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Nonradiative recombination of a localized exciton

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Abstract. In this work a simple model of nonradiative recombination of a localized exciton is rigorously studied. Depending on the details of the linear coupling Hamiltonian to single-mode phonons coupled to a big reservoir of fast modes, different results are obtained. Exponential exciton decay has been found just in special situations.

1. Introduction

In this work we study the following situation. Matter with a periodical structure which contains impurity sites is subjected to the influence of a short pulse of light. The resulting exciton moves through the matter until it is trapped in one of these impurities. We consider the potential corresponding to the impurity to be sufficiently deep that the thermal excitation cannot re-excite the exciton back to cause moving of the exciton again. Further the exciton is supposed to be localized in the first excited electronic level of the substitute molecule (atom). As the interaction of the trapped exciton with surrounding sites is too weak compared to the potential well, it only leads to a small renormalization of the excited state of the substitute molecule (atom). Hence we will not have to distinguish between the excited and renormalized excited states.

Further the exciton interacts with surrounding ions, which vibrate around their equilibrium positions. For the sake of clarity we suppose that the acoustic vibrations (responsible for translational vibrations) do not much influence the situation, therefore, only optical vibrations are taken into account in the exciton–phonon interaction, which is a standard case in polar crystals [1]. The typical energy gap for the excited state is about 2–5 eV; for optical vibrations the energy is about 0.1–0.3 eV. These optical vibrations are not isolated, but also interact with very fast electronic states and with remaining acoustic modes. The time behaviour of the trapped exciton can thus be well described by a two-level system which interacts with phonons. In general, the problem of the interaction of a two-level system with the environment is coupled with a problem of quantum tunnelling in a double-well potential for low temperatures (the problem of tunnelling was introduced by Hund [2] and later developed by Oppenheimer [3], Gamow [4], Gurney and Condon [5]). In the last decade a great deal of interest in quantum tunnelling was stimulated by macroscopic quantum tunnelling in a Josephson system [6] and the theoretical work of Caldeira and Leggett [7]. There are many works concerning quantum tunnelling in the presence of coupling to many degrees of freedom, such as phonons, quasiparticles and electrons. Among them are the work on deep inelastic collisions of heavy ions by Brink *et*

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al [8] and by Möhring and Smilansky [9]. Quantum tunnelling also has a very long history in solid state physics [10–12]. The model exciton–phonon Hamiltonian introduced below can be transformed by an appropriate unitary transformation to a form similar to the well known spin boson Hamiltonian [13]. If we linearize the exciton–phonon interaction we have the situation discussed by many authors (see e.g. [14]). It would be quite confusing to list all important works which have been done in that field. For simplicity we mention the work of Wagner [15] (see also references therein), in which the double-well potential interacting with one phonon mode was treated. The two parameters appearing in the interaction and the energy gap of the double-well potential were changed in various hierarchies. Wagner then calculated the probability of finding the particle in the left minima for these competing models in some perturbative way. Another interesting work was performed by Denner and Wagner [16]. These authors showed that the static base and adiabatic base approaches led to different results in the first order of perturbation.

Similarly to the works mentioned we also consider one phonon mode. Another feature of our work, similar to [15], is changing the coupling parameters. However, we stress that *all our treatment is unperturbative*. We succeeded in computing the probability of localization of the electron at the upper level for times of about 5–30 in the units of the inverse of the exciton energy gap. Furthermore, if we realize that the exciton energy gap is about 10 times greater than the energy of phonons, the perturbation technique would then require a very high order. This limitation does not apply to our treatment here. All approximations assumed here are of numerical character only and were correspondingly checked in the course of calculations.

It is practically impossible to measure nonradiative relaxation of the exciton experimentally. We conjecture that the more complicated time behaviour of the nonradiative exciton relaxation can be transferred into the radiative exciton relaxation. There exist luminescence quenching experiments [17] which have a component corresponding to nonexponential decay (we admit that this nonexponential decay may be of a different origin than in our case). Numerical simulation of the exciton tunnelling in a continuum of phonons (ohmic case) [18] proved no simple time dependence.

2. The physics of the problem and model Liouville superoperator

We put time $t = 0$ at the moment when the exciton is already trapped in the immobile hole in the first electronic excited state. Here we restrict the motion to the first two lowest energy levels. This two-level system is described by the well known Pauli σ matrices. The optical modes of vibrations are described by one characteristic mode of a harmonic oscillator. Fast electronic states of the environment (ions, molecules, ...) of the exciton and remaining acoustic vibrations form a big reservoir, the dynamics of which is considered as being very fast compared to the optical mode. Then the influence of that big reservoir on the vibrational mode fulfils the condition for stochastic modelling. In such a defined physical model we postulate our task as the problem of finding the time dependence of the probability of occurrence of the exciton in the first electronic excited level if the exciton is kept there at the time $t = 0$. It is very useful to realize that in the beginning we assume the phonons to be unrelaxed. If there exist the first excited and the ground levels only, the vibration should be unrelaxed, because at the moment when the exciton is trapped, the vibration is in thermal equilibrium at the temperature T. If higher excitonic levels exist, we assume the vibration to be relaxed (or partially relaxed) around the higher level at the moment when the exciton jumps down to the first electronic excited level. Then we renormalize the vibration around the higher level, but this renormalized vibration is unrelaxed with respect to the first excited level. This corresponds to the situation where the jump of the exciton is caused by very fast degrees of freedom (this fast reservoir is not taken into account explicitly except for its assumed role in formation of the initial state) and the energy is transferred to these fast degrees of freedom. But we stress that the preceding history of the initial state is not of interest in this work.

Let $|1\rangle, |2\rangle$ be the first electronic excited and ground electronic levels with energies ϵ and $-\epsilon$, respectively, and $b, b^\dagger$ be the phonon annihilation and creation operators. Then for the Hamiltonian of the central phonon–exciton system (stochastic influence will be discussed later) we assume

$$H = \hbar\Omega\left[[b^\dagger b + \epsilon\sigma_z] + \left[\frac{(b+b^\dagger)}{\sqrt{2}}(D\sigma_z + \Delta\sigma_x)\right]\right] = H_0 + H_1. \tag{1}$$

Here Ω is the phonon frequency, 2ϵ is the relative energy gap of the exciton measured in units of the phonon frequency, D and Δ are the relative coupling strengths of the exciton to the optical mode. The so-called Pauli matrices are defined in an obvious way

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

The interaction term H_1 is linear in the phonon displacement and is otherwise taken in a quite general form.

As the phonon mode is in interaction with a bath of very fast electronic states we can use the generalized Haken–Strobl–Reineker model [19] for description of that interaction. If L' is the Liouville superoperator of the central exciton–phonon system and L^s is the Liouville superoperator describing the influence of the bath on the phonons then for the total Liouville superoperator L we can write

$$L = L' + L^s \tag{2}$$

$$L' \cdots = \frac{1}{\hbar}[H, \ldots]. \tag{3}$$

Denoting the phonon eigenstates by Greek letters and the exciton eigenstates by Latin ones the stochastic contribution in the simplest approximation reads [20]

$$\begin{aligned} L^s_{\alpha\beta\gamma\delta} = \mathrm{i}\bigg(2\delta_{\alpha\beta}\delta_{\gamma\delta}\Big[\gamma_{\alpha\gamma} - \delta_{\alpha\gamma}\sum_\epsilon \gamma_{\epsilon\alpha}\Big] \\ -(1-\delta_{\alpha\beta})\delta_{\alpha\gamma}\delta_{\beta\delta}\sum_\epsilon[\gamma_{\epsilon\alpha} + \gamma_{\epsilon\beta}] + 2(1-\delta_{\alpha\beta})\delta_{\alpha\delta}\delta_{\beta\gamma}\bar{\gamma}_{\delta\beta}\bigg). \end{aligned} \tag{4}$$

Here the coefficients $\bar{\gamma}_{\alpha\beta}$ will be omitted. For details we refer to [20]. For the coefficients $\gamma_{\alpha\beta}$ we take the following equation

$$\gamma_{\alpha\beta} = \tilde{k}\left[(\alpha+1)\delta_{\beta,\alpha+1} + \alpha\exp\left(-\frac{\hbar\omega}{kT}\right)\delta_{\beta,\alpha-1}\right]. \tag{5}$$

These coefficients are introduced according to [21]. The coefficient $\tilde{k}$ determines the strength of the interaction of the harmonic oscillator with the bath. We should realize that in the stochastic model the coefficient $\tilde{k}$ need not be small.

