Collective coordinates for nuclear spectral densities in energy transfer and femtosecond spectroscopy of molecular aggregates

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A theory for Frenkel exciton dynamics in molecular aggregates which incorporates coupling to vibrational motions (intramolecular, intermolecular and solvent) with multiple spectral densities of arbitrary nature and interpolates between the coherent and the incoherent limits is developed. A rigorous procedure for identifying the relevant collective nuclear coordinates necessary to represent a given set of spectral densities is obtained. Additional coordinates are required as the temperature is lowered. Exciton dynamics is calculated by following the evolution of wavepackets representing the electronic density matrix in the collective coordinates phase space. The signatures of excitonic and nuclear motions in ultrafast fluorescence spectroscopy are explored using a hierarchy of reduction schemes with varying numbers of collective coordinates. © *1996 American Institute of Physics.* [S0021-9606(96)00134-1]

I. INTRODUCTION

Femtosecond spectroscopy of molecular aggregates has become recently an area of special interest; this is connected with intensive studies of the nature of energy transfer in biological systems, such as reaction center and light harvesting photosynthetic antennae.[1] Ultrafast energy transfer between different pigment pools in LHCII[2] and in FMO trimers in the Green bacterium,[3] coherent nuclear motion, which shows up as quantum beats in pump-probe signals,[4] photon echo and transient grating signals[5] from light harvesting complexes, long-time quantum beats in the fluorescence from LH-1 complexes,[6] hole-burning studies of energy transfer in B800-B850 antenna complex[7] and LH-2 complexes[8] show a complicated interplay of intermolecular interactions, coherent nuclear motions, solvent dynamics and static disorder. Similar issues have been addressed earlier in the studies of *J*-aggregates and molecular crystals.[9–15] The theoretical modeling of molecular aggregates should incorporate the complex dynamics of nuclear motions and solvent degrees of freedom coupled to the elementary electronic excitations, the Frenkel excitons.[9,10] Discovery of the crystal structure of an integral membrane light-harvesting complex from photosynthetic bacteria[16] had opened up new levels of modeling the photosynthesis processes, unveiling possible pathways of energy transfer, and allowing a good estimate of intermolecular interactions.

In this paper we develop a theoretical framework for calculating excitonic motions in aggregates, including interactions with molecular and solvent nuclear degrees of freedom with an arbitrary distribution of timescales. Progress in ultrafast experimental techniques had made it possible to measure the spectral densities associated with nuclear motions both in neat liquids and for solvated chromophores.[17] Theoretical methods for calculating these spectral densities have been developed as well.[18] An important open problem addressed in this paper is how to incorporate these spectral densities in the modeling of excitonic motions and what are their spectroscopic signatures. We shall focus on ultrafast fluorescence measurements, but the formalism can be directly applied to other nonlinear optical techniques such as photon echoes, pump-probe, etc.

The electronic structure of a molecular aggregate can be described by the Frenkel exciton Hamiltonian[9]

$$\hat{H}_e = \sum_m \hat{H}_m + \hat{H}', \tag{1.1}$$

where $\hat{H}_m$, the Hamiltonian of the mth molecule, can be written in the form

$$\hat{H}_m = \sum_\alpha E_{m\alpha} \hat{B}^+_{m\alpha} \hat{B}_{m\alpha}. \tag{1.2}$$

Here $E_{n\alpha}$ is the energy of the αth exciton state of molecule m (with the ground state energy taken to be zero), and α runs over the relevant excited states. The exciton operators obey the following commutation relations:

$$[\hat{B}_{m\alpha}, \hat{B}^+_{n\beta}] = \delta_{mn} \left\{ \delta_{\alpha\beta} \prod_\mu (1 - \hat{B}^+_{m\mu} B_{m\mu}) - \hat{B}^+_{m\beta} \hat{B}_{m\alpha} \right\}. \tag{1.3}$$

$\hat{H}'$ represents intermolecular hopping of excitons due to dipole-dipole or exchange interactions.[9,10,19] Neglecting for the sake of simplicity, the matrix elements of the dipole operator between excited states, and the ground state permanent dipole (these can be easily incorporated in the model), $\hat{H}'$ assumes the form

$$\hat{H}' = \sum_{mn\alpha\beta} J_{m\alpha,n\beta} \hat{B}^+_{m\alpha} \hat{B}_{n\beta}. \tag{1.4}$$

This form, which conserves the number of excitons, is known as the Heitler-London approximation.

In many applications it is sufficient to consider a single excited state on each molecule, and the Frenkel exciton model then represents interacting two-level molecules.[19] In this case we may omit the Greek indices in Eqs. (1.2) and (1.4), and the commutation relations adopt the standard form

$$[\hat{B}_m,\hat{B}_n^+]=\delta_{mn}(1-2\hat{B}_m^+\hat{B}_m). \tag{1.5}$$

The interaction of electronic degrees of freedom with intramolecular, intermolecular and solvent nuclear motions can be incorporated through the dependence of the transition frequencies E and intermolecular coupling J on nuclear coordinates.[9,12] The combined electronic and nuclear Hamiltonian is

$$\hat{H}_{ep}=\hat{H}_e(\hat{Q})+\hat{H}_{ph}. \tag{1.6}$$

Here $\hat{H}_{ph}$ represents nuclear degrees of freedom $\hat{Q}$, and $\hat{H}_e$ depends on Q through the Q-dependence of the site energies $E_{m\alpha}$ (diagonal coupling) and the hopping elements $J_{m\alpha,n\beta}$ (off diagonal coupling). Assuming that $\hat{H}_{ph}$ represents a set of harmonic oscillators, and retaining only linear terms in the expansion of $\hat{H}_e$ in Q, we obtain Davydov's exciton-phonon Hamiltonian.[9] Finally, the total Hamiltonian of the aggregate interacting with a time-dependent external field $\varepsilon(\tau)$ is

$$\hat{H}_T(\tau)=\hat{H}_{ep}-\varepsilon(\tau)\hat{\mu}, \tag{1.7}$$

the polarization operator $\hat{\mu}$ in the dipole approximation is given by[19]

$$\hat{\mu}=\sum_{m\alpha}\mu_{m\alpha}(\hat{B}_{m\alpha}+\hat{B}_{m\alpha}^+), \tag{1.8}$$

and $\mu_{m\alpha}$ are the molecular transition dipoles.

Since the electronic subsystem is coupled to a large number of nuclear degrees of freedom, even the dynamics of small molecular aggregates constitutes a complicated many-body problem. The only practical way to proceed is by developing a reduced description based on following the evolution of a few relevant variables. Projection operator techniques[20] provide a formal procedure for developing a reduced description in terms of any chosen set of dynamical variables. The difficulty is then hidden in evaluating the coefficients of the resulting generalized master equation[20–22] which constitutes a closed equation for the evolution of relevant variables.

The simplest reduction scheme is based on keeping only the electronic variables, completely eliminating all nuclear degrees of freedom. This yields a closed system of equations for the excitonic reduced density matrix.[21] However, the necessary memory kernels can only be calculated in two limiting cases. The first is the coherent (weak exciton-phonon coupling) limit. The bath variables can then be eliminated by a perturbative calculation of the kernels in exciton-phonon coupling, which leads to the standard band theories of transport.[23] Under these conditions, time- and frequency-resolved fluorescence and coherent four-wave mixing can be described using a unified theory formulated in terms of exciton transport (treated, e.g., using the Boltzmann equation) and exciton-exciton scattering.[11,15] The second case is the limit of incoherent transport, where the coupling to the bath is diagonal, and intermolecular coupling is weak compared to the dephasing rate (the absorption linewidth). This limit corresponds to Holstein's small polaron theory.[24] Since the model of a single molecule linearly coupled to a harmonic bath can be solved exactly,[19,25] the kernels can be obtained by a perturbative calculation in intermolecular coupling. The master equation for molecular electronic populations represents in this case the incoherent transport theory of Forster and Dexter.[26,27] A theory which interpolates between these two limits has been developed for diagonal[28] as well as off diagonal coupling.[29] This theory is based on equations of motion for the evolution of polaron populations and is, therefore, valid in both limiting cases.

None of the above theories, which focus on the electronic variables alone holds for ultrafast transport observed, e.g., in the biological antenna complexes and the reaction center. The polaron theory[28,29] is inapplicable when the transport timescale is comparable with the timescale of polaron formation. Calculations of the intermolecular coupling parameters[30] in LH2 antennae complexes based on their geometrical structure give $J\sim 300\ \ \mathrm{cm}^{-1}$ which is comparable to the absorption and fluorescence linewidths. This makes Forster's incoherent limit inapplicable. An attempt to approach the problem from the coherent limit faces the following difficulty. Elimination of nuclear degrees of freedom can be effectively done only when the exciton-phonon coupling is much smaller than the inverse bath relaxation time. The latter cannot be faster than $\hbar/kT$ due to the Matsubara frequencies which show up in the expansion of the bath correlation function.[19,31] Physically, this implies that bath degrees of freedom with frequencies $\omega > kT/\hbar$ are frozen, and in the limit of weak exciton-phonon coupling the typical energy transfer time $\tau_{tr}\gg\hbar/kT$. At room temperatures $\hbar/kT\sim 30$ fs, which is comparable with the observed transport timescale $\tau_{tr}<100$ fs.[2,3] The above inequality is only marginally satisfied, and the weak exciton-phonon coupling approach cannot be used. The only practical way to address the problem is to adopt a less reduced description, retaining additional information about the system, such as relevant collective degrees of freedom representing nuclear motions and solvent dynamics.

When the bath is weakly coupled to the collective coordinates, a reduced description in terms of electronic and collective variables can be obtained by applying the Redfield theory.[32] Theoretical modeling of charge transfer[33] (which is formally equivalent to the problem of energy transfer) for two electronic states coupled to a single collective nuclear mode using the Redfield theory has been carried out in Ref. 34. This approach makes it possible to explore a broad range of parameters, interpolating between coherent and incoherent transport, and providing a clear physical picture of transport. It has, however, two limitations. First, since it is based on a weak coupling approximation for eliminating the bath, it has difficulties in describing femtosecond transport. Second, the procedure of calculating the components of the Redfield tensor involves diagonalizing the Hamiltonian of the electronic system coupled to the collective coordinate, which is a serious numerical problem even for the case of two electronic levels and a single nuclear coordinate. This approach is, therefore, not practical for large aggregates. Recently a nonperturbative approach has been proposed[35] which treats strong coupling of the collective coordinate to the Gaussian-

Markovian bath, and results in a hierarchy of kinetic equations. This approach has been generalized to multistate systems[36] and formally applied to low temperatures and arbitrary spectral densities,[37] where it yields complicated multidimensional hierarchies of kinetic equations.

In this paper we introduce an alternative approach based on modeling the relevant bath properties by a finite number of collective bath coordinates. The number of collective coordinates depends on the form of the bath spectral density as well as the temperature.

In Section II we start with a model which assumes that the electronic degrees of freedom are coupled to a few primary effective nuclear coordinates which in turn are linearly coupled to a harmonic bath. This model is general enough to represent an arbitrary nuclear spectral density. We then show how the bath microscopic degrees of freedom may be eliminated, resulting in a reduced description which includes the electronic as well as the collective nuclear variables.[19] These variables represent the primary oscillators, collective bath coordinates as well as Matsubara modes which enter at low temperatures. A systematic method for constructing these coordinates is obtained using a trace-conserving transformation in Liouiville space. We obtain closed equations for wavepackets which depend on the primary coordinates and momenta and a finite set of additional coordinates representing the bath. The evolution of these additional coordinates is described by the Smoluchowski equation. In Section III we show that when the temperature is high compared with the characteristic frequency of collective nuclear motion $kT \gg \hbar\omega_c$, the bath variables can be eliminated,[38] which yields the Fokker-Planck equation for the reduced density matrix. (This limit is not applicable to femtosecond transport in antenna complexes at room temperature where $kT \sim 200 \quad \mathrm{cm}^{-1}$ and ω_c is in hundreds wavenumbers, e.g., $\omega_c \sim 100 \ \mathrm{cm}^{-1}$ in Ref. 6.) Two additional levels of reduction corresponding to overdamped primary mode with and without the high temperature approximations are presented as well. In Section IV we represent the time- and frequency-resolved fluorescence signal in terms of the Green functions of these equations of motion. We then develop a procedure for computing these Green functions using Gaussian wavepackets in phase space. In Section V we eliminate intermolecular electronic coherences and derive a generalized master equation for electronic population variables, assuming that the primary nuclear motions are overdamped (the spectral diffusion limit). The solution of these equations using Gaussian wavepackets is given in Section VI. Section VII summarizes the hierarchy of levels of reduction and discusses their applicability. The results of Ref. 37 can be recovered by representing the equations in the basis set of eigenstates of the Smoluchowski operator, and the dimensionality of the corresponding hierarchical equations is equal to the number of additional coordinates. Our approach gives a clear physical insight by representing the bath by a finite number of relevant collective variables, and suggests powerful methods of solving them using Gaussian phase-space wavepackets.[19] The resulting equations for the wavepacket parameters can be solved numerically even for very large aggregates. Since the approach is nonperturbative, it naturally describes ultrafast (femtosecond) transport. The condition $\hbar\omega_c \ll kT$ can further be relaxed by including a few additional coordinates. In the following sections we set $\hbar = 1$ which is equivalent to measuring energies in the units of frequency (e.g., cm^{-1}). However, in some places in the text we retain the Planck constant $\hbar$ to emphasize the quantum nature of certain effects.

