

Retardation Effects in the Dynamics of Open Molecular Systems

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March 7, 2001

Abstract. The non-Markovian version of the Quantum Master Equation responsible for the time-evolution of a reduced density operator is discussed with emphasis on the influence of external field-pulses. Different methods to account for the retardation effect in the course of the numerical solution of the Quantum Master Equation are reviewed. An application is given for femtosecond optical transitions in molecular systems and the resulting vibrational relaxation processes. The expansion in terms of Laguerre polynomials is introduced as an effective scheme for the numerical description of retarded vibrational energy dissipation. As a result of numerical simulations one can state that retardation effects become more and more pronounced with decreasing duration of the exciting laser pulse. Finally, analytical solutions are presented for non-trivial versions of the non-Markovian Quantum Master Equation.

PACS.

1 Introduction

In nearly all experiments on molecular systems or condensed matter systems one is faced with the special feature that a direct access, for example via the coupling to external fields, is only possible to a particular subset of the system degrees of freedom (DOF). These DOF are usually named *active* DOF whereas the remaining DOF are called *passive* DOF. The latter one influence the experimental output and the observed dynamics only in an indirect way.

If a quantum description of the system dynamics is necessary one takes notice of this circumstance by working with probability distributions reduced to the active DOF. In the most general description this leads to the concept of the reduced density operator. All the ideas behind are discussed in the field of dissipative quantum dynamics. This field is well-established since the fifties and early sixties and has been documented in various excellent textbooks (for a more recent overview see [1–6]). It is also a well-known fact that the equation governing the probability distribution of the active DOF shows retardation effects. These retardation effects are caused by the coupling to the passive DOF (in most cases the DOF of a thermal environment surrounding the small active subsystem) and can be accounted for by certain correlation functions.

Of course, these retardation effects are the result of the *mathematical description* of the system and not of its *physical properties*. Retardation only expresses the fact that the motion of the active system does not appear decoupled from the remaining set of DOF. Therefore, it is matter of course to state that non-Markovian behavior is only caused by the point of view we occupied when de-

scribing a system. What appears as a retardation effect in one approach may be the result of the coupling among a somewhat larger set of DOF in another one. But having chosen a particular description the need to account for retardation naturally arises.

If the time-evolution of the reduced density operator is concerned the type of equations showing retardation effects are known as non-Markovian equations of motion, and the neglect of the retardation is usually termed Markov approximation. To put all this into a more concrete form, first, let us denote the active system by S and the passive system (the reservoir) by R . The complete system $S + R$ is described by the nonequilibrium time-dependent quantum statistical operator $\hat{W}(t)$. Consequently, the reduced statistical operator $\hat{\rho}(t)$ is obtained from $\hat{W}(t)$ by taking the trace with respect to the states related to the passive DOF (reservoir states), i.e.

$$\hat{\rho}(t) = \text{tr}_R \{ \hat{W}(t) \}. \quad (1)$$

Since the equation of motion determining $\hat{\rho}$ is of the operator type, retardation and thus non-Markovian behavior is governed by a superoperator acting in a time non-local manner on $\hat{\rho}$

$$\hat{D}(t, t_0; \hat{\rho}) = - \int_{t_0}^t dt \mathcal{M}(t, \bar{t}) \hat{\rho}(\bar{t}). \quad (2)$$

The quantity \mathcal{M} defines the (superoperator) memory kernel. It depends on the difference of t and \bar{t} if any time-dependent external perturbation is absent. According to the well-established approach leading to the Nakajima-Zwanzig equation for $\hat{\rho}(t)$ an exact expression for $\mathcal{M}(t)$ is

known (see, e.g. [2,7]), which usually saves as a starting point for a perturbational expansion. The decay of $\mathcal{M}(t)$ with increasing t fixes the characteristic time-scale τ_{mem} for which retardation (memory effects) are important.

The approach described so far is based on the construction of an equation of motion to get $\hat{\rho}$. Alternatively one can try to derive directly a closed expression for the density matrix. As it is well-known this becomes possible in using the path integral representation of quantum mechanics. (For a recent overview on the application to chemical physics problems we refer to [8].) If $\hat{\rho}$ has been taken in the coordinate representation the respective density matrix is given as a double path integral including all possible paths which connect the coordinate distribution at the initial time t_0 with that at the actual time t . Here, again retardation appears which is accounted for by the so-called influence functional. This quantity stems from the passive DOF and is nonlocal in time. The approach incorporates the coupling between the active and passive DOF in an exact manner beyond any perturbation theory, but it is numerically strongly demanding what restricts its present applications to active systems with a number of quantum levels less than 10.

Beside many other applications the concept of dissipative quantum dynamics has been used to describe relaxation phenomena in molecular systems and to achieve a quantum mechanical foundation of chemical reaction dynamics. Focusing on optical experiments, electronic transitions and vibrational motion, the research work done up to the dawn of fs-spectroscopy can be characterized by the following peculiarity. The time-scale of preparing an excited molecular state appeared to be much longer than the characteristic time nuclear DOF need to reach equilibrium. In the course of numerical simulations this aspect allowed for the neglect of particular coherence effects and justifies a certain time coarse graining. The coarse graining is achieved in removing unimportant ultrafast fluctuations from the description and, in this way, non-Markovian, i.e. retardation effects disappear.

Meanwhile optical pulses with a duration less than 10fs are available and one can detect coherent nuclear dynamics (dynamics unaffected by environmental fluctuations) [9–12]. This experimental achievement initiated a renaissance of the theory of the dissipative quantum dynamics putting emphasis on the description of ultrafast nuclear dynamics in polyatomic molecules and molecular systems in the condensed phase [7,10–12]. And, there is an argument that one has to expect pronounced retardation effects just in this limit of ultrashort optical excitation. Obviously, if the excitation process i.e. the preparation of a non-equilibrium initial state is long or even comparable to the time τ_{mem} characterizing retardation there will be not any chance to observe non-Markovian effects. However, in the opposite case where the initial state preparation process is fast retardation effects may become observable. Such an observation of retardation has to be understood in the sense that the experimental data should deviate from a related simulation which works completely in the Markovian limit. We will demonstrate this in comparing

the Markovian as well as the non-Markovian description of an optical excitation process (using a sufficient simple model for a molecular system).

But it is not the aim of the present contribution to remain at a single example. Instead, we will give an overview on recent theoretical achievements to incorporate retardation effects into the description of open quantum systems. Although a parallel development took place in solid state physics (see, e.g. [13] and references therein) the present paper concentrates on the field of chemical physics putting emphasis on optical transitions and electron-vibrational dynamics in molecular systems. Since it is a task by itself to clarify the importance of non-Markovian effects when solving density matrix equations we will not comment on the experimental background.

The paper is organized as follows. In the next section a sufficient general model is introduced and we give the basic equation of motion for the reduced density operator. According to the structure of the dissipative part, Eq. (2) a treatment possible in many applications will be explained. The respective idea is made somewhat more concrete in Section 3. The Fourier-Laplace transformation method is discussed in Section 4. In Section 5 the expansion by means of Laguerre polynomials is applied to describe optical excitation into an excited potential energy surface (PES) and to study resulting vibrational relaxation. In the last section analytical solutions of the non-Markovian density operator equations are presented.

2 The Non-Markovian Quantum Master Equation

2.1 The Model

According to the introduction of active DOF our discussion will start with a respective separation of the complete Hamiltonian

$$H = H_S(t) + H_{S-R} + H_R, \quad (3)$$

which is standard in dissipative quantum dynamics. The first part describes the molecular system of interest (active system with Hamiltonian H_{mol}) together with its coupling to an external radiation field (with Hamiltonian $H_{\text{field}}(t)$)

$$H_S(t) = H_{\text{mol}} + H_{\text{field}}(t). \quad (4)$$

The part H_{S-R} accounts for the coupling of the active system to the reservoir, whereas the reservoir is described by H_R . The molecular contribution to H_S will be given by the expression

$$H_{\text{mol}} = \sum_a H_a(Q) |\varphi_a\rangle \langle \varphi_a|. \quad (5)$$

It corresponds to an expansion with respect to the adiabatic electronic states φ_a (with electronic quantum number a) and the neglect of any non-adiabatic coupling. The vibrational Hamiltonian $H_a = T_{\text{vib}} + U_a(Q)$ contains the

kinetic energy operator T_{vib} and the respective PES U_a defined with respect to the set $Q = \{Q_j\}$ of active vibrational DOF. The *eigenfunctions* of the various H_a will be denoted as $\chi_{aM}(Q)$, where M stands for the set of related vibrational quantum numbers.

