

# Quantum master equation, Lindblad-type of dissipation and temperature dependent Monte Carlo wave-function propagation

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**Abstract.** So-called quantum-trajectory techniques have been introduced to reveal single-quantum system dynamics contained in the average ensemble description. Main application could be addressed to quantum optics of single atoms where one usually starts with the Lindblad-type of density matrix equations. Here, emphasis is put on the dissipative dynamics of *molecular* systems. The derivation of a *temperature-dependent* quantum-trajectory technique is presented starting from the widely used quantum master equation (QME) for the reduced density operator. Different applications of the resulting Monte Carlo wave-function (MCWF) method being valid for molecular systems are given.

**PACS.** 05.30.Ch Quantum ensemble theory – 82.20.Fd Stochastic and trajectory models, other theories and models

## 1 Introduction

In the late eighties experimental data became accessible on the interaction of single atoms with the radiation field. These measurements highlighted the importance of *quantum jumps*, *i.e.* electronic transitions which proceed instantaneously on the time-scale of the particular experiment. Such transitions are originated by the coupling of the atomic electronic levels to the reservoir of the radiation-field modes. The quantum-trajectory methods have been introduced as the theoretical framework to describe such a behavior of a single open quantum system [1–5] (for a recent review see also [6]).

The general picture for the related reduced-system dynamics is the assumption that the coupling to the environment leads to interruptions of the coherent motion. The latter is described by a Schrödinger-like wave equation whereas the quantum jumps representing instantaneous deviations from the coherent motion have to be introduced by additional assumptions. The concept of quantum jumps has been elaborated in [1, 2, 4, 5] and is known as the Monte Carlo wavefunction (MCWF) method. The idea of the quantum state diffusion model differing in some respects from the MCWF method has been first proposed in [3]. A common approach based on a probability distributions on a projective Hilbert space is given in [7–9]. But independently of the specific features of the single-quantum system dynamics and its description the ensemble average should result in well-established equations of motion for the related *reduced* density operator  $\hat{\rho}(t)$ .

One can also take the point of view that the MCWF-method represents an alternative and sometimes more efficient technique to determine  $\hat{\rho}(t)$  as proceeding with a direct integration of the QME. Since the numerical effort necessary for the time-propagation of  $\hat{\rho}(t)$  is proportional to  $N^2$ , where  $N$  denotes the dimension of the respective state space, the usage of quantum-trajectory techniques seems advisable for problems defined in a large state-space or characterized by a larger number of degrees of freedom. Because in quantum-trajectory techniques the reduced system density operator is constructed by averaging over various effective wave-functions  $|\Psi(t)\rangle$  the numerical effort for the propagation in time of one effective wave-function is proportional to  $N$  only. (Clearly, the resulting numerical efficiency depends essentially on the number of wavefunctions one needs to achieve good statistics.)

All quantum-trajectory techniques make use of the Lindblad-form of dissipation [10], which has been originally introduced to guarantee the positivity of the density matrix (for a first attempt to find a generalization see [11]). The dissipative part of the density operator equation can be abbreviated by the Lindblad-type of superoperator  $\mathcal{D}_L$  and is usually written in the following form

$$-\mathcal{D}_L \hat{\rho}(t) = - \sum_A \left\{ \frac{1}{2} \left( L_A L_A^\dagger, \hat{\rho} \right)_+ - L_A^\dagger \hat{\rho} L_A \right\}. \quad (1)$$

It has to be specified separately in which manner the *Lindblad*-operators  $L_A^\dagger$  and  $L_A$  act and what the meaning of the labels  $A$  is. Based on this type of dissipative superoperator one determines a bundle of  $N$  different time-dependent wave-functions (state vectors)  $|\Psi_\eta(t)\rangle$  which are

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generated in a consistent manner with certain rules. Then, the statistical operator reduced to a selected number of atomic or molecular degrees of freedom is constructed according to

$$\hat{\rho}(t) = \lim_{N \rightarrow \infty} \sum_{\eta=1}^N \frac{1}{N} |\Psi_{\eta}(t)\rangle \langle \Psi_{\eta}(t)|. \quad (2)$$

This assumes that the reduced statistical operator  $\hat{\rho}$  describes a mixed state built up by pure-state contributions  $|\Psi_{\eta}\rangle$ . However,  $\hat{\rho}$  is a result of a reduction-procedure onto the small number of degrees of freedom of the considered quantum system. This is achieved *via* a trace with respect to the environmental states, *i.e.* we set  $\hat{\rho}(t) = \text{tr}_{\text{R}}\{\hat{W}(t)\}$ . Usually, the statistical operator of the common large system (small active system plus environment) is understood as describing a mixed state according to  $\hat{W}(t) = \sum_n w_n |\Psi_n(t)\rangle \langle \Psi_n(t)|$ . Hence, it is a particular hypothesis to provide the structure given in equation (2) for the reduced statistical operator.

Accepting this hypothesis one works within the MCWF-method, on which will we concentrate in the following, time-step  $\delta t$  by time-step  $\delta t$  (see [2]). If one starts with  $|\Psi(t)\rangle$  at time  $t$  one determines the change of the state vector linear in  $\delta t$ . For this reason the anti-Hermitian contribution  $\Delta H = -i\hbar \sum_A L_A L_A^+ / 2$  is added to the Hamiltonian  $H_S$ . We get a state vector at time  $t + \delta t$  which is not normalized

$$|\tilde{\Psi}(t + \delta t)\rangle = \left(1 - \frac{i}{\hbar} (H_S + \Delta H) \delta t\right) |\Psi(t)\rangle. \quad (3)$$

The reduction  $\delta \mathcal{N}$  of the proper normalization (linear in  $\delta t$ ) reads

$$\begin{aligned} \delta \mathcal{N} &= \frac{2i}{\hbar} \langle \Psi(t) | \Delta H | \Psi(t) \rangle \delta t \\ &\equiv \sum_A \delta \mathcal{N}_A = \sum_A \langle \Psi(t) | L_A L_A^+ | \Psi(t) \rangle \delta t. \end{aligned} \quad (4)$$

Choosing a random number  $\varepsilon$  between zero and one we introduce a so-called quantum jump if  $\varepsilon < \delta \mathcal{N}$ . (Since  $\delta \mathcal{N}$  is a small number the quantum jump is a relatively rare event.) Otherwise the state vector obtained according to equation (3) is normalized only, and we set at time  $t + \delta t$

$$|\Psi(t + \delta t)\rangle = \frac{1}{\sqrt{1 - \delta \mathcal{N}}} |\tilde{\Psi}(t + \delta t)\rangle. \quad (5)$$

But if a quantum jump has to be carried out we write

$$|\Psi(t + \delta t)\rangle = \frac{1}{\sqrt{\delta \mathcal{N}_A / \delta t}} L_A^+ |\Psi(t)\rangle. \quad (6)$$

Which operator  $L_A^+$  has to be used is decided in proportion to the probability distribution  $\delta \mathcal{N}_A / \delta \mathcal{N}$ . According to the randomness of this procedure one may generate different state vectors  $|\Psi_{\eta}(t)\rangle$ . Then, the density matrix can be constructed according to equation (2).

Meanwhile different generalizations of the original stochastic wavefunction methods have been undertaken,

aimed to propagate nonlinear density matrix equations [12], to include non-Markovian effects [11,13–15], and to simulate so-called pure dephasing processes [16]. Although these approaches seem to be very appealing it has already been underlined in the original paper [2] that it is not yet clear whether or not the single wave function  $|\Psi_{\eta}(t)\rangle$  describes the stochastic dynamics of a single quantum system. One reason for this uncertainty would be the fact that the Lindblad-type of dissipation in its original version has been introduced in using a *general* reasoning (semigroup approach) instead of a microscopic model for the interaction with a certain environment. Consequently, any temperature dependence of the Lindblad-operators  $L_A^+$  is absent. Indeed, the derivations below are aimed to demonstrate that this should be not necessarily the case. Consequently, the given approach specifies earlier treatments of atoms interacting with the quantized radiation field [17,18].

In contrast, the standard equation of motion for  $\hat{\rho}(t)$  (the QME) is based on a microscopic model for the coupling of the considered quantum system to a reservoir and describes dissipation *via* thermal equilibrium reservoir correlation functions (see for example [19–21]). This approach is a standard tool in theoretical chemical physics and theoretical chemistry [22], but experienced a renaissance in the last decade in connection with the description of subpicosecond phenomena in molecules (so-called femtochemistry, see [23]). It exists a less amount of work concerning the application of stochastic wavefunction methods to molecular systems [24–26]. And, apart from the observation of single-atom dynamics in a cavity meanwhile one is also able to spectroscopically characterize single molecules (see *e.g.* [27]).

It is the aim of the present paper to promote the use of the MCWF-method to study molecular systems in the condensed phase. A prerequisite to do this is to have a microscopically founded dissipative superoperator at hand. It should include the temperature of the reservoir and should be of the Lindblad-type, equation (1). Here, we will follow the idea of [28] to derive a type of dissipative superoperator which is indeed of the Lindblad-type and originates from a microscopic coupling model, too. A derivation based on probability distributions on a projective Hilbert space has been given recently [7–9]. In contrast, it is the particular intention of the present contribution to bridge the gap between standard QME approaches to molecular systems, on the one side, and temperature dependent Lindblad-types of dissipation and MCWF propagation techniques for molecular degrees of freedoms, on the other side.

To do this we start in Section 2 with the well established QME [19–22] and carry out a certain averaging procedure. From this it becomes possible to deduce microscopically founded and temperature dependent Lindblad-operators in Section 3. This enables us to extend the MCWF-method to finite temperatures for any type of system (beyond the harmonic oscillator which has been treated in [2,24,25]). The application of the state representation is compared with the use of the coordinate

representation. Different examples, among them electron and exciton transfer in molecular systems, are considered in Section 4.