II. REDUCED DESCRIPTION USING COLLECTIVE NUCLEAR COORDINATES

In this section we develop a procedure for modeling exciton dynamics in molecular aggregates, based on keeping a finite number of molecular and solvent relevant nuclear degrees of freedom, and deriving closed equations for the reduced density matrix. Adopting Davydov's exciton-phonon Hamiltonian, we represent the nuclear degrees of freedom as a set of harmonic oscillators with the momenta and coordinate operators $\hat{p}_j'$ and $\hat{q}_j'$. The Hamiltonian [Eq. (1.6)] then assumes the form

$$\hat{H}_{ep} = \sum_n E_n \hat{B}_n^+ \hat{B}_n + \sum_{mn} J_{mn} \hat{B}_m^+ \hat{B}_n - \sum_{jmn} m_j' \omega_j'^2 d_{j,mn}' \hat{B}_m^+ \hat{B}_n \hat{q}_j' + \sum_j \left(\frac{\hat{p}_j'^2}{2m_j'} + \frac{m_j' \omega_j'^2 \hat{q}_j'^2}{2} \right), \tag{2.1}$$

where $\hat{H}_e$ is given by the first three terms, and the last term is the phonon Hamiltonian $\hat{H}_{ph}$. Here m_j' and ω_j' are the masses and the frequencies of the oscillators representing nuclear (molecular and solvent) motions, and $d_{j,mn}'$ is the displacement of the jth oscillator induced by molecular populations $(m=n)$ and intermolecular coherences $(m \neq n)$, representing the diagonal and off diagonal coupling to nuclei, respectively. All nuclear properties which affect the electronic motion are contained in the matrix of spectral densities $C_{mn,kl}(\omega)$ which is a direct generalization of the standard spectral density $C(\omega)$[19] and is given by

$$C_{mn,kl}(\omega) \equiv \sum_j \frac{m_j' \omega_j'^3}{4} d_{j,mn}' d_{j,kl}' 2\pi [\delta(\omega - \omega_j') - \delta(\omega + \omega_j')]. \tag{2.2}$$

This matrix represents the dynamics of the collective nuclear coordinates,

$$\hat{q}_{mn}^{(c)} \equiv \sum_j m_j' \omega_j'^2 d_{j,mn}' \hat{q}_j', \tag{2.3}$$

and is given by the Fourier transform of their correlation functions

$$C_{mn,kl}(\omega) = \frac{i}{2} \int_{-\infty}^{\infty} d\tau \, \exp(i\omega\tau) \langle [\hat{q}_{mn}^{(c)}(\tau), \hat{q}_{kl}^{(c)}(0)] \rangle, \tag{2.4}$$

where the time evolution of $\hat{q}^{(c)}_{mn}(\tau)$ is calculated using the nuclear Hamiltonian $\hat{H}_{ph}$ [the last term in Eq. (2.1)].

To obtain a reduced description in terms of relevant collective variables, we recast the Hamiltonian of Eq. (2.1) in a different form, by introducing a set of primary oscillators with variables $\hat{P}_a, \hat{Q}_a$, coupled to the electronic degrees of freedom and to a set of secondary oscillators $\hat{p}_j, \hat{q}_j$.[19,35–39] The exciton-phonon Hamiltonian is then partitioned in the form

$$\hat{H}_{ep} = \hat{H}_S + \hat{H}_B, \tag{2.5}$$

where the system Hamiltonian $\hat{H}_S$ describes the electronic degrees of freedom coupled to the primary oscillators:

$$\begin{aligned}\hat{H}_S = {} & \sum_n E_n \hat{B}^+_n \hat{B}_n + \sum_{mn} J_{mn} \hat{B}^+_m \hat{B}_n \\ & + \sum_a \left(\frac{\hat{P}^2_a}{2M_a} + \frac{M_a \Omega^2_a \hat{Q}^2_a}{2} \right) \\ & - \sum_{amn} M_a \Omega^2_a d_{a,mn} \hat{B}^+_m \hat{B}_n \hat{Q}_a,\end{aligned} \tag{2.6}$$

and $\hat{H}_B$ represents the bath oscillators and their coupling to the primary oscillators,

$$\hat{H}_B = \sum_{ja} \left[\frac{\hat{p}^2_{ja}}{2m_{ja}} + \frac{m_{ja}\omega^2_{ja}}{2} \left(\hat{q}_{ja} - \frac{c_{ja}}{m_{ja}\omega^2_{ja}} \hat{Q}_a \right)^2 \right]. \tag{2.7}$$

The system-bath coupling is now given by the c_{ja} parameters, and the relevant properties of the bath are represented by a new set of spectral densities $J_a(\omega)$,[19,35–37,39]

$$J_a(\omega) \equiv \sum_j \frac{c^2_{ja}}{4m_{ja}\omega_{ja}} 2\pi [\delta(\omega - \omega_{ja}) - \delta(\omega + \omega_{ja})]. \tag{2.8}$$

These can be expressed in terms of correlation functions of the collective coordinates,

$$\hat{q}^{(c)}_a \equiv \sum_j c_{ja} \hat{q}_{ja}, \tag{2.9}$$

in the following way:

$$J_a(\omega) = \frac{i}{2} \int_{-\infty}^{\infty} d\tau \exp(i\omega\tau) \langle [\hat{q}^{(c)}_a(\tau), \hat{q}^{(c)}_a(0)] \rangle. \tag{2.10}$$

Here the dynamics of $\hat{q}^{(c)}_a(\tau)$ is given by the Hamiltonian Eq. (2.7) with $c_{ja} = 0$.

The transformation from Eqs. (2.5) through (2.7) to Eq. (2.1) is straightforward: using a standard canonical transformation, one can represent a system of coupled harmonic oscillators with variables $\hat{P}_a, \hat{Q}_a, \hat{p}_j, \hat{q}_j$ as a system of uncoupled harmonic oscillators with canonical variables $\hat{p}'_j, \hat{q}'_j$ which constitute the normal mode representation of Eq. (2.1). In particular, this procedure connects the spectral densities $J_a(\omega)$ to the matrix of spectral densities $C_{mn,kl}(\omega)$. Expressions of $C(\omega)$ in terms of $J(\omega)$ for the case of a single primary mode were given in Refs. 19 and 39. A straightforward generalization yields

$$\begin{aligned}C_{mn,kl}(\omega) = {} & \sum_a \frac{M_a \Omega^4_a}{2} d_{mn,a} d_{kl,a} \\ & \times \frac{2M^{-1}_a J_a(\omega)}{(\omega^2 - \Omega^2_a)^2 + [M^{-1}_a J_a(\omega)]^2}.\end{aligned} \tag{2.11}$$

The inverse transformation is, however, not unique. This gives a great deal of flexibility in representing Eq. (2.1) in a form of Eqs. (2.5)–(2.7), i.e., in the choice of collective variables. We can see from Eq. (2.7) that each primary oscillator has its own bath, and that these baths are uncorrelated. We obtain, however, nontrivial correlations in the spectral densities $C_{mn,kl}(\omega)$, allowing each primary oscillator to couple to all electronic populations and intermolecular coherences (the coupling constants are determined by $d_{a,mn}$).

By recasting the Hamiltonian (2.1) in the form of (2.5) we highlighted more clearly the role of the (few) primary oscillators, which makes it easier to develop a simple physical picture. Hereafter, we shall, therefore, adopt the form of Eq. (2.5). For clarity, we assume a single primary oscillator; the generalization to an arbitrary number of oscillators is straightforward.

We first recast the system Hamiltonian in a form

$$\hat{H}_S = \frac{\hat{P}^2}{2M} + V(\hat{Q}), \tag{2.12}$$

where V is a matrix in the electronic space with each matrix element depending on the primary nuclear coordinates. For the Hamiltonian of Eq. (2.6) V only contains terms not higher than quadratic in $\hat{Q}$, however, the following derivation applies for any functional dependence V on $\hat{Q}$ which allows us to treat arbitrary anharmonic potentials. At this point we introduce Liouville space notation which will allow us to recast our results in a compact form. Given an ordinary (Hilbert space) operator $\hat{A}$, we define the following superoperators acting in Liouville space: A_L (action from left), A_R (action from right), A_+ (anticommutator) and A_- (commutator),

$$\begin{aligned}& A_L \hat{\rho} \equiv \hat{A}\hat{\rho}, \quad A_R \hat{\rho} \equiv \hat{\rho}\hat{A}, \\ & A_- \equiv A_L - A_R, \quad A_+ \equiv \tfrac{1}{2}(A_L + A_R).\end{aligned} \tag{2.13}$$

Using this notation, the system's Liouville operator L is expressed in terms of the Hamiltonian $\hat{H}$ as $L = H_-$. Obviously, $A_- \hat{\rho} \equiv [\hat{A}, \hat{\rho}]$, $\hat{A}_+ \hat{\rho} = \frac{1}{2}(\hat{A}\hat{\rho} + \hat{\rho}\hat{A})$.

We now apply a canonical transformation in the complete (system and bath) Liouville space, i.e.,

$$\hat{\rho}' = U\hat{\rho}, \tag{2.14}$$

with

$$\mathrm{Tr}(U\hat{\rho}) = \mathrm{Tr}(\hat{\rho}). \tag{2.15}$$

Here $\hat{\rho}$ is any ordinary operator belonging to our Liouville space, and the superoperator U is

$$U \equiv \exp\left(-iQ_+ \sum_j \frac{c_j}{m_j \omega^2_j} p_{j-} \right). \tag{2.16}$$

This is an invertible, trace-conserving linear transformation. According to Eqs. (2.14) and (2.15), superoperators are transformed as

$$A' = UAU^{-1}, \tag{2.17}$$

with the property

$$\mathrm{Tr}(A_1 \ldots A_n \hat{\rho}) = \mathrm{Tr}(A'_1 \ldots A'_n \hat{\rho}'). \tag{2.18}$$

A straightforward calculation gives for the Liouville operator corresponding to the Hamiltonian $\hat{H}_{ep}$ of Eq. (2.5),

$$L = \frac{1}{M} P_+ P_- + V_-(\hat{Q}) + L_B - qQ_- - \frac{1}{M} P_+ p, \tag{2.19}$$

where the first two terms represent the system, and the third term is the bath Liouville operator,

$$L_B \equiv \sum_j \left(\frac{p_{j+} p_{j-}}{m_j} + m_j \omega_j^2 q_{j+} q_{j-} \right). \tag{2.20}$$

The system-bath coupling is given by the last two terms which depend on the collective bath coordinate q and its conjugate momentum p, represented by the superoperators

$$q \equiv \sum_j c_j q_{j+}, \quad p \equiv \sum_j \frac{c_j}{m_j \omega_j^2} p_{j-}. \tag{2.21}$$

These satisfy the commutation relation

$$[p,q] = -i \sum_j \frac{c_j^2}{m_j \omega_j^2} = -i \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{2J(\omega)}{\omega}. \tag{2.22}$$

We next introduce the time ordered correlation functions $\langle q(\tau) q(0) \rangle$ and $\langle q(\tau) p(0) \rangle$. Here the time evolution is in the bath Liouville space and given by $q(\tau) \equiv \exp(iL_B \tau) q \exp(-iL_B \tau)$. ''Time ordered'' means that the superoperators in these correlation functions should be reordered in a way that superoperators with later time arguments stand to the left of those with earlier time arguments. These correlation functions are given by

$$\begin{aligned} \langle q(\tau) q(0) \rangle &= \int \frac{d\omega}{2\pi} J(\omega) \coth\left(\frac{\omega}{2kT} \right) \cos(\omega\tau), \\ \langle q(\tau) p(0) \rangle &= \theta(\tau) \int \frac{d\omega}{2\pi} \frac{2iJ(\omega)}{\omega} \cos(\omega\tau), \\ \langle p(\tau) p(0) \rangle &= 0. \end{aligned} \tag{2.23}$$

Here $\theta(\tau)$ is the Heaviside step function. It arises since for $\tau < 0$ the $p(0)$ superoperator acts from the left. Since this is a ''minus'' operator, it gives a commutator whose trace vanishes.

Applying a path-integral representation for the Liouville space evolution in the spirit of Refs. 35–39, and integrating over bath variables, we see that the only information about the bath relevant for the system dynamics is contained in these correlation functions. This observation has the following important implication: The dynamics of any system variable calculated using the Liouville operator [Eq. (2.19)] will be unaffected if we can model these correlation functions using a different Liouville operator L_B, which is quadratic in the canonical bath variables. This gives us a great deal of flexibility in modifying L_B, which can be used to simplify the calculations.

We next represent the spectral density in the form

$$J(\omega) = M \sum_{\alpha=1}^{N_0} \frac{\gamma_\alpha \Lambda_\alpha^2 \omega}{\omega^2 + \Lambda_\alpha^2}. \tag{2.24}$$

This expansion constitutes essentially a Laplace transform of $J(t)$, and by taking a sufficient number of terms in the r.h.s. of Eq. (2.24) we can approximate any spectral density.

Substituting Eq. (2.24) into Eqs. (2.23) we obtain

$$\begin{aligned} \langle q(\tau) p(0) \rangle &= \theta(\tau) iM \sum_{\alpha=1}^{N_0} \gamma_\alpha \Lambda_\alpha e^{-\Lambda_\alpha \tau}, \\ \langle q(\tau) q(0) \rangle &= \sum_{\alpha=1}^{N_0} \sigma_\alpha e^{-\Lambda_\alpha |\tau|} + \sum_{n=1}^{\infty} \overline{\sigma_n} e^{-2\pi n kT |\tau|}, \end{aligned} \tag{2.25}$$

where

$$\begin{aligned} \sigma_\alpha &\equiv \frac{1}{2} M \gamma_\alpha \Lambda_\alpha^2 \cot\left(\frac{\Lambda_\alpha}{2kT} \right), \\ \overline{\sigma_n} &\equiv \sum_{\alpha=1}^{N_0} M \gamma_\alpha \Lambda_\alpha^2 \frac{4\pi n (kT)^2}{(2\pi n kT)^2 - \Lambda_\alpha^2}. \end{aligned} \tag{2.26}$$

By truncating the infinite sum over $n (n=1,\ldots,N_1)$ in Eqs. (2.25), we can model the correlation functions in Eqs. (2.25) in the following way. Instead of the bath variables q_j and p_j we introduce a new set of $N = N_0 + N_1$ collective coordinates q_α $\alpha = 1,\ldots,N$. The effective Liouville operator is still given by Eq. (2.19). However, the bath operator L_B adopts the form

$$L_B = i \sum_{\alpha=1}^{N} \Lambda_\alpha \frac{\partial}{\partial q_\alpha} \left(q_\alpha + \sigma_\alpha \frac{\partial}{\partial q_\alpha} \right), \tag{2.27}$$

and the superoperators q and p are replaced by

$$\begin{aligned} q &\equiv \sum_{\alpha=1}^{N} q_\alpha, \\ p &= -i \sum_{\alpha=1}^{N} M \gamma_\alpha \Lambda_\alpha \frac{\partial}{\partial q_\alpha}. \end{aligned} \tag{2.28}$$

The first N_0 coordinates are required in order to fit the spectral density [Eq. (2.24)] with Λ_α and σ_α given by Eqs. (2.24) and (2.26). The remaining N_1 coordinates q_α, $\alpha = N_0 + 1,\ldots,N$ are Matsubara oscillators which are required to model the system if the temperature is not sufficiently high. For these oscillators we define

$$\Lambda_\alpha \equiv 2\pi(\alpha - N_0) kT, \quad \sigma_\alpha \equiv \overline{\sigma_{\alpha - N_0}}, \quad \gamma_\alpha \equiv 0; \quad \alpha > N_0. \tag{2.29}$$

It should be emphasized that our effective dynamical system defined by the coordinates q_α, cannot be represented by reduced effective Hamiltonian in the q_α space, but only by an effective Liouville operator. This is why it is essential to perform all our transformations in Liouville space. An effective Liouivillian can represent much more general dynamics than an effective Hamiltonian.