The molecular Hamiltonian is general enough to carry out different considerations. Performing concrete numerical calculations (see [14,15]) it will be further reduced to the minimal model used in [16,17] for the simulation of ultrafast optical data obtained for a dissolved dye molecule. In particular, this model will serve as a reference system to study the interplay of the external field excitation of the molecule and the non-Markovian relaxation of the vibrational DOF in the excited electronic state. The minimal model consists of two electronic levels modulated by a single effective vibrational coordinate Q . In this case the $H_a(Q)$ are vibrational Hamiltonian corresponding to the ground ($a = g$) as well as to the excited electronic states ($a = e$) and incorporating harmonic oscillator PES

$$U_a(Q) = U_a^{(0)} + \frac{\hbar\omega_{\text{vib}}}{4}(Q - Q_a)^2. \quad (6)$$

For the coupling to the radiation field we have in mind a description within the electric dipole approximation

$$H_{\text{field}}(t) = -\mathbf{E}(t)\hat{\mu}. \quad (7)$$

Here $\mathbf{E}(t)$ is the electric field-strength of a laser pulse (or a sequence of pulses). It reads in detail

$$\mathbf{E}(t) = \mathbf{n}A\mathcal{E}(t)e^{-i\omega_0 t} + \text{c.c.}, \quad (8)$$

where \mathbf{n} is the polarization unit vector, A the complex field amplitude, $\mathcal{E}(t)$ the normalized pulse envelope and ω_0 the carrier frequency. Furthermore, we introduced in Eq. (7) the molecular dipole operator

$$\hat{\mu} = \sum_{a,b} (1 - \delta_{a,b}) \mathbf{d}_{ab} |\varphi_a\rangle \langle \varphi_b|, \quad (9)$$

which only contains off-diagonal contributions connecting different electronic states. \mathbf{d}_{ab} is the related transition matrix element. In the concrete computations it will only connect the ground state φ_g with a single excited state φ_e .

A common notation of the system reservoir coupling is given by the following multiple factorized expression

$$H_{S-R} = \sum_u \mathcal{K}_u \Phi_u, \quad (10)$$

where the \mathcal{K}_u are operators exclusively defined in the state space of the active system and the Φ_u are operators acting in the reservoir state space. Noting the specification of the molecular systems of interest we identify u and v with the electronic quantum numbers a and b , and set

$$\mathcal{K}_a = K_a(Q) |\varphi_a\rangle \langle \varphi_a|. \quad (11)$$

The assumption of a coupling diagonal with respect to the electronic states is not the most general one but reasonable for the present case where the electronic levels are

connected by optical transitions. The dependence of the $K_a(Q)$ on the Q remains arbitrary whereas it represents a widely used *ansatz* to set

$$\Phi_a = \hbar \sum_{\xi} k_{\xi}(a) Z_{\xi}, \quad (12)$$

i.e. the Φ_a depend linearly on the reservoir DOF. The latter are often understood as decoupled harmonic oscillators.

2.2 The Density Operator Equation

It is well-established how to get an exact equation of motion for $\hat{\rho}(t)$ via the Nakajima-Zwanzig identity (see, e.g. [2,7,18,19]). The respective memory kernel superoperator \mathcal{M} , Eq. (2) includes the complete perturbation expansion with respect to the system reservoir coupling via a particular S -matrix type superoperator. According to this complicated structure, however, there is no chance to compute \mathcal{M} beyond some trivial examples. But this difficulty may be overcome, for example, by a time-dependent projection operator approach as suggested in [20,21] allowing for an partial summation with respect to H_{S-R} .

As an alternative, and this is the point of view we will take for the following, one can try to define the active system large enough to cover all strong coupled DOF. Then, the coupling to the remaining passive system should be weak enough to be treated in a perturbational approach. Providing weak or intermediate system reservoir coupling one can carry out the so-called second Born approximation. This is achieved by approximating the equation of motion for $\hat{\rho}$ in the second order with respect to H_{S-R} (fourth-order approximations have been discussed in [22,23] and just higher contributions in [24,25]).

We will not recall the derivation of the equation of motion for $\hat{\rho}$ here since it can be found in many textbooks (see, e.g. [1,2,7]). It follows

$$\begin{aligned} \frac{\partial}{\partial t} \hat{\rho}(t) &= \hat{I}(t, t_0) \\ &- \frac{i}{\hbar} [H_S(t) + H_{\text{mf}}, \hat{\rho}(t)]_- + \hat{D}(t, t_0; \hat{\rho}). \end{aligned} \quad (13)$$

This equation is usually called Quantum Master Equation (QME). The first term on the right-hand side is responsible for the decay of correlations between the active system and the reservoir, which are present at the initial time t_0 . The appearance of such initial correlations corresponds to a non-factorized form (into a system and into a reservoir part) of the complete statistical operator (at the initial time t_0). We will not further comment on it here but refer to the recent nice discussion in [26].

The contribution H_{mf} which extends H_S on the right-hand side is the so-called mean-field term

$$H_{\text{mf}} = \sum_u \langle \Phi_u \rangle_R \mathcal{K}_u, \quad (14)$$

with $\langle \dots \rangle_R$ denoting the thermal average with respect to the reservoir states.

In accordance with Eq. (2) the dissipative part $\hat{D}(t, t_0; \hat{\rho})$ incorporates the convolution of the density operator $\hat{\rho}(t)$ and a memory kernel (memory superoperator) $\mathcal{M}(t, \bar{t})$. Its definition is given by the following equation

$$\begin{aligned} \hat{D}(t, t_0; \hat{\rho}) = & \\ & - \sum_{u,v} \int_{t_0}^t d\bar{t} \left(C_{uv}(t - \bar{t}) \left[\mathcal{K}_u, U_S(t, \bar{t}) \mathcal{K}_v \hat{\rho}(\bar{t}) U_S^+(t, \bar{t}) \right]_- \right. \\ & \left. - C_{vu}(-t + \bar{t}) \left[\mathcal{K}_u, U_S(t, \bar{t}) \hat{\rho}(\bar{t}) \mathcal{K}_v U_S^+(t, \bar{t}) \right]_- \right). \end{aligned} \quad (15)$$

Beside the direct appearance of the external field in the QME via the commutator with H_S the field also enters in an indirect way. Such an indirect field-dependence of the memory kernel is induced by the time-evolution operator U_S which is defined by H_S . The reservoir correlation functions read

$$C_{uv}(t) = \frac{1}{\hbar^2} \left(\langle U_R^+ \Phi_u U_R \Phi_v \rangle_R - \langle \Phi_u \rangle_R \langle \Phi_v \rangle_R \right). \quad (16)$$

For some further application it is useful to introduce the interaction representation of the QME, which should be defined here by the complete system Hamiltonian, Eq. (4). The respective representation of the density operator follows as

$$\hat{\rho}^{(I)}(t) = U_S^+(t, t_0) \hat{\rho}(t) U_S(t, t_0). \quad (17)$$

The QME for $\hat{\rho}^{(I)}(t)$ is obtained in similarity to Eq. (13) but without $H_S(t)$ on the right-hand side. Furthermore, \hat{I} , H_{mf} , and \hat{D} have to be translated into the interaction representation. For the latter quantity one obtains

$$\begin{aligned} \hat{D}^{(I)}(t, t_0; \hat{\rho}^{(I)}) = & \\ & - \sum_{u,u} \int_{t_0}^t d\bar{t} \left(C_{uv}(t - \bar{t}) \left[\mathcal{K}_u^{(I)}(t), \mathcal{K}_v^{(I)}(\bar{t}) \hat{\rho}^{(I)}(\bar{t}) \right]_- \right. \\ & \left. - C_{vu}(-t + \bar{t}) \left[\mathcal{K}_u^{(I)}(t), \hat{\rho}^{(I)}(\bar{t}) \mathcal{K}_v^{(I)}(\bar{t}) \right]_- \right). \end{aligned} \quad (18)$$

Usually one takes this expression to change to the Markov-limit by replacing the density operator with time argument \bar{t} by the one at time t (see, e.g.[7]).

Finally, we remind on the well-known fact that the perturbational treatment of the system reservoir coupling may lead to some wrong behavior of the density operator, i.e. the violation of its positivity. This property can be ensured by taking the so-called Lindblad-type of dissipation. However, the latter provide the Markov approximation together with a neglect of certain parts of the time-local dissipative superoperator (secular type approximations, for a recent discussion see, e.g. [27]).

2.3 Introduction of Auxiliary Density Operators

To characterize the retardation effects and to construct time-local equations of motion it will be of great advan-

tage to change the notation of the dissipative part, Eq. (15). Therefore, we write $\hat{D} = \hat{D}_1 + \hat{D}_2$ and identify \hat{D}_2 with the contribution given by the time-independent part $C_{uv}^{(2)} = - \langle \Phi_u \rangle_R \langle \Phi_v \rangle_R / \hbar^2$ of C_{uv} , Eq. (16). The first contribution \hat{D}_1 follows from the time-dependent first term in Eq. (16).