3. The mathematical formulation and solution of the problem

To get the probability of occurrence of the exciton on the first electron excited level we should solve the following Liouville equation:

$$\frac{\partial}{\partial t}\rho(t) = -\mathrm{i}L\rho(t) \tag{6}$$

with the initial condition for the density matrix operator

$$\rho(0) = |1\rangle\langle 1| \otimes \rho^R. \tag{7}$$

Here ρ^R is the phonon canonical density matrix operator. One can easily realize that such a choice of the initial condition term really describes the situation of the nonrelaxed excited electron.

To exclude superfluous information contained in the solution of the Liouville equation we come to the Nakajima–Zwanzig identity. It was shown [29] that this convolution-type equation retains information on the initial state for a very long time in the second order. Here we stress that no perturbation expansion is made here. The above-mentioned Nakajima–Zwanzig identity reads [22, 23]

$$\frac{\partial}{\partial t}P\rho(t) = -\mathrm{i}PLP\rho(t) - PL\int_0^t \exp\{\mathrm{i}(1-P)L(\tau-t)\}(1-P)LP\rho(\tau)\,\mathrm{d}\tau$$
$$-\mathrm{i}PL\exp\{-\mathrm{i}(1-P)Lt\}(1-P)\rho(0) \tag{8}$$

containing idempotent superoperator P ($P = P^2$). In the literature we often meet various types of P (e.g. Argyres–Kelley operator [24], Peier operator [25]). Instead of these usual forms of P we use the so-called partition projection superoperator [26]. Although this superoperator was originally used for description of the so-called sink model, we can use it here, too, because it projects in the excitonic space onto one matrix element only. We take P in the form

$$PA \equiv |1\rangle\langle 1| \otimes \rho^R Tr_{ph}\langle 1|A|1\rangle. \tag{9}$$

Here ρ^R is the canonical phonon density matrix operator

$$\rho^R = \frac{\exp(-\beta H_{ph})}{Z} \tag{10}$$

with

$$Z = Tr_{ph}(\exp(-\beta H_{ph})). \tag{11}$$

If we take the initial condition according to (7), the first and the third terms on the right-hand side of (8) disappear and we arrive at a single scalar equation

$$\frac{\partial}{\partial t}\rho_{11}(t) = -\int_0^t w(t-\tau)\rho_{11}(\tau)\,\mathrm{d}\tau \tag{12}$$

with the following definition of the scalar memory function:

$$w(t) = Tr_{ph}\langle 1|L\exp\{-\mathrm{i}(1-P)Lt\}(1-P)L\{|1\rangle\langle 1| \otimes \rho^R\}|1\rangle. \tag{13}$$

We have introduced the reduced exciton density matrix operator $\rho_{nm}(t)$ defined as

$$\rho_{nm}(t) = Tr_{ph}\langle n|\rho(t)|m\rangle. \tag{14}$$

Definition (9) of the superoperator P led to equation (12), which is a scalar integrodifferential equation without the time local and initial condition terms. Instead of usual methods of solution of (12), e.g. the Laplace transformation, we use a so far little-used method of Skála and Bílek [27].

Let us define the following set of functions:

$$\bar{J}_i(t) \equiv \frac{(i+1)J_{i+1}(t)}{t} \qquad i = 0, 1, \ldots \tag{15}$$

where $J_i(t)$ are the Bessel functions of the first kind. From our point of view, these functions have the following important properties:

$$\frac{\mathrm{d}}{\mathrm{d}t}\bar{J}_0(t) = -\frac{1}{2}\bar{J}_1(t) \tag{16}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\bar{J}_i(t) = \frac{1}{2}(\bar{J}_{i-1}(t) - \bar{J}_{i+1}(t)) \tag{17}$$

$$\int_0^t \bar{J}_i(t-s)\bar{J}_j(s)\,\mathrm{d}s = \bar{J}_{i+j+1}(t) \tag{18}$$

$$\bar{J}_i(0) = \tfrac{1}{2}\delta_{i0} \qquad i \equiv 1, 2, \ldots \tag{19}$$

and form a complete set [28]. We assume now that $\rho_{11}(t)$ and $w(t)$ are expanded in terms of the functions $\bar{J}_i(t)$.

$$\rho_{11}(t) = \sum_{i=0}^{\infty} p_i \bar{J}_i(t) \tag{20}$$

$$w(t) = \sum_{i=0}^{\infty} w_i \bar{J}_i(t). \tag{21}$$

Equation (12) and relations (16)–(21) lead to the recurrent relations

$$\begin{aligned} p_0 &= 2\rho_{11}(0) \equiv 2 \\ p_1 &= 0 \\ p_2 &= p_0 - 2w_0 p_0 \\ p_{i+1} &= p_{i-1} - 2\sum_{j=0}^{i-1} w_j p_{i-1-j} i \geqslant 1. \end{aligned} \tag{22}$$

Thus the problem of solving equation (12) is replaced by the problem of solving the algebraic system of equations. Given the set of w_i onc can easily calculate the set of p_i. However, the set of w_i is still unknown and should be determined. At first one may consider using some numerical methods, but what is really surprising is the fact that the set of $\bar{J}_i(t)$ functions makes it possible to obtain analytical expressions for the w_i coefficients.

The expansion of a given function in terms of the functions $\bar{J}_n(t)$ is one of the forms of the Neumann series of the first kind [28]. Any function $f(t)$ which can be expanded into the power series

$$f(t) = \sum_{l=0}^{\infty} b_l t^l \tag{23}$$

can also be expanded into the series

$$f(t) = \sum_{n=0}^{\infty} a_n \bar{J}_n(t) \tag{24}$$

with the same radius of convergence. The mutual relation between the coefficients of these series is given by [28]

$$a_n = 2^{n+1} \sum_{s=0}^{\leqslant[\frac{n}{2}]} \frac{(n-s)!}{2^{2s} s!} b_{n-2s} \tag{25}$$

$$b_l = \frac{2^{-l-1}}{(l+1)!} \sum_{m=0}^{\leqslant [\frac{l}{2}]} \frac{(-1)^m}{l-2m+1} \binom{l+1}{m} a_{l-2m}. \tag{26}$$

If we expand the exponential in (13) into the power series we find the relation

$$w(t) = \sum_{n=0}^{\infty} \tilde{w}_n \frac{t^n}{n!} \tag{27}$$

where

$$\tilde{w}_n = \mathrm{i} Tr_{ph} \langle 1 | L R^{n+1} \{ |1\rangle\langle 1| \otimes \rho^R \} | 1 \rangle \tag{28}$$

$$R = -\mathrm{i}(1-P)L. \tag{29}$$

Using (25) we obtain the following result:

$$w_n = 2^{n+1} \sum_{s=0}^{\leqslant [\frac{n}{2}]} \frac{(n-s)!}{2^{2s} s!} \tilde{w}_{n-2s}. \tag{30}$$

Another important question is the rate of convergence of these series and the possibility of their truncation. It may appear in this context that the expansion in terms of the functions $\bar{J}_l(At)$ (here A means a real number) instead of $\bar{J}_l(t)$ is more convenient. That method is called the time scaling method.