Adopting the Wigner representation for the primary oscillator variables, the density matrix can be considered as an operator $\hat{\rho}(P,Q;q_1,\ldots,q_N)$ in the full electronic space of states (i.e., the complete space of states of the electronic subsystem with all possible numbers of electronic excitations), where each matrix element between any pair of electronic states depends on the momentum P and coordinate Q of the primary oscillator and collective bath variables $q_1,\ldots,q_N$. The equation of motion for the reduced density matrix $\hat{\rho}$ for the system driven by an external field becomes

$$\begin{aligned}\frac{\partial\hat{\rho}}{\partial\tau}={}&-i[\hat{H}_e,\hat{\rho}]-\frac{1}{2}M\Omega^2\sum_{mn}d_{mn}\left[\hat{B}_m^+\hat{B}_n,\frac{\partial\hat{\rho}}{\partial P}\right]_+\\&+iM\Omega^2Q\sum_{mn}d_{mn}[\hat{B}_m^+\hat{B}_n,\hat{\rho}]-\frac{1}{M}P\frac{\partial\hat{\rho}}{\partial Q}\\&+M\Omega^2Q\frac{\partial\hat{\rho}}{\partial P}+\sum_{\alpha=1}^{N}\Lambda_\alpha\frac{\partial}{\partial q_\alpha}\left(q_\alpha+\sigma_\alpha\frac{\partial}{\partial q_\alpha}\right)\hat{\rho}\\&-\sum_{\alpha=1}^{N}q_\alpha\frac{\partial\hat{\rho}}{\partial P}+P\sum_{\alpha=1}^{N}\gamma_\alpha\Lambda_\alpha\frac{\partial\hat{\rho}}{\partial q_\alpha}+i\varepsilon(\tau)[\hat{\mu},\hat{\rho}],\end{aligned}\tag{2.30}$$

where $[\ ,\ ]_+$ denotes an anticommutator.

Equation (2.30) with $N_1=\infty$ describes the exact evolution of the electronic degrees of freedom and primary oscillators for the Hamiltonian with the spectral density given by Eq. (2.24). In practice, it is sufficient to use N_1 which satisfies the condition $kTN_1>\hbar\Omega$. Generalization of Eq. (2.30) to include additional primary oscillators is straightforward.

In summary, our procedure for modeling the optical and energy transfer processes in aggregates consists of the following steps: (i) start with the Hamiltonian of Eq. (2.1) with the matrix of spectral densities given by Eq. (2.2). These spectral densities can often be extracted from experiment; (ii) transform to the Hamiltonian of Eqs. (2.5) through (2.7), and choose the set of primary oscillators, with parameters and spectral densities $J_a(\omega)$ of Eq. (2.8) which reproduce the given $C_{mn,kl}(\omega)$ by means of Eq. (2.11); (iii) expand $J_a(\omega)$ in a form of Eq. (2.24) which yields the collective coordinates $q_{a\alpha}$, $\alpha=1,\ldots,N_{0a}$; (iv) add collective variables $q_{aN_{0a}+1},\ldots,q_{aN_a}$ with $N_a\equiv N_{0a}+N_{1a}$, where $N_{1a}\sim\hbar\Omega_a/kT$; (v) the multidimensional extension of Eq. (2.30) to include several primary oscillators finally describes the ultrafast exciton and nuclear dynamics of the aggregate.

In the coming sections we develop several approximate schemes for solving Eq. (2.30).

III. FURTHER REDUCTIONS: THE MULTISTATE FOKKER-PLANCK AND THE SMOLUCHOWSKI EQUATIONS

In Section II we have shown that the secondary oscillators can be modeled by collective variables q_α, provided the spectral densities are represented in the form of Eq. (2.24). The relevant bath relaxation rates are then $\Lambda_{a\alpha}$ as well as the Matsubara frequencies $2\pi nkT/\hbar$. Our reduced description can be further simplified in the high-temperature $kT\gg\hbar\Omega_a$ limit, provided the bath, formed by the secondary oscillators, is fast compared with the frequencies of our primary system. In this case the secondary variables q_α can be eliminated, which results in closed equations of motion for system (electronic and primary oscillators) coordinates alone. This level of reduction had been accomplished for a single electronic state using the path-integral technique of Caldeira and Leggett,[38] and subsequently generalized to the multi-state case that yields the multistate Fokker-Planck equation.[36]

In this section we derive these results as a limiting case of the more general (i.e., less reduced) level of description developed in Section II. To that end, we note that the frequencies ω in $J(\omega)$ [Eq. (2.19)] relevant for the system dynamics are of the order of the primary system frequencies Ω_a. When all bath timescales are fast $kT/\hbar$, $\Lambda_{a\alpha}\gg\Omega_a$, we can use the low-frequency part of $J(\omega)$, taking $\omega\ll\Lambda_\alpha$. This yields the Ohmic spectral density

$$J_a(\omega)=M_a\gamma_a\omega,\tag{3.1}$$

where

$$\gamma_a\equiv\sum_{\alpha=1}^{N_{0a}}\gamma_{a\alpha}.\tag{3.2}$$

Note that since the bath relaxation rates include the Matsubara frequencies $2\pi nkT/\hbar$, this is also necessarily a high temperature limit, i.e., kT is large compared with the primary frequencies Ω_a.

Upon evaluating the Liouville space Green functions of the primary variables, neglecting their coupling to the electronic subsystem we notice that they can be modeled by the following effective Liouville operator (for details see Appendix B):

$$\begin{aligned}L_0=\sum_a\Bigg[&\frac{1}{M_a}P_{a+}P_{a-}+M_a\Omega_a^2Q_{a+}Q_{a-}+\gamma_aQ_{a-}P_{a+}\\&-i\gamma_aM_akT(Q_{a-})^2\Bigg].\end{aligned}\tag{3.3}$$

The Liouville equation written in the Wigner representation for $\hat{\rho}(\mathbf{P},\mathbf{Q},\tau)$ adopts the form of the multi-state Fokker-Planck equation:

$$\begin{aligned}\frac{\partial\hat{\rho}}{\partial\tau}={}&-i[\hat{H}_e,\hat{\rho}]-\frac{1}{2}\sum_{mna}M_a\Omega_a^2d_{mn,a}\left[\hat{B}_m^+\hat{B}_n,\frac{\partial\hat{\rho}}{\partial P_a}\right]_+\\&+i\sum_{mna}M_a\Omega_a^2d_{mn,a}Q_a[\hat{B}_m^+\hat{B}_n,\hat{\rho}]\\&-\sum_a\Bigg[\frac{1}{M_a}P_a\frac{\partial\hat{\rho}}{\partial Q_a}-M_a\Omega_a^2Q_a\frac{\partial\hat{\rho}}{\partial P_a}\\&-\gamma_a\frac{\partial}{\partial P_a}\left(P_a+M_akT\frac{\partial}{\partial P_a}\right)\hat{\rho}\Bigg]+i\varepsilon(\tau)[\hat{\mu},\hat{\rho}].\end{aligned}\tag{3.4}$$

Further reduction may be made in the limit of strongly overdamped nuclear motion, $\gamma_a \gg \Omega_a$, where the collective momenta P_a are much faster than the collective primary coordinates Q_a and may be eliminated. Using the terminology of Section II, the relevant Liouville space correlation functions of nuclear variables can be modeled using distribution functions in configuration space which only depend on the collective coordinates Q_a (excluding the momenta P_a). The procedure is presented in Appendix B and yields the multistate Smoluchowski equation for $\rho(\mathbf{Q},\tau)$:

$$\frac{\partial\hat{\rho}}{\partial\tau} = -i[\hat{H}_e,\hat{\rho}] - \frac{1}{2}\sum_{mna}\frac{\Omega_a^2}{\gamma_a} d_{mn,a}\left[\hat{B}_m^+\hat{B}_n,\frac{\partial\hat{\rho}}{\partial Q_a}\right]_+ + i\sum_{mna} M_a\Omega_a^2 d_{mn,a} Q_a [\hat{B}_m^+ B_n,\hat{\rho}] + \sum_a \frac{\Omega_a^2}{\gamma_a}\frac{\partial}{\partial Q_a}\left(Q_a + \frac{kT}{M_a\Omega_a^2}\frac{\partial}{\partial Q_a}\right)\hat{\rho} + i\varepsilon(\tau)[\hat{\mu},\hat{\rho}]. \tag{3.5}$$

Finally we consider a different level of reduction which applies when the primary modes are overdamped, however, the temperature is not necessarily high. This situation can be described by the following matrix of spectral densities:

$$C_{mn,kl}(\omega) = 2\sum_a d_{a,mn} d_{a,kl}\frac{M_a\Omega_a^2}{2}\frac{\omega(\Omega_a^2/\gamma_a)}{\omega^2 + (\Omega_a^2/\gamma_a)^2}. \tag{3.6}$$

In this case the Liouville space correlation functions of operators $\hat{Q}_a$ responsible for the system-bath interactions can be modeled in the configuration space defined by the coordinates Q_a and the associated Matsubara modes $Q_{an}, n = 1,2,\ldots$. The equation of motion derived in Appendix C becomes

$$\frac{\partial\hat{\rho}}{\partial\tau} = -i[\hat{H}_e,\hat{\rho}] - \frac{1}{2}\sum_{mna}\bar{\Lambda}_a d_{mn,a}\left[\hat{B}_m^+ B_n,\frac{\partial\hat{\rho}}{\partial Q_a}\right]_+ + i\sum_{mna} M_a\Omega_a^2 d_{mn,a}\left(Q_a + \sum_s Q_{as}\right)[\hat{B}_m^+\hat{B}_n,\hat{\rho}] + \sum_a \bar{\Lambda}_a\frac{\partial}{\partial Q_a}\left(Q_a + \bar{\sigma}_a\frac{\partial}{\partial Q_a}\right)\hat{\rho} + \sum_{as}\bar{\Lambda}_{as}\frac{\partial}{\partial Q_{as}}\left(Q_{as} + \bar{\sigma}_{as}\frac{\partial}{\partial Q_{as}}\right)\hat{\rho} + i\varepsilon(\tau)[\hat{\mu},\hat{\rho}], \tag{3.7}$$

where we have used the notation

$$\bar{\Lambda}_a \equiv \frac{\Omega_a^2}{\gamma_a}, \quad \bar{\sigma}_a \equiv \frac{\bar{\Lambda}_a}{2M_a\Omega_a^2}\cot\left(\frac{\bar{\Lambda}_a}{2kT}\right), \quad \bar{\Lambda}_{an} \equiv 2\pi nkT, \quad \bar{\sigma}_{an} \equiv \frac{\bar{\Lambda}_a}{M_a\Omega_a^2}\frac{4\pi n(kT)^2}{(2\pi nkT)^2 - \Lambda_a^2}. \tag{3.8}$$

In summary, we have obtained four equations of motion representing different levels of reduction. These include the most general equation that holds for an arbitrary spectral density [Eq. (2.30)], the fast bath, high temperature limit [Eq. (3.4)], the overdamped primary nuclear motion [Eq. (3.7)], and the high temperature limit of the latter, Eq. (3.5). All of these equations can be written in a unified compact form by introducing variables x_α which represent the relevant reduced variables for each case. Equations (2.30), (3.4), (3.5), and (3.7) then adopt the common form

$$\frac{\partial\hat{\rho}}{\partial\tau} = -i[\hat{H}_e,\hat{\rho}] - \frac{1}{2}\sum_{mn\alpha} D_{mn,\alpha}\left[\hat{B}_m^+\hat{B}_n,\frac{\partial\hat{\rho}}{\partial x_\alpha}\right]_+ + i\sum_{mn\alpha}\overline{D}_{mn,\alpha} x_\alpha[\hat{B}_m^+\hat{B}_n,\hat{\rho}] + \sum_{\alpha\beta} A_{\alpha\beta}\frac{\partial}{\partial x_\alpha}(x_\beta\hat{\rho}) + \sum_\alpha B_\alpha\frac{\partial^2\hat{\rho}}{\partial x_\alpha^2} + i\varepsilon(\tau)[\hat{\mu},\hat{\rho}]. \tag{3.9}$$

The parameters $D,\overline{D},A$, B, and C for all four cases are listed in Appendices A, B, and C. In the following sections we will use Eq. (3.9) to analyze the dynamics of aggregates.

IV. GAUSSIAN PHASE-SPACE WAVEPACKETS FOR TIME- AND FREQUENCY-RESOLVED FLUORESCENCE

In this section we express the time- and frequency-resolved fluorescence signal in terms of Green functions of the Liouville equation [Eq. (3.9)]. We then propose a convenient approximation scheme for calculating these Green functions, based on a Gaussian ansatz for the wavepackets representing the dynamics of collective coordinates in phase space.

In Section III we have derived the equation of motion [Eq. (3.9)] for the density matrix in Liouville space, that includes both electronic and nuclear variables x_α. The latter include primary relevant modes as well as collective coordinates representing the relevant secondary oscillators. The density matrix in Eq. (3.9) is represented as an $\mathbf{x}$-dependent operator $\hat{\rho}(\mathbf{x})$ in the full electronic space of states. We shall introduce matrix elements $\rho_{m_1\ldots m_N,n_1\ldots n_{N'}}(\mathbf{x})$ of $\hat{\rho}(\mathbf{x})$ in the electronic space by

$$\rho_{m_1\ldots m_N,n_1,\ldots,n_{N'}}(\mathbf{x}) \equiv \langle 0|\hat{B}_{m_1}\ldots\hat{B}_{m_N}\hat{\rho}(\mathbf{x})\hat{B}_{n_1}^+\ldots\hat{B}_{n_{N'}}^+|0\rangle. \tag{4.1}$$

This allows us to recast Eq. (3.9) in a form of a set of coupled equations of motion for nuclear wavepackets $\rho_{\mathbf{mn}}(\mathbf{x})$ where $\mathbf{m} \equiv m_1\ldots m_N, \mathbf{n} \equiv n_1\ldots n_{N'}$. $\rho_{\mathbf{mn}}(x)$ represents electronic coherences between N-exciton and N'-exciton states (N-exciton states populations are a special case whereby $N = N'$).