We start to give an alternative notation for \hat{D}_1 . It is obvious from Eq. (15) that we can write $\hat{D}_1 = \sum_u [\mathcal{K}_u, \hat{\Sigma}_u]_-$ (where $\hat{\Sigma}_u$ is easily deduced from Eq. (15)). This expression removes the time non-locality from the QME. Unfortunately, one cannot derive a separate equation of motion for $\hat{\Sigma}_u$. This only becomes possible if the various correlation function $C_{uv}^{(1)}$, which depend on the two time-arguments t and \bar{t} can be replaced by the following multiple factorization *ansatz*

$$C_{uv}^{(1)}(t - \bar{t}) = \frac{1}{\hbar^2} \sum_s \alpha_{uv}^{(s)}(t) \beta_{uv}^{(s)}(\bar{t}). \quad (19)$$

Such an expression may be constructed by a double expansion with respect to an orthogonal set of functions. Providing the multiple factorization of $C_{uv}^{(1)}$ we can introduce the following new auxiliary density operators (note the use of the interaction representation, Eq. (17))

$$\hat{\sigma}_{s,uv}^{(I+)}(t) = \frac{i}{\hbar} \int_{t_0}^t d\bar{t} \beta_{uv}^{(s)}(\bar{t}) U_S^+(\bar{t}, t_0) \mathcal{K}_v \hat{\rho}(\bar{t}) U_S(\bar{t}, t_0), \quad (20)$$

and

$$\hat{\sigma}_{s,uv}^{(I-)}(t) = \frac{i}{\hbar} \int_{t_0}^t d\bar{t} \beta_{vu}^{(s)}(-\bar{t}) U_S^+(\bar{t}, t_0) \hat{\rho}(\bar{t}) \mathcal{K}_v U_S(\bar{t}, t_0), \quad (21)$$

which remove the time-nonlocality in \hat{D}_1 to give

$$\begin{aligned} \hat{D}_1(t) = & \frac{i}{\hbar} \sum_{u,v} \sum_s \\ & \left[\mathcal{K}_u, \alpha_{uv}^{(s)}(t) \hat{\sigma}_{s,uv}^{(+)}(t) - \alpha_{vu}^{(s)}(-t) \hat{\sigma}_{s,uv}^{(-)}(t) \right]_- \end{aligned} \quad (22)$$

The equations of motion for the auxiliary operators read

$$\frac{\partial}{\partial t} \hat{\sigma}_{s,uv}^{(+)}(t) = -\frac{i}{\hbar} [H_S(t), \hat{\sigma}_{s,uv}^{(+)}(t)]_- + \frac{i}{\hbar} \beta_{uv}^{(s)}(t) \mathcal{K}_v \hat{\rho}(t), \quad (23)$$

and

$$\frac{\partial}{\partial t} \hat{\sigma}_{s,uv}^{(-)}(t) = -\frac{i}{\hbar} [H_S(t), \hat{\sigma}_{s,uv}^{(-)}(t)]_- + \frac{i}{\hbar} \beta_{vu}^{(s)}(-t) \hat{\rho}(t) \mathcal{K}_v, \quad (24)$$

We note that the term stemming from initial correlations can be handled in a similar manner [26]. However, for the description of the external field influence initial correlations are of less importance. Any simulation can be performed without this term in letting the external field pulse start to act definitely after the decay of the initial correlations.

Next we deal with term \hat{D}_2 determined by the time-independent part of C_{uv} . It can be rewritten by introducing a single additional density operator $\hat{\sigma}$

$$\hat{D}_2(t, t_0) = -\frac{i}{\hbar} [H_{\text{mf}}, \hat{\sigma}(t)]_- . \quad (25)$$

Using the interaction representation as introduced in Eq. (17) the new operator reads

$$\hat{\sigma}^{(I)}(t) = \frac{i}{\hbar} \int_{t_0}^t d\bar{t} U_S^+(\bar{t}, t_0) [H_{\text{mf}}, \hat{\rho}(\bar{t})]_- U_S(\bar{t}, t_0) . \quad (26)$$

This expression can be related to the following equation of motion (in the Schrödinger representation)

$$\frac{\partial}{\partial t} \hat{\sigma}(t) = -\frac{i}{\hbar} [H_S(t), \hat{\sigma}(t)]_- - \frac{i}{\hbar} [H_{\text{mf}}, \hat{\rho}(t)]_- . \quad (27)$$

The introduction of the auxiliary operators $\hat{\sigma}_{s,uv}^{(\pm)}$ and $\hat{\sigma}$ demonstrates that the time-nonlocality can be removed with any accuracy one needs. In which manner the two types of auxiliary operators contribute depends on the properties of the reservoir correlation functions. If the time-independent part dominates the dissipation one may have the chance to find an analytical solution of the non-Markovian QME (cf. Section 7).

2.4 Expansion with Respect to Electronic States

It is of basic importance for the description of optical transitions and the simulation of nonlinear optical experiments to expand the density operator and the QME with respect to the electronic states $|\varphi_a\rangle$. It results the set of quantities $\hat{\rho}_{ab}(t) = \langle \varphi_a | \hat{\rho}(t) | \varphi_b \rangle$, which just represent operators in the state space of the vibrational coordinates. To deal with formulas which are not too complicated we assume $\langle \Phi_u \rangle_R = 0$ and get from Eq. (13)

$$\begin{aligned} \frac{\partial}{\partial t} \hat{\rho}_{ab}(t) &= \hat{I}_{ab}(t) - \frac{i}{\hbar} (H_a \hat{\rho}_{ab}(t) - \hat{\rho}_{ab}(t) H_b) \\ &+ \frac{i}{\hbar} \mathbf{E}(t) \sum_c (\mathbf{d}_{ac} \hat{\rho}_{cb}(t) - \mathbf{d}_{cb} \hat{\rho}_{ac}(t)) + \hat{D}_{ab}(t, t_0) . \end{aligned} \quad (28)$$

The electronic matrix elements of the dissipative part are obtained as

$$\begin{aligned} \hat{D}_{ab}(t, t_0) &= -\sum_{c,d} \int_{t_0}^t d\bar{t} \\ &\left(C_{ac}(t-\bar{t}) K_a U_{ac}(t, \bar{t}) K_c \hat{\rho}_{cd}(\bar{t}) U_{bd}^+(t, \bar{t}) \right. \\ &+ C_{db}(-t+\bar{t}) U_{ac}(t, \bar{t}) \hat{\rho}_{cd}(\bar{t}) K_d U_{bd}^+(t, \bar{t}) K_b \\ &- C_{bc}(t-\bar{t}) U_{ac}(t, \bar{t}) K_c \hat{\rho}_{cd}(\bar{t}) U_{bd}^+(t, \bar{t}) K_b \\ &\left. - C_{da}(-t+\bar{t}) K_a U_{ac}(t, \bar{t}) \hat{\rho}_{cd}(\bar{t}) K_d U_{bd}^+(t, \bar{t}) \right) \end{aligned} \quad (29)$$

Note Eq. (11) and $U_{ab} = \langle \varphi_a | U_S | \varphi_b \rangle$.

It remains to specify the various C_{ab} . In the case where the simple expression (12) is valid and where the reservoir DOF can be considered as coordinates obtained from a normal mode analysis, i.e. the Z_ξ form a set of independent harmonic oscillators it is advantageously to introduce

$$J_{ab}(\omega) = \sum_{\xi} k_{\xi}(a) k_{\xi}(b) \delta(\omega - \omega_{\xi}) . \quad (30)$$

These quantities are known as spectral densities (coupling-strength weighted density of normal-mode oscillator frequencies). They determine the correlation functions according to (note the vanishing of $\langle \Phi_a \rangle_R$)

$$C_{ab}(t) = \int d\omega e^{-i\omega t} (1 + n(\omega)) (J_{ab}(\omega) - J_{ab}(-\omega)) , \quad (31)$$

with $n(\omega) = 1/(\exp(\hbar\omega/k_B T) - 1)$ being the Bose-Einstein distribution. A common *ansatz* for $j(\omega)$ representing the normalized part (in the frequency interval between 0 and ∞) of a certain J_{ab} is given by $j(\omega) = \omega \exp(-\omega/\omega_c)/\omega_c^2$. The inverse of the cut-off frequency ω_c gives an estimate of the characteristic time τ_{mem} for which the correlations of the reservoir DOF decay. We will denote the inverse of ω_c by t_c .

2.5 Time-Dependent Markov Approximation

As an alternative to the Nakajima-Zwanzig equation an equation of motion for $\hat{\rho}(t)$ has been suggested which is exact but local in time. Now, dissipation is described by $\mathcal{D}(t)\hat{\rho}(t)$ where $\mathcal{D}(t)$ is an explicitly time-dependent superoperator. Such an approach is known as the time-convolutionless density matrix equation [28] (see also the discussion in [29]). Within this approach the absence of the time-nonlocality has been achieved by introducing into $\mathcal{D}(t)$ the reverse time-evolution from the actual time back to the initial time. This can be understood as the presence of additional partial expansions with respect to the perturbation (the system reservoir coupling H_{S-R}).

Both types of density operator equations may be related one to another if one changes to the interaction representation, Eq. (17) and expands $\hat{\rho}^{(I)}(t-\tau)$, after replacing \bar{t} in Eq. (18) by $\tau = t-\bar{t}$, in powers of τ [30]. This procedure, if carried out at the non-Markovian QME, leads again to a dissipative term of type $\mathcal{D}(t)\hat{\rho}(t)$ (of course with \mathcal{D} defined in the second-order with respect to H_{S-R}). Since any non-Markovian effect has been removed we will call this approximation the time-dependent Markov approximation. If the second-order version of $\mathcal{D}(t)$ with respect to H_{S-R} is taken a nearly correct reproduction of the non-Markovian dynamics (of this second-order perturbation type) can be obtained [14]. Other applications of the time-dependent Markov approximation can be found in [17, 31–34].

3 Ansatz for the Reservoir Correlation Function

Before dealing with techniques based on a certain expansion of the density operator and the QME we refer to methods which try to solve the non-Markovian QME directly, i.e. in the time-domain. In [35] the introduction of the fictitious bath modes to simulate a spectral density of the bath has been suggested. Behind this idea is the common observation that a given non-Markovian process can be related to a Markovian process of a system with a larger set of DOF. The easiest way would be to enlarge the system in question by a single fictitious harmonic-oscillator mode. If the latter interacts with a zero-correlation time bath, the spectral density obtained after tracing over the fictitious mode turns out to be of a Lorentzian shape. Although originally suggested for the Monte Carlo wavefunction method [35], where the scaling of the problem (related to the involved level number) is much more favorable than that of the density matrix approach, it is obvious that the system cannot be enlarged by more than a few fictitious modes. Therefore, the flexibility to chose a particular shape of the effective spectral density is rather small.