Here we calculate the matrix elements of L and $(1-P)L$. To achieve this we realize that Latin (Greek) letters designate the exciton (phonon) degrees of freedom of motion so that we can rewrite their definition into the matrix form. Doing this we write

$$P_{i\alpha;j\beta;k\gamma;l\delta} = \delta_{i,1}\delta_{j,1}\delta_{k,1}\delta_{l,1}(\alpha|\rho^R|\beta)\delta_{\gamma;\delta} \tag{31}$$

$$L'_{i\alpha;j\beta;k\gamma;l\delta} = \frac{1}{\hbar}[H_{i\alpha;k\gamma}\delta_{j\beta;l\delta} - H_{l\delta;j\beta}\delta_{k\gamma;i\alpha}] \tag{32}$$

$$(PL')_{i\alpha;j\beta;k\gamma;l\delta} = \frac{1}{\hbar}\delta_{i,1}\delta_{j,1}(\alpha|\rho^R|\beta)[H_{1\delta;k\gamma}\delta_{l;1} - H_{l\delta;1\gamma}\delta_{k;1}]. \tag{33}$$

As L^0 corresponds to H_0 and L^1 corresponds to H_1 one can write the following equations using (1):

$$L^0_{i\alpha;j\beta;k\gamma;l\delta} = \Omega\delta_{i\alpha;k\gamma}\delta_{j\beta;l\delta}[\alpha - \beta + 2\epsilon(j-i)] \tag{34}$$

$$\begin{aligned} L^1_{i\alpha;j\beta;k\gamma;l\delta} = \Omega\Big[& (\sqrt{\alpha+1}\delta_{\alpha;\gamma-1} + \sqrt{\alpha}\delta_{\alpha;\gamma+1}) \\ & \times \left(\frac{D}{\sqrt{2}}(\delta_{i,1}\delta_{k,1} - \delta_{i,2}\delta_{k,2}) + \frac{\Delta}{\sqrt{2}}(\delta_{i,1}\delta_{k,2} + \delta_{i,2}\delta_{k,1}) \right) \delta_{j\beta;l\delta} \\ & -(\sqrt{\beta+1}\delta_{\beta;\delta-1} + \sqrt{\beta}\delta_{\beta;\delta+1}) \\ & \times \left(\frac{D}{\sqrt{2}}(\delta_{j,1}\delta_{l,1} - \delta_{j,2}\delta_{l,2}) + \frac{\Delta}{\sqrt{2}}(\delta_{j,1}\delta_{l,2} + \delta_{j,2}\delta_{l,1}) \right) \delta_{i\alpha;k\gamma} \Big]. \end{aligned} \tag{35}$$

Further, we must realize that the stochastic contribution L^s cannot be written as a commutator, but we combine (4) and (5) to obtain

$$\begin{aligned} L^s_{m\alpha;n\beta;p\gamma;q\delta} = \mathrm{i}\delta_{m;p}\delta_{n;q}\tilde{k}\Bigg[& 2\delta_{\alpha\beta}\delta_{\gamma\delta}\Bigg(\left((\alpha+1)\delta_{\gamma;\alpha+1} + \alpha\exp\left(\frac{-\hbar\omega}{kT}\right)\delta_{\gamma;\alpha-1} \right) \\ & -\delta_{\gamma\alpha}\left(\alpha + (\alpha+1)\exp\left(\frac{-\hbar\omega}{kT}\right)\right)\Bigg) \\ & -(1-\delta_{\alpha\beta})\Bigg(\delta_{\alpha\gamma}\delta_{\beta\delta}\left(\alpha+\beta+(\alpha+\beta+2)\exp\left(\frac{-\hbar\omega}{kT}\right)\right) \end{aligned}$$

$$-2\delta_{\alpha\delta}\delta_{\beta\gamma}\left((\alpha+1)\delta_{\beta;\alpha+1}+\alpha\delta_{\beta;\alpha-1}\exp\left(\frac{-\hbar\omega}{kT}\right)\right)\Bigg]. \tag{36}$$

Using relations (31), (34)–(36) we find

$$PL^0 = 0 \tag{37}$$

$$PL^s = 0 \tag{38}$$

$$PL^1_{i\alpha;j\beta;k\gamma;l\delta} = \delta_{i,1}\delta_{j,1}(\alpha|\rho^R|\beta)\frac{\Omega\Delta}{\sqrt{2}}(\delta_{k,2}\delta_{l,1}-\delta_{l,2}\delta_{k,1})(\sqrt{\delta+1}\delta_{\delta;\gamma-1}+\sqrt{\delta}\delta_{\delta;\gamma+1}) \tag{39}$$

that is,

$$PL^1_{i\alpha;j\beta;k\gamma;l\delta} = \delta_{i,1}\delta_{j,1}\frac{\exp(-\Omega\alpha/kT)}{Z}\delta_{\alpha,\beta}\frac{\Omega\Delta}{\sqrt{2}}(\delta_{k,2}\delta_{l,1}-\delta_{l,2}\delta_{k,1}) \tag{40}$$

$$\times(\sqrt{\delta+1}\delta_{\delta;\gamma-1}+\sqrt{\delta}\delta_{\delta;\gamma+1}). \tag{41}$$

Then for the total Liouville operator we have the equation

$$L = L^0 + L^1 + L^s. \tag{42}$$

Operator $(1-P)L$ is a sum, which can be expressed in the form

$$(1-P)L = L^0 + L^1 + L^s - PL^1. \tag{43}$$

We do not write the explicit formulae for these operators, because they are too complicated.

4. Numerical results

In the calculation of $\rho(t)$ we must overcome two problems connected with infinite sums. The first problem is the convergence of equations (20) and (21). The second is an infinite sum over the phonon states in (28), which must be truncated using the maximum phonon cut-off number N. To overcome these difficulties we must realize that there are two possibilities of calculating the memory function $w(t)$. First, we can use definition (21) with w_l defined according to (28) and (30) ('analytical method'). Second, we can use definition (13) and calculate the memory function for a given set of discrete values of t. We can adopt the latter as a convenient method of determination of N. Here we put $t = 0.05i$ $(i = 0, 1, \ldots, 100)$ and keep N as a moving parameter. Trying the convergence of the set $w(0.05i)$ with respect to N we come to the result that the value $N = 8$ is sufficient. We thus obtain a set S of $w(0.05i)$ numbers (for $N = 8$), which is also suitable for overcoming the first problem, because we can calculate $w(t)$ for $t = 0.05i$ using the analytical method. The convergence in (21) with respect to the number of $\bar{J}_l(t)$ can thus be independently tested with respect to the set S. For a good convergence we must take 80–130 $\bar{J}_l(t)$ functions. All calculations are made in Ωt time units. In expansion (21) we must also use the time-scaling method (see above).

For the sake of simplicity we denote $\rho_{11}(t)$ as

$$P(t) \equiv \rho_{11}(t). \tag{44}$$

To obtain time-dependent $P(t)$ we must define a time scale first. We take t in Ω^{-1} units (or Ωt units) which is equivalent to the choice

$$\Omega \equiv 1. \tag{45}$$

If we denote the inverse temperature of the bath and phonons as T^{-1}, the maximum (cut-off) phonon number as N, the relative (compared to Ω) exciton–phonon interaction constants as D and Δ, the relative (compared to Ω) phonon coupling strength to the bath as $\tilde{k}$ and the relative (also compared to Ω) exciton energy gap as 2ϵ, we obtain table 1 of input parameters studied (we calculate 23 $P(t)$ dependences for individual input parameters and draw 16 output graphs for interesting combinations of input parameters and $P(t)$ dependences). In the table, k means the Boltzmann constant. Varying one parameter with other parameters fixed we come to various features of the $P(t)$ dependence. That is why we plot several curves in one graph for varying parameters in the following figures.