## 2 The quantum master equation

Considering an open quantum system one is usually faced with the problem to describe a comparable small set of active degrees of freedom (the relevant system  $S$  with Hamiltonian  $H_S$ ) which interacts with a macroscopic environment (the reservoir  $R$  with Hamiltonian  $H_R$ ). If the measurements of interest only concern observables exclusively defined in the state space of the active system  $S$  one can reduce the whole description to the determination of the reduced statistical operator  $\hat{\rho}(t)$ . The Nakajima-Zwanzig equation includes a retarded interaction between the active system and reservoir (time convolution between the memory kernel and  $\hat{\rho}$ ) and establishes an exact framework to determine  $\hat{\rho}(t)$  (see *e.g.* [20–22], the convolution-less alternative is shortly mentioned in Appendix B).

For most applications it suffices to take the coupling between the active system and the reservoir as

$$H_{S-R} = \sum_u K_u \Phi_u. \quad (7)$$

The system part  $K_u$  acts in the state-space of system degrees of freedom (DOF) whereas the reservoir part  $\Phi_u$  is defined in the state-space of reservoir DOF. Every term  $K_u \Phi_u$  of the system-reservoir coupling is not necessarily a Hermitian operator, but the complete coupling Hamiltonian  $H_{S-R}$  is Hermitian.

In cases where the system-reservoir coupling is not too strong one can reduce the exact equation of motion for  $\hat{\rho}$  to an equation resulting from a second order perturbation theory (second Born-approximation). The result is the widely used QME. It reads in the interaction representation

$$\begin{aligned} \frac{\partial}{\partial t} \hat{\rho}^{(I)}(t) = & -\frac{1}{\hbar^2} \sum_{u,v} \int_0^\infty d\tau \\ & \times \left\{ C_{uv}(\tau) \left( K_u(t), K_v(t-\tau) \hat{\rho}^{(I)}(t) \right)_- \right. \\ & \left. - C_{vu}(-\tau) \left( K_u(t), \hat{\rho}^{(I)}(t) K_v(t-\tau) \right)_- \right\}. \quad (8) \end{aligned}$$

The appearance of  $\hat{\rho}^{(I)}(t)$  instead of  $\hat{\rho}^{(I)}(t-\tau)$  indicates the application of the Markov approximation. (The use of the upper bound of the integral at  $t = \infty$  expresses that the initial time has been put to  $-\infty$ .) Resulting from the action of time-evolution operator  $\exp -iH_S t/\hbar$  the operators  $K_v$  are time-dependent. The reservoir correlation function reads

$$C_{uv}(t) = \text{tr}_R \{ \hat{R}_{\text{eq}} \Phi_u(t) \Phi_v \}, \quad (9)$$

with time-dependent  $\Phi_u$  defined *via* the time-evolution operator given by the reservoir Hamiltonian  $H_R$ . The

quantity  $\hat{R}_{\text{eq}}$  denotes the equilibrium statistical operator of the reservoir. Note, that the structure of the correlation function as well as the form of equation (8) provides  $\text{tr}_R \{ \hat{R}_{\text{eq}} \Phi_u \} = 0$ . (Otherwise,  $C_{uv}(t)$  has to be generalized by subtracting its factorized part, and one has to include the so-called mean-field term into the QME [22].)

For the following it is useful to introduce the half-sided Fourier transformation of the correlation function

$$\hat{C}_{uv}(\omega) = \int_0^\infty d\tau e^{i\omega\tau} C_{uv}(\tau) = - \int \frac{d\bar{\omega}}{2\pi i} \frac{C_{uv}(\bar{\omega})}{\omega - \bar{\omega} + i\varepsilon} \quad (10)$$

where the completely Fourier transformed correlation function has been denoted by  $C_{uv}(\omega)$ .

To have an example for the correlation function at hand we specify the reservoir part  $\Phi_u$  of the system reservoir coupling, equation (7) somewhat. In the spirit of a power expansion with respect to the reservoir coordinates  $Z_\xi$  we set

$$\Phi_u = \sum_\xi \hbar g_\xi(u) Z_\xi. \quad (11)$$

Additionally, we consider the reservoir as a large set of independent harmonic oscillators. Then, as it is well-known, all reservoir properties can be deduced from the spectral density (coupling strength weighted density of states)

$$J_{uv}(\omega) = \sum_\xi g_\xi(u) g_\xi(v) \delta(\omega - \omega_\xi), \quad (12)$$

where the  $\omega_\xi$  give the oscillator frequencies. Using the spectral density the Fourier transformed correlation function can be expressed as ( $n(\omega)$  denotes the Bose-Einstein distribution)

$$C_{uv}(\omega) = 2\pi\hbar^2 (1 + n(\omega)) (J_{uv}(\omega) - J_{uv}(-\omega)). \quad (13)$$

To derive the Lindblad-type of dissipation from the QME we will take equation (8) formulated in the interaction representation as the starting point. For the presentation of the standard QME in the Schrödinger representation we refer to Appendix A.

### 2.1 Time-averaging procedure

It is well-known that the standard QME as given in Appendix A may violate the positivity of the density matrix. But it has been already proposed by *Davies* in [28] how to overcome this defect. Below we will follow this approach to get a type of dissipative superoperator which guarantees the positivity of  $\hat{\rho}(t)$  by just becoming a superoperator of the Lindblad-type.

The approach is based on the idea to average the density matrix equation with respect to unimportant fast oscillations. The derivation appears as the operator version of the well-known secular approximation (see *e.g.* [19, 22]). To carry out the averaging we go back to the interaction

representation, equation (8) where the time-dependence of the density matrix is only determined by the dissipative part of the original QME. Now, it is easy to average out any oscillation of the dissipative part. Therefore, the right-hand side of equation (8) is expanded with respect to the system Hamiltonian *eigenstate*  $|\alpha\rangle, |\beta\rangle$ , etc. The related *eigenvalues* are denoted as  $E_\alpha$ , and  $E_\beta$  with transition frequencies  $\omega_{\alpha\beta} = (E_\alpha - E_\beta)/\hbar$ . One obtains

$$\begin{aligned} \frac{\partial}{\partial t} \hat{\rho}^{(I)}(t) = & -\frac{1}{\hbar^2} \sum_{u,v} \sum_{\alpha,\beta,\gamma,\delta} \int_0^\infty d\tau e^{-i\omega_{\gamma\delta}\tau} \\ & \times \exp(i(\omega_{\alpha\beta} + \omega_{\gamma\delta})(t - t_0)) K_{\alpha\beta}^{(u)} K_{\gamma\delta}^{(v)} \\ & \times \left( C_{uv}(\tau) |\alpha\rangle\langle\beta| \times |\gamma\rangle\langle\delta| \hat{\rho}^{(I)}(t) \right. \\ & + C_{vu}(-\tau) \hat{\rho}^{(I)}(t) |\gamma\rangle\langle\delta| \times |\alpha\rangle\langle\beta| \\ & - C_{uv}(\tau) |\gamma\rangle\langle\delta| \hat{\rho}^{(I)}(t) |\alpha\rangle\langle\beta| \\ & \left. - C_{vu}(-\tau) |\alpha\rangle\langle\beta| \hat{\rho}^{(I)}(t) |\gamma\rangle\langle\delta| \right). \end{aligned} \quad (14)$$

The time-averaging only concerns the oscillating term with frequency combination  $\omega_{\alpha\beta} + \omega_{\gamma\delta}$ . It leads to the demand  $\omega_{\alpha\beta} + \omega_{\gamma\delta} = 0$ . Additionally, the first term on the right-hand side of equation (14) requires  $\beta = \gamma$  and the second term  $\delta = \alpha$ . To carry out the time-averaging we suppose that the only way to solve  $\omega_{\alpha\beta} + \omega_{\gamma\delta} = 0$  is to set  $\alpha = \beta$  and  $\gamma = \delta$ , or  $\alpha = \delta$  and  $\beta = \gamma$ . This solution excludes spectra incorporating degenerated levels as well as spectra with a unique distance between neighboring levels (harmonic oscillator). As a result, equation (14) is reduced to

$$\begin{aligned} \frac{\partial}{\partial t} \hat{\rho}^{(I)}(t) \approx & -\frac{1}{\hbar^2} \sum_{u,v} \sum_{\alpha,\beta} \int_0^\infty d\tau \left\{ K_{\alpha\beta}^{(u)} K_{\beta\alpha}^{(v)} e^{i\omega_{\alpha\beta}\tau} \right. \\ & \times \left( C_{uv}(\tau) |\alpha\rangle\langle\alpha| \hat{\rho}^{(I)}(t) + C_{vu}(-\tau) \hat{\rho}^{(I)}(t) |\beta\rangle\langle\beta| \right. \\ & - C_{uv}(\tau) |\beta\rangle\langle\alpha| \hat{\rho}^{(I)}(t) |\alpha\rangle\langle\beta| \\ & - C_{vu}(-\tau) |\alpha\rangle\langle\beta| \hat{\rho}^{(I)}(t) |\beta\rangle\langle\alpha| \\ & - K_{\beta\beta}^{(u)} K_{\alpha\alpha}^{(v)} C_{uv}(\tau) |\alpha\rangle\langle\alpha| \hat{\rho}^{(I)}(t) |\beta\rangle\langle\beta| \\ & \left. \left. - K_{\alpha\alpha}^{(u)} K_{\beta\beta}^{(v)} C_{vu}(-\tau) |\alpha\rangle\langle\alpha| \hat{\rho}^{(I)}(t) |\beta\rangle\langle\beta| \right) \right\}. \end{aligned} \quad (15)$$

It is easy to go back to the Schrödinger representation. Doing this one notices that the whole structure of the dissipative part of the QME remains unchanged. It is only necessary to replace  $\hat{\rho}^{(I)}(t)$  by  $\hat{\rho}(t)$ . To have a compact notation we introduce

$$\hat{\Gamma}_{\alpha\rightarrow\beta} = \frac{1}{\hbar^2} \sum_{u,v} \hat{C}_{uv}(\omega_{\alpha\beta}) K_{\alpha\beta}^{(u)} K_{\beta\alpha}^{(v)}. \quad (16)$$