When the external field is switched off, the Hamiltonian (and the equations of motion) conserve the number of excitons. This implies that equations for wavepackets $\rho_{\mathbf{mn}}(\mathbf{x})$ are uncoupled for different values of (N',N). The perturbative solution of Eqs. (3.9) in $\varepsilon(\tau)$ involves solving equations of motion for wavepackets $\rho_{\mathbf{mn}}(\mathbf{x},\tau)$ in the absence of the field.[19] Setting $\varepsilon(\tau) \equiv 0$ in Eq. (3.9) and projecting it into the electronic subspace with up to one excitation in the bra and the ket states of the electronic system, we obtain

$$\frac{d\rho_{mn}}{d\tau}=-i\sum_{k}\ (E_{mk}\rho_{kn}-\rho_{mk}E_{kn})$$
$$-\frac{1}{2}\sum_{k\alpha}\left(D_{mk,\alpha}\frac{\partial\rho_{kn}}{\partial x_{\alpha}}+\frac{\partial\rho_{mk}}{\partial x_{\alpha}}D_{kn,\alpha}\right)$$
$$+i\sum_{k\alpha}x_{\alpha}(\overline{D}_{mk,\alpha}\rho_{kn}-\rho_{mk}\overline{D}_{kn,\alpha})$$
$$+\sum_{\alpha\beta}A_{\alpha\beta}\frac{\partial}{\partial x_{\alpha}}(x_{\beta}\rho_{mn})+\sum_{\alpha}B_{\alpha}\frac{\partial^{2}\rho_{mn}}{\partial x_{\alpha}^{2}}. \tag{4.2}$$

Here latin indices can also assume zero values. $|0\rangle$ denotes the ground electronic state of the system and $|m\rangle$ denotes the state whereby only the mth molecule is excited and all other molecules are in the ground state. We have used the following notation. If $m=0$, or $n=0$, $E_{mn}=0$, $D_{mn,\alpha}=0$, and $\overline{D}_{mn,\alpha}=0$. For $m,n\neq 0$ we have

$$E_{mn}\equiv E_{n}\delta_{mn}+J_{mn}. \tag{4.3}$$

We have thus expressed the density matrix of the system in the complete Liouville space as a matrix in the electronic subspace and as an operator in the nuclear subspace. Each electronic matrix element ρ_{nm} is now a wavepacket in nuclear space. Equation (4.2) allows the calculation of the density matrix by solving coupled equations of motion for these wavepackets. As shown in Ref. 19 the signal, to linear order in pump intensity, can be obtained by following evolution of the wavepackets $\hat{\rho}_{00},\hat{\rho}_{0m},\hat{\rho}_{m0}$, and $\hat{\rho}_{mn}$ calculated in the absence of the external field. Allowing latin indices to assume the value 0 we can obtain the Liouville equation for the wavepackets [Eq. (4.2)] in a form

$$\frac{d\hat{\rho}_{mn}(\mathbf{x},\tau)}{d\tau}+i\sum_{pq}\mathscr{L}_{mn,pq}(\mathbf{x})\hat{\rho}_{pq}(\mathbf{x},\tau)=0. \tag{4.4}$$

We next introduce the Green function solution of the Liouville equation,

$$\hat{\rho}_{mn}(\tau)=\sum_{pq}\mathscr{G}_{mn,pq}(\tau-\tau')\hat{\rho}_{pq}(\tau'). \tag{4.5}$$

The time- and frequency-resolved fluorescence signal is given by[11,40–42]

$$S(\omega_{s},t)=\int_{-\infty}^{t}dt'[e^{i\omega_{s}(t-t')}\tilde{\mathscr{C}}(t,t')+e^{i\omega_{s}(t'-t)}\tilde{\mathscr{C}}(t',t)], \tag{4.6}$$

where $\tilde{\mathscr{C}}$ is the correlation function of the polarization operator,[11,40–42]

$$\tilde{\mathscr{C}}(t,t')=\langle\tilde{\mu}(t)\tilde{\mu}(t')\rangle. \tag{4.7}$$

Here $\tilde{A}(\tau)$ denotes the Heisenberg operator related to a Schrödinger operator $\hat{A}$ whose evolution is given by the full Hamiltonian $\hat{H}_{T}(\tau)$ [Eq. (1.7)]. Equation (4.6) represents an ideal signal.[19] In reality we need to convolute it with the temporal and spectral profiles of the detection (gating) device.[42] For our model we have

$$\tilde{\mathscr{C}}(t,t')=\sum_{mn}\mu_{m}\mu_{n}\tilde{\mathscr{C}}_{mn}(t,t'). \tag{4.8}$$

In Eqs. (4.8)–(4.11) latin indices do not assume zero values.

When the signal is calculated, we find that it naturally separates into two contributions that differ by the time ordering of the various interactions. These are responsible for the Raman and the fluorescence components and will be denoted by superscripts R and F, respectively.[19] We thus have

$$\tilde{\mathscr{C}}(t,t')=\tilde{\mathscr{C}}^{(R)}(t,t')+\tilde{\mathscr{C}}^{(F)}(t,t'), \tag{4.9}$$

with

$$\tilde{\mathscr{C}}^{(R)}_{mn}(t,t')=\theta(t-t')\sum_{kl}\int_{t'}^{t}d\tau\int_{-\infty}^{t'}d\tau'\langle\mathscr{G}_{m0,k0}(t-\tau)\mathscr{G}_{00,00}(\tau-t')\mathscr{G}_{0n,0l}(t'-\tau')\hat{\rho}_{g}\rangle\varepsilon_{k}(\tau)\varepsilon_{l}^{*}(\tau')$$
$$+\theta(t'-t)\sum_{kl}\int_{t}^{t'}d\tau'\int_{-\infty}^{t}d\tau\langle\mathscr{G}_{0n,0l}(t'-\tau')\mathscr{G}_{00,00}(\tau-t)\mathscr{G}_{m0,k0}(t-\tau)\hat{\rho}_{g}\rangle\varepsilon_{k}(\tau)\varepsilon_{l}^{*}(\tau') \tag{4.10}$$

and

$$\tilde{\mathscr{C}}^{(F)}_{mn}(t,t')=\theta(t-t')\sum_{klpq}\int_{-\infty}^{t'}d\tau\int_{\tau}^{t'}d\tau'\langle\mathscr{G}_{m0,q0}(t-t')\mathscr{G}_{qn,pl}(t'-\tau')\mathscr{G}_{p0,k0}(\tau'-\tau)\hat{\rho}_{g}\rangle\varepsilon_{k}(\tau)\varepsilon_{l}^{*}(\tau')$$
$$+\theta(t-t')\sum_{klpq}\int_{-}^{t'}d\tau'\int_{\tau'}^{t'}d\tau\langle\mathscr{G}_{m0,q0}(t-t')\mathscr{G}_{qn,kp}(t'-\tau)\mathscr{G}_{0p,0l}(\tau-\tau')\hat{\rho}_{g}\rangle\varepsilon_{k}(\tau)\varepsilon_{l}^{*}(\tau')$$
$$+\theta(t'-t)\sum_{klpq}\int_{-\infty}^{t}d\tau'\int_{\tau'}^{t}d\tau\langle\mathscr{G}_{0n,0q}(t'-t)\mathscr{G}_{mq,kp}(t-\tau)\mathscr{G}_{0p,0l}(\tau-\tau')\hat{\rho}_{g}\rangle\varepsilon_{k}(\tau)\varepsilon_{l}^{*}(\tau')$$
$$+\theta(t'-t)\sum_{klpq}\int_{-\infty}^{t}d\tau\int_{\tau}^{t}d\tau'\langle\mathscr{G}_{0n,0q}(t'-t)\mathscr{G}_{mq,pl}(t-\tau')\mathscr{G}_{p0,k0}(\tau'-\tau)\hat{\rho}_{g}\rangle\varepsilon_{k}(\tau)\varepsilon_{l}^{*}(\tau'). \tag{4.11}$$

Here ρ_g is the equilibrium ground state wavepacket, $\langle \cdots \rangle$ stands for the trace over bath variables, and $\varepsilon_k(\tau) \equiv \mu_k \varepsilon(\tau)$.

As shown in this and the preceding sections, the dynamics of excitonic variables can be modeled by following the evolution of reduced wavepackets $\rho(x_\alpha, \tau)$ (x_α representing the relevant collective variables) given by Eq. (3.9). Since the polarization operator is expressed in terms of electronic variables alone, and the latter do not change under the canonical transformation defined by Eqs. (2.14) and (2.16), the signal is given by Eqs. (4.10) and (4.11), with the Green functions defined by Eqs. (4.4) and (4.5) where the wavepackets $\hat{\rho}_{mn}$ are represented by functions $\rho_{mn}(x_\alpha)$, the Liouville operators $\mathscr{L}_{mn,pq}$ are defined by Eq. (4.2), and

$$\langle \hat{\rho}(\tau) \rangle = \mathrm{Tr}[\hat{\rho}(\mathbf{x}, \tau)] = \int d\mathbf{x} \rho(\mathbf{x}, \tau). \tag{4.12}$$

Equations (4.8)–(4.11) together with the definitions of the Liouville space Green functions $\mathscr{G}_{mn,pq}$ given by Eqs. (4.2) and (4.5), form a closed system of equations that relate the fluorescence spectra to exciton transport.

A convenient method for computing the necessary Green functions is obtained by making a Gaussian ansatz for the wavepackets in the collective variables x_a,

$$\begin{aligned}\rho_{mn}(\mathbf{x}, \tau) = & \frac{a_{mn}(\tau)}{\sqrt{\det(2\pi\sigma_{mn}(\tau))}} \\ & \times \exp\left[-\frac{1}{2} \sum_{\alpha\beta} (\sigma_{mn}^{-1}(\tau))_{\alpha\beta} (x_\alpha - x_{mn,\alpha}(\tau)) \right. \\ & \left. \times (x_\beta - x_{mn,\beta}(\tau)) \right].\end{aligned} \tag{4.13}$$

This form depends on the following time dependent parameters: The overall normalization $a_{mn}(\tau)$, average portions $x_{mn}(\tau)$, and a covariance matrix $\sigma_{mn}(\tau)$. To obtain equations of motion for these parameters, we substitute the ansatz Eq. (4.13) into Eq. (4.2) and require that they reproduce the first and the second moments of the collective coordinates x_α.[19] These equations of motion are given in Appendix D. Instead of solving a coupled set of partial different equations we now solve trajectories representing the evolution of these parameters. This solution immediately yields the Green functions necessary for calculating the fluorescence. It is important to note that we are making a Gaussian ansatz for the evolution of the free system without the external driving electric field. Therefore, this ansatz yields only the Green functions. The actual density matrix or correlation functions involve time-integrations, and after these integrations are performed, the wavepacket is no longer a Gaussian. In the terminology of Ref. 19 these wavepackets merely give the Liouville space generating function for the signal. Had we made the Gaussian ansatz on the solution of the equation with the driving field, we would have obtained a much cruder approximation for the signal.

Finally we note that in this section we have shown how to model the time- and frequency-resolved fluorescence signal by following the evolution of reduced wavepackets. The same procedure can be applied to calculate other types of optical signals. For example, four-wave mixing measurements may be calculated by following the evolution of wavepackets of Eq. (4.2) as well as wavepackets representing the coherences between two-exciton and ground electronic states. The latter can be represented by $\rho_{mn,0}(\mathbf{x}, \tau)$ with $\rho_{mn,0} = \rho_{nm,0}$ and $\rho_{mm,0} = 0$. The corresponding equation of motion, obtained from Eq. (3.9), reads

$$\begin{aligned}\frac{\partial \rho_{mn,0}}{\partial \tau} = & -i(E_m + E_n)\rho_{mn,0} - i \sum_k (J_{mk}\rho_{kn,0} + J_{nk}\rho_{mk,0}) \\ & - \frac{1}{2} \sum_{k\alpha} \left(D_{mk,\alpha} \frac{\partial \rho_{kn,0}}{\partial x_\alpha} + D_{nk,\alpha} \frac{\partial \rho_{mk,0}}{\partial x_\alpha} \right) \\ & + i \sum_{k\alpha} x_\alpha (\bar{D}_{mk,\alpha}\rho_{kn,0} + \bar{D}_{nk,\alpha}\rho_{mk,0}) \\ & + \sum_{\alpha\beta} A_{\alpha\beta} \frac{\partial}{\partial x_\alpha} (x_\beta \rho_{mn,0}) + \sum_\alpha B_\alpha \frac{\partial^2 \rho_{mn,0}}{\partial x_\alpha^2}.\end{aligned} \tag{4.14}$$

Equation (4.2) together with Eq. (4.14) contains all the necessary information for calculating any time-resolved or frequency-resolved four-wave mixing process.

V. EXCITON TRANSPORT AND FLUORESCENCE IN THE SPECTRAL DIFFUSION LIMIT

In this section we assume diagonal coupling of the electronic system to a bath, modeled by a finite number of overdamped modes whose dynamics is described by the Smoluchowski equation. In the spectral-diffusion limit we can eliminate the reduced wavepackets representing intermolecular electronic coherences. This leads to a closed set of Smoluchowski equations for electronic population wavepackets.

