Influence of Complex Exciton-Phonon Coupling on Optical Absorption and Energy Transfer of Quantum Aggregates

Jan Roden and Alexander Eisfeld

Max-Planck-Institut für Physik komplexer Systeme, Nöthnitzer Straße 38, D-01187 Dresden, Germany

Wolfgang Wolff

Marie-Curie-Gymnasium, Giersbergstraße 39, D-79199 Kirchzarten, Germany

Walter T. Strunz

Institut für Theoretische Physik, Technische Universität Dresden, D-01062 Dresden, Germany

We present a theory that efficiently describes the quantum dynamics of an electronic excitation that is coupled to a continuous, highly structured phonon environment. Based on a stochastic approach to non-Markovian open quantum systems, we develop a dynamical framework that allows us to handle realistic systems where a fully quantum treatment is desired yet the usual approximation schemes fail. The capability of the method is demonstrated by calculating spectra and energy transfer dynamics of mesoscopic molecular aggregates, elucidating the transition from fully coherent to incoherent transfer.

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One often encounters the situation where a quantum particle or an elementary excitation couples to a complex environment. Examples range from the classical polaron problem [1] over electron-phonon interaction in superconductors [2], ultracold impurity atoms immersed in a Bose-Einstein condensate and trapped in a tight optical lattice [3], molecular aggregates and crystals [4–6], atoms or molecules in photonic band gap materials [7] or light-harvesting units in photosynthesis [8]. We speak of a quantum aggregate (QA), if the excitation can reside on N different sites, if it can be handed over from site n to site m mediated by a matrix element V_{nm}, and, importantly, if the excitation couples to a complex environment. In the following we will use the language of exciton-phonon coupling in molecular aggregates, although this scenario is obviously much more general.

For very small QAs ($N < 10$) it may be possible to extract the few most relevant phonon modes and treat them fully quantum mechanically [5,9]. Then, however, the overall irreversible nature of the dynamics caused by the existence of many more environmental modes is ignored. Other approaches, like the coherent exciton scattering approximation [10], are best suited for large aggregates ($N \rightarrow \infty$), yet fail for a small number of monomers. If the overall influence of the vibrational environment is small, a perturbative approach (Redfield) may be appropriate [11,12].

All these established approaches fail for the QAs we are interested in: a quantum excitation that may reside on a finite number of sites, significantly coupled to a complex environment of phonons that consists of a few distinct vibrations embedded in an overall dissipative bath. We tackle this intricate regime of complex dynamics fully quantum mechanically using ideas from a stochastic de-

scription of non-Markovian open quantum systems [13] (see also [11]). We present a dynamical framework based on a stochastic Schrödinger equation (SSE) that allows us to determine the quantum dynamics emerging from a significant exciton-phonon coupling in complex QAs. We are able to treat QAs consisting of a very small to a large number of monomers, bridging a gap in previous approaches. Moreover, being nonperturbatively, in a single unified theory we may describe exciton-dynamics ranging from fully coherent, over weakly perturbed, to strongly affected by the vibrations. To demonstrate the capability of the method, it is applied to study optical absorption and the coherent-incoherent transition of energy transfer in ring-shaped molecular aggregates [6], as they appear, e.g., in the light-harvesting units of some bacteria.

We consider QAs where the wave functions of different monomers do not overlap (tight binding) and each monomer has two electronic states with a transition energy ε_n for monomer n. A state in which monomer n is electronically excited and all other monomers are in their electronic ground state is denoted by $|\pi_n\rangle$. The Holstein model [14] includes the crucial influence of (possibly damped) vibrations on each monomer and is given by the Hamiltonian

$$H = H_{\text{el}} + H_{\text{int}} + H_{\text{vib}}. \tag{1}$$

Here,

$$H_{\text{el}} = \sum_{n,m=1}^{N} (\varepsilon_n \delta_{nm} + V_{nm}) |\pi_n\rangle\langle\pi_m|, \tag{2}$$

