{1 - \zeta^2} (\cos \omega t - \zeta^2 \cos \omega_0 t),$$

$$\phi_b(t) = \frac{\zeta}{1 - \zeta^2} (\sin \omega t - \zeta \sin \omega_0 t), \quad (\zeta \equiv \omega/\omega_0).$$

Figs. 1 and 2 show one of the possible scenarios for the development of TLS kinetics at room temperature in the presence of a non-resonant ( $\omega \neq \omega_0$ ) and resonant ( $\omega \simeq \omega_0$ ) external field, controlling the TLS – environment coupling.

## RESULTS FOR TLS WITH A PERIODIC COUPLING TO THE OHMIC PHONON BATH

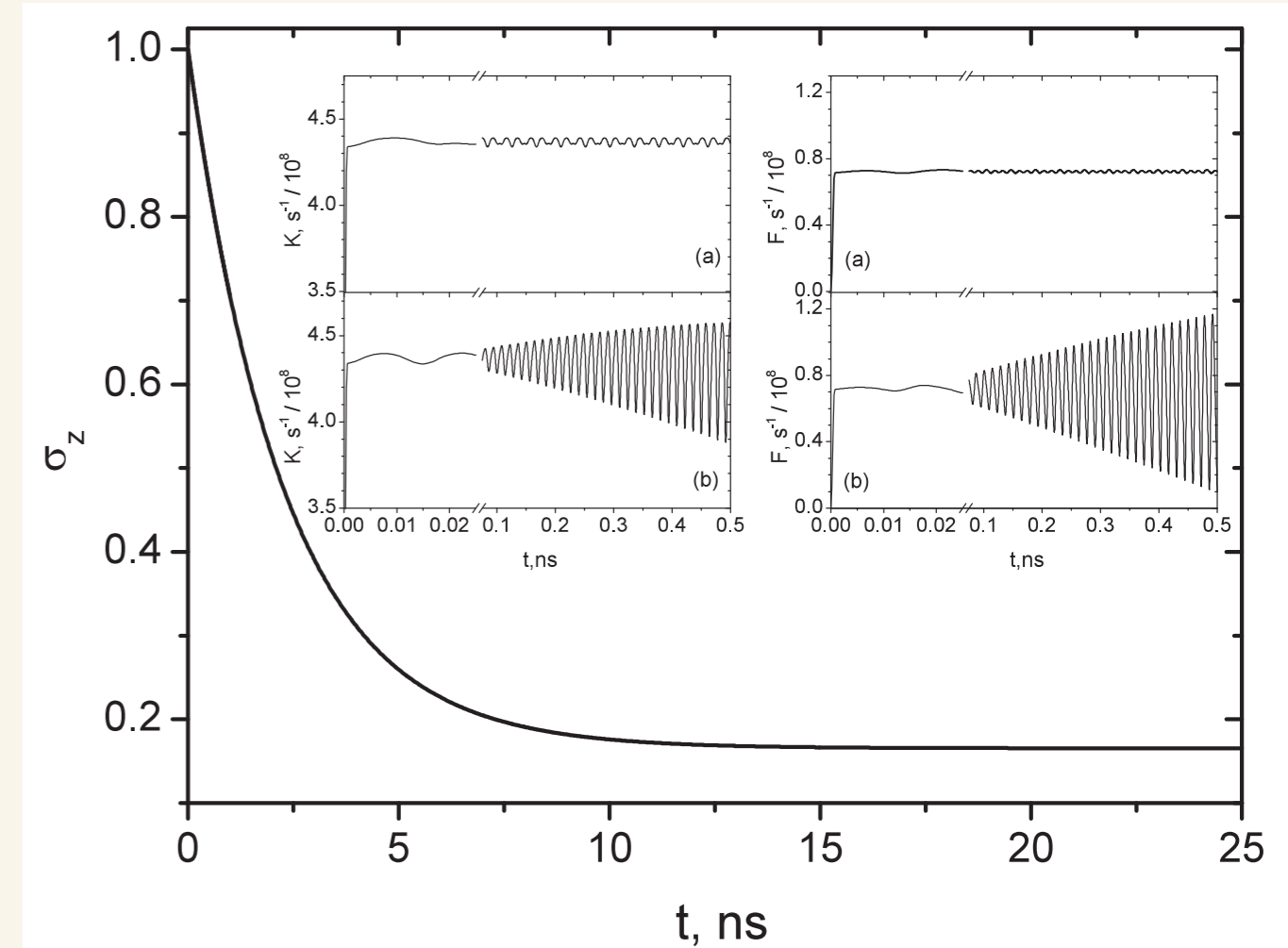


Figure 1: Temporal behavior of the occupation probabilities of electronic states of an open TLS with periodic changes in the electron-phonon coupling  $\kappa(t)$ . The insets on the left and right show the time dependences of both the transition rate and the free term of the kinetic equation under conditions of non-resonant (a) and resonant (b) influence of a periodic field on  $\kappa(t)$ . Three characteristic times of temporal evolution are clearly observed at scales  $\Delta t \sim 0.1$  ns, 0.01 ns and 1 ns. Calculations with parameters  $T = 300$  K,  $E_r = 50$  cm<sup>-1</sup>,  $\hbar\omega_0 = 15$  cm<sup>-1</sup>,  $\hbar\omega_s = 70$  cm<sup>-1</sup>,  $\hbar v = 5$  cm<sup>-1</sup>,  $\alpha = 0.25$ ,  $\beta = 0.1$ . The resonant regime of  $1 \rightarrow 2$  transitions is estimated at  $\omega \simeq \omega_0 = 15$  cm<sup>-1</sup>.

