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Anharmonic Oscillator Approach to the Exciton-Exciton Annihilation Dynamics in Molecular Aggregates

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The dynamics of Frenkel excitons in aggregates of coupled electronic three-level molecules in the presence of strong external fields is investigated. Particular emphasis is paid to the microscopic inclusion of exciton-exciton annihilation. It appears as a combination of exciton fusion and internal conversion processes which are taken into account within perturbation theory. The influence of an environment on the exciton dynamics is treated by means of stochastic fluctuations of the electronic transition energies. A closed set of equations of motion is derived and it is shown how nonlinear optical spectra can be calculated nonperturbatively.

I. INTRODUCTION

During the last decades the study of the electronic properties of such distinct systems like organic semiconductors, polymers strands, dye aggregates and biological chromophore complexes made the Frenkel exciton model a common concept in condensed matter physics.[1,2] A prominent example for Frenkel excitons can be found in the chlorophyll-protein complexes of photosynthetic light-harvesting antennae (LHAs).[3,4] Besides the outstanding importance of photosynthesis, it was the determination of atomic-scale resolution structures for several antenna complexes which attracted the interest of a more physico-chemical oriented research.[3-5] Meanwhile all ultrafast spectroscopic techniques have been applied to investigate the energy and charge transfer dynamics in photosynthetic pigment-protein complexes;[4] the interpretation of these experiments in turn stimulated the development of the standard Frenkel exciton theory.[3,5]

Two aspects characterize the activities in the field of photosynthetic antenna systems. First, there is the general point of guiding biologists and biophysicists in their attempt to reveal the basics of life. Second, pigment-protein complexes can be viewed as any other physical system, i.e., they represent a particular type of molecular nanostructures. In this spirit experiments are often carried out under conditions far away from being physiological. For example, every non-linear optical experiment on LHAs includes transitions into

electronic states which are of no importance for the functionality of the antennae. Nevertheless, by means of these techniques one gets access to relaxation rates and energy levels which are of central importance for the excitation energy transfer. Furthermore, one is able to clarify the influence of the ubiquitous static and dynamic disorder introduced by the protein environment. Finally, increasing the light intensities it becomes possible to distinguish between different relaxation channels.

In the case of high intensity excitation the dynamics of Frenkel excitons is influenced by exciton-exciton annihilation (EEA). This can be considered as a two step process (cf. Fig. 1): First, the mutual Coulomb interaction between two excitons leads to an excitation of one molecule into a
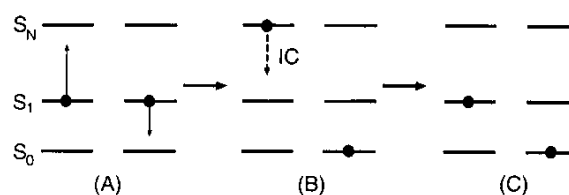

Fig. 1. Exciton-exciton annihilation in coupled electronic three level systems. The dipole-dipole interaction between two S_1 excitons leads to a double excitation of one three level molecule: (A) → (B). Internal conversion causes a de-excitation (B) and a single exciton is annihilated (C).

higher excited state, the other molecule gets de-excited. In the second step the highly excited state relaxes back to the original state via internal conversion. As a result a single exciton has been annihilated and heat is released into the local environment.

The investigation of EEA has a long history in particular in the context of molecular crystals. The appropriate theoretical frame has been provided by Suna[6] and later by Kenkre.[7,8] In Ref. 6 it was shown that the classical continuum model leading to the kinetic equation

$$\frac{\partial n(\mathbf{r};t)}{\partial t} = -\gamma_{\mathrm{anni}}[n(\mathbf{r};t)]^2 \qquad (1.1)$$

for the exciton density $n(\mathbf{r};t)$ results from a low density limit of a hierarchy of equations for a set of many-particle distribution functions. In particular an expression for the phenomenological bimolecular annihilation rate γ_{anni} could be derived. Moreover, Ref. 6 contains a quantum statistical formulation of exciton hopping based on multi-exciton density matrices. This approach reveals that Eq. 1.1 results from a certain type of mean field approximation. Similar conclusions have been reached in Ref. 7 where also a Generalized Master Equation description of exciton transfer and EEA incorporating spatial coherences on the lattice was given. The latter effect was shown to influence quantum yields and fluorescence intensity.