This quantity can be understood as a generalized transition rate. It enables us to abbreviate the first two terms on the right-hand side of equation (15).  $\hat{C}(\omega)$  denotes the

half-sided Fourier transformation of the correlation function and has already been introduced in equation (10). If  $\hat{C}(\omega)$  is replaced by  $C(\omega)$  we will write  $\Gamma_{\alpha\rightarrow\beta}$  instead of  $\hat{\Gamma}_{\alpha\rightarrow\beta}$ . One can verify that

$$\Gamma_{\alpha\rightarrow\beta} = \hat{\Gamma}_{\alpha\rightarrow\beta} + \hat{\Gamma}_{\alpha\rightarrow\beta}^*, \quad (17)$$

demonstrating that  $\Gamma_{\alpha\rightarrow\beta}$  is a real quantity. It comprises the third and fourth term on the right-hand side of equation (15). To abbreviate the remaining two terms we introduce

$$\tilde{\Gamma}_{\alpha\beta} = \frac{1}{\hbar^2} (1 - \delta_{\alpha,\beta}) \sum_{u,v} C_{uv}(\omega = 0) K_{\beta\beta}^{(u)} K_{\alpha\alpha}^{(v)}. \quad (18)$$

Before further proceeding this last expression needs a short comment. A detailed inspection of the respective contribution to equation (15) shows that it violates probability conservation, *i.e.* it results in  $\sum_\alpha \partial \rho_{\alpha\alpha} / \partial t \neq 0$ . Therefore, the Markov-approximation and the time-averaging procedure ask for a careful discussion whenever applied to those parts of  $\mathcal{D}\hat{\rho}$  leading to equation (18). For the present applications and as it has already been done in equation (18) we neglect the diagonal contributions.

The complete dissipative part of the QME will be symbolized by the action of the time-averaged dissipative superoperator according to

$$\begin{aligned} -\overline{\mathcal{D}}\hat{\rho}(t) = & -\sum_{\alpha} \left( \sum_{\beta} \hat{\Gamma}_{\alpha\rightarrow\beta} |\alpha\rangle\langle\alpha| \hat{\rho}(t) + \hat{\rho}(t) \sum_{\beta} \hat{\Gamma}_{\alpha\rightarrow\beta}^* |\alpha\rangle\langle\alpha| \right) \\ & + \sum_{\alpha,\beta} \Gamma_{\alpha\rightarrow\beta} |\beta\rangle\langle\alpha| \hat{\rho}(t) |\alpha\rangle\langle\beta| + \sum_{\alpha,\beta} \tilde{\Gamma}_{\alpha\beta} |\alpha\rangle\langle\alpha| \hat{\rho}(t) |\beta\rangle\langle\beta|. \end{aligned} \quad (19)$$

To get a deeper insight into the derived structure we will give a short interpretation of the various terms. We start with the term proportional to  $\Gamma_{\alpha\rightarrow\beta}$ , which comprises, left and right from  $\hat{\rho}$ , transitions from the states  $|\alpha\rangle$  to the states  $|\beta\rangle$ . This becomes somewhat more concrete if we use expression (13) for the correlation function which is valid if the coupling to the reservoir is linear with respect to the reservoir coordinates. The transition rate reads

$$\begin{aligned} \Gamma_{\alpha\rightarrow\beta} = & 2\pi \sum_{u,v} K_{\alpha\beta}^{(u)} K_{\beta\alpha}^{(v)} \\ & \times \left( (1 + n(\omega_{\alpha\beta})) J_{uv}(\omega_{\alpha\beta}) + n(\omega_{\beta\alpha}) J_{uv}(\omega_{\beta\alpha}) \right). \end{aligned} \quad (20)$$

It represents the standard rate expression for energy relaxation. The transition processes proceed from level  $\alpha$  to lower-lying levels (proportional to  $1 + n(\omega_{\alpha\beta})$ ) and to higher-lying levels (proportional to  $n(\omega_{\beta\alpha})$ ). Next we concentrate on the terms proportional to  $\hat{\Gamma}_{\alpha\rightarrow\beta}$ . They form a non-Hermitian extension  $\Delta\overline{H}$  of the system Hamiltonian which can be written as

$$\Delta\overline{H} = -i\hbar \sum_{\alpha,\beta} \hat{\Gamma}_{\alpha\rightarrow\beta} |\alpha\rangle\langle\alpha|. \quad (21)$$

Taking this definition the complete dissipative part, equation (19) reads

$$-\overline{\mathcal{D}}\hat{\rho}(t) = -\frac{i}{\hbar}\left(\Delta\overline{H}\hat{\rho}(t) - \hat{\rho}(t)\Delta\overline{H}^+\right) - \Delta\overline{\mathcal{D}}\hat{\rho}(t), \quad (22)$$

where  $\Delta\overline{\mathcal{D}}\hat{\rho}$  comprises the third and the fourth term in equation (19). The latter are usually named sandwich terms since they incorporate the simultaneous action on  $\hat{\rho}$  from the left and the right. In contrast those terms proportional to  $\tilde{\Gamma}$  describe scattering processes where no energy exchange takes part (pure dephasing processes).

## 2.2 Energy representation

It is instructive to relate the result of the time-averaging procedure to the well-known secular approximation [19, 22]. For this reason we present the energy (state) representation of some formulas of the preceding section. It enables us to write the energy representation of the non-Hermitian Hamiltonian, equation (21) as

$$-\frac{i}{\hbar}\langle\alpha|\Delta\overline{H}|\beta\rangle = -\delta_{\alpha,\beta}\sum_{\gamma}\hat{\Gamma}_{\alpha\rightarrow\gamma}, \quad (23)$$

and the total dissipative part of the QME reads

$$-\langle\alpha|\overline{\mathcal{D}}\hat{\rho}(t)|\beta\rangle = -\left(\sum_{\gamma}\hat{\Gamma}_{\alpha\rightarrow\gamma} + \sum_{\gamma}\hat{\Gamma}_{\beta\rightarrow\gamma}^*\right)\rho_{\alpha\beta}(t) + \delta_{\alpha,\beta}\Gamma_{\gamma\rightarrow\alpha}\rho_{\gamma\gamma}(t) + \tilde{\Gamma}_{\alpha\beta}\rho_{\alpha\beta}(t). \quad (24)$$

Next, we give a notation of this equation which contains a complete ordering with respect to diagonal and off-diagonal density matrix elements

$$-\langle\alpha|\overline{\mathcal{D}}\hat{\rho}(t)|\beta\rangle = -\delta_{\alpha,\beta}\left(\sum_{\gamma}\Gamma_{\alpha\rightarrow\gamma}\rho_{\alpha\alpha}(t) - \sum_{\gamma}\Gamma_{\gamma\rightarrow\alpha}\rho_{\gamma\gamma}(t)\right) - (1 - \delta_{\alpha,\beta})\left(\sum_{\gamma}(\hat{\Gamma}_{\alpha\rightarrow\gamma} + \hat{\Gamma}_{\beta\rightarrow\gamma}^*) - \tilde{\Gamma}_{\alpha\beta}\right)\rho_{\alpha\beta}(t). \quad (25)$$

The diagonal part describes population redistribution according to an ordinary rate equation. The decay of the off-diagonal density matrix elements is governed by the rates  $\hat{\Gamma}$  where the real part can be interpreted as a standard dephasing-rate.

The derived state representation of the dissipative part of the QME, equation (25) coincides with the result obtained from an approach based on the Redfield-tensor and on the application of the secular approximation [29].

## 2.3 Pure dephasing contributions

Pure dephasing is characterized as the type of interaction (scattering) process between the active system and the reservoir which proceeds without energy exchange. Therefore, those transition rates entering equation (25) may

contribute to pure dephasing rates for which the diagonal parts ( $\alpha \rightarrow \alpha$ ) do not vanish. A closer inspection of the part of equation (25) describing dephasing (off-diagonal part) shows that besides  $\tilde{\Gamma}$  also the two generalized rates  $\hat{\Gamma}$  may contribute. Indeed, if the diagonal part of  $K_{\alpha\beta}^{(u)}$  exists  $\hat{\Gamma}_{\alpha\rightarrow\beta}$ , equation (16) contains a zero-frequency contribution of the correlation function. We write

$$\hat{\Gamma}_{\alpha\rightarrow\beta} = \delta_{\alpha,\beta}\hat{\Gamma}_{\alpha}^{(\text{dia})} + (1 - \delta_{\alpha,\beta})\hat{\Gamma}_{\alpha\rightarrow\beta}^{(\text{od})}. \quad (26)$$

The first part together with  $\tilde{\Gamma}$  gives the complete pure dephasing rate

$$r_{\alpha\beta}^{(\text{pd})} = (1 - \delta_{\alpha,\beta})\frac{1}{\hbar^2}\sum_{u,v}\left(\hat{C}_{uv}(\omega=0)K_{\alpha\alpha}^{(u)}K_{\alpha\alpha}^{(v)} + \hat{C}_{uv}^*(\omega=0)K_{\beta\beta}^{(u)}K_{\beta\beta}^{(v)} - C_{uv}(\omega=0)K_{\beta\beta}^{(u)}K_{\alpha\alpha}^{(v)}\right). \quad (27)$$

It depends on the frequency dependence of the correlation functions and, in particular, on the limit  $\omega \rightarrow 0$  if pure dephasing rates exist.