Diagonal coupling implies that the exciton-bath interaction constants $d_{mn,\alpha}$, are given by

$$d_{mn,\alpha} = \delta_{mn} d_{m,\alpha}, \tag{5.1}$$

where Greek indices denote the collective overdamped coordinates. The matrix of spectral densities of Eq. (2.11) also assumes a diagonal form,

$$C_{mn,kl}(\omega) = \delta_{mn}\delta_{kl} C_{mk}(\omega). \tag{5.2}$$

In the overdamped limit $\gamma_\alpha \gg \Omega_\alpha$, the matrix of spectral densities represents a collection of overdamped Brownian oscillators,[19]

$$C_{mn}(\omega) = \sum_\alpha \bar{d}_{m,\alpha} \bar{d}_{n,\alpha} \frac{2\lambda_\alpha \bar{\Lambda}_\alpha}{\omega^2 + \bar{\Lambda}_\alpha^2}. \tag{5.3}$$

Here we have introduced the notation

$$\bar{\Lambda}_\alpha \equiv \frac{\Omega_\alpha^2}{\gamma_\alpha}, \quad \Delta_\alpha \equiv \sqrt{2\lambda_\alpha kT}, \tag{5.4}$$

$$\lambda_\alpha \equiv \frac{M_\alpha \Omega_\alpha^2}{2} \sum_m (d_{m,\alpha})^2,$$
$$\overline{d}_{m,\alpha} \equiv d_{m,\alpha} \left[\sum_n (d_{n,\alpha})^2 \right]^{-1/2}. \tag{5.5}$$

Defining the dimensionless collective coordinates q_α,

$$q_\alpha \equiv Q_\alpha \left[\sum_m (d_{m,\alpha})^2 \right]^{-1/2}, \tag{5.6}$$

we can recast the Smoluchowski equation [Eq. (3.5)] in a form

$$\begin{aligned}\frac{d\hat{\rho}}{d\tau} = & -i[\hat{H}_e,\hat{\rho}] + i \sum_{m\alpha} 2\lambda_\alpha \overline{d}_{m,\alpha} q_\alpha [\hat{B}_m^+ \hat{B}_m,\hat{\rho}] \\ & + \sum_\alpha \overline{\Lambda}_\alpha \frac{\partial}{\partial q_\alpha} \left[q_\alpha + \left(\frac{\Delta_\alpha}{2\lambda_\alpha} \right)^2 \frac{\partial}{\partial q_\alpha} \right] \hat{\rho} \\ & - \frac{1}{2} \sum_{m\alpha} \overline{\Lambda}_\alpha \overline{d}_{m,\alpha} \left[\hat{B}_m^+ \hat{B}_m, \frac{\partial \hat{\rho}}{\partial q_\alpha} \right]_+ + i\varepsilon(\tau)[\hat{\mu},\hat{\rho}].\end{aligned} \tag{5.7}$$

Upon taking electronic matrix elements of this equation, we obtain the equations of motion for the wavepackets [Eq. (4.2)],

$$\begin{aligned}\frac{d\rho_{mn}(\mathbf{q},t)}{d\tau} = & -i(E_m - E_n)\rho_{mn}(\mathbf{q},t) \\ & + i \sum_\alpha 2\lambda_\alpha (\overline{d}_{m,\alpha} - \overline{d}_{n,\alpha}) q_\alpha \rho_{mn}(\mathbf{q},t) \\ & + \sum_\alpha \overline{\Lambda}_\alpha \frac{\partial}{\partial q_\alpha} \left[\left(q_\alpha - \frac{\overline{d}_{m,\alpha} + \overline{d}_{n,\alpha}}{2} \right) \right. \\ & \left. + \left(\frac{\Delta_\alpha}{2\lambda_\alpha} \right)^2 \frac{\partial}{\partial q_\alpha} \right] \rho_{mn}(\mathbf{q},t) \\ & - i \sum_k (J_{mk}\rho_{kn} - J_{kn}\rho_{mk}(\mathbf{q},t)).\end{aligned} \tag{5.8}$$

We have thus shown that the system described by a spectral density of Eqs. (5.2) and (5.3) can be modeled in the high temperature limit $\Lambda_\alpha \ll kT$ using Eq. (5.8).

To proceed further we need to take a closer look at the various timescales of the system. The evolution timescale of the coherence wavepackets ρ_{0m}, ρ_{m0}, and ρ_{mn} (for $m \neq n$) is $\tau_c \sim \Delta^{-1}$. Two timescales appear in the evolution of the population wavepackets: $\tau_p^{(1)} \sim \overline{\Lambda}^{-1}$ reflecting the relaxation of the collective coordinates, and $\tau_p^{(2)} \sim W^{-1}$ related to intermolecular transport (here W is the energy transfer rate). When $W \ll \Lambda$ we have $\tau_p^{(1)} \ll \tau_p^{(2)}$, the collective coordinates are fully relaxed at all times, and we recover Forster's transport limit [see Eq. (6.10)]. In the opposite limit $W \gg \Lambda$, nuclear dynamics is too slow to affect the coherent exciton motion. Below we consider the more complex case whereby $W \sim \overline{\Lambda}$. Here we have only one timescale in the evolution of population wavepackets $\tau_p \sim \tau_p^{(1)} \sim \tau_p^{(2)}$. We further assume that the bath is slow compared with the inverse exciton-phonon coupling strength, i.e.,

$$\overline{\Lambda}_\alpha \ll \Delta_\beta. \tag{5.9}$$

This is known as the spectral diffusion limit. Since in this limit we have $\tau_c \ll \tau_p$, and we are interested in the evolution of the signal on a timescale $\tau \gg \tau_c$, we can eliminate the intermolecular coherences and make a Markovian approximation, which yields time-local equations of motion for population wavepackets (without memory).

In the Smoluchowski equations for the coherences [Eqs. (5.8)] $\lambda q \sim \Delta$ since the size of an equilibrated wavepacket is $q \sim \Delta/2\lambda$. Since $\overline{\Lambda} \ll \Delta$ and $W \ll \Delta$, the first two terms in the rhs of Eq. (5.8) dominate the equations of motion for coherence wavepackets (with $m \neq n$). Neglecting the other terms we obtain the following simplified equations for intramolecular and intermolecular coherence wavepackets,

$$\frac{d\rho_{m0}}{d\tau} = -iE_m \rho_{m0} + i \sum_\alpha 2\lambda_\alpha \overline{d}_{m,\alpha} q_\alpha \rho_{m0}, \tag{5.10}$$

$$\begin{aligned}\frac{d\rho_{mn}}{d\tau} = & -i(E_m - E_n)\rho_{mn} + i \sum_\alpha 2\lambda_\alpha (\overline{d}_{m,\alpha} - \overline{d}_{n,\alpha}) q_\alpha \rho_{mn} \\ & + iJ_{mn}(\rho_{mm} - \rho_{nn}); \quad m \neq n.\end{aligned} \tag{5.11}$$

In the rhs of Eq. (5.11) we have also retained the population terms, neglecting the coherences.

Equations (5.10) and (5.11) may be easily solved. As indicated in Section IV, the signal is given by Eqs. (4.9), (4.10), and (4.11) with $\mathscr{G}$ being the Green function of the Smoluchowski equations. We assume that the aggregate is excited by a short pulse with duration $t_p \ll \tau_p$, so that in calculating the signal $\tilde{\mathscr{C}}(t,t')$ for $t,t' \gg t_p, \tau_c$ we can neglect the short-time (Raman) component $\tilde{\mathscr{C}}^{(R)}$. Evolution on the first time interval defined by Eq. (5.10) and represented by Green functions $\mathscr{G}(\tau - \tau')$ and $\mathscr{G}(\tau' - \tau)$ in Eq. (4.11) gives the initial condition for the evolution of populations. Evolution on the second time interval can be described in the following way. The solution of Eq. (5.11) connects the intermolecular coherences to the populations,

$$\begin{aligned}\rho_{mn}(\mathbf{q},\tau) = i \int_0^\infty d\tau' \, \exp\Big[& -i(E_m - E_n)\tau' \\ & + i \sum 2\lambda_\alpha (\overline{d}_{m,\alpha} - \overline{d}_{n,\alpha}) q_\alpha \tau' \Big] J_{mn} \\ & \times [\rho_{mm}(\mathbf{q},\tau) - \rho_{nn}(\mathbf{q},\tau)], \quad m \neq n.\end{aligned} \tag{5.12}$$

[Here we have invoked the Markovian approximation substituting $\rho(\mathbf{q},\tau)$ for $\rho(\mathbf{q},\tau - \tau')$ in the rhs]. Substituting Eq. (5.12) into Eq. (5.8) for $m = n$, we obtain a closed equation for the populations which together with Eq. (5.12) defines the evolution of the excited states wavepackets during the second time interval. Evolution on the last time interval given by Eq. (5.10) connects the signal to the population wavepackets.

Since in this case $\tilde{\mathscr{C}}_{mn}$ vanishes when $m \neq n$, the fluorescence signal only depends on electronic populations and we have

$$
\begin{aligned}
\tilde{\mathscr{C}}(t,t') &= \sum_m \mu_m^2 \\
&\quad \times \int d\mathbf{q}\, \exp\left[-i\left(E_m - \sum_\alpha 2\lambda_\alpha \overline{d_{m,\alpha}} q_\alpha\right)(t-t')\right] \\
&\quad \times \rho_{mn}(\mathbf{q},t).
\end{aligned} \tag{5.13}
$$

The electronic population wavepackets are obtained by solving the master equation

$$
\begin{aligned}
\frac{d\rho_{mm}(\mathbf{q},\tau)}{d\tau}
&= \sum_\alpha \overline{\Lambda}_\alpha \frac{\partial}{\partial q_\alpha}\left[(q_\alpha - \overline{d_{m,\alpha}}) + \left(\frac{\Delta_\alpha}{2\lambda_\alpha}\right)^2 \frac{\partial}{\partial q_\alpha}\right]\rho_{mm}(\mathbf{q},\tau) \\
&\quad + \sum_n 2\pi |J_{mn}|^2 \delta\left[E_m - E_n - \sum_\alpha 2\lambda_\alpha(\overline{d_{m,\alpha}} - \overline{d_{n,\alpha}}) q_\alpha\right] \\
&\quad \times [\rho_{nn}(\mathbf{q},\tau) - \rho_{mm}(\mathbf{q},\tau)],
\end{aligned} \tag{5.14}
$$

with the initial condition

$$
\begin{aligned}
\rho_{mm}(\mathbf{q},\tau=0) &= \int_{-\infty}^{\infty} d\tau'' \int_{-\infty}^{\infty} d\tau' \\
&\quad \times \exp\left[i\left(E_m - \sum_\alpha 2\lambda_\alpha \overline{d_{m,\alpha}} q_\alpha\right)\right. \\
&\quad \left. \times (\tau'' - \tau')\right] \varepsilon_m(\tau'') \varepsilon_m^*(\tau') \rho_g(\mathbf{q}).
\end{aligned} \tag{5.15}
$$

Here $\rho_g(\mathbf{q})$ is the ground state equilibrium wavepacket given by

$$
\rho_g(\mathbf{q}) = \prod_\alpha \frac{2\lambda_\alpha}{\sqrt{2\pi}\Delta_\alpha} \exp\left[-\frac{1}{2}\left(\frac{2\lambda_\alpha}{\Delta_\alpha}\right)^2 q_\alpha^2\right]. \tag{5.16}
$$

Equation (5.13) expresses the signal in terms of $\rho_{mm}(\mathbf{q})$, which is obtained by solving a master equation for electronic populations [Eq. (5.14)] with the initial conditions, Eq. (5.15). The last term in Eq. (5.14) represents the coordinate-dependent transition rate between states n and m. The δ-function signifies that the transition in this approximation takes place only on the curve crossing surface, whereby the energies of both electronic states dressed by the nuclei are degenerate. Assuming a single coordinate q_α, this equation coincides with the result of Zusman[43] and the curve crossing surface is then a point. In the next section we will apply the Gaussian wavepacket approach for the solution of Eq. (5.14).

VI. GAUSSIAN WAVEPACKETS AND THE TIME-DEPENDENT FORSTER RATE

In this section we calculate the fluorescence signal [Eqs. (5.13)–(5.15)] using the Gaussian ansatz [Eq. (4.13)] for the wavepackets $\rho_{mm}(\mathbf{q})$. We assume that each molecule is coupled to its own bath described by a single overdamped mode, and that the various baths are uncorrelated. The wavepacket coordinates will be denoted $\mathbf{x}=(q_1,\dots,q_N)$ where N is the number of molecules. In this case we can use a simplified Gaussian ansatz given by Eq. (4.13) for $m=n$ (since we are dealing with population wavepackets only), taking the matrices σ_{mm} to be diagonal, i.e., $(\sigma_{mm})_{ij}=\delta_{ij}\sigma_{mm,j}$. The equations of motion for the parameters a_{mm}, $q_{mm,j}$, and $\sigma_{mm,j}$ can be obtained by substituting Eq. (5.14) into Eqs. (D1), (D2), and Eq. (D3) for $\alpha=\beta$. The fluorescence signal is expressed in terms of these parameters by substituting Eq. (4.13) into Eq. (5.13). To obtain the initial conditions for these parameters we calculate the zeroth, the first, and the second moments of the collective coordinates for the initial wavepackets [Eq. (5.15)]. This yields the following expression for the signal:

$$
\begin{aligned}
\tilde{\mathscr{C}}(t,t') &= \sum_m \mu_m^2 a_{mm}(t) \exp\{-i[E_m - 2\lambda_m q_{mm,m}(t)] \\
&\quad \times (t-t')\} \exp\left\{-\frac{1}{2}(2\lambda_m)^2 \sigma_{mm,m}(t)(t-t')^2\right\}.
\end{aligned} \tag{6.1}
$$

The equations of motion for the populations $a_{nn}\equiv\int d\mathbf{q}\rho_{nn}(\mathbf{q})$ are

$$
\frac{da_{mm}}{d\tau} = \sum_n W_{mn}(\tau) a_{nn} - \sum_n W_{nm}(\tau) a_{mm}, \tag{6.2}
$$

with

$$
\begin{aligned}
W_{mn}(\tau) &\equiv |J_{mn}|^2 \left[\frac{2\pi}{(2\lambda_m)^2 \sigma_{nn,m} + (2\lambda_n)^2 \sigma_{nn,n}}\right]^{1/2} \\
&\quad \times \exp\left[-\frac{1}{2}\frac{(E_m - 2\lambda_m q_{nn,m} - E_n + 2\lambda_n q_{nn,n})^2}{(2\lambda_m)^2 \sigma_{nn,m} + (2\lambda_n)^2 \sigma_{nn,n}}\right].
\end{aligned} \tag{6.3}
$$

Here the rates $W_{mn}(\tau)$ depend on time through the time evolution of the parameters $\eta\equiv(q_{nn,j}(\tau),\sigma_{nn,j}(\tau))$. Closed equations of motion for these parameters are given in Appendix E.