The scaling problem can be avoided if we view the fictitious bath modes only as a numerical trick for the decomposition of the spectral density. To this end the following parameterization of the correlation function has been suggested in [26] (for a single electronic state, see also [23])

$$J(\omega) = \frac{1}{2} \sum_{s=1}^{\nu} J_s \frac{\pi\omega}{[(\omega + \omega_s)^2 + \gamma_s^2][(\omega - \omega_s)^2 + \gamma_s^2]}, \quad (32)$$

where the parameters J_s , ω_s and γ_s are arbitrary and real. It is the great advantage of such a generalized multi-Lorentzian form that an analytical determination of the time-dependent correlation function according to Eq. (31) becomes possible. One obtains (note the absence of electronic quantum numbers)

$$\begin{aligned} \text{Re } C(t) &= \sum_{s=1}^{\nu} \frac{J_s}{\omega_s \gamma_s} \left(\coth \left(\frac{\beta}{2} (\omega_s + i\gamma_s) \right) e^{i\omega_s t - \gamma_s t} \right) \\ &+ \sum_{s=1}^{\nu} \frac{J_s}{\omega_s \gamma_s} \left(\coth \left(\frac{\beta}{2} (\omega_s - i\gamma_s) \right) e^{-i\omega_s t - \gamma_s t} \right) \\ &+ \frac{2i}{\beta} \sum_{s=1}^{n'} J(i\nu_s) e^{-\nu_s t}, \end{aligned} \quad (33)$$

and

$$\text{Im } C(t) = -i \sum_{s=1}^{\nu} \frac{J_s}{\omega_s \gamma_s} \left(e^{i\omega_s t - \gamma_s t} - e^{-i\omega_s t - \gamma_s t} \right), \quad (34)$$

where $\nu_s = 2\pi s k_B T$ are the Matsubara frequencies. If formulated for the difference time-argument $t - \bar{t}$ the real and imaginary part of the correlation function are just of the type introduced in Eq. (19). Therefore, the original

QME can be completed by the equations of motion for the auxiliary density operators, Eqs. (20) and (21).

The resulting equations would represent the time local equivalent to the original time non-local Eq. (13) if the parameterization (32) is exact. Although this is not the case it has been noted in [26] that it gives a good approximation for an Ohmic spectral density even if one incorporates only a few terms in the expansion Eq. (32). But the main advantage of this method is that one can easily account for an external field influence. So, the approach is suitable for strong field problems as well as for problems of laser pulse control of molecular dynamics, e.g. in the framework of the optimal control scheme [36].

4 Fourier-Laplace Transformation and the Description of Retardation Effects in the Frequency-Domain

Inspecting the general form of the QME, Eq. (13) the idea arises to use the Fourier-Laplace transformation method for the solution of the time non-local problem. Under certain additional conditions and for a few level systems one can obtain results by analytical calculations which are applicable, for example, to the computation of pump-probe spectra (see [30,37-40]).

Omitting any field dependence ($H_S \equiv H_{mol}$), providing that the mean-field term, Eq. (14) does not exist and setting $t_0 = 0$, one easily constructs the Fourier-Laplace transformed version of Eq. (13). Its solution reads

$$\begin{aligned} \hat{\rho}(\omega) &= \{i\omega - i\mathcal{L}_{mol} - \mathcal{M}(\omega)\}^{-1} \\ &\times (\hat{I}(\omega) - \hat{\rho}(t=0)), \end{aligned} \quad (35)$$

where \mathcal{L}_{mol} denotes the Liouville superoperator corresponding to the commutator with H_{mol} and $\mathcal{M}(\omega)$ is the memory kernel, Eq. (2) transformed into the frequency domain. Choosing a concrete representation the respective Fourier-Laplace transformed density matrix can be determined, at least numerically. After a back transformation the time-dependence of the complete set of density matrix elements is available (see, e.g. [41]). But all those problems connected with the presence of a time-dependent external field cannot be treated in this manner. After the transformation into the frequency domain a convolution integral of the Fourier-Laplace transformed field and the density operator occurs. However, if a linearization with respect to the field can be carried out (or some higher-order expansions) the problem becomes tractable again. This will be demonstrated in the following for the case of the linear absorption coefficient.

We start with the time-dependent formulation of the frequency-domain absorption coefficient

$$\alpha(\omega) = \frac{4\pi\omega n_{mol}}{3\hbar c} \text{Re} \int_0^{\infty} dt e^{i\omega t} C_{d-d}^{(-)}(t), \quad (36)$$

where n_{mol} denotes the volume density of the absorbing molecules, and the dipole-dipole correlation function is

given by $C_{d-d}^{(-)}(t)$. For the molecular systems under consideration the dipole operator, Eq. (9) should exclusively act on system DOF and should realize transitions from the electronic ground-state φ_g to the excited state φ_e . Accordingly, the dipole-dipole correlation function can be written as $(\text{tr}_{\text{vib}}\{\dots\})$ denotes the trace with respect to the active vibrational DOF)

$$C_{d-d}^{(-)}(t) = \mathbf{d}_{ge} \text{tr}_{\text{vib}}\{\langle \varphi_e | \hat{\sigma}(t) | \varphi_g \rangle\} + \mathbf{d}_{eg} \text{tr}_{\text{vib}}\{\langle \varphi_g | \hat{\sigma}(t) | \varphi_e \rangle\}. \quad (37)$$

The operator $\hat{\sigma}(t)$ is a solution of the non-Markovian QME but with the initial condition $\hat{\sigma}(0) = [\hat{\mu}, \hat{\rho}_{\text{eq}}]_-$ ($\hat{\rho}_{\text{eq}}$ is the vibrational equilibrium statistical operator in the electronic ground-state, see also [27]). Furthermore, since only electronic off-diagonal matrix elements of $\hat{\sigma}$ are needed the initial correlation term vanishes.

Eq. (37) together with (36) is a generalization of the well-known formula which gives the absorption coefficient at frequency ω via the Fourier transformation of the vibrational wavepacket motion on the excited electronic state PES after an instantaneous transition from the ground-state at time $t = 0$ (see, for example [7]). In this picture the ultrafast wavepacket motion within a sub-picosecond time-region determines the cw-absorption. If the vibrational wavepacket motion on the excited state PES involves dissipation but without retardation effects (Markovian relaxation), or in other words if the coherences responsible for linear absorption decay according to an exponential law the frequency-domain line broadening appears to be of the Lorentzian type. Obviously, non-Markovian effects, i.e. non-exponential decay of the coherences will result in a deviation from the Lorentzian line-shape. This fact is well anticipated in semiconductor optics but has been discussed not in a similar clear fashion in chemical physics. Therefore, we shortly demonstrate the non-Lorentzian line-broadening of a vibrational progression corresponding to an electronic transition coupled to a single vibrational DOF (compare the Hamiltonian Eq. (5)).

To end up with an analytical formula we consider the special case where the coupling of the active vibrational DOF to the reservoir modes is much larger in the excited electronic state than in the ground-state, i.e. we set $K_g = 0$ in Eq. (11). A compact treatment is achieved if we introduce the Green's function type matrix $G_{MN}(t) = \Theta(t) \langle \chi_{eM} | \langle \varphi_e | \hat{\sigma}(t) | \varphi_g \rangle | \chi_{gN} \rangle$.

According to the initial value of $\hat{\sigma}$ we get $G_{MN}(t = 0) = \mathbf{d}_{eg} \langle \chi_{eM} | \chi_{gN} \rangle f(\hbar\omega_{gN})$, where f gives the thermal distribution versus the vibrational levels $E_{gN} = \hbar\omega_{gN}$ of the electronic ground-state. This Green's function enables us to rewrite the first electronic matrix element in Eq. (37). The second matrix element can be neglected since it leads to non-resonant (anti-resonant) contributions. Before giving the equation of motion for G_{MN} we note

$$\alpha(\omega) = \frac{4\pi\omega n_{\text{mol}}}{3\hbar c} \text{Re} \left\{ \mathbf{d}_{eg}^* \sum_{M,N} \langle \chi_{gN} | \chi_{eM} \rangle G_{MN}(\omega) \right\}. \quad (38)$$

Taking the general non-Markovian QME expanded with respect to electronic states (cf. Eq. (28)) and concentrating on a coupling to the reservoir DOF in the excited-state only gives after a Fourier-transformation ($\omega_{eM,gN}$ are respective transition frequencies)

$$-i\omega G_{MN}(\omega) = G_{MN}(t = 0) - i\omega_{eM,gN} G_{MN}(\omega) - \sum_K \tilde{C}_{MK}(\omega + \omega_{gN}) G_{KN}(\omega). \quad (39)$$

The frequency-dependent correlation function has been introduced according to

$$\tilde{C}_{MK}(\omega) = \int_0^\infty dt C_{ee}(t) \langle \chi_{eM} | K_e(Q) U_e(t) K_e(Q) | \chi_{eK} \rangle. \quad (40)$$

The general absorption coefficient is obtained after inverting the matrix formed by the prefactor of G_{MN} in Eq. (39) [42,43]. If one neglects the off-diagonal parts of \tilde{C}_{MK} one obtains

$$\alpha(\omega) = \frac{4\pi\omega n_{\text{mol}} |\mathbf{d}_{eg}|^2}{3\hbar c} \sum_{M,N} f(\hbar\omega_{gN}) |\langle \chi_{gN} | \chi_{eM} \rangle|^2 \text{Re} \tilde{C}_{MM}(\omega + \omega_{gN}) \times \left((\omega - \omega_{eM,gN} + \text{Im} \tilde{C}_{MM}(\omega + \omega_{gN}))^2 + (\text{Re} \tilde{C}_{MM}(\omega + \omega_{gN}))^2 \right)^{-1} \quad (41)$$

The derived expression clearly shows that the correlation function (the quantity being responsible for non-Markovian effects) if transformed into the frequency domain, strongly influences the concrete line-shape of the optical absorption spectrum. The real part of \tilde{C}_{MM} is responsible for a line broadening of the transitions whereas the imaginary part shifts the position of the transitions. But the frequency dependence of both, i.e. $\text{Re} \tilde{C}_{MM}$ and $\text{Im} \tilde{C}_{MM}$ may result in strong deviations from a simple Lorentzian line shape [43].