## 3 Lindblad-type of dissipation

After having discussed in detail the time-averaging procedure of the QME and the obtained expressions we demonstrate how to get the Lindblad-type of dissipation, equation (1). For this aim we need a common form of  $\Delta\overline{H}$ , equation (21) and the remaining part  $-\Delta\overline{\mathcal{D}}$ . This form is obtained if we replace  $\hat{\Gamma}$  by  $\text{Re}\hat{\Gamma} \equiv \Gamma/2$  and neglect the contribution proportional to  $\tilde{\Gamma}$ . Therefore, we rearrange equation (19) according to

$$-\overline{\mathcal{D}}\hat{\rho}(t) = -\mathcal{D}_L\hat{\rho}(t) - \mathcal{D}_{\text{non-L}}\hat{\rho}(t). \quad (28)$$

The first contribution can be written in the Lindblad-form as will be demonstrated below. The second non-Lindblad type reads

$$-\mathcal{D}_{\text{non-L}}\hat{\rho}(t) = -\sum_{\alpha,\beta}i\text{Im}\hat{\Gamma}_{\alpha\rightarrow\beta}|\alpha\rangle\langle\alpha|\hat{\rho}(t) + \hat{\rho}(t)\sum_{\alpha,\beta}i\text{Im}\hat{\Gamma}_{\alpha\rightarrow\beta}|\alpha\rangle\langle\alpha| + \sum_{\alpha,\beta}\tilde{\Gamma}_{\alpha\beta}|\alpha\rangle\langle\alpha|\hat{\rho}(t)|\beta\rangle\langle\beta|. \quad (29)$$

In the state representation this term exclusively determines off-diagonal density matrix elements and does not disturb probability conservation. But the absence of the Lindblad-structure avoids to apply the standard procedure of the MCWF-method as explained in the introduction. A possible treatment of these terms together with the pure-dephasing contribution has been proposed recently in [16].

For the time being we will concentrate on the Lindblad-type of dissipation which reads

$$-\mathcal{D}_L\hat{\rho}(t) = -\sum_{\alpha,\beta}\left\{\frac{1}{2}\left(\Gamma_{\alpha\rightarrow\beta}|\alpha\rangle\langle\alpha|\hat{\rho}(t)\right)_+ - \Gamma_{\alpha\rightarrow\beta}|\beta\rangle\langle\alpha|\hat{\rho}(t)|\alpha\rangle\langle\beta|\right\}. \quad (30)$$

In order to demonstrate that this expression is identical with the Lindblad-form, equation (1) we replace  $|\alpha\rangle\langle\alpha|$  by  $|\alpha\rangle\langle\beta| \times |\beta\rangle\langle\alpha|$  and introduce the *Lindblad*-operator

$$L_A^+ = \sqrt{\Gamma_{\alpha\rightarrow\beta}}|\beta\rangle\langle\alpha| \quad (31)$$

with the identification  $A = (\alpha, \beta)$ . Indeed, equation (1) is reproduced (i) starting from a microscopic model for the system-reservoir coupling, and (ii) including the temperature of the reservoir.

To clearly underline the effect of finite temperature we note equation (20). Furthermore, the assumption of a non-degenerated and heterogeneous spectrum is used and the transition rate can be split off according to

$$\Gamma_{\alpha\rightarrow\beta} = \Gamma_{\alpha\rightarrow\beta}^{(\text{down})} + \Gamma_{\alpha\rightarrow\beta}^{(\text{up})}. \quad (32)$$

The first term on the right-hand side reads

$$\Gamma_{\alpha\rightarrow\beta}^{(\text{down})} = 2\pi \sum_{u,v} K_{\alpha\beta}^{(u)} K_{\beta\alpha}^{(v)} (1 + n(\omega_{\alpha\beta})) J_{uv}(\omega_{\alpha\beta}) \quad (33)$$

and describes transitions proceeding downwards in the spectrum. Upward transitions are incorporated in

$$\Gamma_{\alpha\rightarrow\beta}^{(\text{up})} = 2\pi \sum_{u,v} K_{\alpha\beta}^{(u)} K_{\beta\alpha}^{(v)} n(\omega_{\beta\alpha}) J_{uv}(\omega_{\beta\alpha}). \quad (34)$$

This allows to split off the Lindblad-operators according to

$$L_{\alpha\rightarrow\beta}^+ = \Theta(\omega_{\alpha\beta}) \sqrt{\Gamma_{\alpha\rightarrow\beta}^{(\text{down})}} |\beta\rangle\langle\alpha| + \Theta(\omega_{\beta\alpha}) \sqrt{\Gamma_{\alpha\rightarrow\beta}^{(\text{up})}} |\beta\rangle\langle\alpha|. \quad (35)$$

It describes downwards and upwards transitions from the reference level  $\alpha$ . (The unit-step functions have only been introduced to make the difference between the two terms more obvious.)

### 3.1 The MCWF-method in the state representation

The considerations of the foregoing section are continued in presenting respective formulas necessary to carry out the MCWF-method in the state representation. We introduce the expansion coefficient of the time-dependent state vector generated within the MCWF-method

$$C_\alpha(t) = \langle\alpha|\Psi(t)\rangle. \quad (36)$$

The state representation of equation (3) follows as

$$\begin{aligned} \langle\alpha|\tilde{\Psi}(t + \delta t)\rangle &\equiv \tilde{C}_\alpha(t + \delta t) = \left(1 - \frac{i}{\hbar} E_\alpha \delta t\right) C_\alpha(t) \\ &\quad - \frac{1}{2} \sum_A \langle\alpha|L_A L_A^+|\Psi(t)\rangle \delta t. \end{aligned} \quad (37)$$

If we calculate the state representation of the Lindblad-operator term we get

$$\sum_A \langle\alpha|L_A L_A^+|\beta\rangle = \delta_{\alpha,\beta} \sum_\gamma \Gamma_{\alpha\rightarrow\gamma} \equiv \delta_{\alpha,\beta} / \tau_\alpha. \quad (38)$$

In the last part of this expression we identified the total transition rate out of the state  $|\alpha\rangle$  by the inverse life-time of this state. This enables us to write equation (37) in the following form

$$\tilde{C}_\alpha(t + \delta t) = \left(1 - \left(\frac{i}{\hbar} E_\alpha + \frac{1}{\tau_\alpha}\right) \delta t\right) C_\alpha(t). \quad (39)$$

Accordingly, the change of the norm  $\delta\mathcal{N}$  can be written as

$$\begin{aligned} \delta\mathcal{N} &= \delta t \sum_\alpha \frac{|C_\alpha(t)|^2}{\tau_\alpha} \\ &\equiv \sum_A \delta\mathcal{N}_A = \sum_{\alpha,\beta} |C_\alpha(t)|^2 \Gamma_{\alpha\rightarrow\beta} \delta t. \end{aligned} \quad (40)$$

Here, we can identify  $\delta\mathcal{N}_A$  by  $\delta\mathcal{N}_{\alpha\beta} = |C_\alpha(t)|^2 \Gamma_{\alpha\rightarrow\beta} \delta t$ .

The state representation of the quantum jumps, equation (6) from the initial state  $|\beta\rangle$  to the final state  $|\alpha\rangle$  follows as

$$C_\alpha(t + \delta t) = \sqrt{\frac{\Gamma_{\beta\rightarrow\alpha} \delta t}{\delta\mathcal{N}_{\beta\alpha}}} C_\beta(t) \equiv \frac{C_\beta(t)}{|C_\beta(t)|}. \quad (41)$$

The final state after the jump is the result of a random choice as explained in Section 1, and it is not a superposition state but the state  $|\alpha\rangle$ . This single state, however, carries the phase of the initial state.

If no quantum jump takes place we have

$$C_\alpha(t + \delta t) = \tilde{C}_\alpha(t + \delta t) / \sqrt{1 - \delta\mathcal{N}}. \quad (42)$$

The mentioned procedure generates the expansion coefficients of the state vector for every instant of time  $t \equiv t_n = t_0 + n\delta t$ . According to equation (2) the density matrix follows as

$$\rho_{\alpha\beta}(t) = \sum_{\eta=1}^N \frac{1}{N} C_\alpha^{(\eta)*}(t) C_\beta^{(\eta)}(t). \quad (43)$$

### 3.2 The MCWF-method in the coordinate representation

It is instructive to proof whether or not the coordinate representation offers some technical advantages compared to the energy representation. The coordinate representation is easily obtained from the state representation by introducing the completeness relation  $1 = \int dx |x\rangle\langle x|$  at those parts of the derivation where it would be necessary. The coordinate representation of the basis states is denoted as  $\langle x|\alpha\rangle = \phi_\alpha(x)$  whereas  $\Psi(x, t)$  has to be identified with  $\langle x|\Psi(t)\rangle$ . If quantum jumps are absent one gets

$$\begin{aligned} \tilde{\Psi}(x, t + \delta t) &= \left(1 - \frac{i}{\hbar} H_S\right) \Psi(x, t) \delta t \\ &\quad - \frac{i}{\hbar} \int dy \Delta\bar{H}(x, y) \Psi(y, t) \delta t. \end{aligned} \quad (44)$$

The integral kernel reads

$$\begin{aligned} \frac{i}{\hbar} \Delta \bar{H}(x, y) &= \frac{1}{2} \langle x | \sum_A L_A L_A^\dagger | y \rangle \\ &= \frac{1}{2} \sum_\alpha \phi_\alpha(x) \phi_\alpha^*(y) \frac{1}{\tau_\alpha}. \end{aligned} \quad (45)$$

The related changes of the norm can be obtained from

$$\delta \mathcal{N}_{\alpha\beta} = \left| \int dx \phi_\alpha^*(x) \Psi(x, t) \right|^2 \Gamma_{\alpha \rightarrow \beta} \delta t. \quad (46)$$

