Short time de-excitation dynamics of a two-level electron system. Non-perturbative solution of the master equation

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Abstract. A new general non-perturbative method for the solution of the generalized master equation for a simple two-level model of the electron–phonon system coupled to a thermodynamic reservoir is suggested. The model includes a two-level system interacting linearly with the single-mode phonons coupled to the thermodynamic bath. For the interaction of the bath with the vibrational mode we use a stochastic model generalized to finite temperatures. The results are compared with a direct numerical solution.

1. Introduction

Electron–phonon coupling is one of the basic phenomena encountered in the investigation of the dynamics of the electronic states in molecules and solids. In the usual approach to the description of the transfer phenomena, the two-level model system interacts with a Gaussian stochastic bath, modelling the influence of a large number of phonon modes [1], or is divided into a single mode coupled to the model system and the remaining modes [2–4]. Similar models also play an important role in the description of relaxation of the excited states due to the electron–phonon coupling. Here, a two-level three-mode model [5, 6] or a two-level one mode model [7] have been successfully used.

The dynamics in such systems is usually studied by means of the time-dependent Schrödinger equation [4–6] or a master equation for the reduced density matrix elements [2, 7, 8]. A powerful tool in this respect is the so-called generalized master equation (GME) (see e.g. [9–11]). In this work, we extend a special method for the solution of GME suggested in [12] and first used in [7]. This method is based on the use of interesting properties of some generalized Fourier expansions enabling us to convert integro-differential equations into algebraic ones. In [7], the method allowed us to compute the non-radiative relaxation of the localized exciton in solids in the short time region. The main aim of this paper is to develop a general and accurate method for the solution of the GME and to investigate the time behaviour of the system for both the short and long times.

As a suitable basis for the development of such a method we consider the same model Hamiltonian as in [7]. This choice makes it possible to compare our results in the short time region with those obtained in [7]. Moreover, the relative simplicity of the model allows us to solve the corresponding Liouville equation by a direct numerical method. These results are used to test the accuracy of our method.

In section 2, we introduce the model system. It consists of the above-mentioned electron system modelled by two energy levels, which are subject to the interaction with

one internal optical vibrational mode (phonon mode). This model simulates a diatomic molecule oscillating in the harmonic approximation. We suppose that it can be excited to the first excited level, without changing the vibrational mode. This mode interacts with the thermodynamic reservoir (bath) representing very fast electronic states and remaining acoustic modes in a solid or surrounding molecules in a liquid or a gas. In both cases, the interaction with the bath can be taken as stochastic if the processes in the bath are much faster than the relaxation of the first excited state. To describe the stochastic interaction we use the generalized Haken–Strobl–Reineker model [11]. We generalize this model to include finite-temperature effects analogously to [13, 14]. The direct interaction of the fast modes and the above-mentioned electron levels is not considered.

In section 3, we formulate the GME for our system and obtain a system of coupled integro-differential equations in which the first time derivative of the density matrix depends on the convolution of the so-called memory functions with the density matrix of the system. To solve this system of equations we use some interesting properties of the Laguerre functions (sections 4 and 5), which enable us, using the expansion of the memory functions and density matrix into this orthonormal set, not only to transform these integro-differential equations into algebraic ones, but also to derive interesting analytical results for the memory functions. From known memory functions we can then calculate the time evolution of the reduced density matrix.

The probability of finding the system at the first excited level is given by the corresponding diagonal element of the electron density matrix. Its time dependence is investigated for several different temperatures of the bath and for a few different values of the parameters of the interaction among the components of the system.

One very important feature of our approach is that our treatment does not have perturbative character and all approximations are numerical only. In practical applications, one has to truncate the infinite expansions of the memory functions and density matrix to a finite number of terms. However, the accuracy can be easily checked by controlling the contribution of new terms when the expansion is enlarged. Another important aspect is that our method does not rely either on any concrete form of the model Hamiltonian or the type of the stochastic interaction with the bath. Therefore, this method can easily be applied to other problems where solution of GME is required.

2. Model Hamiltonian and stochastic interaction with the bath

Our Hamiltonian consists of two parts: the most interesting is the two electron levels describing the ground and first excited states of a molecule. The second is the harmonic oscillator describing the vibrational optical phonon interacting linearly with these states. These two parts can, for example, represent an isolated two-state diatomic molecule oscillating in the harmonic approximation. To describe the interaction of this system with the surroundings, we introduce the thermodynamic bath. We suppose that there is an interaction between the optical phonon and thermodynamic bath, which can be described by a generalized stochastic model, and that the bath does not influence the electron levels. Thus, the interaction between the electron levels and the bath is realized via the phonon mode.