EEA has also been studied in dye aggregates[9−12] and photosynthetic complexes. In photosynthesis research it was appreciated early that measuring the fluorescence decay and quantum yields versus pulse intensity can provide valuable information on exciton migration within a so-called domain, that is, a connected assembly of photosynthetic units each consisting of LHAs as well as reaction centers. These domains are for many photosynthetic systems rather planar with 40 to 400 LHAs per reaction center.[13] A phenomenological Master Equation describing the kinetics of the number of excitations in a domain under annihilation and unimolecular loss conditions was given by Paillotin et al.[14] From an analytical solution of the Master Equation by means of the generating function approach it was shown that the fluorescence yield versus intensity curve contains information on the number of connected units in the domain. This approach was later extended by Den Hollander et al.[15] to include the different states (open/closed) of the reaction center. Further, the phenomenological rates were given a microscopic explanation using a random walk model (for an application see Ref. 16). The early work on EEA in LHAs has been summarized in Ref. 17.

More recent studies on energy migration and trapping include the modeling of structural and spectrally inhomo-geneous situations given in Ref. 18 and the extension of the Suna model to include higher excited intramolecular electronic states, trapping, and the excitation process.[19] On the experimental side it has been demonstrated that singlet-singlet and singlet-triplet annihilation can be discriminated upon changing the pulse repetition rate (see, e.g., Ref. 20). Combined with phenomenological theories this allowed study, for instance, of the connectivity of chloroplasts,[21] or energy migration in photosynthetic bacteria; the latter revealed a percolation like nature of the dynamics.[20] Further, pump-probe spectroscopy has been used to elucidate the effect of local heating due to EEA in the so-called FMO complex,[22] to study the interplay between exciton relaxation and EEA in the strongly coupled peripheral LHA of Rps. acidophila,[23] and to investigate spectral redistribution in the LHC-II of green plants.[24]

Concluding this overview we would like to stress that from the theoretical point of view the modeling of energy migration in LHAs has been restricted to phenomenological Master Equations. It was only recently that a more elaborate theory has been formulated and applied to a dimer model of the LHC-II of green plants.[25,26] The approach had been based on a density matrix formulation in terms of multi-exciton vibrational states. EEA followed as a radiationless transition process among different exciton manifolds. The multi-exciton vibrational representation has been motivated by the fact that the intermediate strength of excitonic coupling and dephasing introduced by the protein environment in LHAs makes it necessary to treat them on the same footing. An exact inclusion of both interactions is hardly possible beyond the dimer model of Refs. 25,26. However, the mutual Coulomb interaction has to compete not only with the dynamic exciton-vibrational coupling but also with static disorder. The latter will localize the excitonic wave function on a few pigments and a perturbation theory with respect to both the dynamic disorder and the Coulomb interaction becomes possible.

A convenient tool for dealing with this situation is given by the anharmonic excitonic oscillator approach,[27−31] which is an alternative to the standard Frenkel exciton description. The minimum model for a microscopic description of EEA would include three intramolecular electronic states (we treat only singlet-singlet EEA here). In Ref. 27 it was shown that the dynamics of a system of coupled three-level molecules can be mapped onto a set of coupled anharmonic excitonic oscillators. By construction this model is well suited to describe the nonlinear optical properties of large aggregates. This was shown for the third-order response function in Refs. 27, 28. However, as pointed out in Refs. 25, 26 the description of EEA under intense field conditions requires

going beyond a third order perturbation expansion, i.e., to use an approach which allows in principle a nonperturbative inclusion of the external field interaction.

In the following we will use the anharmonic oscillator model to give a closed expression for the nonlinear optical polarization of large molecular aggregates. This includes a microscopic model for the internal conversion leading to EEA, the exciton transfer, the exciton-vibrational interaction, as well as a nonperturbative treatment of the external field. In Section II we briefly summarize the concept of the anharmonic exciton oscillator representation and define our model Hamiltonian. In Section III the equations of motion for the different dynamic variables are derived starting from the Heisenberg equation for the related quantum operators. Appropriate factorizations of expectation values are discussed together with the perturbation theory which is used to treat the excitonic interactions as well as the coupling to the nuclear degrees of freedom. The connection with nonlinear ultrafast experiments is established in Section IV. The paper is summarized in Section V.