is the purely electronic part of the Hamiltonian and

$$H_{\text{vib}} = \sum_{n=1}^{N} \sum_{j} \hbar\omega_{nj} a_{nj}^{\dagger} a_{nj} \tag{3}$$

describes the collection of phonon modes. Here a_{nj} denotes the annihilation operator of mode j of monomer n with frequency ω_{nj}. For each monomer n, the sum over j takes into account internal vibrations and their coupling to modes of the local environment. The coupling of electronic excitation to these vibrations is contained in

$$H_{\text{int}} = -\sum_{n=1}^{N}\sum_{j}\kappa_{nj}(a_{nj}^{\dagger} + a_{nj})|\pi_n\rangle\langle\pi_n| \qquad (4)$$

where the coupling constants κ_{nj} are related to the dimensionless Huang-Rhys factor X_{nj} through $\kappa_{nj} = \hbar\omega_{nj}\sqrt{X_{nj}}$ [15]. An energy shift $\sum_j \hbar\omega_{nj}X_{nj}$ is incorporated into the transition energy ε_n.

The complex structure of the phonon "bath" of monomer n is encoded in the bath correlation function at temperature T [12]

$$\alpha_n(\tau) = \int d\omega J_n(\omega)\left(\cos(\omega\tau)\coth\frac{\hbar\omega}{2k_BT} - i\sin(\omega\tau)\right) \quad (5)$$

with the spectral density $J_n(\omega) = \sum_j|\kappa_{nj}|^2\delta(\omega - \omega_{nj})$ of monomer n which is usually replaced by a smooth function to guarantee genuine irreversibility. For simplicity we will restrict ourselves in the following to the zero-temperature limit.

We use recently developed ideas from a SSE approach to open quantum system dynamics [13,16] to treat the model with a complicated continuous and structured phonon distribution fully quantum mechanically. In brevity, the SSE approach amounts to a solution of the full Schrödinger equation for a total Hamiltonian of the type of Eq. (1). It may be derived using a (Bargmann) coherent state basis [17] with $|z_{nj}\rangle = \exp(z_{nj}a_{nj}^{\dagger})|0\rangle$ for each environmental (vibrational) degree of freedom. Here $|0\rangle$ is the state where no vibrations are excited and z_{nj} is a complex number. Thus (here for a zero-temperature environment) the full state of system and environment at all times is written in the form [17]

$$|\Psi(t)\rangle = \int \frac{d^2\mathbf{z}}{\pi}e^{-|\mathbf{z}|^2}|\psi(t, \mathbf{z}^*)\rangle|\mathbf{z}\rangle \qquad (6)$$

with $\mathbf{z}$ representing the collection of coherent state labels z_{nj}. Remarkably, in an approximation to be discussed below (see also section III.B of [18]), the dynamics of the Holstein model (1) is now captured in the Schrödinger equation

$$\partial_t|\psi(t, \mathbf{z}^*)\rangle = -\frac{i}{\hbar}H_{\text{el}}|\psi(t, \mathbf{z}^*)\rangle - \sum_m|\pi_m\rangle\langle\pi_m|(z_m^*(t)$$
$$- \bar{D}^{(m)}(t))|\psi(t, \mathbf{z}^*)\rangle \qquad (7)$$

in the small Hilbert space of the electronic degrees of freedom alone—a huge reduction in complexity. In Eq. (7), we use the abbreviations $z_m^*(t) = -\frac{i}{\hbar}\sum_j\kappa_{mj}z_{mj}^*e^{i\omega_{mj}t}$ and