Following [7], we assume that our two level system is excited at time $t = 0$. We assume that $|1\rangle$ and $|2\rangle$ are the first excited and ground states with the energies $\hbar\Omega\epsilon$ and $-\hbar\Omega\epsilon$, respectively. Here, $\hbar$ is the Planck constant and Ω is the single phonon mode frequency. The Hamiltonian of the two-level electron system and the optical vibrational

mode is assumed in the form

$$H_{\text{ex,ph}} = \hbar\Omega(\epsilon\sigma_z + b^+b) \tag{1}$$

where b and b^+ are optical phonon anihilation and creation operators and σ_z denotes the Pauli matrix. The interaction Hamiltonian has the form

$$H_{\text{int}} = \hbar\Omega\frac{(b^+ + b)}{\sqrt{2}}(D\sigma_z + \Delta\sigma_x) \tag{2}$$

where D and Δ are relative coupling constants of the two-level system with the optical mode. The interaction is linear in the phonon displacement. Thus, the complete Hamiltonian assumed in this paper reads

$$H = \hbar\Omega\left[(b^+b + \epsilon\sigma_z) + \frac{b + b^+}{\sqrt{2}}(D\sigma_z + \Delta\sigma_x)\right] = H_{\text{ex,ph}} + H_{\text{int}}. \tag{3}$$

To describe the interaction with the bath we use the generalized Haken–Strobl–Reineker model [11]. Henceforth, we assume that L' denotes the Liouville superoperator of our system without the interaction with the bath

$$L'\ldots = \frac{1}{\hbar}[H, \ldots]. \tag{4}$$

We assume further that L^s denotes the Liouville superoperator describing the interaction with the phonon bath. According to [15], the stochastic contribution reads

$$L^s_{m\alpha,n\beta,p\gamma,q\delta} = i\delta_{mp}\delta_{nq}\left[2\delta_{\alpha\beta}\left(\gamma_{\alpha\gamma} - \delta_{\alpha\gamma}\sum_\epsilon \gamma_{\epsilon\alpha}\right) - (1 - \delta_{\alpha\beta})\delta_{\alpha\gamma}\delta_{\beta\delta}\sum_\epsilon(\gamma_{\epsilon\alpha} + \gamma_{\epsilon\beta})\right]. \tag{5}$$

Here, the phonon eigenstates are denoted by the Greek letters and the energy states by the Latin ones. The $\gamma_{\alpha\beta}$ coefficients ($\neq \gamma_{\beta\alpha}$ owing to the finite temperature effect) are taken in the form [16]

$$\gamma_{\alpha\beta} = \tilde{k}\left[(\alpha + 1)\delta_{\beta,\alpha+1} + \alpha\exp\left(-\frac{\hbar\omega}{k_bT}\right)\delta_{\beta,\alpha-1}\right]. \tag{6}$$

The detailed equilibrium conditions are obeyed by this choice. The coefficient $\tilde{k}$ determines the strength of the interaction between the harmonic oscillator and the bath. We note that $\tilde{k}$ need not be small. The total Liouville superoperator of our system equals

$$L = L' + L^s. \tag{7}$$

3. Generalized master equation

To calculate the density matrix we have to solve the Liouville equation

$$\frac{\partial}{\partial t}\rho(t) = -iL\rho(t) \tag{8}$$

with the initial condition

$$\rho(0) = |1\rangle\langle1| \otimes \rho^R. \tag{9}$$

Here, $\rho^R = \exp(-\beta H_{\text{ph}})/Z$ is the canonical equilibrium phonon density matrix. This initial condition means that the system is excited at $t = 0$. Since we are not interested in the complete information described by the density matrix we use the so-called Argyres–Kelley projection superoperator [17]

$$PA = \sum_{m,n}|m\rangle\langle n| \otimes \rho^R \text{Tr}_{\text{ph}}\langle m|A|n\rangle. \tag{10}$$

This superoperator performs an average over the phonon states and selects the elements of the density matrix describing the two level system. The master equation for the relevant information $P\rho(t)$ follows from the Nakajima–Zwanzig identity [10]

$$\frac{\partial}{\partial t}P\rho(t) = -\mathrm{i}PLP\rho(t) - \mathrm{i}PLP\mathrm{e}^{-\mathrm{i}(1-P)L(t-b)}(1-P)\rho(t_0)$$

$$- \int_{t_0}^{t} PL\mathrm{e}^{-\mathrm{i}(1-P)L(t-\tau)}(1-P)LP\rho(\tau)\mathrm{d}\tau. \tag{11}$$