The quantum jump is generated according to

$$\begin{aligned} \Psi(x, t + \delta t) &= \phi_\alpha(x) \sqrt{\frac{\Gamma_{\beta \rightarrow \alpha} \delta t}{\delta \mathcal{N}_{\beta\alpha}}} \int dy \phi_\beta^*(y) \Psi(y, t) \\ &\equiv \phi_\alpha(x) \frac{\int dy \phi_\beta^*(y) \Psi(y, t)}{\left| \int dy \phi_\beta^*(y) \Psi(y, t) \right|}, \end{aligned} \quad (47)$$

where the procedure to chose the quantum number pair  $(\alpha, \beta)$  has been described in Section 1. If non quantum jump takes place we get

$$\Psi(x, t + \delta t) = \frac{\tilde{\Psi}(x, t + \delta t)}{\sqrt{1 - \delta \mathcal{N}}}. \quad (48)$$

The given formulas show that the use of the coordinate representation does not circumvent the determination of the wavefunctions  $\phi_\alpha(x)$  and the related transition frequencies  $\omega_{\alpha\beta}$  of the spectrum. But under special conditions it should be possible to approximate the integral kernel, equation (45), in using some known basis functions. In this way one may avoid the computation of the  $\phi_\alpha(x)$  and  $\omega_{\alpha\beta}$ . For example, if one introduces a mean inverse life-time  $1/\bar{\tau}$  replacing the various  $1/\tau_\alpha$  in equation (45), the integral kernel becomes local, *i.e.* equal to  $\delta(x-y)/2\bar{\tau}$ . This approximate type of describing dissipation becomes complete if the quantum jumps are carried out into known functions  $\tilde{\phi}(x)$  which approximate the correct *eigenfunctions*. An alternative treatment has been suggested in [26], where a special Lindblad-type of the dissipative term  $-\mathcal{D}\hat{\rho}$  has been derived in using the coordinate representation.

## 4 Applications

In the remaining part of the paper we discuss different examples for the application of the MCWF-method with concentration on the field of molecular and chemical physics.

### 4.1 Relaxation in multi-level system

Let us consider a molecular systems for which the *eigenstates*  $E_\alpha$  of the active part (with Hamiltonian  $H_S$ ) are

known. As a first example we mention the vibrational levels belonging to a given (adiabatic) electronic state. The respective vibrational Hamiltonian reads  $H_{\text{vib}} = T + U(q)$  with the potential energy surface  $U(q)$  characterized by the set  $q = \{q_j\}$  of vibrational coordinates. If the *eigenvalues* of  $H_{\text{vib}}$  can be determined we have to identify  $\alpha$  from  $E_\alpha$  as the set of vibrational quantum numbers. In the most simple case where the potential energy surface is defined by normal-mode oscillations  $\alpha$  separates into the set  $\{N_j\}$  of normal-mode harmonic oscillator quantum numbers [22].

Multi-level systems are also found in connection with the formation of Frenkel-excitons in dye aggregates or chromophore complexes and in connection with electron transferring system. The latter will be discussed in more detail in the following section. For the case of intramolecular excitation energy (Frenkel-exciton) transfer we give the respective active system Hamiltonian [30]. Restricting on the presence of a single excitation in the aggregate it reads

$$H_{\text{ex}} = \sum_{m,n} \left( \delta_{m,n} E_m + (1 - \delta_{m,n}) J_{mn} \right) |m\rangle \langle n|. \quad (49)$$

The  $E_m$  describe the electronic excitation energy of molecule  $m$  in the complex (usually related to the transition from the singlet ground-state to the first excited singlet state  $S_1$ ). The Coulombic coupling (without charge transfer) between different molecules  $m$  and  $n$  is denoted by  $J_{mn}$ , and  $|m\rangle$  gives the state where molecule  $m$  is excited whereas all remaining molecules are in the ground-state. A diagonalization of  $H_{\text{ex}}$  results in the (single) exciton spectrum with energies  $E_\alpha$ . This approach can be generalized to the simultaneous presence of two or more excitations in the complex resulting in two-exciton, three-exciton etc. spectra. If charge transfer between the various constituents of the complex becomes important the concept of Frenkel-excitons loses its meaning and the *eigenenergies*  $E_\alpha$  corresponds to more or less delocalized excited electronic state. This is typical for atomic clusters or nanoparticles.

Having discussed such examples for the *eigenstate*  $|\alpha\rangle$  and *eigenvalues*  $E_\alpha$  of the system Hamiltonian  $H_S$  we specify the coupling Hamiltonian  $H_{S-R}$ , equation (7) in providing that it reduces to a single term. This specification removes all indices  $u$  and  $v$  from the formulas introduced so far. We can directly overtake these general expressions, but have to specify the relaxation rates, equation (20) to

$$\begin{aligned} \Gamma_{\alpha \rightarrow \beta} &= 2\pi |K_{\alpha\beta}|^2 \\ &\times \left( (1 + n(\omega_{\alpha\beta})) J(\omega_{\alpha\beta}) + n(\omega_{\beta\alpha}) J(\omega_{\beta\alpha}) \right). \end{aligned} \quad (50)$$

For concrete computations we can use all formulas given in Section 3.1 or in Section 3.2 to carry out the MCWF propagation. The generalization to a nonlinear system-reservoir coupling is shortly discussed in Appendix C.

## 4.2 Ultrafast electron transfer reactions

Investigating so-called ultrafast electron transfer which usually proceeds on a sub-picosecond time-scale one is confronted with a concerted electronic and nuclear motion, and as a result with the occurrence of electronic and vibrational coherences. A possible treatment of such phenomena can be achieved in an approach where the active system is not only given by the electronic degrees of freedom but by some selected vibrational modes, too [31,32]. The remaining vibrational degrees of freedom are considered to form the thermal bath. If one takes the so-called diabatic representation the respective molecular Hamiltonian is given by

$$H_{\text{mol}} = \sum_{m,n} \left( \delta_{m,n} H_m(q) + (1 - \delta_{m,n}) V_{mn}(q) \right) |\varphi_m\rangle \langle \varphi_n|. \quad (51)$$

The  $|\varphi_m\rangle$  denote the diabatic electronic states and cover the donor level ( $m = D$ ) the acceptor level ( $m = A$ ) and some bridging levels ( $m = B_1, B_2, \dots$ ) in between. Expression (51) contains the vibrational Hamiltonian belonging to the various electronic states and  $V_{mn}$  is the electronic state coupling. Both quantities depend on the set  $q$  of nuclear coordinates. The vibrational wavefunctions defined as *eigenstates* of the vibrational Hamiltonian  $H_m$  are written as  $|\chi_{mM}\rangle$  where  $M$  is the vibrational quantum number set. The coupling of the (active) coordinates  $q$  to other reservoir degrees of freedom is taken in a diagonal form with respect to the electronic quantum numbers. We write

$$H_{\text{S-R}} = \sum_m K_m \Phi_m, \quad (52)$$

where the system part reads

$$K_m = k_m(q) |\varphi_m\rangle \langle \varphi_m|, \quad (53)$$

and  $\Phi_m$  is identical to the expression in equation (11), but with  $u$  replaced by  $m$ .

Of course, the molecular Hamiltonian, equation (51) can be diagonalized leading to the so-called adiabatic representation. If one proceeds in such a manner one derives a representation similar to that discussed in the foregoing section (and all can be reproduced done so far). In many cases, however, some residual nonadiabatic couplings remain, and again we would have a system which is not diagonal. Therefore, to demonstrate how one has to generalize the formulas given in the foregoing section to the case where one uses non-*eigenstates* of the system we will take the diabatic representation. This can be additionally motivated by a restriction to small transfer couplings  $V_{mn}$  (small compared to typical vibrational quanta of the active modes  $q_j$ ). In line with the assumption of small  $V_{mn}$  one can concentrate on the description of dissipation which exclusively proceeds in the diabatic states. (Whenever this approximation becomes inadequate one should leave the diabatic representation and describe the transfer process by means of the adiabatic states.)

To achieve the Lindblad-form of the diabatic description of dissipation, *i.e.* relaxation in non-*eigenstates* one has to change over from the general dissipative terms in the QME to the time-averaged version  $\overline{\mathcal{D}}\hat{\rho}$ , equation (19). To do this we have to use in the dissipative terms the time-evolution operator  $U_S^{(0)} = \exp(-iH_S^{(0)}t/\hbar)$  instead of  $U_S = \exp(-iH_S t/\hbar)$ . Here, the zeroth-order Hamiltonian reads  $H_S^{(0)} = \sum_m H_m(q)$ . As a result we get the following type of Lindblad-operators, equation (31)

$$L_A^+ = \sqrt{\Gamma_{mM \rightarrow nN}} |\varphi_m\rangle \langle \chi_{mM}| \langle \chi_{nN}| \langle \varphi_n|. \quad (54)$$

Inserting the concrete form of the system-reservoir coupling, equation (53) into equation (20) one obtains

$$\begin{aligned} \Gamma_{mM \rightarrow nN} = & \delta_{m,n} 2\pi |k_{mM,mN}|^2 \\ & \times \left( (1 + n(\omega_{mM,mN})) J_{mm}(\omega_{mM,mN}) \right. \\ & \left. + n(\omega_{mN,mM}) J_{mm}(\omega_{mN,mM}) \right). \quad (55) \end{aligned}$$

As expected the transition rates are diagonal with respect to the diabatic electronic quantum numbers.