$$\bar{D}^{(m)}(t) = \int_0^t ds\,\alpha_m(t-s)D^{(m)}(t, s). \qquad (8)$$

Here, $D^{(m)}(t, s)$ represents a $\mathbf{z}^*$-independent operator in the electronic Hilbert space, introduced to approximate a functional derivative $\frac{\delta}{\delta z_m^*(s)}|\psi(t, \mathbf{z}^*)\rangle \approx D^{(m)}(t, s)|\psi(t, \mathbf{z}^*)\rangle$ that appears in the exact equation [19]. The reasoning underlying this approximation is elaborated upon further at the end of this Letter. The operator $D^{(m)}(t, s)$ is obtained by solving

$$\partial_t D^{(m)}(t, s) = \left[-\frac{i}{\hbar}H_{\text{el}}, D^{(m)}(t, s)\right]$$
$$+ \sum_l[|\pi_l\rangle\langle\pi_l|\bar{D}^{(l)}(t), D^{(m)}(t, s)], \quad (9)$$

with initial condition $D^{(m)}(t = s, s) = -|\pi_m\rangle\langle\pi_m|$ [18].

Equation (7) (for the electronic state), together with Eqs. (8) and (9) (for operators in the electronic Hilbert space) is the new dynamical framework which will be used to determine all properties of interest of the QA [20]. Together with expression (6), $|\psi(t, \mathbf{z}^*)\rangle$ constitutes the full state and thus all information about electronic and vibronic degrees of freedom is available.

The cross section for absorption of light with frequency Ω in dipole approximation at zero-temperature turns out to be connected to a simple autocorrelation function:

$$\sigma(\Omega) = \frac{4\pi}{\hbar c}\Omega\text{Re}\int_0^\infty dt\,e^{i\Omega t}\langle\psi(0, \mathbf{z} = \mathbf{0})|\psi(t, \mathbf{z} = \mathbf{0})\rangle.$$
$$(10)$$

The state $|\psi(t, \mathbf{z} = \mathbf{0})\rangle$ is obtained from Eq. (7) with initial condition $|\psi(0, \mathbf{z} = \mathbf{0})\rangle = \sum_{n=1}^{N}(\hat{\mathcal{E}}\cdot\vec{\mu}_n)|\pi_n\rangle$ where the geometry of the aggregate enters explicitly via the transition dipoles $\vec{\mu}_n$ and the polarization of the light $\hat{\mathcal{E}}$. Note that only the projection of the total state onto the vibronic ground state $|0\rangle$ is needed, which is the single solution of Eq. (7) with the choice $z_m^*(t) = 0$.

More involved is the determination of transport properties which requires the reduced density operator $\rho(t) = \text{Tr}_{\text{vib}}|\Psi(t)\rangle\langle\Psi(t)|$. It is found by considering the $z_m^*(t)$ in Eq. (7) to be independent colored stochastic processes with correlations $\langle\langle z_m(t)z_n(s)\rangle\rangle = 0$ and $\langle\langle z_m(t)\rangle\rangle = 0$. The covariance of these processes is connected to the bath correlation function via $\langle\langle z_m^*(t)z_n(s)\rangle\rangle = \alpha_m(t-s)\delta_{mn}$. It follows that the reduced density operator of the electronic part can be obtained as an ensemble mean $\rho_t = \langle\langle|\psi(t, \mathbf{z}^*)\rangle\langle\psi(t, \mathbf{z}^*)|\rangle\rangle$ over the noises $z_1(t), \dots, z_N(t)$.

Our novel approach is now applied to study optical absorption and transfer properties of molecular aggregates [6]. The spectral density of the monomers $J(\omega)$ is taken to be a sum of Lorentzians, see Fig. 1, resulting in the monomer absorption spectrum shown in Fig. 2(a), which nicely resembles that of a typical organic dye [21]. In the following we will take the width Δ (standard deviation) of this monomer spectrum as the unit of energy (for organic dyes Δ is in the order of 0.1 eV). The vibrational progression due to the high-energy modes with energies around 1.5 Δ in the spectral density (see Fig. 1) is clearly visible. The considerable broadening of this progression mainly stems
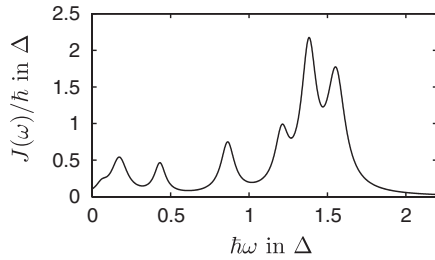
FIG. 1.   The spectral density used for the calculation of spectra in Fig. 2 and energy transfer in Fig. 3. The unit of energy is the width Δ of the resulting monomer absorption spectrum [Fig. 2(a)].