5 Laguerre Polynomial Expansion

To find an alternative to the expansion into a continuous set of functions as discussed in the preceding section one should search for methods using a discrete set. However, this set of functions should possess some special properties to allow for an easy handling of the time derivative and the convolution integral. In [44–46] an expansion has been used based on generalized Bessel functions $\tilde{J}_n(t) = (n+1)J_{n+1}(t)/t$ ($n = 0, 1, 2, \dots$), where $J_n(t)$ are the ordinary Bessel functions of the first kind. One can verify, that the time derivative of a single $\tilde{J}_n(t)$ and the convolution of two $\tilde{J}_n(t)$ can be represented by a linear combination of a restricted number of the generalized Bessel functions. These properties enable one to convert the original set of integro-differential equations into a set

of algebraic equations for the expansion coefficients. The generalized Bessel functions have been successfully used in [47] and [48] to investigate a two-level system interacting with a single harmonic oscillator coupled to a Markovian bath (in analogy to [35]).

A similar system has been investigated in [49] and [50], but using the orthogonal set of Laguerre polynomials (compare also [51, 52]). In [14] and [15] this method has been extended to solve the QME (13). Laguerre polynomials are defined via $L_n(t) = \exp(t) d^n / (dt)^n (t^n \exp(-t)) / n!$ ($n = 0, 1, 2, \dots$) and are orthonormal with respect to the scalar product $(f, g) = \int_0^\infty dt \exp(-t) f(t) g(t)$. Here and in the following the variable t has to be understood as a dimensionless time. It has to be chosen in such a manner that it covers the relevant time-region of the correlation function if expanded in Laguerre polynomials.

It is the key point of the whole approach that the Laguerre polynomials obey the relation

$$\frac{\partial}{\partial t} L_n(t) = - \sum_{m=0}^{n-1} L_m(t), \quad (42)$$

and the relation

$$\int_0^t d\bar{t} L_n(t - \bar{t}) L_m(\bar{t}) = L_{n+m}(t) - L_{n+m+1}(t). \quad (43)$$

Both enable one to transform the non-Markovian QME to an infinite set of algebraic equations (provided any time-dependent external field is absent). First we note the expansion of the density operator

$$\hat{\rho}(t) = \sum_{n=0}^{\infty} \hat{\rho}^{(n)} L_n(t), \quad (44)$$

as well as its back transformation

$$\hat{\rho}^{(n)} = \int_0^\infty dt e^{-t} L_n(t) \hat{\rho}(t). \quad (45)$$

In a similar manner an expansion is possible for the memory kernel \mathcal{M} and the initial correlation term \hat{I} . If one applies this expansion one obtains recursion formulas for the density operator expansion coefficients

$$\begin{aligned} \hat{\rho}^{(n)} &= \left(1 + i\mathcal{L}_{\text{mol}} + \mathcal{M}^{(0)}\right)^{-1} \times \left(\hat{\rho}(t=0) + \hat{I}^{(n)}\right) \\ &- \sum_{k=0}^{n-1} \left\{1 + \mathcal{M}^{(n-k)} - \mathcal{M}^{(n-k-1)}\right\} \hat{\rho}^{(k)}. \end{aligned} \quad (46)$$

Provided we know the expansion coefficients $\mathcal{M}^{(n)}$ of the memory kernel and of the initial correlation term, we are in the position to recursively compute the expansion coefficients of the density operator. Since we have to expand the correlation function to get the expansion coefficients of the memory kernel, any type of correlation function and thus any type of spectral density can be described within this method. Again, as in the case of the Fourier-Laplace transformation, the main disadvantage of the method is its disability to include time-dependent external fields.

But this difficulty can be circumvented if an expansion with respect to field-strength is carried out. In [15] an expansion up to the second order in the field-strength has been used to derive a source term describing a laser excitation of the system. The resulting source term will be introduced in the next section where we show that it can be treated in similarity to the initial correlation term.

6 Interplay of Non-Markovian Relaxation and Optical State Preparation

In order to demonstrate the effect of retardation and of optical state preparation and their interplay, if both proceed on the same time scale, we will consider a simple version of the model introduced in Section 2.1. Furthermore, we will concentrate on the weak-field regime where the field-influence on dissipation can be neglected. Resulting from this assumption the computation can be easily performed in applying the Laguerre polynomial method. Before discussing this in detail we shortly comment on the strong-field limit and the field-alternation of dissipation.

6.1 Field-Modulation of Dissipation

As already mentioned in Section 2.2 there is an indirect field dependence of the QME, Eq. (13), which is induced via a field dependence of the dissipative part, Eq. (15). This indirect field dependence has been discussed in Ref. [17] for the case of vibrational relaxation proceeding after ultrafast photoexcitation of a molecular system into an excited electronic state. The description of the modulation of vibrational relaxation in an electronic ground state after infrared laser pulse excitation can be found in [23, 26, 34].

Additionally, emphasis has been put in [17] on the relation of this field dependence of dissipation to continuous-wave driven open quantum systems (see, e.g. [53]). In a continuous-wave driven situation an external field may change the position and mutual distance of the molecular levels. Since the position of the related transition frequencies within the spectral density (describing the coupling to the reservoir) decides whether or not the dissipation works effectively a change of the transition frequencies may alternate the strength of dissipation. For the field-influence of sub-picosecond pulses, however, one has to change from this frequency domain description to a description in the time-domain [17].

We start our discussion in using the interaction representation of the QME introduced in Eqs. (17) and (18), where the external field influence is completely contained in the time depended operators $\mathcal{K}_u^{(I)}(t)$ and $\mathcal{K}_v^{(I)}(\bar{t})$. Let us introduce the S -operator defined by the external field

$$\begin{aligned} S(t, t_0) &= T \exp \left(- \frac{i}{\hbar} \int_{t_0}^t d\tau U_{\text{mol}}^+(\tau - t_0) H_{\text{field}}(\tau) U_{\text{mol}}(\tau - t_0) \right), \end{aligned} \quad (47)$$

where U_{mol} is the molecular time–evolution operator. Accordingly we may write $\mathcal{K}_u^{(I)}(t) = S^+(t, t_0)U_{\text{mol}}^+(t, t_0)\mathcal{K}_u U_{\text{mol}}^+(t, t_0)S^+(t, t_0)$. This expression is particularly suited to discuss the external field influence on dissipation since separate equations of motion can be derived for $S(t, t_0)$ (its matrix elements within a concrete representation) [17].

In the limit of an impulsive excitation an analytical consideration becomes possible. This limit follows if we set for the external field amplitude $\mathcal{E}(t) = \delta(t - t_F)$. The S –operator simplifies drastically $S(t, t_0) = \Theta(t_F - t) + \Theta(t - t_F)\exp(-i\hat{\phi})$. As long as the pulse is absent S equals the unity operator. After the pulse had been present an operator acts in such a manner that a phase changes appears. The respective operator reads $\hat{\phi} = 2 |A/\hbar| \cos(\omega_0 t_F + \arg(A)) \hat{\mu}^{(\text{mol})}(t_F)$, where here and in the following "mol" indicates the time–dependence given by U_{mol} . According to the type of S –operator introduced so far the following generalized form of the dissipative part $\hat{D}^{(I)}$ of the QME can be computed

$$\begin{aligned} \hat{D}_{\text{gen}}^{(I)}(t, t_0; \hat{\rho}^{(I)}) &= \Theta(t_F - t)\hat{D}^{(\text{mol})}(t, t_0; \hat{\rho}^{(\text{mol})}) \\ &+ \Theta(t - t_F)\left(\hat{d}^{(I)}(t_F, t_0; t; \hat{\rho}^{(I)}) + \hat{\Delta}^{(I)}(t, t_F; \hat{\rho}^{(I)})\right) \end{aligned} \quad (48)$$

The first contribution on the right–hand side is only valid in the time interval before the pulse enters the probe. It is identical with the form introduced in Eq. (18) but with $\mathcal{K}_u^{(I)}(t)$ and $\mathcal{K}_v^{(I)}(\bar{t})$ replaced by $\mathcal{K}_u^{(\text{mol})}(t)$ and $\mathcal{K}_v^{(\text{mol})}(\bar{t})$, respectively. This has to be expected since for $t < t_F$ the quantity $\mathcal{K}_u^{(I)}(t)$ is identical to the field–independent form $\mathcal{K}_u^{(\text{mol})}(t)$. In the time interval after the pulse action we have the contribution proportional to $\hat{d}^{(I)}$. It follows from the general expression Eq. (18) if the upper limit t of the integration is replaced by t_F but with the argument t remaining in the correlation functions $C_{uv}(t - \bar{t})$. Furthermore, $\mathcal{K}_u^{(\text{mol})}(t)$ has to be replaced by $\exp(i\hat{\phi})\mathcal{K}_u^{(\text{mol})}(t)\exp(-i\hat{\phi})$. Finally, $\hat{\Delta}^{(I)}(t, t_F; \hat{\rho}^{(I)})$ is obtained if the lower integration limit is replaced by t_F , and, besides $\mathcal{K}_u^{(\text{mol})}(t)$, also the quantity $\mathcal{K}_v^{(\text{mol})}(\bar{t})$ is replaced by $\exp(i\hat{\phi})\mathcal{K}_v^{(\text{mol})}(\bar{t})\exp(-i\hat{\phi})$.