This equation is called the GME. Taking the Argyres–Kelley projection superoperator (10) and the initial conditions (9), the second term on the right-hand side of (11) disappears and we get a system of equations

$$\frac{\partial}{\partial t}\rho_{mn}(t) = -\sum_{pq}\left[u_{mnpq}\rho_{pq}(t) + \int_{0}^{t} w_{mnpq}(t-\tau)\rho(\tau)\,\mathrm{d}\tau\right]. \tag{12}$$

Here, we introduce the reduced density matrix operator

$$\rho_{mn}(t) = \mathrm{Tr}_{\mathbf{ph}}\langle n|\rho(t)|m\rangle \tag{13}$$

the time local term

$$u_{mnpq} = \mathrm{Tr}_{\mathbf{ph}}\langle m|L(|p\rangle\langle q|\otimes \rho^R)|n\rangle \tag{14}$$

and the so-called memory functions

$$w_{mnpq}(t) = \mathrm{Tr}_{\mathbf{ph}}\langle m|L\exp\{\mathrm{i}(1-P)Lt\}(1-P)L(|p\rangle\langle q|\otimes \rho^R)|n\rangle. \tag{15}$$

4. Use of the Laguerre functions for the solution of the GME

As seen in section 2, our problem leads to the solution of the system of integro-differential equations. We can easily verify that the first derivative of the Laguerre polynomial and the convolution of the two Laguerre polynomials can be expressed as a linear combination of the Laguerre polynomials [18]. In this section, we use these interesting properties of the Laguerre polynomials to convert the GME into algebraic equations.

First we introduce the Laguerre functions as

$$\overline{L}_n(t) = L_n(t)\mathrm{e}^{-at} \tag{16}$$

where $a > 0, a \in \mathbb{R}$ and $n = 0, 1, \ldots$. $L_n(t)$ is the Laguerre polynomial of the nth order

$$L_n(t) = \frac{1}{n!}\mathrm{e}^t\frac{\mathrm{d}^n}{\mathrm{d}t^n}(\mathrm{e}^{-t}t^n). \tag{17}$$

The e^{-at} factor may be useful to reduce the magnitude of $L_n(t)$ for very large time t. These functions are orthonormal with respect to the scalar product with the integration

$$\int_{0}^{\infty}\mathrm{e}^{-(1-2a)t}\ldots\mathrm{d}t \tag{18}$$

and have similar properties with respect to the first derivative and convolution as the Laguerre polynomials.

The GME (11) is the convolution integro-differential equation. To simplify the convolution we use the following property of $\overline{L}_n(t)$ [18]

$$\int_{0}^{t}\overline{L}_n(t-\tau)\overline{L}_m(\tau)\,\mathrm{d}\tau = \overline{L}_{n+m}(t) - \overline{L}_{n+m+1}(t). \tag{19}$$

To transform the time derivative in equation (12) we use the equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\overline{L}_n(t) = -\sum_{m=0}^{n-1} L_m(t)\mathrm{e}^{-at} - aL_n(t)\mathrm{e}^{-at} = \sum_{m=0}^{n-1}\overline{L}_m(t) - a\overline{L}_n(t). \tag{20}$$

Supposing that we can expand $\rho_{pq}(t)$ and $w_{mnpq}(t)$ into the power series in $\overline{L}_n(t)$

$$\rho_{pq}(t) = \sum_k \rho_{pq}^k \overline{L}_k(t) \tag{21}$$

and

$$w_{mnpq}(t) = \sum_k w_{mnpq}^k \overline{L}_k(t) \tag{22}$$

where ρ_{pq}^k and w_{mnpq}^k are expansion coefficients, we can transform equation (12) into an algebraic form. We use the fact that $L_k(t=0) = 1$ for all k. This enables us to introduce the initial condition into the equation, because $\sum_{k=0}^{\infty}\rho_{pq}^k = \rho_{pq}(0)$. In a special case $k=0$ we get

$$\delta_{m1}\delta_{n1} - (1-a)\rho_{mn}^0 = \sum_{pq}^2 [u_{mnpq} + w_{mnpq}^0]\rho_{pq}^0 \tag{23}$$

which can be transformed into

$$B_{mn}^0 = \delta_{m1}\delta_{n1} = \sum_{pq}^2 M_{mnpq}\rho_{pq}^0 \tag{24}$$

where

$$M_{mnpq} = u_{mnpq} + w_{mnpq}^0 + (1-a)\delta_{mp}\delta_{nq}. \tag{25}$$

For $k > 0$ we obtain

$$B_{mn}^k = \delta_{m1}\delta_{n1} - \sum_{j=0}^{k-1}\left[\rho_{mn}^j - \sum_{pq}^2 (w_{mnpq}^{k-j} - w_{mnpq}^{k-j-1})\rho_{pq}^j\right] = \sum_{pq}^2 M_{mnpq}\rho_{pq}^k. \tag{26}$$