FIG. 2.   (a) Absorption spectrum of the monomer [its width Δ (standard deviation) is used as the unit of energy]. (b)–(d) J band spectra of ring-shaped aggregates with $C = -2.6\,\Delta$. The values of N are indicated in the figures.

from the low-energy vibrations below 0.5 Δ in the spectral density.

In the following we focus on aggregates for which the absorption exhibits a narrow band, redshifted with respect to the monomer absorption, the so-called J band [6,22]. We consider an aggregate of N identical monomers arranged equidistantly along a ring with transition dipoles lying in the plane of the ring, such that the angle between the transition dipoles of neighboring monomers is identical for all monomers. In the calculations we have taken into account the interaction $V \equiv V_{n,n+1}$ between neighboring monomers only. For the chosen geometrical arrangement, without coupling to vibrations, the aggregate absorption would be a single line, shifted by an energy $C \equiv 2\,V\cos(2\pi/N)$ with respect to the electronic monomer absorption line.

Figures 2(b)–2(d) show aggregate absorption spectra for $C = -2.6\,\Delta$ for different N. We find that the mean of the aggregate spectrum is shifted by the energy C with respect to the mean of the monomer spectrum, in accordance with sum rules [23]. Furthermore, with increasing N the vibrational structure vanishes and the lowest peak (around -2.6 Δ) becomes narrower by roughly a factor $1/\sqrt{N}$. This is the well-known effect of motional narrowing which leads to the narrow shape of the J band of molecular aggregates [22,24], obtained here from a fully dynamical calculation. Upon increasing $|C|$ further the shape of the aggregate spectrum (especially the width) undergoes only very small changes, hardly noticeable even for $|C| \to \infty$. Therefore one might assume that also other properties of the QA will only slightly change when increasing $|C|$.

However, this is not the case as we will now show considering energy transfer for the same situation as in Fig. 2(d), (i.e., $N = 15$ and $C = -2.6$ Δ). Initially, the electronic excitation is chosen to be localized on monomer number eight. As unit of time we take the typical time $\hbar/|C|$ of intermonomer electronic excitation transfer [25]. In Fig. 3(b) we show the time-dependent probability to be electronically excited as a function of site number and time (note that the aggregate is ring-shaped). For reference, in Fig. 3(a) the case where the electronic transfer does not couple to any vibrational modes is shown [26]. While the transfer in Fig. 3(a), obtained from a purely electronic
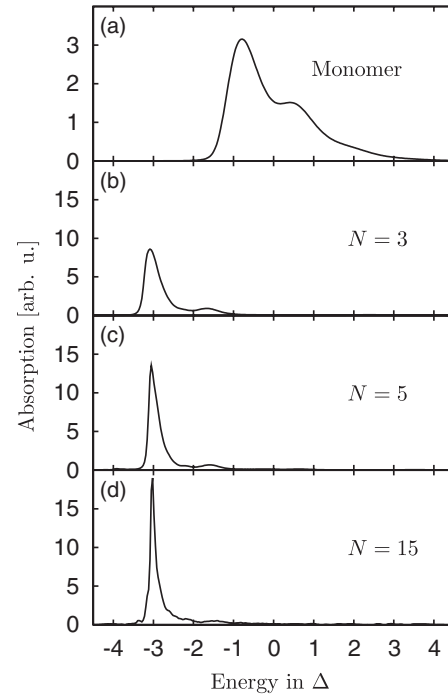
theory, exhibits clear excitation maxima over a long period of time, the excitation in Fig. 3(b) is distributed quickly over all monomers due to the coupling to the vibrational continuum (the transfer shown is averaged over 1000 realizations of the stochastic noise $\mathbf{z}^*$, but was well converged after only 600 realizations). We have found that upon increasing $|C|$ the fast smearing of the excitation in Fig. 3(b) is suppressed and at about $C = -13\,\Delta$ the purely electronic situation of Fig. 3(a) is reached. This is quite remarkable, showing, that from the width of the J band
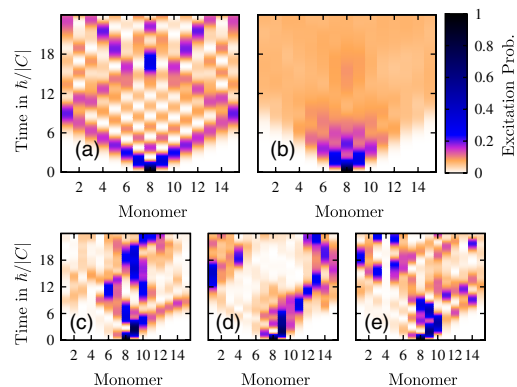