The whole expression Eq. (48) shows on the one–hand side that the ultrafast (impulsive) action of the external field sets up a new initial correlation term given by $\hat{d}^{(I)}(t_F, t_0; t; \hat{\rho}^{(I)})$. As explained, it only depends on the running time t via the correlation functions, and thus decays with the characteristic reservoir correlation time. After the pulse had been excited the molecular system, dissipation acts in similarity to the time before the pulse arrived but with somewhat changed coupling functions to the reservoir DOF.

The finite pulse duration necessary to consider real experimental situations weakens the structure of Eq. (48). The expected initial correlation effects leading to certain oscillation of the time–dependence of the density operator are shown in Fig. 2 for the example of vibrational relaxation rates in an excited electronic state.

6.2 Reduction to a Single Electronic State

After having discussed the strong–field case we concentrate on the opposite situation where the field can be treated within a perturbation expansion. This weak–field limit allows to focus on the interplay of excited state preparation and retardation effects which appear during the relaxation of the active vibrational coordinate. As already stated earlier the initial correlation term can be neglected since the external field pulse should act at a time (set equal to zero in the following) where these correlations already disappeared. Furthermore, the minimal model introduced in Section 2.1 is used for the concrete computations (see also Fig. 1). In the weak field regime the set of equations for $\hat{\rho}_{ab}$ can be reduced to a single effective equation for the diagonal density operator $\hat{\rho}_{ee}$ which describes vibrational dynamics on the excited–state PES only. As it is well–known a closed equation for $\hat{\rho}_{ee}$ is obtained if one determines $\hat{\rho}_{eg}$ linearly with respect to \mathbf{E} and inserts the expression into the equation of motion for $\hat{\rho}_{ee}$. According to Eq. (28) one easily derives the QME for $\hat{\rho}_{eg}$. To have a sufficient simple expression we replace the respective dissipative contribution \hat{D}_{eg} by a time–local expression $\hat{I}_e\hat{\rho}_{eg} + \hat{\rho}_{eg}\hat{I}_g$ and a deviation $\Delta\hat{D}_{eg}$ from this expression. On the one hand side this procedure enables us to derive an analytical formula for the field–dependent source term in the equation of motion for $\hat{\rho}_{eg}$. And, a guideline is established to improve the result step by step. The operators \hat{I}_a realize dephasing and are given by $\hat{I}_a = \int_0^\infty d\tau C_{aa}(\tau)K_a K_a(-\tau)$. Instead of a contribution proportional to $\hat{\rho}_{eg}$, now the equation of motion for $\hat{\rho}_{ee}$ contains a source term. The complete equation reads

$$\begin{aligned} \frac{\partial}{\partial t}\hat{\rho}_{ee}(t) &= \frac{i}{\hbar}\left(H_e, \hat{\rho}_{ee}(t)\right)_- \\ &- \hat{D}_{ee}(t; \hat{\rho}_{ee}) + \hat{F}_{ee}(t, 0; \mathbf{E}) . \end{aligned} \quad (49)$$

For the source term one gets

$$\begin{aligned} &\hat{F}_{ee}(t, 0; \mathbf{E}) \\ &= \frac{1}{\hbar^2} \int_0^t d\bar{t} (\mathbf{d}_{eg}\mathbf{E}(t)) (\mathbf{d}_{ge}\mathbf{E}(\bar{t})) \tilde{U}_e(t - \bar{t}) \hat{\rho}_{\text{eq}} \tilde{U}_g^\dagger(t - \bar{t}) \\ &+ \text{h.c.}, \end{aligned} \quad (50)$$

with the (electronic ground–state) vibrational equilibrium density operator $\hat{\rho}_{\text{eq}}$. The evolution operators $\tilde{U}_e(t)$ and $\tilde{U}_g(t)$ are defined according to $\tilde{U}_a(t) = \exp(-iH_a/\hbar - \hat{I}_a)$ i.e. they are formed by non–hermitian Hamiltonian including the dephasing operators \hat{I}_a .

6.3 Energy Representation

For the numerical computation of the density matrix we have to change from the operator expression to a concrete representation which in the present case is defined via the harmonic oscillator like *eigenstates* of the vibrational Hamiltonian H_e . We neglect the electronic quantum

number and get the respective density matrix as $\rho_{MN}(t) = \langle \chi_{eM} | \hat{\rho}_{ee}(t) | \chi_{eN} \rangle$. The equation of motion follows from Eq. (49) as

$$\begin{aligned} \frac{\partial}{\partial t} \rho_{MN}(t) &= -i\omega_{MN} \rho_{MN}(t) \\ &- \sum_{K,L} \int_0^t d\tau \mathcal{M}_{MN,KL}(\tau) \rho_{KL}(t-\tau) + F_{MN}(t). \end{aligned} \quad (51)$$

Note the abbreviation $\omega_{MN} = (E_{eM} - E_{eN})/\hbar$, where the E_{eM} are the *eigenvalues* of H_e . The tetradic matrix $\mathcal{M}_{MN,KL}(\tau)$ following from the memory kernel superoperator reads in detail

$$\begin{aligned} \mathcal{M}_{MN,KL}(\tau) &= \delta_{M,K} \sum_A M_{LA,AN}(-\tau) e^{i\omega_{AM}\tau} \\ &+ \delta_{N,L} \sum_A M_{MA,AK}(\tau) e^{i\omega_{NA}\tau} \\ &- M_{LN,MK}(-\tau) e^{i\omega_{NK}\tau} - M_{LN,MK}(\tau) e^{i\omega_{LM}\tau}, \end{aligned} \quad (52)$$

with $M_{MN,KL}(\tau) = C_{ee}(\tau) \langle \chi_{eM} | K_e | \chi_{eN} \rangle \langle \chi_{eK} | K_e | \chi_{eL} \rangle$. The energy representation of the inhomogeneity is obtained as

$$\begin{aligned} F_{MN} &= \frac{|\mathbf{d}_{eg}A|^2}{\hbar^2} \sum_L \langle \chi_{eM} | \chi_{gL} \rangle \langle \chi_{gL} | \chi_{eN} \rangle f(E_{gM}) \\ &\times \mathcal{E}(t) \int_0^t d\bar{t} \mathcal{E}(\bar{t}) e^{-i(\omega_{ML} - \Delta\omega)(t-\bar{t})} + \text{c.c.} \end{aligned} \quad (53)$$

Here, $f(E_{gM})$ denotes the thermal distribution versus the electronic ground-state vibrational levels.

For the concrete computations we took the field-pulse envelope as $\mathcal{E}(t) = \sqrt{2/\pi\tau_p^2} \exp(-2(t-\tau_f)^2/\tau_p^2)$. The time τ_f where the pulse reaches its maximum has to be chosen large compared to τ_p in order to get $\mathcal{E}(t=0) \approx 0$. We set $\tau_f = 50$ fs. The field amplitude A (cf. Eq. (8)) together with the transition dipole moment is not specified explicitly. Instead, we choose $A \times \mathbf{nd}_{eg}$ in such a manner to achieve an excited state population sufficiently smaller than 1. For our computation this choice guarantees $\rho_{NN}(t \rightarrow \infty) \approx < 10^{-3}$. Beside the envelope we introduced in Eq. (53) the quantity $\Delta\omega$ giving the detuning between the energetic distance of both PES and the photon energy, i.e. $\Delta\omega = \omega_0 - (U_e^{(0)} - U_g^{(0)})/\hbar$. Eq. (51) is a closed equation of motion for the vibrational dynamics in the excited electronic state involving both, the excitation and the relaxation processes.

To compare the non-Markovian dynamics with those obtained within the standard Markov approximation (see the detailed discussion in [15]) the time-dependence of the vibrational level population $P_M(t) = \rho_{MM}(t)$ (for the first four levels on the PES corresponding to the excited electronic state φ_e) will be drawn. Fig. 3 displays the population dynamics after laser pulse excitation with pulse durations extending from 5 fs up to 30 fs. One can immediately notice that the main difference between the Markovian

and non-Markovian dynamics lies in the different behavior in a time-interval just after the excitation process. The populations achieved just after the laser pulse action are different, and for sufficiently short pulses the oscillatory behavior of the population shows rather different patterns in both cases. Different decay rates of the populations can be also observed.