Introducing the transformation of the indices

$$i = 2m + n - 2 \tag{27}$$

we can rewrite equations (26) and (24) as

$$B_i^k = \sum_{j=0}^4 M_{ij}\rho_j^k \qquad k = 0, 1, 2, \ldots \tag{28}$$

with the solution in the form

$$\rho_i^k = \sum_{j=1}^4 (M^{-1})_{ij} B_j^k. \tag{29}$$

Thus, for given coefficients of the memory function w_{mnpq}^k, we can calculate ρ_{mn}^k. The factor $\delta_{m1}\delta_{n1}$ in B_{mn}^k plays the role of the initial condition and must be always replaced by the corresponding $\rho_{mn}(0)$ in other applications. To solve our problem completely, we must determine the expansion coefficients w_{mnpq}^k.

5. Expansion of the memory functions in terms of the Laguerre functions

In this section, we find the expansion coefficients of the exponential appearing in the definition of the memory function (15) into the Laguerre functions. In this way we obtain a new analytical expression for the expansion coefficients w^k_{mnpq}. Results can be written in a very simple algebraic form.

Using the scalar product (18) we get for the expansion coefficients w^k_{mnpq}

$$w^k_{mnpq} = \mathrm{Tr_{ph}} \langle m | L \left[\int_0^\infty \exp\{-\mathrm{i}(1-P)Lt\} L_k(t) \mathrm{e}^{-at} \mathrm{e}^{-(1-2a)t} \, \mathrm{d}t \right] (1-P)L | p \rangle \langle q | \otimes \rho^R | n \rangle. \tag{30}$$

It can be seen from equation (30) that we have to calculate the following integral

$$\int_0^\infty \exp(-At) L_k(t) \, \mathrm{d}t \tag{31}$$

where

$$A = \mathrm{i}(1-P)L + (1-a) \tag{32}$$

and a is the exponent in the Laguerre function (16). Using another interesting property of the functions $L_k(t)$ [18]

$$\int_0^t L_k(s) \, \mathrm{d}s = L_k(t) - L_{k+1}(t) \tag{33}$$

and with integration by parts in equation (31) we get

$$\int_0^\infty \exp(-At) L_k(t) \, \mathrm{d}t = (A-1)^k A^{-(k+1)}. \tag{34}$$

This integration is valid not only if A is a number, but also if A is a positive definite matrix defined above. We can easily verify that the commutator $[A, (1-P)L]$ equals zero. It also implies that $[A^{-1}, (1-P)L] = 0$ so we can now rewrite equation (30) into the form

$$w^k_{mnpq} = \mathrm{Tr_{ph}} \langle m | L(1-P)LA^{-1}(1-A^{-1})^k | p \rangle \langle q | \otimes \rho^R | n \rangle. \tag{35}$$

This expression is suitable for numerical calculations. To obtain the coefficient $w^{k=0}_{mnpq}$ we perform the trace over the phonon states of the operator $L(1-P)LA^{-1}$ in equation (35). For $k > 0$ this operator must be multiplied by $(1-A^{-1})^k$.

At this point we have the w^k_{mnpq} coefficients necessary for the evaluation of the ρ^k_{mn} coefficients. The last remaining step is to write down the matrix elements of L and $(1-P)L$. The matrix elements of L^s are given in equation (5). For the matrix elements of L we get

$$L_{i\alpha,j\beta,k\gamma,l\delta} = \frac{1}{\hbar} (H_{i\alpha,k\gamma} \delta_{l\delta,j\beta} - H_{l\delta,j\beta} \delta_{k\gamma,i\alpha}) \tag{36}$$

where

$$H_{i\alpha,k\gamma} = \hbar\Omega[\alpha\delta_{\alpha\gamma} + \epsilon(\delta_{i1}\delta_{k1} - \delta_{i2}\delta_{k2})] + \hbar\Omega \left(\sqrt{\gamma}\delta_{\alpha+1,\gamma} + \sqrt{\gamma+1}\delta_{\alpha-1,\gamma} \right)$$

$$\times \left[\frac{D}{\sqrt{2}} (\delta_{i1}\delta_{k1} - \delta_{i2}\delta_{k2}) + \frac{\Delta}{\sqrt{2}} (\delta_{i1}\delta_{k2} + \delta_{i2}\delta_{k1}) \right]. \tag{37}$$