II. AGGREGATE HAMILTONIAN IN ANHARMONIC OSCILLATOR REPRESENTATION

A. Exciton Hamiltonian

In the following we will be concerned with aggregates made of N_{mol} molecules each having three electronic states S_0, S_1, and S_N, denoted by $f = 0, 1, 2$, respectively. This situation is commonly described on the basis of the Frenkel exciton Hamiltonian[1,2]

$$H_{\text{frenkel}} = \sum_{n, f=(1,2)} E_n^{(f)} b_{nf}^\dagger b_{nf} + \sum_{mn} \beta_{mn} d_m d_n \qquad (2.1)$$

The Frenkel exciton creation and annihilation operators $b_{nf}^\dagger$ and b_{nf}, respectively, obey Pauli-commutation relations $[b_{nf}, b_{n'f'}^\dagger] = \delta_{nn'}\delta_{ff'}(1 - 2b_{nf}^\dagger b_{nf})$. They are defined via the Frenkel exciton state vectors $|f_n\rangle$, where the index $f_n = (0, 1, 2)$ counts the three possible states of the n-th molecule according to: $b_{n1}^\dagger = |1_n\rangle\langle 0_n|$ and $b_{n2}^\dagger = |2_n\rangle\langle 1_n|$.

In what follows we assume that only the $S_0 \rightarrow S_1$ and the $S_1 \rightarrow S_N$ transitions have finite matrix elements of the transition dipole moment, $\mu_n^{(10)}$ and $\mu_n^{(21)}$. Thus the molecular dipole operator $\vec{d}_n = d_n \vec{e}_n$ is given by

$$\vec{d}_n = \vec{e}_n \mu_n^{(10)} [(b_{n1}^\dagger + b_{n1}) + \kappa_n (b_{n2}^\dagger + b_{n2})] \qquad (2.2)$$

Here, we introduced the ratio between the dipole matrix elements as

$$\kappa_n = \mu_n^{(21)} / \mu_n^{(10)} \qquad (2.3)$$

and $\vec{e}_n$ is the unit vector pointing along the dipole vector $\vec{d}_n$ (For simplicity we take both transition dipoles to have the same orientation.). The molecules are assumed to interact via dipole-dipole forces; the matrix β_{mn} in Eq. 2.1 contains the orientations of the $S_0 \rightarrow S_1$ transition dipoles of molecules m and n, and is proportional to the third power of the inverse distance between the center of masses of the two molecules:

$$\beta_{mn} = \frac{\vec{e}_m \vec{e}_n}{r_{mn}^3} - 3\frac{(\vec{r}_{mn}\vec{e}_m)(\vec{r}_{mn}\vec{e}_n)}{r_{mn}^5} \qquad (2.4)$$

Here, $\vec{r}_{mn}$ is the distance vector between the mth and the nth molecule.

In Ref. 27 it was shown that the nonlinear optical properties of this kind of molecular system are conveniently described in terms of the anharmonic oscillator picture (see also Ref. 32). This approach is based on the observation that upon introduction of oscillator creation and annihilation operators according to the general prescription

$$B_n^\dagger = \sum_{f=0}^{F-1} \frac{\mu_n^{(f+1,f)}}{\mu_n^{(10)}} |f_n + 1\rangle\langle f_n| \qquad (2.5)$$

(here, $f = 0 \ldots F - 1$ counts the intramolecular electronic states, i.e., $F = 3$ in the present case) the dipole operator takes the simple form

$$\vec{d}_n = \vec{e}_n \mu_n (B_n + B_n^\dagger) \qquad (2.6)$$

(note that $\mu_n^{(10)} = \mu_n$ will be used for brevity). The new operators satisfy the commutation relations

$$[B_m, B_n^\dagger] = \delta_{mn}\left(1 - \sum_{f=0}^{F-1} q_n^{(f)}(B_n^\dagger)^f (B_n)^f\right) \qquad (2.7)$$

By construction the dipole-dipole interaction term in Eq. 2.1 has a simple form while for the on-site contribution the following ansatz is made

$$\sum_{n,f} E_n^{(f)} b_{nf}^\dagger b_{nf} = \sum_{n,f} \frac{1}{f!} \hbar \Omega_n^{(f)} (B_n^\dagger)^f (B_n)^f \qquad (2.8)$$