As it has to be expected a change of the laser pulse length results in a change of the level population (except that of the second excited one, which is excited resonantly). Therefore, in part A of Fig. 3 the shortest pulse results in a moderate population of all shown levels and gives a pronounced deviation of the non-Markovian dynamics from the Markovian one. While the curves corresponding to the Markov approximation show regular oscillations with the period $2\pi/\omega_{vib}$ the corresponding non-Markovian curves display oscillations with a larger amplitude and a larger period approximately twice that of the Markov case. The origin of this change of the oscillation period will be discussed in the next section.

A similar behavior as in part A can be found in part B of Fig. 3. Interestingly, in this case and even for longer pulses the Markovian approximation fails to guarantee the positivity of the populations. This effect has been discussed at length in [54] and [32, 33]. There, so-called slippage of the initial condition valid for the Markovian equations of motion has been proposed to assure the positivity and to reproduce the non-Markovian dynamics within the Markovian approximation. In the present case, however, due to the deviations between the oscillatory patterns such a slippage of the level population just after the laser pulse action would not lead to the reproduction of non-Markovian results within a Markovian description. On the other hand, looking at part C and D of Fig. 3 where the pulse length has been further increased the possible reproduction of the non-Markovian populations by a Markovian theory comes into question. Now, any oscillations of the populations are absent, and it should become possible that a careful choice of the parameters in the Markovian model would allow to reproduce the non-Markovian dynamics.

Additionally to the present considerations one may find in [15] results showing the influence of the system-bath coupling strength and the length of the bath correlation time. In all cases the same typical non-Markovian effects, as discussed so far, have been found. For short laser pulses an increase of the system-bath coupling makes the non-Markovian effects to be visible for shorter bath correlation times and vice versa.

7 Analytical Description of Non-Markovian Effects

In this section we present two examples for an analytical solution of the non-Markovian QME. The possibility for such a treatment is related to a time-independent part of the correlation function, Eq. (16). The basic ideas to remove the time non-locality from the QME have been

explained in Section 2.3. In both examples we will describe the motion of a vibrational DOF which proceeds in an excited-state PES after photo-excitation.

The first example deals with the dynamics of a vibrational wavepacket showing non-Markovian relaxation. The situation will be characterized by the inequality $\tau_{\text{mem}} > 1/\omega_{\text{vib}}$. It corresponds to the case in which the internal motion of the vibrational DOF is faster than the retardation effect resulting from the environmental influence. Furthermore, we will provide $t < \approx \tau_{\text{mem}}$, what reduces the actual time to the interval from the beginning of the evolution up to times not larger than τ_{mem} . Both inequalities enable us to replace the correlation functions $C(t-\bar{t})$ and $C(-t+\bar{t})$ from Eq. (15) by the common and real value $C(0)$ (note that the restriction to a single PES allows to disregard the electronic quantum numbers). According to Section 2.3 we identify $i\hbar\sqrt{C(0)}K$ with H_{mf} of Eq. (14) leading to the single auxiliary operator $\hat{\sigma}$. Or alternatively we set $\alpha_{uv}^{(s)}(t)$ and $\beta_{uv}^{(s)}(\bar{t})$ from Eq. (19) equal to $i\hbar\sqrt{C(0)}$.

One easily verifies that an equation of motion for $\hat{\sigma}$ is given by Eq. (27) (or by one of the two Eqs. (23) and (24)). A decoupling of the equations of motion for $\hat{\rho}$ and $\hat{\sigma}$ becomes possible after introducing the new density operators $\hat{w}^{(\pm)} = \hat{\rho} \pm \hat{\sigma}$ with initial conditions $\hat{w}^{(\pm)}(0) = \hat{\rho}(0)$ (note $t_0 = 0$ and $\hat{\sigma}(0) = 0$). To be able to carry out an analytic calculation two additional assumptions are necessary. First, we assume a linear dependence of K on the vibrational coordinate Q , and second, we provide that the initial state is the result of an impulsive photo-excitation process from the electronic ground-state. Accordingly, the initial state can be taken as the displaced vibrational ground-state. The resulting initial value of the density operator reads $\hat{\rho}(t=0) = D^+(g)|\chi_0\rangle\langle\chi_0|D(g)$. Here, we introduced the well-known displacement operator D^+ of harmonic oscillator coordinates shifting the wavefunction localized at $Q=0$ to the new position $Q=-2g$ (g denotes the electron vibrational coupling constant, see e.g. [7]).

Now, the contribution $\sqrt{C(0)}Q$ resulting from non-Markovian dissipation can be incorporated into the oscillator Hamiltonian H_{mol} by defining shifted PES $U^{(\pm)}(Q) = \hbar\omega_{\text{vib}}(Q \mp Q_c)^2/4 - \hbar C(0)/\omega_{\text{vib}}$, with the origin of the PES displaced to $Q_c = 2\sqrt{C(0)}/\omega_{\text{vib}}$. The Hamiltonian $H_{\text{mol}}^{(\pm)}$ following from the replacement of the PES U by $U^{(\pm)}$ define dissipation-less equations of motion for $\hat{w}^{(\pm)}$ which solution is obtained as $\hat{w}^{(\pm)}(t) = \exp(-iH_{\text{mol}}^{(\pm)}t/\hbar)\hat{\rho}(0)\exp(iH_{\text{mol}}^{(\pm)}t/\hbar)$. Since the initial state has been chosen as a pure state, the states the density operators $\hat{w}^{(\pm)}$ describe at later times remain pure. These states result from the propagation of the displaced vibrational ground-state $D^+(g)|\chi_0\rangle$ in the displaced oscillator potential $U^{(\pm)}$. Changing to the coordinate representation the solution follows as the moving wavepacket (see, e.g. [7])

$$\begin{aligned} \psi^{(\pm)}(Q, t) &= \langle Q | \exp\left(-\frac{i}{\hbar}H_{\text{S}}^{(\pm)}t\right) D^+(g) | 0 \rangle \\ &= \chi_0(Q^{(\pm)}(t))e^{i\varphi^{(\pm)}(t)}. \end{aligned} \quad (54)$$

Here, $\chi_0(Q)$ denotes the oscillator ground-state wavefunction which reads in the present notation $(\mu_{\text{vib}}\omega_{\text{vib}}/\pi\hbar)^{1/4}\exp(-Q^2/4)$ (the phase $\varphi^{(\pm)}(t)$ can be found in [7]). The time-dependent coordinate $Q^{(\pm)}(t) = Q \mp Q_c + (2g \pm Q_c)\cos(\omega_{\text{vib}}t)$ results in a harmonic and shape invariant motion of the wavepacket.

Although the density operators $\hat{w}^{(\pm)}(t)$ describe pure states $\hat{\rho}(t)$ will describe a mixed state. There does not appear a (coherent) superposition of the two types of wavefunctions $\psi^{(\pm)}(Q, t)$, but a superposition of the related pure-state density operators. This can be demonstrated by introducing the coordinate distribution function

$$\begin{aligned} P(Q, t) &= \langle Q | \hat{\rho}(t) | Q \rangle = \frac{1}{2} \langle Q | \hat{w}^{(+)}(t) + \hat{w}^{(-)}(t) | Q \rangle \\ &= \chi_0^2(Q^{(+)}(t)) + \chi_0^2(Q^{(-)}(t)), \end{aligned} \quad (55)$$

which is obtained as the (phase insensitive) superposition of two independent coordinate distribution functions. In contrast to the case of Markovian dissipation where a single wavepacket is moving the given superposition introduces a specific structure into the coordinate distribution $P(Q, t)$ [15].

As a second example of an analytical solution of the non-Markovian QME we consider as similar system as in the foregoing example but with a different type of coupling to the reservoir DOF. It is taken in the form $\Phi = \sum_{\xi} \hbar\omega_{\xi}(g_I(\xi)Z_{\xi} + g_{II}(\xi)Z_{\xi}^2)$ where a nonlinear contribution in Z_{ξ} has been included besides the linear standard term. These two contributions result in a separation of the correlation function $C(t)$ into the part $C_I(t)$ defined by the linear part of Φ and into $C_{II}(t)$ given by the quadratic part of Φ . Furthermore, the computation of $C_{II}(t)$ leads to two contributions $C_{II}^{(1)}(t)$ and $C_{II}^{(2)}$, where the latter becomes independent on time (note that $C_{II}^{(2)}$ is different from the factorized part of $C_{II}(t)$, see also the detailed discussion in [55]). The concrete expressions are

$$\begin{aligned} C_{II}^{(1)}(t) &= \frac{1}{2} \int d\omega \omega^2 e^{-i\omega t} (1 + n(\omega/2))^2 \\ &\quad \left(J_{II}(\omega) + J_{II}(-\omega) \right), \end{aligned} \quad (56)$$

but with the new spectral density $J_{II}(\omega) = \sum_{\xi} g_{II}^2(\xi) \delta(\omega - 2\omega_{\xi})$. The frequency argument $2\omega_{\xi}$ indicates that the considered type of system-reservoir coupling results in relaxation processes where transitions within the spectrum of the active system are accompanied by the emission or absorption of two reservoir quanta. For the second, time-independent part of the correlation function one obtains

$$C_{II}^{(2)} = \int_0^{\infty} d\omega \omega^2 n(\omega/2) (1 + n(\omega/2)) J_{II}(\omega). \quad (57)$$

In the following we will concentrate on the influence of the time-independent part $C_{II}^{(2)}$ what would be justified if $C_{II}^{(2)}$ dominates on $C_{II}^{(1)}$. According to Eqs. (56) and