The projection superoperator P is given, according to (10), by its matrix elements

$$P_{i\alpha,j\beta,k\gamma,l\delta} = \delta_{ik}\delta_{jl}(\alpha|\rho^R|\beta)\delta_{\gamma\delta}. \tag{38}$$

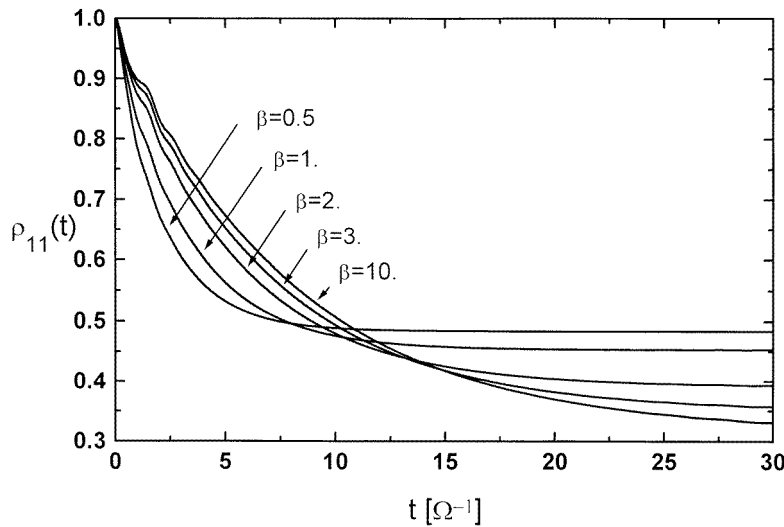The elements of $(1-P)L$ can be obtained by a matrix multiplication.

Figure 1. Dependence of the probability $\rho_{11}(t)$ of finding the system at the excited state on different values of the reciprocal temperature β for the parameters $\epsilon = 3, \tilde{k} = 1, D = 1$ and $\Delta = 1$.

The method suggested above transforms the Liouville equation into the system of algebraic equations for the reduced density matrix elements (13). The use of the complete set of the Laguerre functions makes it possible to derive new analytical expressions (35) for the memory functions. We show in the following section that equation (35) yields accurate results even for surprisingly long times.

6. Numerical results

First, we define the timescale for describing the dynamics of our system. We put $\Omega = 1$, which is equivalent to the choice of the time unit Ω^{-1}. We denote the maximum (cut-off) number of phonons as N. Similarly to [7] we take $N = 8$. Tests show that further increase of N leads to negligible changes for all the investigated cases. The a constant in the Laguerre function definition (16) is taken as 0.3 in all computations. The probability $\rho_{11}(t) = \sum_\gamma \rho_{1\gamma,1\gamma}(t)$ of finding the system at the first excited state is calculated for several values of the parameters $\epsilon, \tilde{k}, D, \Delta$ and $\beta = \frac{1}{k_B T}$, where k_B is the Boltzmann constant and T is the temperature of the bath (see figures 1–6).

In figure 1, we show the probability $\rho_{11}(t)$ for different temperatures and the strong interaction of the electron system with the bath $\tilde{k} = 1$. We see that by increasing temperature to $T = 1/(k_B \beta)$ we get a steeper decay of $\rho_{11}(t)$ for short times t and a higher equilibrium value of $\rho_{11}(t)$ at long times. Owing to the strong interaction with the bath the oscillations of $\rho_{11}(t)$ are small. The short time region of figure 1 is shown in figure 2. It is seen that the time derivative of $\rho_{11}(t)$ at $t = 0$ equals zero, in contrast to the results following from the Pauli master equation (PME).