To obtain an expression for the time-dependent rate $W(\tau)$ which closely resembles the Forster's formula[26] we make a further approximation based on the following observation. The initial conditions [Eq. (E8)] for the wavepacket parameters $q_{mm,j}$ and $\sigma_{mm,j}$ for $j \neq m$ are represented by their equilibrium values $q_{mm,j}(0)=0$ and $\sigma_{mm,j}(0) = (\Delta_j/2\lambda_j)^2$. Neglecting in Eqs. (E1) and (E4) the intermolecular-interactions-induced terms we obtain

$$
q_{mm,j}(\tau)=0, \quad \sigma_{mm,j}(\tau) = \left(\frac{\Delta_j}{2\lambda_j}\right)^2. \tag{6.4}
$$

The set of evolving wavepacket parameters is now represented by $\eta=(q_{nn,n},\sigma_{nn,n})$. Substituting Eq. (6.4) into Eqs. (E2) and (E5) we obtain a closed system of equations that describe the dynamics of wavepackets parameters $q_{nn,n}$ and $\sigma_{nn,n}$. This system can be alternatively derived by making a simplified Gaussian ansatz using Eq. (6.4) for $\sigma_{mm,j}$ and $q_{mm,j}$ for $j \neq m$ and only allowing the evolution of the parameters $q_{mm,m}$ and $\sigma_{mm,m}$. The expression for the time-dependent rate [Eq. (6.3)] under this approximation adopts a form:

$$W_{mn}(\tau)=|J_{mn}|^2\left[\frac{2\pi}{\Delta_m^2+(2\lambda_n)^2\sigma_{nn,n}(\tau)}\right]^{1/2}\times\exp\left\{-\frac{1}{2}\frac{[E_n-E_m-2\lambda_n q_{nn,n}(\tau)]^2}{\Delta_m^2+(2\lambda_n)^2\sigma_{nn,n}(\tau)}\right\}. \tag{6.5}$$

This result can be represented in a form that closely resembles Forster's rate,

$$W_{mn}(\tau)=|J_{mn}|^2\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}f_m(\omega)f_n'(\omega;\tau). \tag{6.6}$$

The rate is given by the overlap of absorption $f_m(\omega)$,

$$f_m(\omega)=\left(\frac{2\pi}{\Delta_m^2}\right)^{1/2}\exp\left[-\frac{(\omega-E_m)^2}{2\Delta_m^2}\right], \tag{6.7}$$

and time-dependent fluorescence $f_n'(\omega;\tau)$,

$$f_n'(\omega;\tau)=\left[\frac{2\pi}{(2\lambda_n)^2\sigma_{nn,n}(\tau)}\right]^{1/2}\times\exp\left\{-\frac{1}{2}\frac{[\omega-E_n-2\lambda_n q_{nn,n}(\tau)]^2}{(2\lambda_n)^2\sigma_{nn,n}(\tau)}\right\}. \tag{6.8}$$

These lineshapes are normalized to a unit area:

$$\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}f_m(\omega)=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}f_n'(\omega;\tau)=1. \tag{6.9}$$

In the Forster's limit $J^2/\Delta \ll \Lambda$ the wavepacket parameters equilibrate much faster than the population dynamics, and upon substituting the equilibrium values $q_{mm,n}=\delta_{mn}, \sigma_{mm,n}=(\Delta_m/2\lambda_m)^2$ into Eq. (6.3) we obtain the Forster time-independent rate,

$$W_{mn}=|J_{mn}|^2\left(\frac{2\pi}{\Delta_m^2+\Delta_n^2}\right)^{1/2}\exp\left[-\frac{1}{2}\frac{(E_n-2\lambda_n-E_m)^2}{\Delta_m^2+\Delta_n^2}\right]. \tag{6.10}$$

This rate can be obtained from Eq. (6.6) upon substitution of the spectral-diffusion forms of the absorption $f_m(\omega)$ [Eq. (6.7)] and the relaxed fluorescence spectra $f_n'(\omega)$,

$$f_n'(\omega)=\left(\frac{2\pi}{\Delta_n^2}\right)^2\exp\left[-\frac{(\omega-E_n+2\lambda_n)^2}{2\Delta_n^2}\right]. \tag{6.11}$$

$f_n'(\omega)$ is the relaxed (long-time) form of Eq. (6.8) with $q_{mm,m}=1, \sigma_{nn,n}=(\Delta_n/2\lambda_n)^2$.

Equation (6.2) generalizes Forster's equations to account for finite nuclear relaxation rates (compared with the transfer rate). This results in time-dependent rates associated with the nonequilibrium nuclear wavepackets.

In concluding this section, we shall consider a simpler approximation. Neglecting intermolecular coupling in the equations of motion for the wavepacket parameters $q_{nn,n}$ and $\sigma_{nn,n}$ [Eqs. (E2) and (E5)] (which means that we neglect the influence of J on the evolution of the form of wavepackets, retaining its influence on the evolution of populations), we can solve these equations and obtain

$$q_{nn,n}(\tau)=1+[q_{nn,n}(0)-1]\exp(-\overline{\Lambda}_n\tau),$$
$$\sigma_{nn,n}(\tau)=\left(\frac{\Delta_n}{2\lambda_n}\right)^2+\left[\sigma_{nn,n}(0)-\left(\frac{\Delta_n}{2\lambda_n}\right)^2\right]\exp(-2\overline{\Lambda}_n\tau). \tag{6.12}$$

Substituting Eq. (6.12) into Eq. (6.5) or into Eqs. (6.6) and (6.8) we obtain an explicit expression for $W_{mn}(\tau)$.[45] Similar expressions for $W(\tau)$ based on the Fermi Golden Rule were presented in Ref. 46. It should be noted further that Eqs. (6.10) and (6.5) reproduce the rate in the nonadiabatic limit i.e., to (large J) second order in J. Equations (5.14) or (6.3), however, can interpolate between the nonadiabatic and the adiabatic limits.[47]

VII. DISCUSSION

This paper is focused on theoretical modeling of ultrafast electronic and nuclear motions in molecular aggregates that can be probed by various femtosecond spectroscopic techniques. Although we gave explicit expressions only for time- and frequency-resolved fluorescence, the Green functions obtained here can be used in the calculation of numerous other nonlinear techniques such as pump-probe and photon echo.

Given the macroscopic number of solvent degrees of freedom, ultrafast dynamics of aggregates is a complex many-body problem. When the coupling to the bath is not weak, and perturbative many-body techniques are not applicable, the only practical way to treat the problem is by using a reduced description based on keeping a few relevant collective bath coordinates.

The simplest reduction schemes only retains electronic variables. This leads to equations of motion that adopt a form of the master, Boltzmann, Redfield, or Forster equations.[11,20–23,26–29] In all of these cases, it is assumed that the bath relaxation time is much faster than the exciton dynamics timescale. This assumption usually fails in the case of femtosecond energy transfer in biological systems, and one needs to keep at least those bath variables whose relaxation times are comparable to the exciton transport timescale; only the faster bath degrees of freedom can be eliminated. In the case of a harmonic bath linearly coupled to the electronic system, all relevant bath information is contained in the matrix of spectral densities [Eq. (2.2)] that represents the antisymmetrized correlation functions [Eq. (2.4)] of collective coordinates [Eq. (2.3)] which couple the bath to the electronic variables. In the case of a Gaussian-Markovian (GM) spectral density [given by Eq. (2.24) for $N_0=1$] such a correlation function decays exponentially in time and can be modeled by a single stochastic variable. Since any spectral density can be approximated by a superposition of GM spectral densities (which amount to a discrete Laplace transform), the antisymmetrized correlation functions of the collective coordinate can be modeled by a set of stochastic variables. However, an important result of the present paper is that to describe the exciton dynamics one needs to model not only the antisymmetrized correlation functions of collective coordinates but the symmetrized ones as well. The latter depend on temperature and contain infinite sums involving Matsubara frequencies $2\pi nkT/\hbar, n=1,2,\ldots$ [see Eq. (2.26)]. As can be seen from Eq. (2.26), each term in the infinite sum is represented by a stochastic variable with the correlation time given by the inverse Matsubara frequency $2\pi nkT/\hbar$. This implies that the Matsubara frequencies constitute a set of additional relaxation rates. In practice it should be possible to keep only a finite number of stochastic variables representing the Matsubara frequencies with $n \leqslant N_0$ where $(2\pi N_0 kT/\hbar)^{-1}$ is equal to the fastest system timescale.

When the temperature is sufficiently high, i.e., when even the first Matsubara correlation time $(2\pi nkT/\hbar)^{-1}$ is fast, one does not need to incorporate stochastic variables representing the Matsubara frequencies, and the bath is described on the classical level. On the other hand, even if the bath is infinitely fast on the classical level [this corresponds to the case $\Lambda_\alpha \rightarrow \infty$ in Eq. (2.24)], its relaxation time may not be faster than $(2\pi kT/\hbar)^{-1}$; this is a quantum effect that naturally becomes stronger at lower temperatures.

The approach presented in the paper is based on calculating the relevant (antisymmetrized and symmetrized) correlation functions of collective coordinates using the given spectral densities (which may be obtained either from experiment or theory) and modeling them with correlation functions of a set of effective collective variables evolving with closed equations using an effective Liouville operator. The modeling procedure is not unique and we have developed a hierarchy of reduction schemes and provided guidance as to how to choose an adequate reduced description scheme in each case.

The hierarchy of reduced reduction schemes is depicted in Fig. 1. Each box represents a different level of reduction, the first line in a box is a list of variables, the second line represents the values assumed by indices, and the third line shows the total number of bath variables. A solid line with an arrow means a unique transformation, a dashed line represents a non-unique transformation.

Case (1) in Fig. 1 is the full description of the nuclear variables represented by a set of oscillator variables p_j', p_j' with the Hamiltonian given by Eq. (2.1). In Case (2) the bath oscillators are represented by a few primary oscillators $P_a Q_a$ coupled to the electronic system and a macroscopic set of solvent oscillator variables p_{aj}, q_{aj} coupled to the primary oscillators. In Case (1) the relevant properties of the bath are given by the matrix $C_{mn,kl}(\omega)$ [Eq. (2.2)], in Case (2) they are given by spectral densities $J_a(\omega)$ [Eq. (2.8)]. The transformations $(2) \rightarrow (1)$ is unique and given by Eq. (2.11). The transformation $(1) \rightarrow (2)$ is not unique. The description (2) is useful since the spectral densities $C_{mn,kl}(\omega)$ typically have a set of maxima related to coherent nuclear motions coupled to solvent degrees of freedom. Level (2) is very convenient formally for modeling a spectral density with a set of maxima. As shown in Section II, Case (2) can be successfully modeled by a reduction scheme (3) based on introducing a finite set of stochastic variables $q_{aj_a}^{(c)}$ instead of a macroscopic set of solvent variables. The spectral densities $J_a(\omega)$ describing the coupling of solvent variables to the primary modes should be modeled in the form of Eq. (2.24).

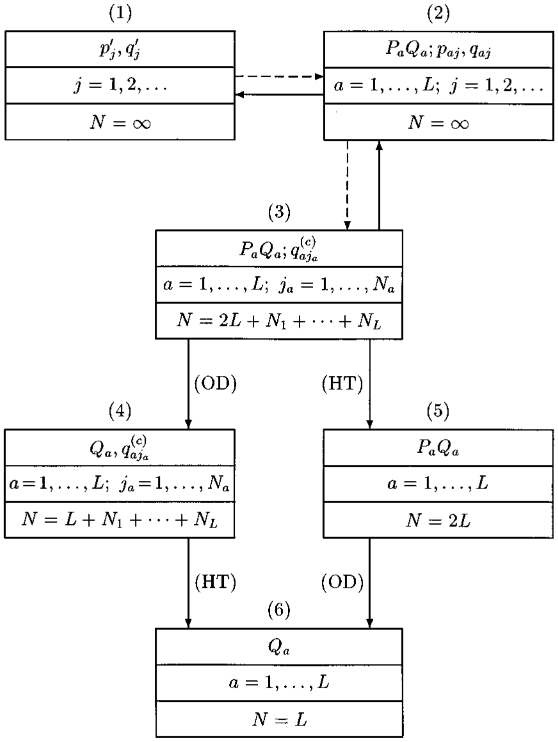

FIG. 1. The hierarchy of reduction schemes considered in the paper. The first line in a box is a list of variables representing nuclear motions; the second line shows the values assumed by the indices; the third line gives the total number of reduced variables. A solid line represents a unique transformation; a dashed line stands for a non-unique transformation. OD and HT denote reductions due to overdamped motion of primary oscillators (OD) or the high temperature limit (HT).

The equation of motion for the reduced wavepackets adopts the form of Eq. (2.30). As shown in Section II, the number of Matsubara variables N_1 is given by $N_1 \sim \hbar\Omega/kT$ and is manageable provided the temperature is not too low. It is not possible to use a fast bath $\Lambda \gg \Omega$ for modeling in a situation $\hbar\Omega \sim kT$, since one needs to incorporate the Matsubara oscillators with $nkT < \hbar\Lambda$ which will increase the number of collective variables.

When the spectral densities $C(\omega)$ do not have strong features one can model directly the spectral densities $C(\omega)$ as a superposition of overdamped contributions [Eq. (3.6)]. This leads to level (4) in terms of variables Q_a, Q_{as} (Q_{as} are denoted as $q_{aj_a}^{(c)}$ in Fig. 1), and the resulting equation of motion for reduced wavepackets is Eq. (3.7). In Section III the reduction has been obtained by modeling the spectral densities of Eq. (3.6) directly, however, it can be alternatively derived by eliminating the fast momentum variables P_a in case (3) when the primary oscillators are overdamped.

When $\hbar\Omega_a < kT$ (high temperature limit) all secondary variables can be eliminated; this leads to level (5) retaining only the primary variables P_a, Q_a. The resulting equation of motion is the multi-state Fokker-Planck equation [Eq. (3.4)]. Again this level can be obtained in two ways: starting either with (3), or directly with (2), and eliminating the secondary variables. Finally, level (6) is obtained by assuming both the high temperature limit and overdamped primary oscillators. The reduced wavepacket which depends on the variables Q_a satisfy the multi-state Smoluchowski equation [Eq. (3.5)]. This can be derived by either taking the high temperature limit of (4) and eliminating the Matsubara variables Q_{as}, or by applying the overdamped limit to (5) and eliminating the fast variables P_a in a standard way.[19]

The hierarchy of Fig. 1 is related to various reduction schemes with respect to nuclear variables. Reduction of electronic variables (e.g., elimination of electronic coherences) can be obtained at all levels of this hierarchy, provided exciton-phonon interaction is weak (Redfield theory) or intermolecular coupling is small (Forster theory).

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APPENDIX A: CANONICAL TRANSFORMATIONS IN LIOUIVILLE SPACE AND THE GENERALIZED FOKKER-PLANCK EQUATION

In this appendix we present the details of the canonical transformation introduced in Section II [Eqs. (2.14)–(2.16)] and give the values of the parameters D,D,A, and B in Eq. (3.9) which generalizes Eq. (2.30) to an arbitrary number of primary oscillators.

The motivation for performing a canonical transformation is the following. As can be seen from Eqs. (2.5)–(2.7), the Liouville operator $L_{ep} \equiv H_{ep-}$ related to the Hamiltonian $\hat{H}_{ep}$ in the case of a single primary oscillator can be written in a form

$$L_{ep} = \frac{1}{M} P_+ P_- + V_-(\hat{Q}) + \sum_j \left[\frac{p_{j+} p_{j-}}{m_j} + m_j \omega_j^2 \left(q_{j+} - \frac{c_j}{m_j \omega_j^2} Q_+ \right) \times \left(q_{j-} - \frac{c_j}{m_j \omega_j^2} Q_- \right) \right], \tag{A1}$$

where we have used the notation introduced in Eq. (2.12). The system-bath interaction involves the (commuting) bath superoperators q_{j+} and q_{j-}. Our goal is to obtain a reduced description in terms of wavepackets that depend on collective coordinates alone (no collective momenta). However, the algebra of superoperators $p_{j\pm}$ and $q_{j\pm}$ can be represented in the space of wavepackets which depend on coordinates and momenta (the Wigner representation). On the other hand, the superoperators p_{j-} and q_{k+} form a closed algebra with $[p_{j-}, q_{k+}] = -i\delta_{jk}$ which can be represented in the space of wavepackets depending on coordinates alone. However, to apply this representation one should recast the system-bath interaction in a form which involves the operators p_{j-} and q_{j+}, not q_{j-} and q_{j+}. This can be achieved by applying the canonical transformation in Liouville space represented by Eqs. (2.14)–(2.16).