(57) this should be the case for higher temperatures [55]. Then, we can proceed as in the foregoing case and obtain the reduced density operator as a superposition of the $w^{(\pm)}$. Again the initial value of the density operator is understood as the result of an impulsive excitation and we construct it from the displaced vibrational ground-state wavefunction. For the present purposes it is most appropriate to consider the time-dependence of the vibrational level population

$$P_M(t) = |A_M^{(+)}(t)|^2 + |A_M^{(-)}(t)|^2, \quad (58)$$

where the transition amplitudes read $A_M^{(\pm)}(t) = \sum_N f_{\text{FC}}(M, N) \tilde{f}_{\text{FC}}(N, 0) \exp(-i\omega_{\text{vib}}Nt)$. The Frank-Condon factors $f_{\text{FC}} = \langle \chi_M | \chi_N^{(\pm)} \rangle$ and $\tilde{f}_{\text{FC}} = \langle \chi_N^{(\pm)} | \chi_{g0} \rangle$ describe the overlap between different oscillator states. The first overlap concerns a wavefunction (with quantum number M) from the excited state PES (where the actual vibrational motion proceeds) and the displaced oscillator wavefunction corresponding to the Hamiltonian $H_{\text{mol}}^{(\pm)}$. The second type of Frank-Condon factors includes the functions related $H_{\text{mol}}^{(\pm)}$ and the electronic-ground state vibrational function $|\chi_{g0}\rangle$, respectively. Obviously, $P_M(t)$ should display constructive and destructive interferences among the various contributions oscillating with multiples of ω_{vib} . But we expect additional contributions stemming from the two independent contribution $|A_M^{(\pm)}(t)|^2$ to the level population.

In Fig. 4 we compare the analytical solution, Eq. (58) with the results of the numerical calculation. For the latter the reservoir correlation time has been taken as $t_c = 50\text{fs}$ what is large enough to achieve a pronounced non-Markovian behavior. Looking at the oscillatory pattern of the analytical solution (part B of the Fig. 4) we note clear similarities with the behavior shown by the numerical solution of the non-Markovian QME (at least within the first few periods of the oscillator motion after an impulsive excitation). At the end of the 300 fs time window one observes that the oscillatory patterns of the populations obtained within the non-Markovian approach converge to those resulting from a Markov approximation (dashed line in part A of Fig. 4). This shows that the non-Markovian effect demonstrated here for the vibrational level population originates from the adaption of the system to a new initial condition (which has been set up by the photo-excitation process). Once the adaption is complete the systems dynamics become very similar to that obtained within the Markov approximation.

8 Conclusions

This contribution has been aimed to give an overview on the present status of describing non-Markovian behavior in open molecular systems. Different schemes have been presented to account for retardation effects in the course of numerical calculations. For the process of vibrational relaxation following ultrafast optical excitation of a poly-

atomic molecule the non-Markovian dynamics of the vibrational level population has been discussed in detail.

Although it has been demonstrated in the present paper and in those we referred to that non-Markovian behavior cannot be assumed to be of a really large influence, it may result in a notable change of relaxation processes after an optical state preparation. In particular this should become observable if pulses are used which length is below 10 fs. Since such pulses are really at the borderline of that what is possible at the moment in ultrafast optical spectroscopy concrete examples for retarded vibrational relaxation processes are not available.

Despite this particular situation, however, it is valuable at all to clarify the importance of retardation effects. Only such studies enables one to decide whether or not one has to incorporate non-Markovian terms when solving the Quantum Master Equation. But having clarified this it would be of great importance to gain further insight how to extend the validity of the non-Markovian Quantum Master Equation in going beyond the second Born-approximation.

We gratefully acknowledge financial support by the *Deutsche Forschungsgemeinschaft* through Sfb 450.

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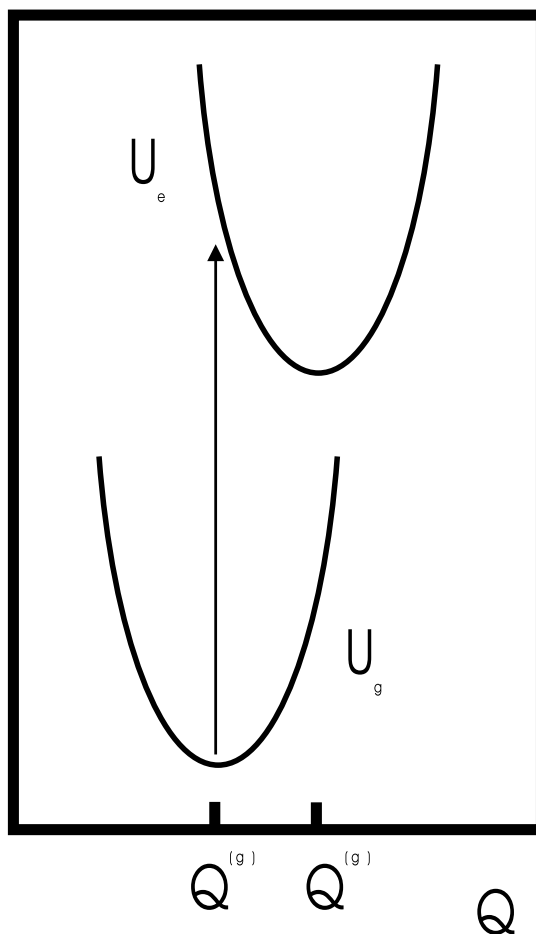


Fig. 1. Scheme of the minimal model of two PES connected by an optical transition.

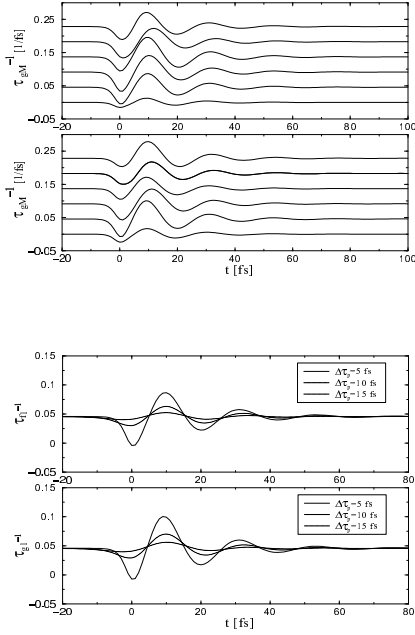


Fig. 2. Laser pulse modulation of vibrational energy dissipation. (a) Field-dependent relaxation rates (inverse life times) τ_{aM}^{-1} (in units of fs^{-1}) for the molecular parameters as in [16] and for $t_c=100$ fs, $\alpha = \mathbf{nd}_{eg}A\langle\chi_{e2}|\chi_{g0}\rangle=1.5$, and pulse duration $\tau_p=5$ fs. The vibrational quantum numbers $M = 0-5$ are assigned from bottom to top. (b) Field-dependent relaxation rate for the excited vibrational state $M = 1$ in dependence on the laser pulse length τ_p (other parameters as in (a)).

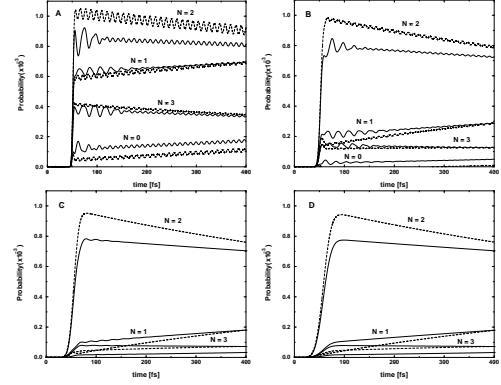


Fig. 3. Population of the first four vibrational levels of an excited electronic state in dependence on the pulse-length τ_p . Full line: solution of the non-Markovian QME; dashed-line: Markov approximation. Part A: $\tau_p = 5$ fs, part B: $\tau_p = 10$ fs, part C: $\tau_p = 20$ fs, and part D: $\tau_p = 30$ fs. Parameters of the system are: $U_e^{(0)} - U_g^{(0)} = 2$ eV, $Q_e - Q_g = \sqrt{10}$, $\hbar\omega_{vib} = 190$ meV, $d_{eg} = 1D$, $t_c = 30$ fs and $J(\omega_{vib}) = 1.9 \times 10^{-4}/fs$. The field strength has been chosen to achieve a small population of the excited electronic level, here $\approx 10^{-3}$.

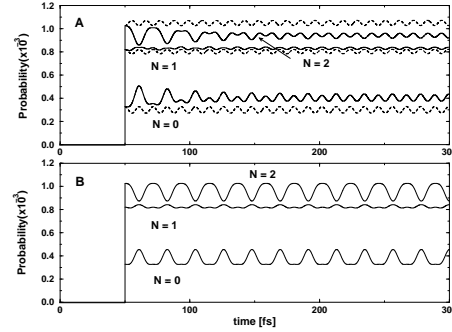


Fig. 4. Population dynamics of the vibrational ground state and the first two excited states of an excited electronic level after an impulsive excitation. Part A: case of a correlation time $t_c = 50$ fs considered for the non-Markovian description (full line) and for the Markov approximation (dashed line), part B: analytical results from Eq. 58 corresponding to the case of an infinitely long correlation time t_c . (Other parameters like those in Fig. 3).