Eqs. 2.7 and 2.8 contain the yet unknown parameters $q_m^{(f)}$ and $\Omega_n^{(f)}$. In Ref. 27 it was shown that these parameters can be determined from the requirement that the matrix elements of the on-site Hamiltonian and the commutation relations are identical in the Frenkel and the oscillator picture. This results in recursion relations from which one obtains for the present case of three level systems $q_n^{(1)} = 2 - \kappa_n^2$, $q_n^{(2)} = (\kappa_n^2 - \kappa_n^4 - 1)/\kappa_n^2$, $\hbar\Omega_n^{(1)} = E_n^{(1)}$, and $\hbar\Omega_n^{(2)} = 2(E_n^{(2)}/\kappa_n^2 -$
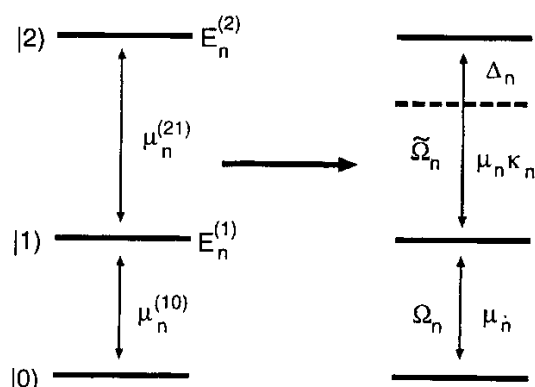
Fig. 2. Mapping of the Frenkel exciton states (left) onto the anharmonic excitonic oscillator states (right). Note that $E_n^{(0)}$ is chosen to be zero.

$E_n^{(1)}$). Collecting the different terms the Frenkel exciton Hamiltonian Eq. 2.1 transforms into

$$H_{\text{ex}} = \sum_n \left[E_n B_n^\dagger B_n + \frac{g_n}{2} (B_n^\dagger)^2 (B_n)^2 \right] + \sum_{mn} [J_{mn} B_m^\dagger B_n + \text{c.c.}] \tag{2.9}$$

Here we introduced the matrix elements of the dipole-dipole interaction as $J_{mn} = \beta_{mn}\mu_n\mu_m$. The parameter g_n is related to the anharmonicity of the n-th oscillator, $\hbar\Delta_n = E_n^{(2)} - 2E_n^{(1)}$, through $\hbar\Delta_n = \kappa_n^2 g_n/2 + (\kappa_n^2 - 2)E_n^{(1)}$. The mapping procedure is illustrated in Fig. 2. In the following we will use the notation $\Omega_n \equiv \Omega_n^{(1)}$ and $\tilde{\Omega}_n \equiv \Omega_n^{(2)} - \Omega_n^{(1)}$. The various limits of the oscillator model, in particular the two-level limit, $\kappa_n = 0$, and the harmonic oscillator limit for which $\kappa_n = \sqrt{2}$ and $\Delta_n = 0$ have been discussed previously.[27,28]

B. Internal Conversion

Exciton-exciton annihilation is a consequence of the breakdown of the Born-Oppenheimer approximation, i.e., the adiabatic separation of electronic and nuclear motions.[5] If two excitons are in the S_1-state at different sites, J_{mn} includes a resonant interaction process which leads to the de-excitation of the m-th molecule and the simultaneous excitation of the n-th molecule into its S_N-state. This situation is shown in Fig. 1. Owing to the nonadiabatic coupling between the S_N- and S_1-states, internal conversion will occur as indicated in panel (B) of Fig. 1. This is usually a rather fast process (see also Ref. 33). The overall outcome is the annihilation of one exciton as shown in Fig. 1(C).

In the oscillator picture we can incorporate internal conversion by adding the following term to the Hamiltonian

Eq. 2.9

$$H_{\text{IC}} = \sum_n V^{(\text{IC})}(R)[B_n^\dagger (B_n)^2 + \text{h.c.}] \tag{2.10}$$

Here, $V^{(\text{IC})}(R)$ is an operator defined with respect to the particular set of nuclear degrees of freedom, $R \equiv \{R\}$, which is responsible for the internal conversion process. Note that in terms of the Frenkel exciton states Eq. 2.11 corresponds to

$$H_{\text{IC}} = \sum_n V^{(\text{IC})}(R)\kappa_n[|1_n\rangle\langle 2_n| + \text{h.c.}] \tag{2.11}$$

In passing we mention that in principle exciton-exciton annihilation is not restricted to a three level scheme. Different exciton processes involving higher excited S_N-states can be straightforwardly incorporated (see also Ref. 19).