In figure 3, the cases of the switched-on and switched-off interaction with the bath are compared. Thus, for small time t the missing interaction with the bath ($\tilde{k} = 0$) leads to a steeper decay of $\rho_{11}(t)$. However, the probability $\rho_{11}(t)$ does not converge to any equilibrium value. We see that the interaction with one phonon mode without the interaction
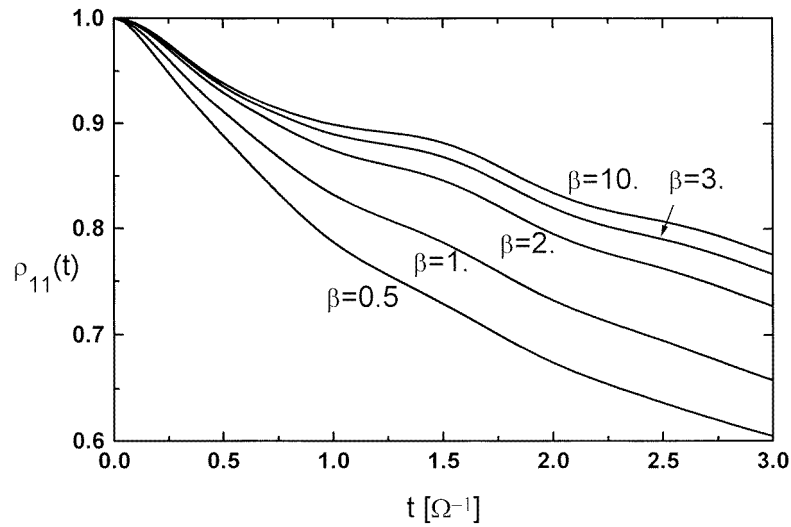
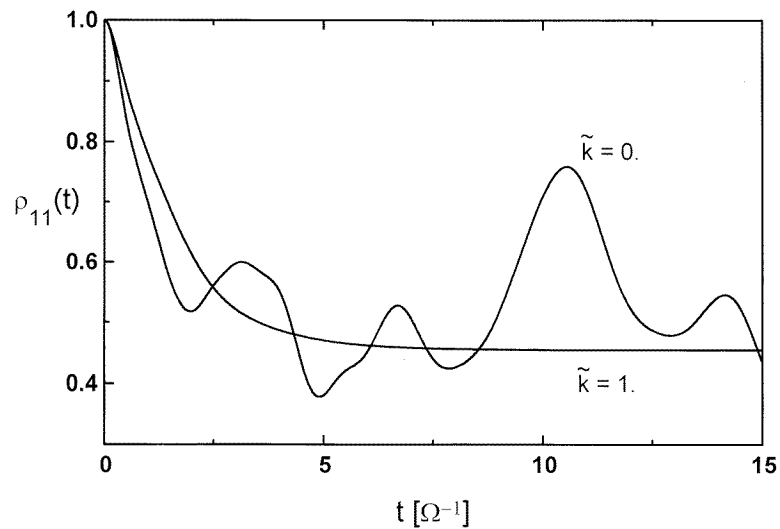**Figure 2.** Detail of the short time region of figure 1.

Figure 3. Comparison of the cases of the switched-on ($\tilde{k} = 1$) and switched-off ($\tilde{k} = 0$) interaction with the bath for the parameters $\epsilon = 1$, $\beta = 1$, $D = 1$ and $\Delta = 1$.

with the bath is not sufficient for approaching the equilibrium state of the electron system.