Table 1.

Input	D	Δ	$\tilde{k}$	ϵ	$(kT)^{-1}$	N
1	1	1	1	3	0.5	8
2	0.1	0.1	0.1	5	1	8
3	1	1	1	3	1	8
4	1	1	5	3	1	8
5	1	1	1	10	1	8
6	1	1	0	10	1	8
7	1	1	0	3	1	8
8	1	1	1	3	2	8
9	1	1	1	3	3	8
10	1	1	1	3	5	8
11	1	1	1	3	10	8
12	1	1	1	2	1	8
13	1	0	1	3	5	8
14	0	1	1	3	1	8
15	1	1	1	1	1	8
16	1	1	0	1	1	8
17	1	1	0	1	3	8
18	1	1	0	1	5	8
19	0	1	1	5	1	8
20	0	1	0	3	1	8
21	0	1	5	3	1	8
22	0	1	1	10	1	8
23	0	1	0	1	1	8

In figure 1, we can study the dependence of $P(t)$ on varying temperature. Increasing temperature causes steeper decay of $P(t)$, but the temperature dependence is not too strong. This corresponds to the fact that phonons must exchange energy with the exciton to cause the jump of the exciton to the lower electronic energy level. For smaller temperatures we succeeded in calculating $P(t)$ for greater values of the argument t. However, it should be noted that here no strong oscillations have occurred. This is the result of the stochastic influence, which leads not only to the relaxation of the phonons but also to the relaxation of the exciton. Steeper decay of $P(t)$ with increasing temperature can also be confirmed in figure 2, but this fact is not so easily evident because oscillations occur, due to the switched-off stochastic influence. The local damping character is thus added to the oscillation character. For short times the situation with lower temperature leads to a steeper decay of $P(t)$, but the overall decay is a little weaker. We should also remember a strong amplitude of the oscillations for removed stochastic influence, which is a quite different case from that if the stochastic field were taken into account.

A comparison of situations for switched-on and switched-off stochastic fields is studied in figure 3. The stochastic field causes strong damping, while in the situation with the switched-off stochastic field oscillations with a large amplitude are added to the damping. This causes a stronger decay of $P(t)$ for short time. We should also note that the overall

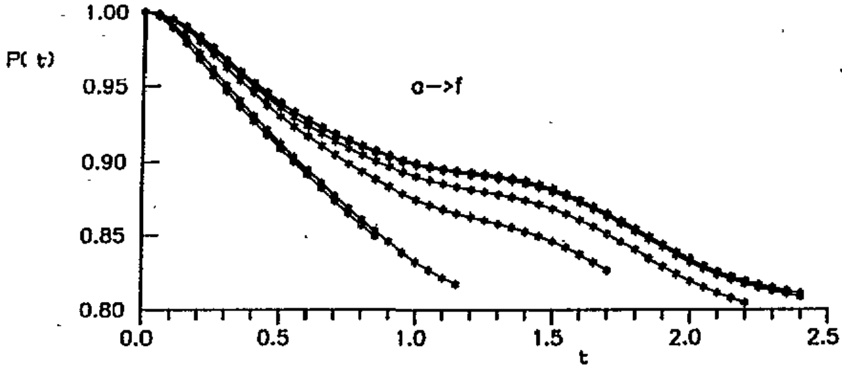

Figure 1. The dependence of $P(t)$ for the input parameters $D = 1$, $\Delta = 1$, $\tilde{k} = 1$, $\epsilon = 3$, $N = 8$, $(kT)^{-1} = 0.5$, 1, 2, 3, 5, 10 for (a), (b), (c), (d), (e), (f).

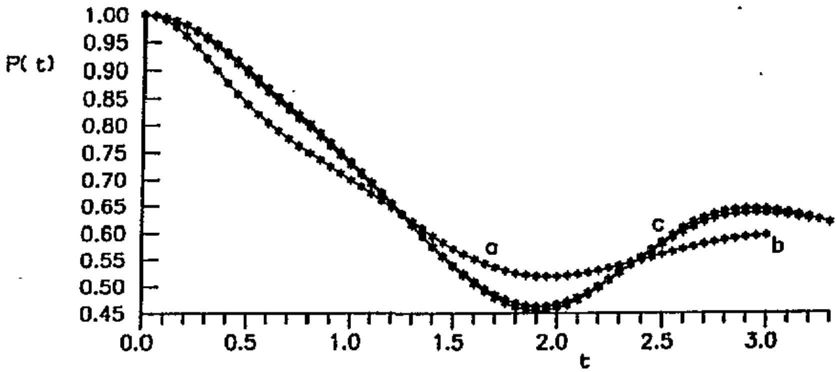

Figure 2. The dependence of $P(t)$ for the input parameters (a) $D = 1$, $\Delta = 1$, $\tilde{k} = 0$, $\epsilon = 1$, $(kT)^{-1} = 1$, $N = 8$, (b) $D = 1$, $\Delta = 1$, $\tilde{k} = 0$, $\epsilon = 1$, $(kT)^{-1} = 3$, $N = 8$ or (c) $D = 1$, $\Delta = 1$, $\tilde{k} = 0$, $\epsilon = 1$, $(kT)^{-1} = 5$, $N = 8$.

decay of $P(t)$ for the switched-on stochastic influence is faster than for the situation without it. A very similar situation is shown in figure 4. Here we study the same situation except for a lowered exciton energy gap. All quantities have been preserved there. If we change the exciton energy gap tenfold and other parameters are left unchanged we get the situation in figure 5. The stochastic influence leads to a greater damping and removes fast oscillations which occur for vanishing stochastic field. Comparing the last three figures we can also verify that lowering of the exciton energy gap leads to a stronger decay of $P(t)$.

The dependence of $P(t)$ on the exciton energy gap is studied in figure 6. The fact that the narrower exciton energy gap leads to much stronger decay is confirmed. The reason for that behaviour is in the fact that for a narrower exciton energy gap the probability of jumping down of the exciton is greater (although virtual phonons do not require energy conservation, the probability of cascading down of the exciton is lowered for a greater exciton energy gap because the probability of multiphonon processes is lowered, too). Another interesting feature is the strong dependence of the frequency of oscillations on the exciton energy gap in the Ω^{-1} units. However, in the $(2\epsilon)^{-1}$ time units (the inverse of the exciton energy gap) the dependence is removed. In this time scale the period is about 7.3. Another interesting situation is seen in figure 7. Here not only is the stochastic influence removed but also the interaction constant D is set to fulfil $D = 0$. There are some changes compared to the

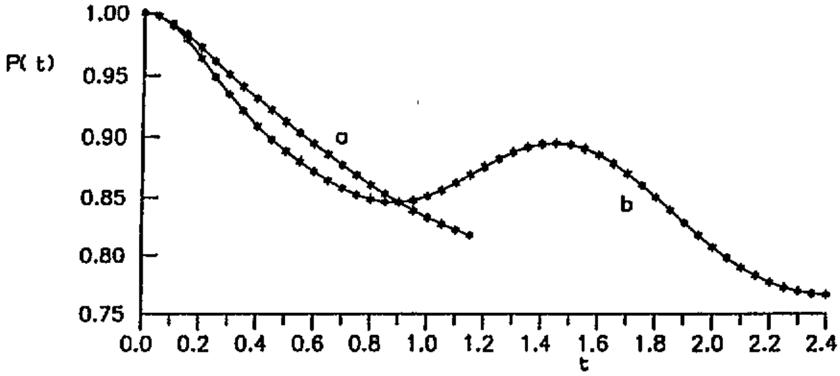

Figure 3. The dependence of $P(t)$ for the input parameters (a) $D = 1$, $\Delta = 1$, $\tilde{k} = 1$, $\epsilon = 3$ $(kT)^{-1} = 1$, $N = 8$ or (b) $D = 1$, $\Delta = 1$, $\tilde{k} = 0$, $\epsilon = 3$, $(kT)^{-1} = 1$, $N = 8$.