Next we present an expansion of the reduced density operator in terms of electronic states

$$\hat{\rho}_{mn}(t) = \langle \varphi_m | \hat{\rho}(t) | \varphi_n \rangle. \quad (56)$$

This quantity is an operator in the state-space of the nuclear DOF. The QME follows as

$$\begin{aligned} \frac{\partial}{\partial t} \hat{\rho}_{mn}(t) = & -\frac{i}{\hbar} (H_m \hat{\rho}_{mn}(t) - \hat{\rho}_{mn}(t) H_n) \\ & - \langle \varphi_m | \mathcal{D}_L \hat{\rho}(t) | \varphi_n \rangle, \quad (57) \end{aligned}$$

where the electronic matrix element of the dissipative part can be rewritten by introducing the newly defined Lindblad operators

$$l_{mM \rightarrow nN}^+ = \sqrt{\Gamma_{mM \rightarrow nN}} |\chi_{nN}\rangle \langle \chi_{mM}|. \quad (58)$$

These operators exclusively act in the state space of the vibrational degrees of freedom and describe excitations and deexcitations in the diabatic vibrational spectrum. The electronic matrix element of the dissipative part reads

$$\begin{aligned} - \langle \varphi_m | \mathcal{D}_L \hat{\rho}(t) | \varphi_n \rangle = & -\frac{1}{2} \sum_{M,N} l_{mM \rightarrow nN} l_{mM \rightarrow mN}^+ \hat{\rho}_{mn}(t) \\ & - \hat{\rho}_{mn}(t) \frac{1}{2} \sum_{M,N} l_{nM \rightarrow nN} l_{nM \rightarrow mN}^+ \\ & + \delta_{m,n} \sum_{M,N} l_{mM \rightarrow mN}^+ \hat{\rho}_{mm}(t) l_{mM \rightarrow mN}. \quad (59) \end{aligned}$$

An initial condition for the reduced density operator would be a thermal distribution *versus* the vibrational levels of the donor state  $\varphi_D$ , *i.e.* we set

$$\hat{\rho}_{mn}(t_0) = \delta_{m,n} \delta_{m,D} \frac{\exp(-(H_D/k_B T))}{\text{tr}_{\text{vib}} \{ \exp(-(H_D/k_B T)) \}}. \quad (60)$$

$H_D$  is the donor vibrational Hamiltonian and  $\text{tr}_{\text{vib}}\{\dots\}$  denotes the trace with respect to the vibrational DOF. (In the case of photoinduced ultrafast ET, of course, one has to consider the optical preparation process of the donor state in detail.)

If we concentrate on the part of equation (59) being diagonal with respect to the diabatic electronic quantum numbers it is again of the Lindblad type. In contrast, the sandwich terms disappear for the off-diagonal part. Such a result is caused by the structure of the system reservoir coupling, equation (53) diagonal with respect to the diabatic electronic quantum numbers. Consequently, the dissipative superoperator acts exclusively from the left or from the right on  $\hat{\rho}_{mn}$ . The absence of the sandwich-type term means that quantum jumps do not appear if the MCWF-method is applied. This conclusion becomes immediately obvious if one notices that quantum jumps create the sandwich-type terms if one changes from the MCWF-method to equation of motion for the density operator equation (2) [2].

A considerable simplification is achieved if one follows [25], where spectral densities  $J_{mm}$  have been used independent on the diabatic electronic quantum numbers. Furthermore, a harmonic oscillator model has been adopted for the description of a single vibrational coordinates  $q$ . Changing to a dimensionless vibrational coordinate  $Q = C + C^+$ , built up by oscillator annihilation and creation operators  $C$ , and  $C^+$ , respectively, we can write the potential energy surfaces as  $U_m(Q) = U_m^{(0)} + \hbar\omega_{\text{vib}}(Q - Q_m^{(0)})^2/4$ . The quantity  $Q_m^{(0)}$  denotes the actual displacement of the coordinate upon the presence of the transferred electron at diabatic level  $m$ . Furthermore, we set  $k_m(Q) = Q - Q_m^{(0)}$ . This enables us to introduce the following simplification

$$\frac{1}{2} \sum_{M,N} l_{mM \rightarrow mN} l_{mM \rightarrow mN}^+ = \pi n(\omega_{\text{vib}}) J(\omega_{\text{vib}}) C C^+ + \pi(1 + n(\omega_{\text{vib}})) J(\omega_{\text{vib}}) C^+ C. \quad (61)$$

However, for the sandwich-type term we obtain the somewhat larger expression

$$\begin{aligned} \sum_{M,N} l_{mM \rightarrow mN}^+ \hat{\rho}_{mm}(t) l_{mM \rightarrow mN} &= 2\pi \sum_N \left( n(\omega_{\text{vib}}) J(\omega_{\text{vib}}) \right. \\ &\times |\chi_{mN}\rangle \langle \chi_{mN}| C^+ \hat{\rho}_{mm}(t) C |\chi_{mN}\rangle \langle \chi_{mN}| \\ &\quad \left. + (1 + n(\omega_{\text{vib}})) J(\omega_{\text{vib}}) \right) \\ &\times |\chi_{mN}\rangle \langle \chi_{mN}| C \hat{\rho}_{mm}(t) C^+ |\chi_{mN}\rangle \langle \chi_{mN}|. \quad (62) \end{aligned}$$

The derived formulas have been used in [25] to describe ET in a donor-acceptor complex with three accepting modes.

### 4.3 Linear optical absorption

Linear absorption is treated here to demonstrate how the MCWF-method is modified if exclusively off-diagonal electronic contributions are considered. As it is well-known

the linear absorption coefficient  $\alpha(\omega)$  is determined by the (half-sided) Fourier-transformed dipole-dipole correlation function  $C_{d-d}^{(-)}(t)$ . Neglecting inhomogeneous broadening, introducing an orientational averaging and denoting the volume density of molecular systems by  $n_{\text{mol}}$  one obtains (see *e.g.* [22])

$$\alpha(\omega) = \frac{4\pi\omega n_{\text{mol}}}{3\hbar c} \text{Re} \int_0^\infty dt e^{i\omega t} C_{d-d}^{(-)}(t). \quad (63)$$

If a molecular system embedded in a thermal environment is considered and optical transitions (in the chosen frequency range) exclusively proceed in the molecular system the dipole-dipole correlation function can be transformed into a reduced representation. In this reduced representation all environmental degrees of freedom have been removed and the time-evolution is described by the dissipative dynamics of the reduced (active) system  $S$ . We get the expression

$$C_{d-d}^{(-)}(t) = \text{tr}_S \{ \hat{\mu} \mathcal{U}(t) (\hat{\mu}, \hat{\rho}_{\text{eq}})_- \}. \quad (64)$$

Here, the time-evolution superoperator  $\mathcal{U}(t)$  is of such a type that it generates the correct solution of the QME. The trace concerns the state-space of the active system only, and the dipole operator has been denoted as  $\hat{\mu}$ . Together with the equilibrium reduced density operator  $\hat{\rho}_{\text{eq}}$  it defines the initial value of the dissipative time-evolution. The given formula is useful whenever optical absorption can be described *via* a direct propagation of a small set of active degrees of freedom. Within this approach one circumvents the determination of the active system *eigenstates* what is advisable if, for example, the motion in a non-bonding potential energy surface is considered (see *e.g.* [33, 34]).

We comment how the MCWF method works in this case. To do this we describe the molecular system by a two-state model with the electronic ground-state  $\varphi_g$  and the excited state  $\varphi_e$ . The respective Hamiltonian is given by

$$H_{\text{mol}} = \sum_{a=g,e} H_a(q) |\varphi_a\rangle \langle \varphi_a|. \quad (65)$$

The  $H_a$  denote the related vibrational Hamiltonian depending on the set  $q = \{q_j\}$  of vibrational coordinates. Furthermore, any diagonal element of the dipole operator is neglected, and we have

$$\hat{\mu} = \mathbf{d}_{\text{eg}} |\varphi_e\rangle \langle \varphi_g| + \text{h.c.} \quad (66)$$

In the sense of a Condon-approximation the vectorial transition dipole moment  $\mathbf{d}_{\text{eg}}$  does not depend on the vibrational coordinates. According to these specifications the dipole-dipole correlation function, equation (64) can be simplified in carrying out the electronic part of the trace. It remains a trace with respect to the vibrational state-space

$$C_{d-d}^{(-)}(t) = \mathbf{d}_{\text{ge}} \text{tr}_{\text{vib}} \{ \langle \varphi_e | \hat{\sigma}(t) | \varphi_g \rangle \} + \mathbf{d}_{\text{eg}} \text{tr}_{\text{vib}} \{ \langle \varphi_g | \hat{\sigma}(t) | \varphi_e \rangle \}, \quad (67)$$

with

$$\hat{\sigma}(t) = \mathcal{U}(t)(\hat{\mu}, \hat{\rho}_{\text{eq}})_-. \quad (68)$$

Obviously, one only has to propagate off-diagonal reduced density operators. They have to be understood as generalizations of  $\hat{\rho}_{\text{eg}}$  and  $\hat{\rho}_{\text{ge}}$  (with the initial condition  $\hat{\sigma}(0) = (\hat{\mu}, \hat{\rho}_{\text{eq}})_-$ ). To carry out the propagation we will use the same coupling of the active coordinates  $q_j$  to the reservoir degrees of freedom as in the foregoing Section 4.2. But here we have to understand equation (53) as a relation which concerns the two adiabatic levels  $\varphi_a$  instead of diabatic levels as in the original relation.

According to equation (59) which is a direct consequence of the state-diagonal coupling *ansatz*, equation (53) we obtain the dissipative part of the QME governing the dynamics of  $\hat{\rho}_{\text{eg}}$  as

$$-\langle \varphi_e | \mathcal{D}_L \hat{\rho} | \varphi_g \rangle = -\frac{1}{2}(\hat{\gamma}_e \hat{\rho}_{\text{eg}} + \hat{\rho}_{\text{eg}} \hat{\gamma}_e). \quad (69)$$

The newly introduced  $\gamma$ -operators read

$$\hat{\gamma}_a = \sum_{M,N} \Gamma_{aM \rightarrow aN} |\chi_{aM}\rangle \langle \chi_{aN}|, \quad (70)$$

and the transition rates are defined similar to those introduced in equation (55), but related here to the adiabatic electronic states. The  $M, N, \dots$  label the set of vibrational quantum numbers and  $\chi_{aM}$  denotes the vibrational wavefunction of adiabatic electronic state  $a$ .