Figure 4 shows the case of the large energy gap ϵ. In the case of the switched-on interaction between vibrational mode and the bath ($\tilde{k} = 1$) we see only a slow decay of $\rho_{11}(t)$. At the same time, the probability $\rho_{11}(t)$ oscillates around a very high mean value. Increasing the energy gap ϵ we get a slower decay of $\rho_{11}(t)$. This can be seen better in figure 5 where we show the dependence of $\rho_{11}(t)$ on the energy gap ϵ for the switched-on interaction with the bath. We see that the large energy gap leads to a slow decay of $\rho_{11}(t)$. The same situation can be found in case of the switched-off interaction with the reservoir ($\tilde{k} = 0$). Let us note that in this situation with $\tilde{k} = 0$, the second-order PME yields no relaxation at all.
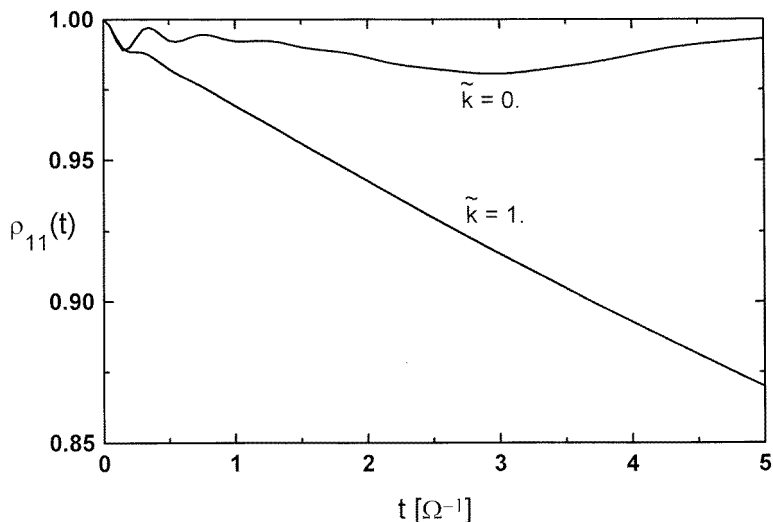
Figure 4. Comparison of the switched-on and switched-off interaction with the thermodynamic bath in case of the large energy gap $\epsilon = 10$ and the parameters $\beta = 1$, $D = 1$ and $\Delta = 1$.
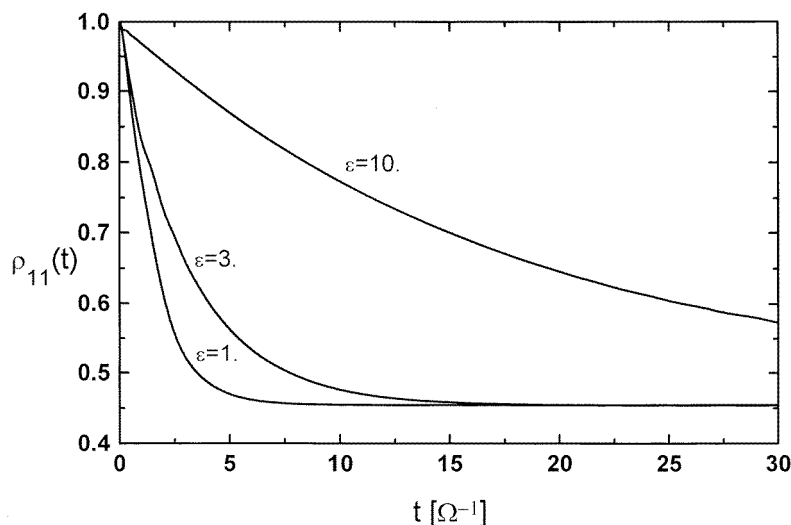

Figure 5. Dependence of $\rho_{11}(t)$ on the increasing energy gap ϵ for the parameters $\tilde{k} = 1, \beta = 1, D = 1$ and $\Delta = 1$.

Figure 6 compares the results for the weak coupling ($\tilde{k} = 0.1$) with the switched-off interaction with the bath ($\tilde{k} = 0$). Strong oscillations occur in case of the switched-off coupling. However, significant oscillations can be also observed in case of the weak coupling. It is seen that even for the weak interaction with the bath the system approaches the equilibrium state for sufficiently large t.

The dependence of $\rho_{11}(t)$ on D and Δ was discussed in detail in [7] and will not be given here.
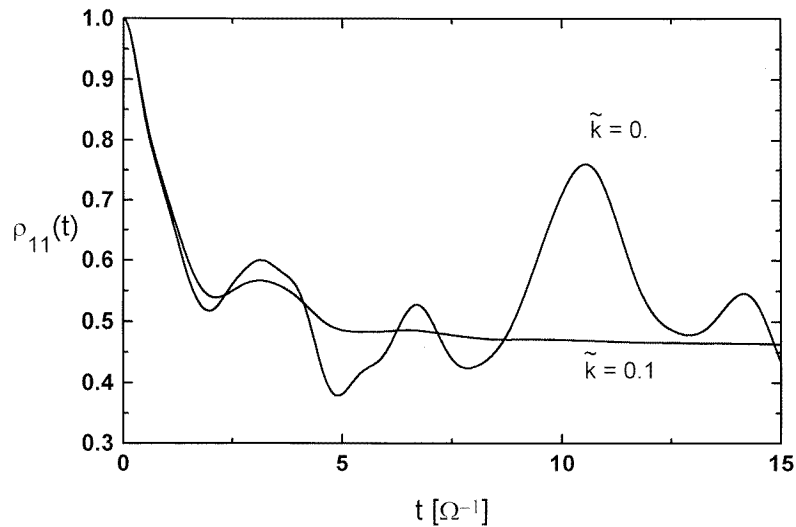
Figure 6. Comparison of the weak coupling case ($\tilde{k} = 0.1$) with the switched-off interaction with the bath ($\tilde{k} = 0$) for the parameters $\epsilon = 1, \beta = 1, D = 1$ and $\Delta = 1$.