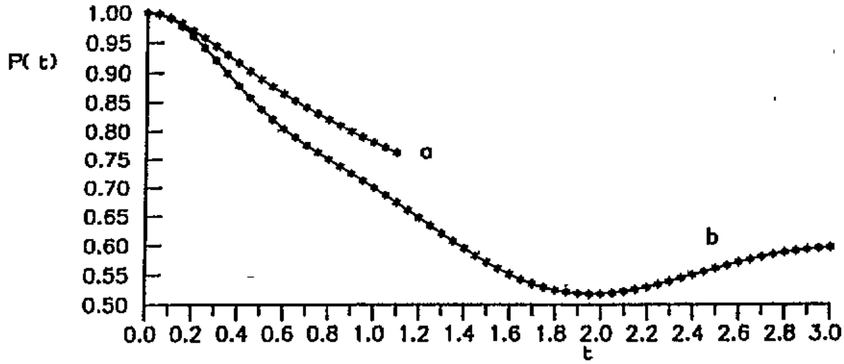

Figure 4. The dependence of $P(t)$ for the input parameters (a) $D = 1$, $\Delta = 1$, $\tilde{k} = 1$, $\epsilon = 1$, $(kT)^{-1} = 1$, $N = 8$ or (b) $D = 1$, $\Delta = 1$, $\tilde{k} = 0$, $\epsilon = 1$, $(kT)^{-1} = 1$, $N = 8$.

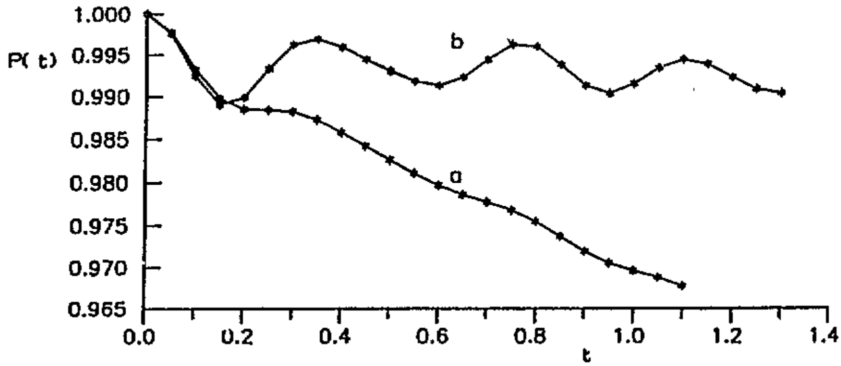

Figure 5. The dependence of $P(t)$ for the input parameters (a) $D = 1$, $\Delta = 1$, $\tilde{k} = 1$, $\epsilon = 10$, $(kT)^{-1} = 1$, $N = 8$ or (b) $D = 1$, $\Delta = 1$, $\tilde{k} = 0$, $\epsilon = 10$, $(kT)^{-1} = 1$, $N = 8$.

previous figure. First, the decay is not so strong as for $D = 1$. The greater exciton energy gap leads to the lower probability decay only in the $(2\epsilon)^{-1}$ time units, not in the Ω^{-1} ones. The frequency of the oscillation of the probability is not conserved either in the $(2\epsilon)^{-1}$ time units, or in the Ω^{-1} ones. This is caused by the fact that the tendency to the polaron effect is now removed ($D = 0$). The dependence of $P(t)$ on the exciton energy gap is drawn for the stochastic field in figure 8. The relation between the exciton energy gap and the decay of $P(t)$ is confirmed again. Because of the stochastic influence the oscillations are removed. Here we put $D = 0$. The relation between the exciton energy gap and the decay of $P(t)$ is also studied in figure 9. $P(t)$ decreases more rapidly for smaller values of the exciton energy gap again. In this figure the stochastic influence is taken into account and $D = 1$. Oscillations are removed again. So far we have considered the behaviour of $P(t)$ with respect to temperature, exciton energy gap and stochastic influence. We now turn our attention to the dependence of $P(t)$ on interaction parameters more deeply. In figure 10 one curve is plotted for very small interaction parameters. $\Delta = 0.1$ causes only a very small decrease of $P(t)$. Here we see that the very small value of $\tilde{k} = 0.1$ leads to rapid oscillations of $P(t)$ because the stochastic influence is almost switched off. The case of $\Delta = 0$ gives $P(t) = 1$ because the exciton–phonon interaction leads to a polaron only. A very important problem is the influence of the parameter D on the time behaviour of $P(t)$.

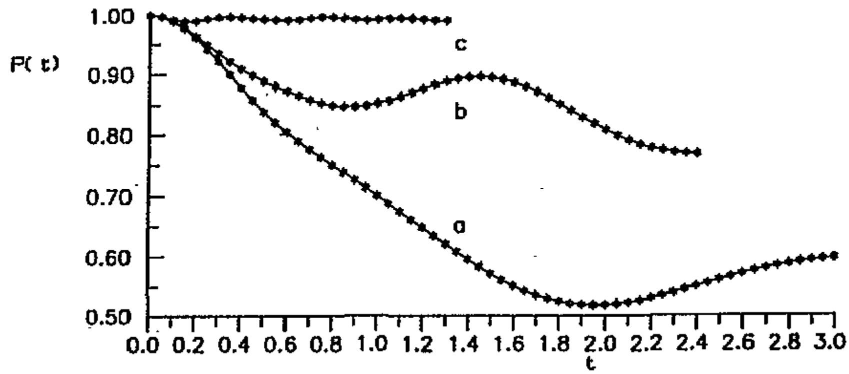

Figure 6. The dependence of $P(t)$ for the input parameters (a) $D = 1$, $\Delta = 1$, $\tilde{k} = 0$, $\epsilon = 1$, $(kT)^{-1} = 1$, $N = 8$, (b) $D = 1$, $\Delta = 1$, $\tilde{k} = 0$, $\epsilon = 3$, $(kT)^{-1} = 1$, $N = 8$ or (c) $D = 1$, $\Delta = 1$, $\tilde{k} = 0$, $\epsilon = 10$, $(kT)^{-1} = 1$, $N = 8$.

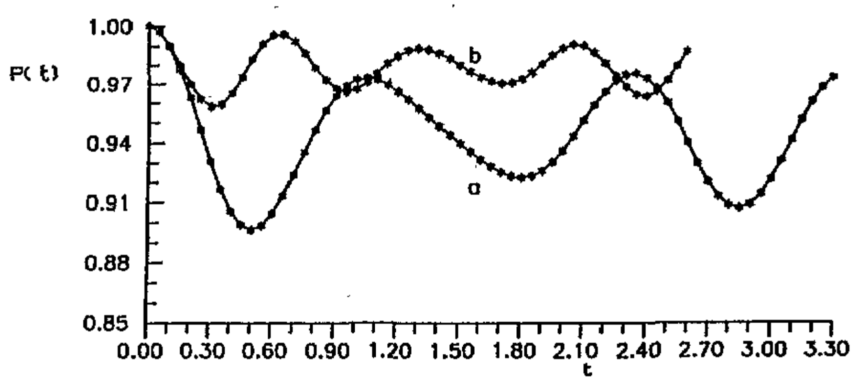

Figure 7. The dependence of $P(t)$ for the input parameters (a) $D = 0$, $\Delta = 1$, $\tilde{k} = 0$, $\epsilon = 3$, $(kT)^{-1} = 1$, $N = 8$ or (b) $D = 0$, $\Delta = 1$, $\tilde{k} = 0$, $\epsilon = 1$, $(kT)^{-1} = 1$, $N = 8$.