A quantum canonical transformation in the Schrödinger space is a linear unitary transformation $\hat{U}_0$ in the space of states. It must be unitary to conserve the basic structure of the space of states, i.e., the scalar product. The basic structure of the Liouville space is the trace. A canonical transformation in Schrödinger space generates a canonical transformation U acting in Liouville space defined as

$$U\hat{\rho} \equiv \hat{U}^+ \hat{\rho} U, \tag{A2}$$

which conserves the trace, i.e., $\mathrm{Tr}(U\hat{\rho}) = \mathrm{Tr}\, \hat{\rho}$. However, one can use a more general class of transformations than Eq. (A2) which consists of all linear invertible trace-conserving operators U acting in Liouville space [see Eqs. (2.14) and (2.15)]. One can apply a canonical transformation to operators, such a transformation should satisfy the property given by Eq. (2.18); this leads to the definition given by Eq. (2.17).

Consider a canonical transformation U defined by Eq. (2.16) which satisfies Eq. (2.15). Applying Eq. (2.17) to our basic operators we obtain

$$Q'_\pm = Q_\pm, \quad p'_{j\pm} = p_{j\pm}, \quad q'_{j-} = q_{j-}, \quad P'_+ = P_+, \\ q'_{j+} = q_{j+} - \frac{c_j}{m_j \omega_j^2} Q_+, \quad P'_- = P_- + \sum_j \frac{c_j}{m_j \omega_j^2} p_{j-}. \tag{A3}$$

The Liouville operator L_{ep} from Eq. (A1) written in transformed variables adopts the form of Eq. (2.19) where we omitted the primes. The system-bath interaction in Eq. (2.19) involves the superoperators p_{j-} and q_{j+} only [see Eq. (2.21)]. The equation of motion [Eq. (2.30)] is derived in Section II starting with Eq. (2.19).

Generalization of Eq. (2.30) to include an arbitrary number of primary oscillators is straightforward. Consider Eq. (2.30) with L primary oscillators described by the variables P_a, Q_a with $a = 1,\ldots,L$. Instead of Greek indices we need to use double indices $a\alpha$, where a denotes the primary oscillator coupled to the secondary variables $q_{a\alpha}$, $\alpha = 1,\ldots,N_a$. The equation of motion has a form of Eq. (3.9). The vector $\mathbf{x}$ of variables $x_\alpha, \alpha = 1,\ldots,2L + N_1 + \cdots + N_L$ is given by $\mathbf{x} = (P_1, Q_1, q_{11}, \ldots, q_{1N_1}; P_2, Q_2, q_{21}, \ldots, q_{2N_2}; \ldots; P_L, Q_L, q_{L1}, \ldots, q_{LN_L})$. The non-zero components of D and D are

$$D_{mn,\mu(a)} = \bar{D}_{mn,\mu(a)+1} \equiv M_a \Omega_a^2 d_{mn,a}, \tag{A4}$$

with

$$\mu(a) \equiv 2(a-1) + N_1 + \ldots + N_{a-1} + 1. \tag{A5}$$

Non-zero components of B have the form

$$B_{\nu(a,\alpha)} \equiv \Lambda_{a\alpha} \sigma_{a\alpha}, \tag{A6}$$

with $0 < \alpha \leqslant N_a$ and

$$\nu(a,\alpha) \equiv 2(a-1) + N_1 + \cdots + N_{a-1} + \alpha + 2. \tag{A7}$$

The non-zero components of A are

$$A_{\mu(a)+1,\mu(a)} \equiv -\frac{1}{M_a}, \quad A_{\mu(a),\mu(a)+1} \equiv M_a \Omega_a^2, \\ A_{\mu(a),\nu(a,\alpha)} = -1, \quad A_{\nu(a,\alpha),\mu(a)} = \gamma_{a\alpha} \Lambda_{a\alpha}, \\ A_{\nu(a,\alpha),\nu(a,\alpha)} = \Lambda_{a\alpha}. \tag{A8}$$

APPENDIX B: DERIVATION OF THE MULTISTATE FOKKER-PLANCK AND SMOLUCHOWSKI EQUATIONS

In this appendix we outline the derivation of the multistate Fokker-Planck [Eq. (3.4)] and multistate Smoluchowski [Eq. (3.5)] equations.

In the high temperature limit for the Ohmic spectral density [Eq. (3.1)] the evolution can be described by the multistate Fokker-Planck equation,[36] which can be rederived using the scheme of Section II as follows.

Adopting the Wigner representation for primary oscillators, we introduce the reduced wavepackets $\hat{\rho}(\mathbf{P},\mathbf{Q})$ which are operators in the electronic space; the operators $P_{a\pm}, Q_{a\pm}$ in this representation are

$$P_{a-} \equiv -i\frac{\partial}{\partial Q_a}, \quad P_{a+} \equiv P_a,$$
$$Q_{a-} \equiv i\frac{\partial}{\partial P_a}, \quad Q_{a+} \equiv Q_a. \tag{B1}$$

Consider the Liouville operator L_0 given by Eq. (3.3) that acts in the space of reduced wavepackets $\hat{\rho}(\mathbf{P},\mathbf{Q})$. The equilibrium reduced wavepacket is the stationary point of the Liouville equation with the Liouville operator L_0, it has the form

$$\rho_g(\mathbf{P},\mathbf{Q}) = \prod_a \frac{\Omega_a}{2\pi kT} \exp\left[-\left(\frac{P_a^2}{2M_a kT} + \frac{M_a\Omega_a^2 Q_a^2}{2kT} \right) \right]. \tag{B2}$$

A straightforward calculation shows that the Liouville space Green functions of the superoperators $P_{a\pm}, Q_{a\pm}$ in the reduced system calculated with respect to the equilibrium density matrix of Eq. (B2) reproduce the high temperature limit for the Green function of the corresponding superoperators in the complete Liouville space, with the Liouville operator

$$\begin{aligned} L_0' = \sum_a & \left(\frac{1}{M} P_{a+}P_{a-} + M_a\Omega_a^2 Q_{a+}Q_{a-} \right) \\ & + \sum_j \left[\frac{1}{m_{ja}} p_{ja+}p_{ja-} \right. \\ & - m_{ja}\omega_{ja}^2 \left(q_{ja+} - \frac{c_{ja}}{m_{ja}\omega_{ja}^2} Q_{a+} \right) \\ & \left. \times \left(q_{ja-} - \frac{c_{ja}}{m_{ja}\omega_{ja}^2} Q_{a-} \right) \right]. \end{aligned} \tag{B3}$$

Since the secondary-oscillator variables are not involved in interactions with electronic degrees of freedom, this immediately yields the multi-state Fokker-Plank equation [Eq. (3.4)].

Equation (3.4) can be also written in a form of Eq. (3.9). In this case, the vector $\mathbf{x}$ of the variables $x_\alpha, \alpha = 1,\ldots,2L$ is given by $\mathbf{x} = (P_1, Q_1, \ldots, P_L, Q_L)$ and non-zero components of D, D, A, and B are given by

$$D_{mn,2a-1} = \overline{D}_{mn,2a} = M_a\Omega_a^2 d_{mn,a},$$
$$A_{2a,2a-1} = -\frac{1}{M_a}, \quad A_{2a-1,2a} = M_a\Omega_a^2, \tag{B4}$$
$$A_{2a-1,2a-1} = \gamma_a, \quad B_{2a-1} = \gamma_a M_a kT.$$

To derive the multistate Smoluchowski equation we represent the matrix of spectral densities in the overdamped limit in a form

$$C_{mn,kl}(\omega) = 2\sum_a d_{a,mn} d_{a,kl} \frac{M_a\Omega_a^2}{2} \frac{\omega(\Omega_a^2/\gamma_a)}{\omega^2 + (\Omega_a^2/\gamma_a)^2}. \tag{B5}$$

Since the nuclear variables in Eqs. (2.1) and (2.6) are connected by a linear canonical transformation we have

$$\hat{Q}_a = \sum_j \overline{c_{aj}} \hat{q}_j', \tag{B6}$$

and comparing the last terms in Eqs. (2.1)–(2.6) we obtain

$$d_{j,mn}' = \sum_a \frac{d_{a,mn} M_a \Omega_a^2}{m_j' \omega_j'^2} \overline{c_{aj}}. \tag{B7}$$

Combining Eqs. (2.2), (B5), and (B7) yields

$$\overline{J_{ab}}(\omega) = \delta_{ab} \frac{1}{M_a\Omega_a^2} \frac{\omega(\Omega_a^2/\gamma_a)}{\omega^2 + (\Omega_a^2/\gamma_a)^2}, \tag{B8}$$

where

$$\overline{J_{ab}}(\omega) \equiv \sum_j \frac{\overline{c_{aj}}\,\overline{c_{bj}}}{4m_j'\omega_j'} 2\pi[\delta(\omega - \omega_j') - \delta(\omega + \omega_j')]. \tag{B9}$$

Equations (B6)–(B9) imply the following form of the correlation functions of $Q_{a\pm}$ operators in a system were the coupling of the electronic degrees of freedom to the nuclear is neglected,

$$\langle Q_{a+}(\tau) Q_{b+}(0) \rangle = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \overline{J_{ab}}(\omega) \coth\left(\frac{\omega}{2kT} \right) \cos(\omega\tau), \tag{B10}$$

$$\langle Q_{a+}(\tau) Q_{b-}(0) \rangle = -i\theta(\tau) \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} 2\overline{J_{ab}}(\omega) \sin(\omega\tau). \tag{B11}$$

The Liouville space operator $L \equiv H_{ep-}$ corresponding to the Hamiltonian $\hat{H}_{ep}$ of Eq. (2.1) can be presented in a form

$$L = L_e + L_B + L_{int}, \tag{B12}$$

with $L_e \equiv H_{e-}$ and

$$\begin{aligned} L_B & \equiv \sum_j \frac{1}{m_j'} p_{j+}' p_{j-}' + m_j' \omega_j'^2 q_{j+}' q_{j-}', \\ L_{int} & = -\sum_{amn} M_a\Omega_a^2 d_{a,mn} (B_m^+ B_n)_+ Q_{a-} \\ & \quad - \sum_{amn} M_a\Omega_a^2 d_{a,mn} (B_m^+ B_n)_- Q_{a+}. \end{aligned} \tag{B13}$$

The interaction of the bath with the electronic degrees of freedom involves the operators $Q_{a\pm}$ only. The correlation functions of these operators with respect to the Liouville operator L_B [Eq. (B13)] are given by Eqs. (B10) and (B11) and in the high-temperature limit adopt a form

$$\langle Q_{a+}(\tau)Q_{b+}(0)\rangle=\delta_{ab}\frac{kT}{M_a\Omega_a^2}\ \exp[-(\Omega_a^2/\gamma_a)|\tau|], \tag{B14}$$

$$\langle Q_{a+}(\tau)Q_{b-}(0)\rangle=-i\,\delta_{ab}\theta(\tau)\frac{\Omega_a^2/\gamma_a}{M_a\Omega_a^2}\ \exp[-(\Omega_a^2/\gamma_a)\tau]. \tag{B15}$$

These can be modeled as correlation functions of the operators

$$Q_{a+}\equiv Q_a,\quad Q_{a-}\equiv i\frac{\Omega_a^2/\gamma_a}{M_a\Omega_a^2}\frac{\partial}{\partial Q_a}, \tag{B16}$$

which act in the space of wavepackets $\rho(\mathbf{Q})$ with the free-bath Liouville operator L_B of a form

$$L_B=i\sum_a\frac{\partial}{\partial Q_a}\left(Q_a+\frac{kT}{M_a\Omega_a^2}\frac{\partial}{\partial Q_a}\right). \tag{B17}$$

Substituting Eq. (B17) into Eq. (B12) yields the Liouville operator L in a form

$$\begin{aligned}L=L_e&-\sum_{mna}M_a\Omega_a^2 d_{a,mn}Q_a(B_m^+B_n)_-\\&-i\sum_{mna}\frac{\Omega_a^2}{\gamma_a}d_{a,mn}(B_m^+B_n)_+\frac{\partial}{\partial Q_a}\\&+i\sum_a\frac{\Omega_a^2}{\gamma_a}\frac{\partial}{\partial Q_a}\left(Q_a+\frac{kT}{M_a\Omega_a^2}\frac{\partial}{\partial Q_a}\right).\end{aligned} \tag{B18}$$

By including the external field, the Liouville equation with L given by Eq. (B18) yields the multi-state Smoluchowski equation [Eq. (3.5)] that can also be represented in the form of Eq. (3.9)

In the case described by Eq. (3.5) the vector of $\mathbf{x}$ of variables $x_\alpha,\alpha=1,\dots,L$ is represented by $\mathbf{x}=(Q_1,\dots,Q_L)$ with the parameters of Eq. (3.9) given by

$$\begin{aligned}&D_{mn,a}=\frac{\Omega_a^2}{\gamma_a}d_{mn,a},\quad \overline{D}_{mn,a}=M_a\Omega_a^2 d_{mn,a},\\&A_{aa}=\frac{\Omega_a^2}{\gamma_a},\quad B_a=\frac{kT}{\gamma_a M_a}.\end{aligned} \tag{B19}$$

APPENDIX C: EQUATIONS OF MOTION FOR OVERDAMPED PRIMARY MODES

In this appendix we develop a reduction scheme which applies when the primary bath oscillators are overdamped, but, the temperature is not necessarily high.