As already claimed in the foregoing section the Lindblad-type of dissipation valid for the off-diagonal density operator is free of the sandwich term and any quantum jump will be absent if changed to the MCWF method. As a consequence of the absence of quantum jumps the norm of the propagated wavefunction decreases. This conclusion can be directly related to the fact that the off-diagonal density operator  $\hat{\rho}_{ab}$  vanishes for  $t \rightarrow \infty$ . (In contrast, we have  $\text{tr}_{\text{vib}}\{\hat{\rho}_{\text{gg}} + \hat{\rho}_{\text{ee}}\} = 1$ .)

The mentioned property offers an easy way to compute the off-diagonal density operators. We note that the initial value  $\hat{\rho}_{\text{eq}} = R_{\text{eq}}^{(\text{g})} |\varphi_g\rangle \langle \varphi_g|$  incorporates the thermal equilibrium statistical operator  $R_{\text{eq}}^{(\text{g})}$  with respect to the vibrational states of the electronic ground-state (in similarity to Eq. (60)). Taking the off-diagonal matrix elements of equation (68) one obtains

$$\begin{aligned} \langle \varphi_e | \hat{\sigma}(t) | \varphi_g \rangle &= \mathbf{d}_{\text{eg}} \exp \left\{ \left( -\frac{i}{\hbar} H_e - \hat{\gamma}_e/2 \right) t \right\} R_{\text{eq}}^{(\text{g})} \\ &\times \exp \left\{ \left( \frac{i}{\hbar} H_g - \hat{\gamma}_g/2 \right) t \right\}. \end{aligned} \quad (71)$$

The equilibrium statistical operator (of a mixed state)  $R_{\text{eq}}^{(\text{g})}$  contains the pure-state contributions  $|\chi_{gN}\rangle \langle \chi_{gN}|$  projecting on a particular vibrational state of the electronic ground-state. These states are propagated from the left with an effective Hamiltonian  $H_e - i\hbar\hat{\gamma}_e/2$  and from the right with  $H_g + i\hbar\hat{\gamma}_g/2$ . If one carries out the trace with

respect to the vibrational degrees of freedom *via* the states  $\chi_{eN}$  of the excited electronic states one obtains the correlation function, equation (67) as

$$\begin{aligned} C_{\text{d-d}}^{(-)}(t) &= |\mathbf{d}_{\text{ge}}|^2 \\ &\times \sum_{M,N} \langle \chi_{eM} | \exp \left\{ \left( -\frac{i}{\hbar} E_{eM} - \frac{1}{2\tau_{eM}} \right) t \right\} | \chi_{gN} \rangle \\ &\times \langle \chi_{gN} | f(E_{gN}) \exp \left\{ \left( \frac{i}{\hbar} E_{gN} - \frac{1}{2\tau_{gN}} \right) t \right\} | \chi_{eM} \rangle. \end{aligned} \quad (72)$$

The part proportional  $\langle \varphi_g | \hat{\sigma}(t) | \varphi_e \rangle$  could be neglected since it leads to non-resonant contributions in the absorption coefficient. Inverse vibrational state life-times have been introduced in similarity to equation (38) as  $1/\tau_{aM} = \sum_N \Gamma_{aM \rightarrow aN}$ , and we abbreviated  $\langle \chi_{gN} | R_{\text{eq}}^{(\text{g})} | \chi_{gN} \rangle$  by the distribution function  $f(E_{gN})$ .

To be complete we present the final result for the absorption coefficient. Therefore, we have to insert the derived expression for the correlation function into equation (63)

$$\begin{aligned} \alpha(\omega) &= \frac{4\pi\omega n_{\text{mol}}}{3\hbar c} |\mathbf{d}_{\text{ge}}|^2 \sum_{M,N} |\langle \chi_{eM} | \chi_{gN} \rangle|^2 f(E_{gN}) \\ &\times \frac{1/2\tau_{eM} + 1/2\tau_{gN}}{(\omega - (E_{eM} - E_{gN})/\hbar)^2 + (1/2\tau_{eM} + 1/2\tau_{gN})^2}. \end{aligned} \quad (73)$$

A formula for the absorption coefficient has been obtained built up by various contributions with a Lorentzian-like line-shape.

#### 4.4 Some generalizations

As already pointed out for linear absorption electronic transitions (in molecular systems) induced by external light-fields are characterized by the presence of density matrix elements which are off-diagonal with respect to the electronic level index. These matrix elements oscillate with a frequency comparable to that of the light-wave and we will shortly comment how to derive for such a situation a Lindblad-type of dissipation. First we note, that the time averaging procedure of Section 2.1 to derive the Lindblad-type of dissipation would fail. There exist different possibilities to overcome this problem. Here, we mention the approach which is based on the following quasi-Fourier expansion of the density operator

$$\hat{\rho}(t) = \sum_{n=-\infty}^{\infty} e^{-in\omega_L t} \hat{\rho}^{(n)}(t). \quad (74)$$

The frequency  $\omega_L$  is that of the externally applied laser-pulse, and the expansion coefficients obey the equations of motion which have to be derived from the original QME. To do this we take again the dipole approximation with coupling Hamiltonian  $-\mathbf{E}(t)\hat{\mu}$  to the radiation field. The field is assumed to be quasi-monochromatic  $\mathbf{E}(t) = E(t)\mathbf{n} \exp(-i\omega_L t) + \text{c.c.}$ , with carrier frequency

$\omega_L$  and unit vector  $\mathbf{n}$  of polarization. We use the carrier-wave expansion of the density operator, and if we order the complete QME with respect to the carrier-waves we obtain

$$\begin{aligned} \left(\frac{\partial}{\partial t} + i\omega_L\right)\hat{\rho}^{(n)}(t) &= -\frac{i}{\hbar}\left(H_S, \hat{\rho}^{(n)}\right)_- - \mathcal{D}\hat{\rho}^{(n)} \\ &+ \frac{i}{\hbar}\left(E(t)((\mathbf{n}\mu), \hat{\rho}^{(n-1)})_- + E^*(t)((\mathbf{n}\mu), \hat{\rho}^{(n+1)})_-\right). \end{aligned} \quad (75)$$

This set of equations can be used to repeat the time-averaging procedure of Section 2.1. Here, we only note that equation (75) contains the additional approximation of a field-independent dissipative superoperator. At higher field-intensities this approximation becomes questionable [35,37].

## 5 Conclusions

To describe the dynamic behavior of a single quantum system feeling the dissipative influence of a certain environment the MCWF-method might be the method of the choice. But based on a very general type of dissipative superoperator it is questionable if this technique gives the proper single-system description. Therefore, it is useful to underline the relation of the Lindblad-type of dissipative superoperator to a concrete model.

One way to get such a relationship has been presented here by constructing a Lindblad-type of dissipation from a microscopic *system-environment* Hamiltonian. And, according to this approach the Lindblad-type of dissipation becomes temperature dependent. The method is general and can be applied to different systems studied in molecular and chemical physics.

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## Appendix A: The standard quantum master equation

Changing from equation (8) back to the Schrödinger representation gives the standard QME [19–22, 36, 38, 39]

$$\frac{\partial}{\partial t}\hat{\rho}(t) = \frac{i}{\hbar}[H_S, \hat{\rho}(t)]_- - \mathcal{D}\hat{\rho}(t) \quad (A.1)$$

with the dissipative part

$$-\mathcal{D}\hat{\rho}(t) = -\frac{i}{\hbar}\left(\Delta H\hat{\rho}(t) - \hat{\rho}(t)\Delta H^+\right) - \Delta\mathcal{D}\hat{\rho}(t). \quad (A.2)$$

There appear non-Hermitian contributions to the Hamiltonian

$$\Delta H = -\frac{i}{\hbar}\sum_u K_u A_u. \quad (A.3)$$

Additionally, equation (A.2) includes the so-called *sandwich* term

$$-\Delta\mathcal{D}\hat{\rho}(t) = \frac{1}{\hbar^2}\sum_u \left(A_u\hat{\rho}K_u + K_u\hat{\rho}A_u^+\right). \quad (A.4)$$

The newly introduced operators  $A_u$  read

$$A_u = \sum_v \int_0^\infty d\tau C_{uv}(\tau)K_v(-\tau). \quad (A.5)$$

The notation of the dissipative part, equation (A.2) of the QME is equivalent to the various forms derived in literature (see *e.g.* [19–22, 31, 32]). As it is well-known the given type of QME comprises among various advantages the main disadvantage of violating the positivity of the density matrix.

## Appendix B: The dissipative superoperator

The Lindblad-type of dissipation gives respective terms in the density operator equation which are time-local, *i.e.* free of retardation (non-Markovian) effects. If one starts from the Nakajima-Zwanzig equation an additional approximation, the Markov-approximation is necessary to come into contact to the Lindblad-type of dissipation. However, there exist an alternative approach which is exact but ends up with a time-local dissipative terms in the density operator equation. This approach is known as the description resulting in a convolution-less density operator equation [40]. In the following we shortly discuss what general types of dissipative superoperator have to be expected in the convolution-less approach.