In figure 11 we test situations for $D = 1$ and $D = 0$ when the stochastic influence is taken into account. We can observe that both the curves provide a similar $P(t)$ dependence and that $D = 1$ gives a little stronger decay of $P(t)$. A practically equivalent result has

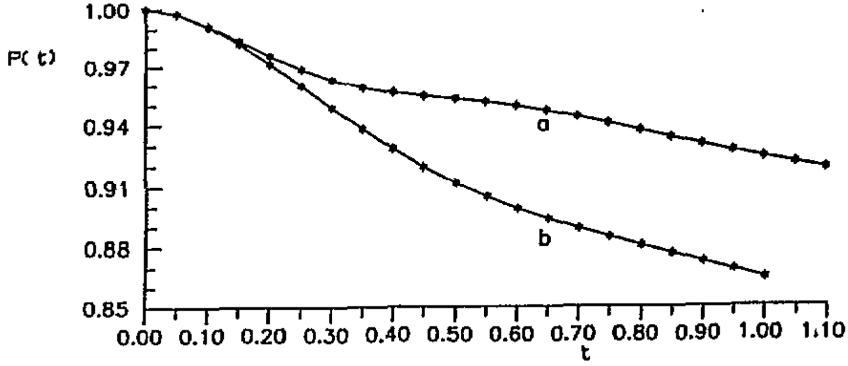

Figure 8. The dependence of $P(t)$ for the input parameters (a) $D = 0$, $\Delta = 1$, $\tilde{k} = 1$, $\epsilon = 5$, $(kT)^{-1} = 1$, $N = 8$ or (b) $D = 0$, $\Delta = 1$, $\tilde{k} = 1$, $\epsilon = 3$, $(kT)^{-1} = 1$, $N = 8$.

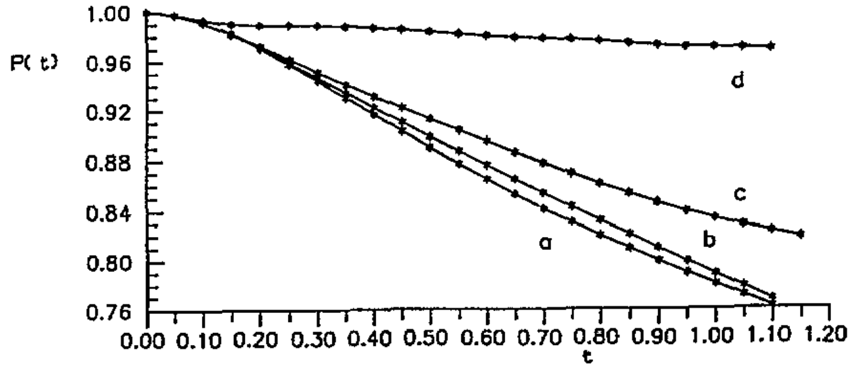

Figure 9. The dependence of $P(t)$ for the input parameters (a) $D = 1$, $\Delta = 1$, $\tilde{k} = 1$, $\epsilon = 1$, $(kT)^{-1} = 1$, $N = 8$, (b) $D = 1$, $\Delta = 1$, $\tilde{k} = 1$, $\epsilon = 2$, $(kT)^{-1} = 1$, $N = 8$, (c) $D = 1$, $\Delta = 1$, $\tilde{k} = 1$, $\epsilon = 3$, $(kT)^{-1} = 1$, $N = 8$ or (d) $D = 1$, $\Delta = 1$, $\tilde{k} = 1$, $\epsilon = 10$, $(kT)^{-1} = 1$, $N = 8$.

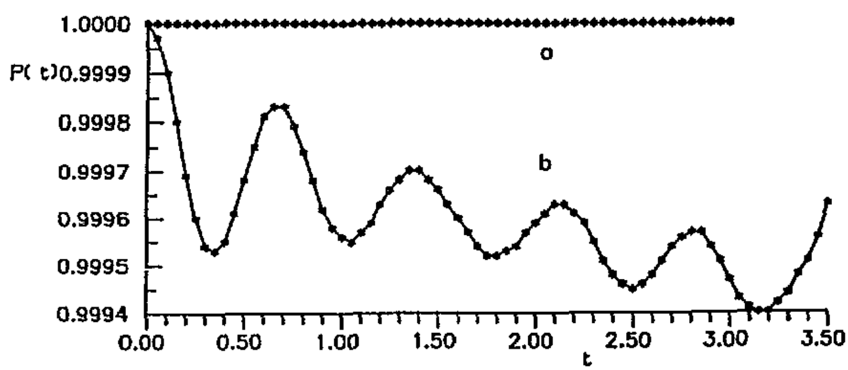

Figure 10. The dependence of $P(t)$ for the input parameters (a) $D = 1$, $\Delta = 0$, $\tilde{k} = 1$, $\epsilon = 3$, $(kT)^{-1} = 1$, $N = 8$ or (b) $D = 0.1$, $\Delta = 0.1$, $\tilde{k} = 0.1$, $\epsilon = 5$, $(kT)^{-1} = 1$, $N = 8$.

been obtained in figure 12 where we have changed the exciton energy gap to a smaller value. Then we come to the conclusion that the stochastic influence of the reservoir tends to destroy the inclination of the phonons to create a polaron as a result of taking $D = 1$. Let us examine whether a very strong stochastic influence gives equivalent results for $D = 0$ and $D = 1$. To answer that question one obstacle should be overcome. A large value of $\tilde{k}$ leads to a memory function which is practically nonzero in the time interval (0, 0.2) only. This implies a problem of expanding such a memory function into a power series of the Bessel-like functions for nonzero times. We have thus succeeded in calculating $P(t)$ only for time interval (0, 0.2) in Ω^{-1} units. But the $P(t)$ dependence can be extended for an arbitrary time in the following manner. If we plot the memory functions for the set of parameters (1, 1, 5, 3, 1, 8) and (0, 1, 5, 3, 1, 8) in figure 13 and figure 14, respectively, we can really see that they are practically nonzero in the time interval (0, 0.2) only. But in that interval $P(t)$ approximately satisfies the relation $P(t) = 1$. Realizing this fact we can perform the well known Markovian approximation outside the time interval (0, 0.2). Then for $t > 0.2$ we can replace the memory function by a delta function. This approximation leads to the exponential decay of $P(t)$. If we realize that the exponential decay is linear for short times we can measure the lifetime of the exponential decay by measuring the derivative of $P(t)$ near the point $t = 0.2$. We obtain for the lifetime a value of about 11–12 (in the Ω^{-1} units), which is the same number for both situations. Analysing figure 15 we come to the conclusion that for strong stochastic influence the behaviour of $P(t)$ is independent of the value of D. The case of the switched-off stochastic field is plotted in figure 16. The values $D = 0$ and $D = 1$ give absolutely different results. The situation with $D = 1$ gives strong damping and oscillations both with a large period (of the order of several units of Ω^{-1}) and an appreciable amplitude (about 0.1) and $P(t)$ decreases for $t = 2$ to a value of nearly 0.5. $D = 0$ causes rapid oscillations (the period of the oscillation is about 0.7) with a very small fluctuating amplitude (about 0.03) without any detectable decay. This result may appear surprising because the interaction term involving D does not cause cascading down of the exciton directly, but promotes the phonons to create a polaron only. This interaction term comes into effect through another interaction term (which involves constant Δ) only via its influence on the phonon states (caused by nonzero D). Many authors think that both the shifted and unshifted phonon states give the same result. That is why they omit the term with the parameter D. We have found that this step may be justified if the stochastic effect of the fast reservoir is taken into account.