7. Comparison with direct numerical solution

As an alternative to the method suggested in sections 4 and 5 and in order to check the power of our method we also solved the system of complex linear differential equations (8) by numerical integration. This equation can be written as $2(2N + 2)^2$ (in our case $N = 8$), real linear differential equations for real and imaginary parts of the elements of the density matrix $\rho_{i\alpha j\beta}$.

This system of equations was solved by the Bulirsch–Stoer Runge–Kutta method [19]. To check the stability and accuracy of the solution, we performed several calculations with different step lengths and numerical accuracies. Even for the oscillating case with the parameters ($\epsilon = 1, D = 1, \Delta = 1, \beta = 1, \tilde{k} = 0$) and for time going up to $t = 50$, 10 decimal digits of accuracy of the solution were attainable. The computational time depends substantially on the timestep, maximum time, demanded accuracy and character of the solution. Typically, it takes from several tens of minutes to several hours on an HP 715 workstation.

In comparison with this advanced numerical method, our suggested approach requires several times shorter computational time. In table 1, we see the comparison of the Runge–Kutta computational time for the timestep $dt = 0.05$ and $dt = 0.25$ with the times for the polynomial computations. The demanded accuracy is six and eight digits, respectively, for time t up to 50. The parameters of these computations are those of figure 1. The results obtained by the polynomial method can be computed for any value of t and do not depend on the timestep. By increasing the number of terms in the expansion in the case of the strong coupling to the bath the contribution of added terms goes down very quickly (see table 2). Checking the contribution of the last few terms of the polynomial series provides a good means to check the accuracy of the computation.

Using the new method we can obtain the results at least three times quicker than by using the standard approach. Any further increase of the timestep can lead to the loss of the details in the short time region. This may be important for larger systems, when the

Table 1. Comparison of the computational times of the Runge–Kutta and our new (polynomial) method for given accuracy of the results.

Accuracy	Timestep	R–K	Polynomial method
10^{-6}	0.05	$0:15:47$	$0:04:35$
10^{-6}	0.25	$1:09:15$	$0:04:35$
10^{-8}	0.05	$0:17:37$	$0:05:10$
10^{-8}	0.25	$1:12:12$	$0:05:10$

Table 2. Absolute values of the contributions of the last 10 terms of the series in the Laguerre functions for an increasing number of terms at various times t.

Number of terms	$t = 1$	$t = 10$	$t = 30$	$t = 50$
21–30	7×10^{-4}	2×10^{-3}	5×10^{-2}	4×10^{-1}
41–50	7×10^{-6}	3×10^{-6}	1×10^{-5}	8×10^{-3}
91–100	9×10^{-8}	1×10^{-8}	2×10^{-6}	2×10^{-5}
141–150	1×10^{-9}	1×10^{-8}	4×10^{-8}	3×10^{-6}
171–180	6×10^{-10}	1×10^{-9}	7×10^{-9}	7×10^{-8}
261–270	1×10^{-11}	1×10^{-11}	7×10^{-10}	4×10^{-9}
351–360	2×10^{-13}	4×10^{-13}	1×10^{-11}	7×10^{-10}

computational time becomes of the order of days. Another aspect of this comparison is that we compare the results of our new method of the solution of the set of integro-differential equations with those obtained by the direct solution of the Liouville equation. However, the method is not restricted to the full GME derived from the Liouville equation, and can be applied to the solution of other linear integro-differential equations.

In [7], the calculations were performed until time t, about 10 times shorter than in our case, i.e. for time when $\rho_{11}(t)$ is still far from its equilibrium value. Further extension of the method was technically impossible. For these times, our results based on the above modification agree with those of [7].

8. Conclusions

In this paper, we suggested a new general method of the solution of the GME, and used it for investigation of the time behaviour of the model electron–phonon system. The Laguerre functions used in this paper allow us to derive a new analytical expression (35) for the expansion coefficients of the memory function and to increase the computational accuracy. The advantage of the method suggested in this paper is that it is non-perturbative and is in principle applicable to any Hamiltonian and Liouville superoperator. Results indicate, in many situations and in contrast to PME, an appreciably non-exponential relaxation.

The accuracy of our results and the power of our method were checked by comparison with the direct numerical solution of the Liouville equation and the results of [7]. In contrast to [7], our method makes it possible to perform calculations for time t when the probabilities $\rho_{11}(t)$ and $\rho_{22}(t)$ approach their equilibrium values.

Acknowledgments

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