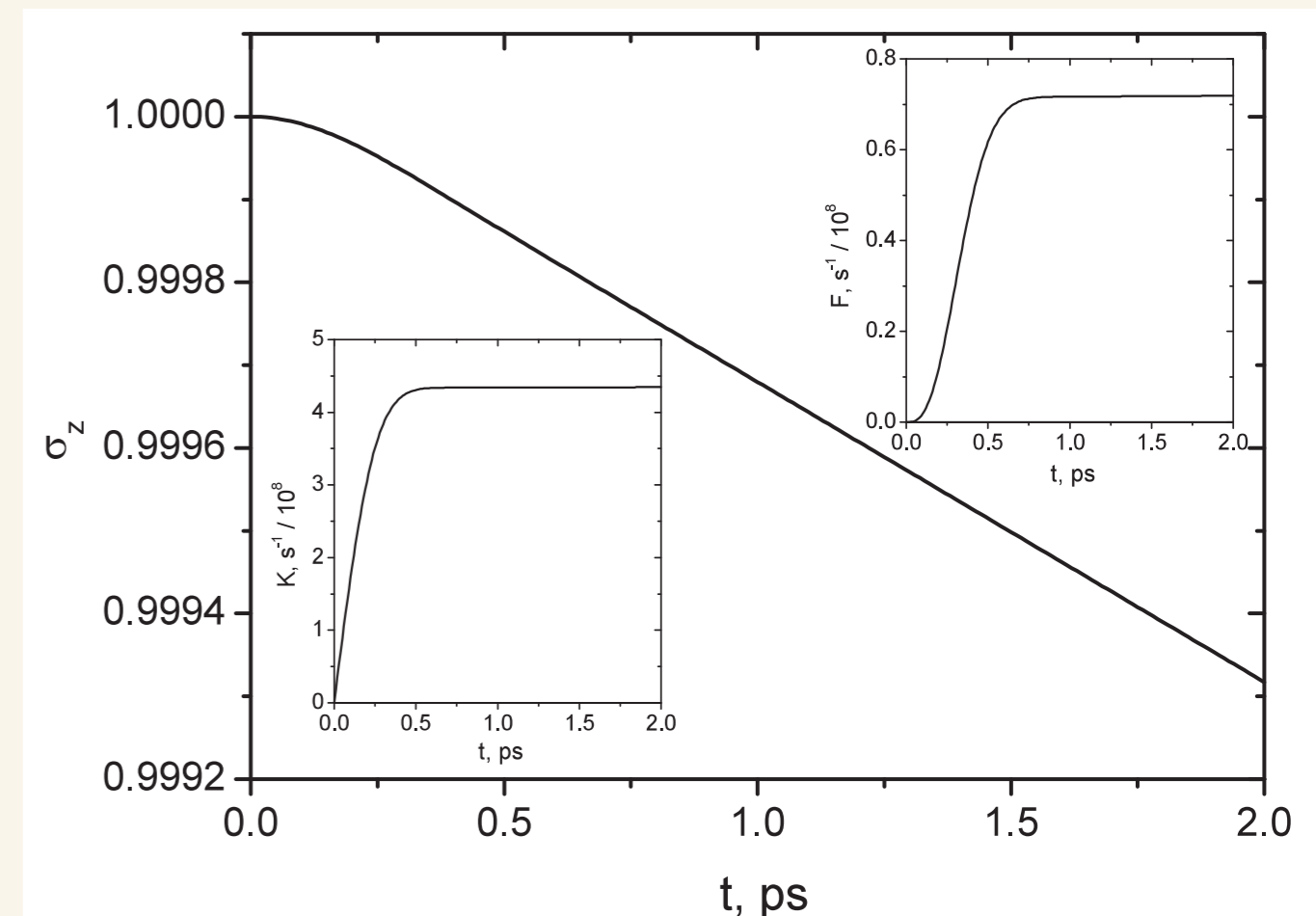


Figure 2: The initial stage of development of kinetics (scale  $\Delta t \sim 0.1$  ps), at which the change in the occupation probabilities of TLS states is insignificant, but the rate  $K(t)$  of transition between states increases the evolution time scale to  $\Delta t \sim 0.01$  ns.

The formation of the transition rate  $K(t)$  (and the free term  $F(t)$ ) is due to the development in time of three stages of the kinetic process.

1. The fastest stage can be estimated by expanding the functions  $G_B(\tau)$  and  $G_S(t, t-\tau)$  near  $t \simeq 0, \tau = 0$ . At room temperature, when  $n(\omega_D), n(\omega_0) \gg 1$ , and with use of the Ohmic form of the bath spectral density we get

$$G_B(\tau) \approx i(E_r/\hbar)\tau + (2\omega_D k_B T/\hbar)\tau^2,$$

$$G_S(t, t-\tau) \approx (\alpha + \beta)^2 [i\omega_0 \tau + (2\omega_0 k_B T/\hbar)\tau^2].$$

Thus,  $\tau_{fast}^{-1} \simeq \sqrt{(2k_B T/\hbar)[\omega_D + (\alpha + \beta)^2 \omega_0]}$ . For the values of  $\omega_D, \omega_0$  and  $T$  we use, this gives a value of  $\tau_{fast} \approx 0.25$  ps, which is in good agreement with the data presented in Fig. 2.

2. The second kinetic stage is fixed on the time scale  $\Delta t \sim \omega_0^{-1} \sim 0.02$  ns (Fig. 1). This stage reflects a purely dynamic process that has little effect on the change in the probabilities  $P_n(t)$  of occupation of the TLS states.

3. Real changes in the occupation probabilities are associated with the third, slowest stage of kinetics, which is fixed on the time scale  $\Delta t \sim 1$  ns. The stage is controlled by the the matrix elements  $V_{nr}$  so that the inverse characteristic time of the slowest stage is equal to  $\tau_{tr}^{-1} \sim v^2 \tau_{fast}$ . This gives  $\tau_{tr} \sim 1$  ns, which is in good agreement with the time behavior of  $\sigma_z = \sigma_z(t)$  shown in Figure 1.