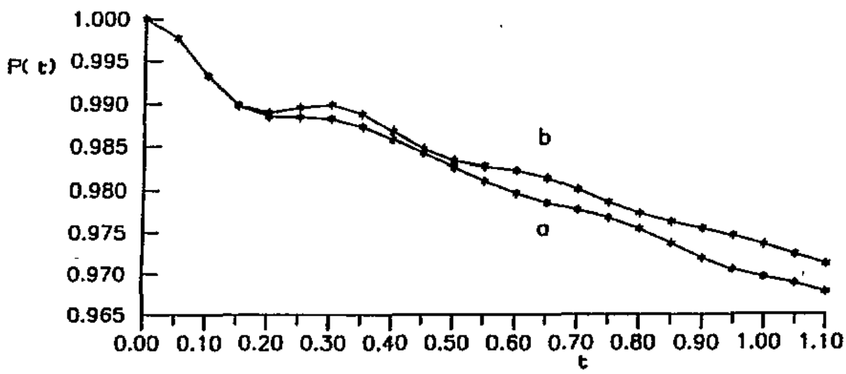

Figure 11. The dependence of $P(t)$ for the input parameters (a) $D = 1$, $\Delta = 1$, $\tilde{k} = 1$, $\epsilon = 10$, $(kT)^{-1} = 1$, $N = 8$ or (b) $D = 0$, $\Delta = 1$, $\tilde{k} = 1$, $\epsilon = 10$, $(kT)^{-1} = 1$, $N = 8$.

We have discussed various dependences of the exciton recombination on input parameters for various parameters. We now give a complete review of the obtained properties.

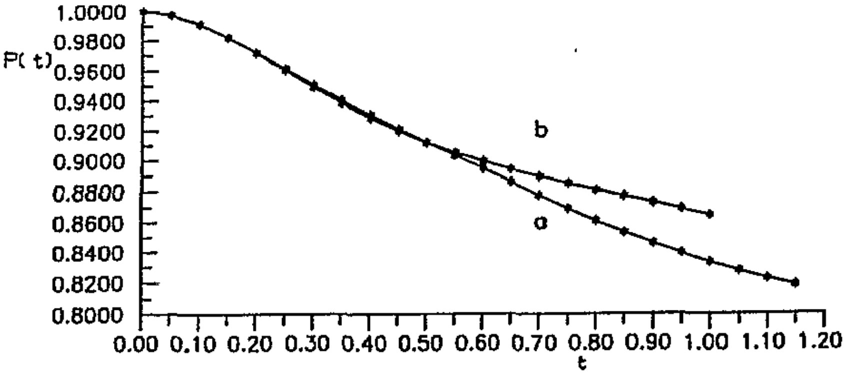

Figure 12. The dependence of $P(t)$ for the input parameters (a) $D = 1$, $\Delta = 1$, $\tilde{k} = 1$, $\epsilon = 3$, $(kT)^{-1} = 1$, $N = 8$ or (b) $D = 0$, $\Delta = 1$, $\tilde{k} = 1$, $\epsilon = 3$, $(kT)^{-1} = 1$, $N = 8$.

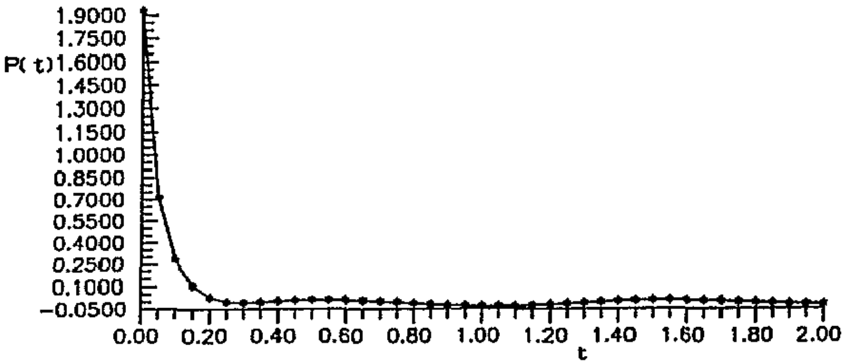

Figure 13. The memory function for the input parameters $D = 1$, $\Delta = 1$, $\tilde{k} = 5$, $\epsilon = 3$, $(kT)^{-1} = 1$, $N = 8$.

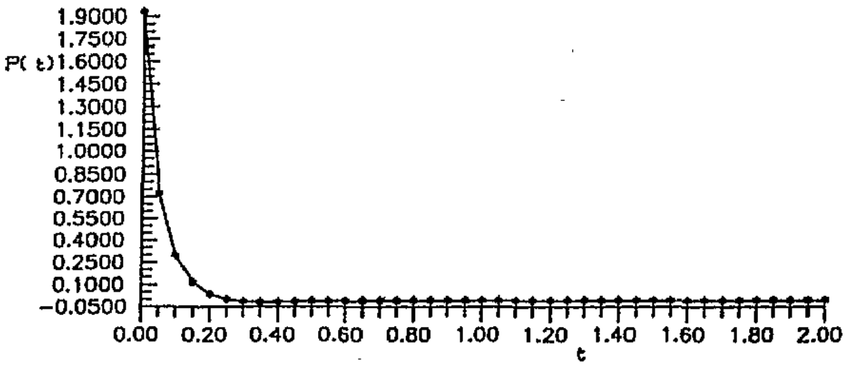

Figure 14. The memory function for the input parameters $D = 0$, $\Delta = 1$, $k = 5$, $\epsilon = 3$, $(kT)^{-1} = 1$, $N = 8$.

Time t. Exponential decay of the exciton state is rather exceptional; if this is the case, then *it occurs from a certain time only. We have found several time scales connected with the* decay and oscillations which could have fluctuating character.

Temperature T. As shown in figure 1 and figure 2, increasing temperature results in a faster

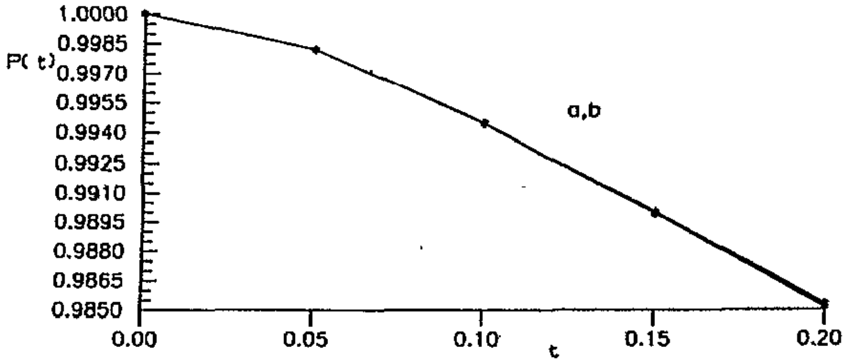

Figure 15. The dependence of $P(t)$ for the input parameters (a) $D = 1$, $\Delta = 1$, $\tilde{k} = 5$, $\epsilon = 3$, $(kT)^{-1} = 1$, $N = 8$ or (b) $D = 0$, $\Delta = 1$, $\tilde{k} = 5$, $\epsilon = 3$, $(kT)^{-1} = 1$, $N = 8$.