FIG. 3 (color online).   Transfer of the electronic excitation energy on a ring-shaped 15-mer for $C = -2.6$ Δ. Initially only monomer 8 is excited. (a) Without coupling to a phonon bath. (b) With coupling to a phonon bath with spectral density of Fig. 1. (c)–(e) Three of the 1000 single realizations over which the transfer in (b) is averaged.

alone it is not easily possible to infer the influence of the phonon bath on transfer properties. To gain deeper insight into the nature of the transfer, in Figs. 3(c)–3(e) three of the 1000 single realizations over which the transfer in Fig. 3(b) is averaged are shown. In these single realizations the excitation stays localized in a small region (about 3 monomers) and performs a random-walk-like motion.

These considerations show that our dynamical framework based on a SSE in the Hilbert space of electronic excitation allows an efficient and detailed description of properties of QAs, including complex vibrational couplings. Therefore an examination of the approximation underlying Eq. (7) is in order. It is based on a functional expansion of $\frac{\delta}{\delta z_m^*(s)}|\psi(t, \mathbf{z}^*)\rangle$ with respect to the noise $\mathbf{z}^*$ [18], taking only the lowest order term into account. This approximation has been confirmed to be true in many cases of interest: it is true near the Markov limit (Lindblad), and contains the weak coupling (Redfield) limit [27]. Moreover, it holds true for many soluble cases, including the case of independent monomers ($V_{nm} = 0$) of this Holstein model. To check the quality of the approximation beyond the usual limits (Markov, Redfield), we investigated the case of a spectral density consisting of a single Lorentzian in more detail. For the dimer ($N = 2$) we were able to compare with spectra obtained from full quantum calculations and found overall good agreement. Last but not least, we have confirmed that the sum rules [23,28] for the first five moments of the absorption spectrum are satisfied.

To conclude, we have developed a new dynamical framework for the determination of optical and transport properties of QAs. This method allows a fully quantum treatment with realistic complex vibrational environments. The usefulness has been shown by considering the emergence of the J band as N grows and by capturing the transition from coherent to incoherent energy transfer. The next step is to investigate the much more complicated case of the H band [29] where the details of the vibrational structure play a more pronounced role. Since the method is based on the time-propagation of a SSE, it is also ideally suited to include external time-dependent fields. This should enable us to efficiently study coherent control schemes or describe multidimensional spectroscopy using realistic spectral densities. Clearly, as indicated in the introduction, the model we solve here and variants thereof appear in many applications well beyond molecular aggregates which will be a subject of future research.

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