To get the convolution-less equation of motion for the reduced statistical operator one makes use of the formal solution of the Liouville-von Neumann equation established for the total statistical operator  $\hat{W}^{(I)}(t)$  [40]. The statistical operator has been taken in the interaction representation defined with respect to the system-reservoir coupling and is obtained as  $\mathcal{U}^{(I)}(t, \bar{t})\hat{W}^{(I)}(\bar{t})$  from its earlier value at time  $\bar{t}$ . The quantity  $\mathcal{U}^{(I)}(t, \bar{t})$  gives the time-evolution superoperator (in the interaction representation). To get the desired equation for the reduced density operator one follows, in a first step, the derivation of the Nakajima-Zwanzig equations (see *e.g.* [22]). Within this derivation one usually introduces the projection superoperator  $\mathcal{P} = \hat{R} \text{tr}_R\{\dots\}$  ( $\hat{R}$  is the reservoir equilibrium statistical operator) and the orthogonal complement  $\mathcal{Q} = 1 - \mathcal{P}$ . Using both projectors one can represent the statistical operator at an earlier time as

$$\hat{W}^{(I)}(\bar{t}) = \mathcal{U}^{(I)+}(t, \bar{t})\left(\mathcal{P}\hat{W}^{(I)}(t) + \mathcal{Q}\hat{W}^{(I)}(t)\right). \quad (B.1)$$

Using this relation together with

$$\mathcal{A}(t, t_0) = \int_{t_0}^t d\tau \mathcal{U}_Q^{(I)}(t, \tau)\mathcal{Q}\mathcal{L}_{S-R}^{(I)}(\tau)\mathcal{P}\mathcal{U}^{(I)+}(t, \tau) \quad (B.2)$$

where  $\mathcal{U}_{\mathcal{Q}}^{(I)}$  is obtained from  $\mathcal{U}^{(I)}$  in replacing the interaction Liouvillian  $\mathcal{L}_{S-R}^{(I)}$  by  $\mathcal{Q}\mathcal{L}_{S-R}^{(I)}$  one can rewrite the equation for  $\mathcal{Q}\hat{W}^{(I)}(t)$  as

$$\left\{1 + i\mathcal{A}(t, t_0)\right\}\mathcal{Q}\hat{W}^{(I)}(t) = -i\mathcal{A}(t, t_0)\mathcal{P}\hat{W}^{(I)}(t). \quad (\text{B.3})$$

This equation can be solved with respect to  $\mathcal{Q}\hat{W}^{(I)}(t)$  and the solution has to be introduced into the equation for  $\mathcal{P}\hat{W}^{(I)}(t)$ . The latter is reduced to an equation of motion for the reduced density operator (in the interaction representation). Changing back to the Schrödinger representation gives the convolution-less equation of motion for the reduced statistical operator

$$\frac{\partial}{\partial t}\hat{\rho}(t) = -\frac{i}{\hbar}[H_S, \hat{\rho}(t)]_- - \mathcal{D}(t)\hat{\rho}(t) \quad (\text{B.4})$$

with the time-dependent dissipative superoperator

$$\begin{aligned} \mathcal{D}(t) &= U_S(t - t_0) \\ &\times \text{tr}_R \left\{ \mathcal{L}_{S-R}^{(I)}(t) (1 + i\mathcal{A}(t, t_0))^{-1} \mathcal{A}(t, t_0) \hat{R} \right\} U_S^\dagger(t - t_0). \end{aligned} \quad (\text{B.5})$$

The time-evolution operator  $U_S$  is defined *via* the system Hamiltonian  $H_S$ .

Although the particular form of the superoperator  $\mathcal{D}(t)$  is known its detailed action is not manageable (if any approximation should be avoided). According to this situation it is advisable to carry out some general considerations. Therefore, we write down the action of  $\mathcal{D}(t)$  as

$$-\mathcal{D}(t)\hat{\rho}(t) = A(t)\hat{\rho}(t) + \hat{\rho}(t)B(t) + \sum_j C_j(t)\hat{\rho}(t)D_j(t). \quad (\text{B.6})$$

This is the most general form possible for  $\mathcal{D}$  to act on  $\hat{\rho}$ , where the quantities  $A(t)$ ,  $B(t)$ ,  $C_j(t)$ , and  $D_j(t)$  are ordinary time-dependent operators. Let us specify these operators in more detail. The property  $\mathcal{D}\hat{\rho} = (\mathcal{D}\hat{\rho})^+$  results in

$$-\mathcal{D}(t)\hat{\rho}(t) = A(t)\hat{\rho}(t) + \hat{\rho}(t)A^\dagger(t) + \sum_j C_j(t)\hat{\rho}(t)C_j^\dagger(t), \quad (\text{B.7})$$

provided the terms in equation (B.6) are linear independent. Next, we use probability conservation which results in the requirement  $\text{tr}\{\mathcal{D}\hat{\rho}\} = 0$ . Using the cyclic invariance of an operator-arrangement to which the trace operation is applied, and the fact that  $\text{tr}\{\mathcal{D}\hat{\rho}\} = 0$  has to be fulfilled for every basis used for the trace operation we get

$$A(t) + A^\dagger(t) = -\sum_j C_j^\dagger(t)C_j(t). \quad (\text{B.8})$$

We may conclude

$$A(t) = -\frac{1}{2}\sum_j C_j^\dagger(t)C_j(t) + i\hat{h}(t), \quad (\text{B.9})$$

where  $\hat{h}$  is a Hermitian operator. As a result, the Lindblad-form, equation (1) is derived, but generalized here to a form including explicitly time-dependent operators

$$\begin{aligned} -\mathcal{D}(t)\hat{\rho}(t) &= -\frac{1}{2}\sum_j \left( C_j^\dagger(t)C_j(t)\hat{\rho}(t) \right)_+ - i\left( \hat{h}(t), \hat{\rho}(t) \right)_- \\ &\quad + \sum_j C_j(t)\hat{\rho}(t)C_j^\dagger(t). \end{aligned} \quad (\text{B.10})$$

If the  $C_j$ -operators are time-independent it is known that this type of dissipation also guarantees the positivity of the density matrix, namely  $\langle \alpha | \hat{\rho}(t) | \alpha \rangle \geq 0$

There exists an alternative to the solution, equation (B.10). This becomes obvious if one groups together pairs of terms  $C_i(t)\hat{\rho}(t)D_i(t)$  and  $C_j(t)\hat{\rho}(t)D_j(t)$  such that one gets a Hermitian expression like  $C_j(t)\hat{\rho}(t)D_j(t) + D_j^\dagger(t)\hat{\rho}(t)C_j^\dagger(t)$ . Here, we identified  $D_i(t) = C_j^\dagger(t)$  and  $C_i(t) = D_j^\dagger(t)$ . Instead of equation (B.8),  $\text{tr}\{\mathcal{D}\hat{\rho}\} = 0$  leads to

$$A(t) + A^\dagger(t) = -\sum_j \left( D_j(t)C_j(t) + C_j^\dagger(t)D_j^\dagger(t) \right) \quad (\text{B.11})$$

with the solution

$$A(t) = -\sum_j D_j(t)C_j(t). \quad (\text{B.12})$$

The dissipative part of the density matrix equation reads

$$\begin{aligned} -\mathcal{D}(t)\hat{\rho}(t) &= -\frac{1}{2}\sum_j \left( D_j(t)C_j(t)\hat{\rho}(t) + \hat{\rho}(t)C_j^\dagger(t)D_j^\dagger(t) \right. \\ &\quad \left. + D_j(t)C_j(t) + C_j^\dagger(t)D_j^\dagger(t) \right)_-. \end{aligned} \quad (\text{B.13})$$

It is just the type of dissipative superoperator one meets in the standard QME shortly presented in Appendix A.

## Appendix C: Nonlinear system-reservoir coupling

The special type of system-reservoir coupling introduced in equation (11) has been motivated by a power expansion with respect to the reservoir coordinates  $Z_\xi$ . In the following we will deal with the quadratic contribution of this expansion and set

$$\Phi_u = \sum_\xi \hbar k_\xi(u) Z_\xi^2. \quad (\text{C.1})$$

This is not the most general type, but to have not too complicated formulas we neglected any off-diagonal contributions with respect to the mode-index.

Before determining the respective form of the correlation function, equation (9) we note

$$\langle \Phi_u \rangle_R \equiv \text{tr}_R \{ \hat{R}_{\text{eq}} \Phi_u \} = \sum_\xi \hbar k_\xi(u) (1 + 2n(\omega_\xi)). \quad (\text{C.2})$$

In contrast to the expression equation (11) where  $\Phi_u$  depends linearly on the reservoir coordinates, here the thermal averaged expectation values  $\Phi_u$  do not vanish. In the QME this property leads to the appearance of the so-called mean-field term  $-i\langle\langle H_{S-R} \rangle\rangle_{\rho}$  with the bracket abbreviating the thermal average over the reservoir equilibrium-state as in equation (C.2). Additionally, the correlation function, equation (9) has to be defined with  $\Delta\Phi_u = \Phi_u - \langle\Phi_u\rangle_{\text{R}}$ . A somewhat lengthy but straightforward calculation gives for the correlation function the formula

$$C_{uv}(t) = C_{uv}^{(1)}(t) + C_{uv}^{(2)}. \quad (\text{C.3})$$

The first time-dependent contribution is obtained as

$$C_{uv}^{(1)}(t) = 2\hbar^2 \int d\omega e^{-i\omega t} (1 + n(\omega/2))^2 \times (\mathcal{J}_{uv}(\omega) + \mathcal{J}_{uv}(-\omega)) \quad (\text{C.4})$$

with a spectral density different from equation (12)

$$\mathcal{J}_{uv}(\omega) = \sum_{\xi} k_{\xi}(u)k_{\xi}(v)\delta(\omega - 2\omega_{\xi}). \quad (\text{C.5})$$

According to the argument  $2\omega_{\xi}$  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. Nevertheless, this part of the correlation function, equation (C.3) can be handled as that defined in equation (13).

For the second, time-independent part of the correlation function, equation (C.3) one obtains

$$C_{uv}^{(2)} = 4\hbar^2 \int_0^{\infty} d\omega n(\omega/2)(1 + n(\omega/2))^2 \mathcal{J}_{uv}(\omega). \quad (\text{C.6})$$

If one changes to the Fourier-transformed correlation function  $C_{uv}(\omega)$  the second part  $C_{uv}^{(2)}$  would become proportional to  $\delta(\omega)$ . This singular frequency dependence indicates that it cannot be handled within those approximations used in Section 2.1. Instead, the absence of any time-dependence shows that  $C_{uv}^{(2)}$  has to be considered within the non-Markovian version of the QME. In particular, the considerations of Section 3 leading to the Lindblad-type of dissipation cannot be applied.

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