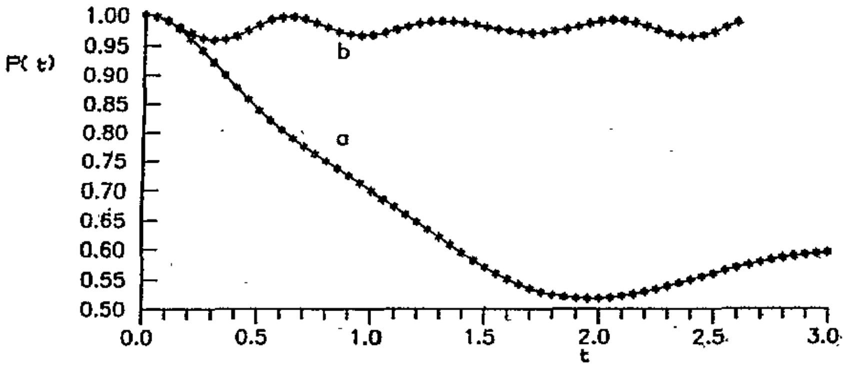

Figure 16. The dependence of $P(t)$ for the input parameters (a) $D = 1$, $\Delta = 1$, $\tilde{k} = 0$, $\epsilon = 1$, $(kT)^{-1} = 1$, $N = 8$ or (b) $D = 0$, $\Delta = 1$, $\tilde{k} = 0$, $\epsilon = 1$, $(kT)^{-1} = 1$, $N = 8$.

decay of the exciton probability $P(t)$. This expected thermal dependence was confirmed.

Exciton energy gap ϵ. Wider exciton energy gap leads to an increased number of phonons involved in the transition process provided that the standard energy conservation law applies. The probability of such a process is therefore suppressed, which leads to a smaller exciton recombination rate, too. This expected dependence was also confirmed. There was, however, an interesting property discovered. If we take $D = 1$ (phonons are promoted to create a polaron) we find that the period of the oscillations is practically conserved in the $(2\epsilon)^{-1}$ time units. Then we come to the following conclusion: if we try to renormalize the central exciton–phonon Hamiltonian in such a way that the effect of the phonon mode should be included in phenomenological constants only, we can write for the central exciton–phonon Hamiltonian H

$$H \approx \hbar\Omega(\alpha(\epsilon)\sigma_z + J(\epsilon, \Delta, D)\sigma_x) \tag{46}$$

with

$$\alpha(\epsilon), J(\epsilon, \Delta, D) \propto \epsilon \tag{47}$$

to produce ϵ-independent oscillation in the $(2\epsilon)^{-1}$ time units. We must also realize that due to the interaction between phonons and the exciton, the system reduced to excitonic degrees of freedom only does not conserve energy (transfer to the phonon mode). However, in the case of a wide exciton energy gap the transfer is slowed and with a good accuracy we may say that in the case of a wide exciton energy gap the energy of the system reduced to excitonic degrees of freedom is conserved. It is not difficult to realize that the modified central exciton–phonon Hamiltonian causes periodical behaviour of $P(t)$. This property is well confirmed in figure 6 for the wide exciton energy gap. Then we can conclude that in the case of $D = 1$, $\tilde{k} = 0$ and the wide exciton energy gap, electronic states and the exciton energy gap could be renormalized due to the interaction with phonons in such a way that the renormalized exciton energy gap is proportional to the bare exciton energy gap. The renormalized exciton energy gap is narrowed approximately sevenfold. Also we may easily verify that the lifetime of that renormalized state increases with an increased value of the exciton energy gap.

Parameter of stochastic influence $\tilde{k}$. The stochastic influence of the bath is assumed to destroy the coherent-like behaviour of our single-mode phonons. We may be interested in whether this property is transferred to the excitonic space. We have verified that the stochastic influence destroys the coherent-like behaviour of the exciton, too. This could have been expected because the probability $P(t)$ of the exciton involves the sum over phonon space, too, and the stochastic influence leads to a finite lifetime. These two facts give a destructive interference effect. Here a question about the accuracy of the stochastic model may be put forward. We have already mentioned that the one-dimensional case of the stochastic model leads to the limit of infinite temperature (measured by diagonal elements of ρ in the representation of true eigenstates of the central system, i.e. exciton + phonons in our case) for a long time. On the other hand, equation (5) makes our approach exceed the limits of the original stochastic model in the sense of the generalized stochastic Liouville equation model [20, 19]. Moreover, in this work we are interested in small or intermediate times only. Another remarkable feature of the stochastic influence is hidden in the result that the cases $D = 0$ and $D = 1$ give very similar results if the phonon system is under a sufficiently strong influence of the stochastic field. Then the stochastic field is supposed to destroy (or suppress) the effect which promotes the phonons to create a phonon cloud resulting from the presence of the nonzero parameter D. For strong stochastic field cases, $D = 0$ and $D = 1$ give practically undetectable differences—see figure 15.

Parameter of symmetric exciton–phonon coupling Δ. Here we have verified an obvious fact that nonzero Δ is a necessary condition for the exciton recombination—see figure 10. For $\Delta = 0$ we have $P(t) = 1$ and for $\Delta = 0.1$ we have $P(t) \sim 1$.

Parameter of antisymmetric exciton–phonon coupling D. This dependence is perhaps more interesting. We have proved that if the stochastic influence is switched off, $D = 0$ and $D = 1$ give very different results—see figure 16. $D = 0$ leads to fast oscillations with a very small fluctuating amplitude without any detectable decay. $D = 1$ provides slow oscillations with a great amplitude and a strong decay for time $t \in (0, 3)$ in Ω^{-1} units. This could be interpreted in the following manner: the oscillating phonon field changes the sign in the $\Delta\sigma_x(b + b^\dagger)$ term which acts against greater amplitude of the probability oscillations and its decay. The interference of the dynamics caused by the σ_x term and one of the phonons leads to fast oscillations and fluctuating amplitude. $D = 1$ promotes the phonons to form a polaron cloud which breaks the dynamics of the phonon system and then the rate of change of the sign in the leading interaction term $\Delta\sigma_x(b + b^\dagger)$ is suppressed. This enables the leading interaction term to come more effectively into action.

5. Conclusions

We calculated the probability $P(t)$ of occurrence of the Frenkel exciton at the lowest excited level for the exciton interacting with single-mode optical phonons. Further we assumed the optical phonons to interact with very fast electronic states (modelled by a stochastic influence). We should like to stress that no simple time dependence is observed. Out of many time scales, one time scale originates from the Nakajima–Zwanzig equation, which gives $\mathrm{d}P(t)/\mathrm{d}t = 0$ for $t = 0$; another time scale is given by the damping of $P(t)$; others arise from the oscillating character of $P(t)$.

Besides expected dependences with respect to the temperature, exciton energy gap and interaction parameters, other interesting properties were found (listed in the previous section). Among them we stress one result more than others. If we take the exciton–phonon interaction Hamiltonian H_{int} in a quite general form with respect to the exciton

$$H_{int} = \hbar\Omega \left[\frac{(b+b^{\dagger})}{\sqrt{2}} (D\sigma_z + \Delta\sigma_x) \right] \tag{48}$$

with the pure excitonic Hamiltonian satisfying

$$H = \hbar\Omega\epsilon\sigma_z \tag{49}$$

we have found that $D = 0$ and $D = 1$ are able to lead to appreciably different results if the stochastic field is sufficiently weak. This result is potentially very important because many authors put simply $D = 0$, which cannot be generally justified. However, if a sufficiently strong stochastic field is switched on, both the situations, $D = 0$ and $D = 1$, give practically the same results. Further we have found that if the stochastic field is removed, $D = 1$ leads to renormalization of the exciton energy gap. The renormalized exciton energy gap is proportional to the original exciton energy gap and is narrowed.

We stress that the method used is *unperturbative* and *applicable* to any form of the interaction Hamiltonian (for example higher orders of the phonon displacement in the interaction Hamiltonian, too).

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