The derivation follows the steps used in obtaining the Smoluchowski equation (see Appendix B). The only difference is that instead of calculating the Liouville space Green functions of the operators $Q_{a\pm}$ [Eqs. (B10) and (B11)] in the high temperature limit [leading to Eqs. (B14) and (B15)], we evaluate these correlation functions exactly, resulting in

$$\langle Q_{a+}(\tau)Q_{b+}(0)\rangle=\delta_{ab}\left[\overline{\sigma_a}\ \exp(-\overline{\Lambda}_a|\tau|)+\sum_{s=1}^{\infty}\overline{\sigma_{as}}\ \exp(-\overline{\Lambda}_{as}|\tau|)\right]. \tag{C1}$$

The correlation function $\langle Q_{a+}(\tau)Q_{b-}(0)\rangle$ still has a form of Eq. (B15) and $\langle Q_{a-}(\tau)Q_{b-}(0)\rangle=0$. The parameters $\overline{\sigma_a},\overline{\Lambda}_a,\overline{\sigma_{as}}$, and Λ_{as} are defined in Section III [Eqs. (3.8)]. To model the Green functions of Eqs. (C1) we introduce wavepackets depending on Q_a and additional coordinates Q_{as} representing the Matsubara frequencies terms in Eq. (C1) given by the sum over s. To model the correlation functions we define the operators Q_{a+} by

$$Q_{a+}=Q_a+\sum_{s=1}Q_{as}. \tag{C2}$$

The operators Q_{a-} have the form of Eq. (B16). The bath operator L_B should be taken in a form

$$\begin{aligned}L_B=&\,i\sum_{a=1}^{L}\overline{\Lambda}_a\frac{\partial}{\partial Q_a}\left(Q_a+\overline{\sigma_a}\frac{\partial}{\partial Q_a}\right)\\&+i\sum_{a=1}^{L}\sum_{s=1}^{N_a}\overline{\Lambda}_{as}\frac{\partial}{\partial Q_{as}}\left(Q_{as}+\overline{\sigma_{as}}\frac{\partial}{\partial Q_{as}}\right).\end{aligned} \tag{C3}$$

Strictly speaking, we need to use $N_a=\infty$ for $a=1,\dots,L$; however, in practice it is suffice enough to keep a finite number of Matsubara frequencies (see the discussion in Section II). Substituting the bath Liouville operator from Eq. (C3) into Eq. (B12) we obtain Eq. (3.7).

To represent Eq. (3.7) in a form of Eq. (3.9) we introduce the vector $\mathbf{x}$ of variables x_α, $\alpha=1,\dots,L+N_1+\dots+N_L$ by $\mathbf{x}=(Q_1,Q_{11},\dots,Q_{1N_1};Q_2,Q_{21},\dots,Q_{2N_2};\dots;Q_L,Q_{L1},\dots,Q_{LN_L})$. The non-zero components of D are

$$D_{mn,\nu(a)}=\frac{\Omega_a^2}{\gamma_a}d_{mn,a}, \tag{C4}$$

where

$$\nu(a)\equiv a+N_1+\cdots+N_{a-1}. \tag{C5}$$

For $\nu(a)\leqslant\alpha<\nu(a+1)$ we have

$$\overline{D}_{mn,\alpha}=M_a\Omega_a^2 d_{mn,a}. \tag{C6}$$

The non-zero components of A and B are

$$A_{\nu(a),\nu(a)}=\overline{\Lambda}_a,\quad B_{\nu(a)}=\overline{\Lambda}_a\overline{\sigma_a}, \tag{C7}$$

and

$$A_{\nu(a)+s,\nu(a)+s}=\overline{\Lambda}_{as},\quad B_{\nu(a)+s}=\overline{\Lambda}_{as}\overline{\sigma_{as}}, \tag{C8}$$

where $0<s<N_a$.

APPENDIX D: TIME EVOLUTION OF GAUSSIAN WAVEPACKETS IN PHASE SPACE

In this appendix we derive equations of motion for the parameters of the Gaussian wavepackets [Eq. (4.13)] assuming that Eq. (4.2) holds for the first and the second moments of collective coordinates x_α.

The time derivatives of the wavepacket parameters [Eq. (4.13)] are related to the time derivatives of its moments as follows:

$$\frac{da_{mn}}{d\tau} = \int d\mathbf{x} \frac{d\rho_{mn}(\mathbf{x})}{d\tau}, \tag{D1}$$

$$\frac{dx_{mn,\alpha}}{d\tau} = \frac{1}{a_{mn}} \int d\mathbf{x} x_\alpha \frac{d\rho_{mn}(\mathbf{x})}{d\tau} - \frac{1}{a_{mn}} x_{mn,\alpha} \int d\mathbf{x} \frac{d\rho_{mn}(\mathbf{x})}{d\tau}, \tag{D2}$$

$$\frac{d\sigma_{mn,\alpha\beta}}{d\tau} = \frac{1}{a_{mn}} \int d\mathbf{x} (x_\alpha - x_{mn,\alpha})(x_\beta - x_{mn,\beta}) \frac{d\rho_{mn}(\mathbf{x})}{d\tau} - \frac{1}{a_{mn}} \sigma_{mn,\alpha\beta} \int d\mathbf{x} \frac{d\rho_{mn}(\mathbf{x})}{d\tau}. \tag{D3}$$

Combining Eqs. (D1)–(D3) with Eq. (4.2), we obtain, after a straightforward calculation,

$$\frac{da_{mn}}{d\tau} = -i \sum_k (E_{mk} a_{kn} - E_{kn} a_{mk}) + i \sum_{k\mu} (\overline{D}_{mk,\mu} x_{kn,\mu} a_{kn} - \overline{D}_{kn,\mu} x_{mk,\mu} a_{mk}). \tag{D4}$$

The equations for the parameters $x_{mn,\alpha}$ have the form

$$\begin{aligned}\frac{dx_{mn,\alpha}}{d\tau} = {} & -\frac{i}{a_{mn}} \sum_k [E_{mk} a_{kn} (x_{kn,\alpha} - x_{mn,\alpha}) - E_{kn} a_{mk} (x_{mk,\alpha} - x_{mn,\alpha})] + \frac{1}{a_{mn}} \sum_k \frac{1}{2} (D_{mk,\alpha} a_{kn} + D_{kn,\alpha} a_{mk}) - \sum_\mu A_{\alpha\mu} x_{mn,\mu} \\ & + \frac{i}{a_{mn}} \sum_{k\mu} \overline{D}_{mk,\mu} [\sigma_{kn,\alpha\mu} + (x_{kn,\alpha} - x_{mn,\alpha}) x_{kn,\mu}] a_{kn} - \frac{i}{a_{mn}} \sum_{k\mu} \overline{D}_{kn,\mu} [\sigma_{mk,\alpha\mu} + (x_{mk,\alpha} - x_{mn,\alpha}) x_{mk,\mu}] a_{mk}.\end{aligned} \tag{D5}$$

Finally we have for the parameters $\sigma_{mn,\alpha\beta}$

$$\begin{aligned}\frac{d\sigma_{mn,\alpha\beta}}{d\tau} = {} & -\sum_\mu (A_{\alpha\mu} \sigma_{mn,\beta\mu} + A_{\beta\mu} \sigma_{mn,\alpha\mu}) + 2\delta_{\alpha\beta} B_\alpha - \frac{i}{a_{mn}} \sum_k E_{mk} a_{kn} [\sigma_{kn,\alpha\beta} - \sigma_{mn,\alpha\beta} + (x_{mn,\alpha} - x_{kn,\alpha})(x_{mn,\beta} \\ & - x_{kn,\beta})] + \frac{i}{a_{mn}} \sum_k E_{kn} a_{mk} [\sigma_{mk,\alpha\beta} - \sigma_{mn,\alpha\beta} + (x_{mn,\alpha} - x_{mk,\alpha})(x_{mn,\beta} - x_{mk,\beta})] + \frac{1}{a_{mn}} \sum_k \frac{1}{2} [D_{mk,\alpha} (x_{kn,\beta} \\ & - x_{mn,\beta}) + D_{mk,\beta} (x_{kn,\alpha} - x_{mn,\alpha})] a_{kn} + \frac{1}{a_{mn}} \sum_k \frac{1}{2} [D_{kn,\alpha} (x_{mk,\beta} - x_{mn,\beta}) + D_{kn,\beta} (x_{mk,\alpha} - x_{mn,\alpha})] a_{mk} \\ & + \frac{i}{a_{mn}} \sum_{k\mu} \overline{D}_{mk,\mu} [\sigma_{kn,\alpha\beta} (x_{kn,\mu} - x_{mn,\mu}) + \sigma_{kn,\alpha\mu} (x_{kn,\beta} - x_{mn,\beta}) + \sigma_{kn,\beta\mu} (x_{kn,\alpha} - x_{mn,\alpha}) + (\sigma_{kn,\alpha\beta} \\ & - \sigma_{mn,\alpha\beta}) x_{mn,\mu}] a_{kn} - \frac{i}{a_{mn}} \sum_{k\mu} \overline{D}_{kn,\mu} [\sigma_{mk,\alpha\beta} (x_{mk,\mu} - x_{mn,\mu}) + \sigma_{mk,\alpha\mu} (x_{mk,\beta} - x_{mn,\beta}) + \sigma_{mk,\beta\mu} (x_{mk,\alpha} - x_{mn,\alpha}) \\ & + (\sigma_{mk,\alpha\beta} - \sigma_{mn,\alpha\beta}) x_{mn,\mu}] a_{mk} + \frac{i}{a_{mn}} \sum_{k\mu} [\overline{D}_{mk,\mu} (x_{kn,\alpha} - x_{mn,\alpha})(x_{kn,\beta} - x_{mn,\beta}) x_{kn,\mu} a_{kn} - \overline{D}_{kn,\mu} (x_{mk,\alpha} - x_{mn,\alpha}) \\ & \times (x_{mk,\beta} - x_{mn,\beta}) x_{mk,\mu} a_{mk}].\end{aligned} \tag{D6}$$

APPENDIX E: EQUATIONS OF MOTION FOR WAVEPACKET PARAMETERS IN THE SPECTRAL DIFFUSION LIMIT

In this appendix we present equations of motion for the wavepacket parameters $\eta = (q_{nn,j}, \sigma_{nn,j})$ and the initial conditions which describe the evolution of the system in the spectral diffusion limit (see Section VI). The collective coordinates satisfy the equations

$$\begin{aligned}\frac{dq_{mm,j}}{d\tau} = {} & -\overline{\Lambda}_j q_{mm,j} \\ & + \sum_n \frac{a_{nn}}{a_{mm}} W_{mn}(\eta)(q_{nn,j} - q_{mm,j}) \\ & - 2\lambda_j \sigma_{jj,j} T_{mj}(\eta) W_{mj}(\eta) \frac{a_{jj}}{a_{mm}} \\ & - 2\lambda_j \sigma_{mm,j} T_{jm}(\eta) W_{jm}(\eta),\end{aligned} \tag{E1}$$

for $j \neq m$ and

$$\frac{dq_{mm,m}}{d\tau} = -\overline{\Lambda}_m(q_{mm,m}-1) + \sum_n \frac{a_{nn}}{a_{mm}} W_{mn}(\eta)(q_{nn,m}-q_{mm,m}) + \sum_n 2\lambda_m \sigma_{nn,m} T_{mn}(\eta) W_{mn}(\eta) \frac{a_{nn}}{a_{mm}} + \sum_n 2\lambda_m \sigma_{mm,m} T_{nm}(\eta) W_{nm}(\eta), \tag{E2}$$

where we have defined

$$T_{mn}(\eta) \equiv \frac{E_m - 2\lambda_m q_{nn,m} - E_n + 2\lambda_n q_{nn,n}}{(2\lambda_m)^2 \sigma_{nn,m} + (2\lambda_n)^2 \sigma_{nn,n}}. \tag{E3}$$

For the second moments σ we have

$$\frac{d\sigma_{mm,j}}{d\tau} = -2\overline{\Lambda}_j \left[\sigma_{mm,j} - \left(\frac{\Delta_j}{2\lambda_j} \right)^2 \right] + \sum_n [(q_{nn,j}-q_{mm,j})^2 + \sigma_{nn,j} - \sigma_{mm,j}] W_{mn}(\eta) \frac{a_{nn}}{a_{mm}} - 4\lambda_j \sigma_{jj,j} T_{mj}(\eta) \times (q_{jj,j}-q_{mm,j}) W_{mj}(\eta) \frac{a_{jj}}{a_{mm}} - (2\lambda_j \sigma_{jj,j})^2 \{[T^{(1)}_{mj}(\eta)]^2 - [T_{mj}(\eta)]^2\} W_{mj}(\eta) \frac{a_{jj}}{a_{mm}} + (2\lambda_j \sigma_{mm,j})^2 \{[T^{(1)}_{jm}(\eta)]^2 - [T_{jm}(\eta)]^2\} W_{jm}(\eta), \tag{E4}$$

for $j \neq m$ and

$$\frac{d\sigma_{mm,m}}{d\tau} = -2\overline{\Lambda}_m \left[\sigma_{mm,m} - \left(\frac{\Delta_m}{2\lambda_m} \right)^2 \right] + \sum_n [(q_{nn,m}-q_{mm,m})^2 + (\sigma_{nn,m} - \sigma_{mm,m})] W_{mn}(\eta) \frac{a_{nn}}{a_{mm}} + \sum_n 4\lambda_m \sigma_{nn,m} T_{mn}(\eta) \times (q_{nn,m}-q_{mm,m}) W_{mn}(\eta) \frac{a_{nn}}{a_{mm}} - \sum_n (2\lambda_m \sigma_{nn,m})^2 \{[T^{(1)}_{mn}(\eta)]^2 - [T_{mn}(\eta)]^2\} W_{mn}(\eta) \frac{a_{nn}}{a_{mm}} + \sum_n (2\lambda_m \sigma_{mm,m})^2 \{[T^{(1)}_{nm}(\eta)]^2 - [T_{nm}(\eta)]^2\} W_{nm}(\eta), \tag{E5}$$

where we have introduced the notation

$$T^{(1)}_{mn}(\eta) \equiv \frac{1}{[(2\lambda_m)^2 \sigma_{nn,m} + (2\lambda_n)^2 \sigma_{nn,n}]^{1/2}}. \tag{E6}$$

The initial conditions are

$$a_{mm}(0) = \int_{-\infty}^{\infty} d\tau' \, d\tau'' \, \exp\left[i\Omega_m(\tau''-\tau') - \frac{\Delta_m^2}{2}(\tau''-\tau')^2 \right] \varepsilon_m(\tau'') \varepsilon_m^*(\tau'), \tag{E7}$$

$$\begin{aligned} q_{mm,j}(0) &= -\delta_{mj} i a_{mm}^{-1}(0) \int_{-\infty}^{\infty} d\tau' \, d\tau'' \frac{\Delta_m^2}{2\lambda_m}(\tau''-\tau') \, \exp\left[i\Omega_m(\tau''-\tau') - \frac{\Delta_m^2}{2}(\tau''-\tau')^2 \right] \varepsilon_m(\tau'') \varepsilon_m^*(\tau'), \\ \sigma_{mm,j}(0) &= \left(\frac{\Delta_j}{2\lambda_j} \right)^2 - \delta_{mj} a_{mm}^{-1}(0) \frac{\Delta_m^4}{(2\lambda_m)^2} \int_{-\infty}^{\infty} d\tau' \, d\tau'' (\tau''-\tau')^2 \, \exp\left[i\Omega_m(\tau''-\tau') - \frac{\Delta_m^2}{2}(\tau''-\tau')^2 \right] \varepsilon_m(\tau'') \varepsilon_m^*(\tau'). \end{aligned} \tag{E8}$$

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