C. Exciton-Vibrational Coupling

Exciton-vibrational interaction plays a fundamental role for the dynamics of many aggregates. It is of particular relevance for the energy transfer in photosynthetic antenna complexes where it provides the means for releasing excess energy thus facilitating energy funneling to the reaction center. There exist different approaches to the inclusion of exciton-vibrational coupling which have been reviewed in Refs. 3,5. Here we adopt a stochastic model (see also Ref. 34) assuming that the on-site electronic transition energies are subject to some fluctuations. Specifically, we will use the Hamiltonian

$$H_{\text{ex-vib}} = \sum_n \delta E_n(t) \left(B_n^\dagger B_n + \alpha_n (B_n^\dagger)^2 (B_n)^2 \right) \tag{2.12}$$

For simplicity we have assumed that the $S_0 \rightarrow S_1$ transition is governed by the same fluctuation $\delta E_n(t)$ as the $S_1 \rightarrow S_N$ transition. Only the magnitude is scaled by some factor γ_n which, introduced in the Frenkel picture, is related to the α_n in Eq. 2.12 via $\alpha_n = (\gamma_n - \kappa_n^2)/\kappa_n^2$.

Next we have to specify the characteristics of the stochastic fluctuations $\delta E_n(t)$. In the context of the stochastic Liouville equation the so-called Haken-Strobl-Reineker parameterization for the correlation functions of $\delta E_n(t)$ is frequently applied.[35] Here the modulation of the electronic energies is described in terms of a Gaussian-Markovian process which is strictly valid only in the high-temperature limit. An extension to finite temperatures was given by Čápek and coworkers.[36]

Below we will use the model of dichotomic noise which has been used in Ref. 37, as an example. As usual the first moment of the fluctuation is set to zero, $\langle \delta E_n(t)\rangle = 0$, while for the second moment we have

$$\langle \delta E_n(t)\delta E_m(t')\rangle = \delta_{mn}\hbar^2\eta^2 \exp\{-(t-t')/\tau_{\text{cor}}\} \tag{2.13}$$

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Here, the fluctuations of different sites have been assumed to be independent; the amplitude η is not dependent on the site index. Also the correlation time τ_{cor} is the same for all pigments. Finally we point out that the dichotomic process switches randomly between the values $+\hbar\eta$ and $-\hbar\eta$, i.e., it holds for any time t the important relation $(\delta E_n(t))^2 = \hbar^2\eta^2$.

D. Interaction with the External Field and Optical Polarization

One of the main reasons for introducing the excitonic oscillator representation was the simple form which is obtained for the molecular dipole operator, Eq. 2.6. This results in the following semiclassical expression for the interaction between the aggregate and the external field

$$H_{\text{field}}(t) = -\sum_n \mathcal{E}(t)\mu_n B_n^\dagger + \text{h.c.} \tag{2.14}$$

Note that we skip the vector notation for the external field as well as for the transition dipoles for brevity. This implies that all dipoles are oriented parallel as is the case, for instance, in some linear aggregates. However, an extension of the obtained results to the case of non-parallel dipoles at different sites is straightforward and requires the implementation of an orientational average for the calculation of nonlinear optical spectra.[38] Concerning the (classical) external field one is usually interested in setups where a sequence of pulses interact with the sample, i.e.,

$$\mathcal{E}(t) = \sum_j \mathcal{E}_{\omega_j}(t)e^{-i(\omega_j t - \mathbf{k}_j \mathbf{r})} + \text{c.c.} \tag{2.15}$$

Here $\mathcal{E}_{\omega_j}(t)$ is the pulse envelope while ω_j and $\mathbf{k}_j$ denote the carrier frequency and the wave vector, respectively (cf. Ref. 32). Throughout this paper we will apply the rotating wave approximation to the system-field coupling, i.e., from Eq. 2.14 only those terms for which an excitation of the system goes together with an energy loss of the external field and vice versa are considered (i.e., $H_{\text{field}} \propto \mathcal{E}_{\omega_j}(t)B_n^\dagger e^{-i(\omega_j t - \mathbf{k}_j \mathbf{r})} + \text{h.c.}$).

All information about the response of the sample to for example, a strong pump pulse, is contained in the expectation value of the polarization. Within the excitonic oscillator representation the polarization operator is defined as[27,28]

$$P(t) = \sum_n \mu_n[B_n^\dagger(t) + B_n(t)] \tag{2.16}$$

Here, the time dependence of the exciton operator is in the Heisenberg representation. Calculation of the expectation value of Eq. 2.16 thus requires the solution of the Heisenberg equations of motion for the operator B_n (or $B_n^\dagger$). As

we will see in the following section this involves in principle the solution of an infinite hierarchy of equations. Our main objective therefore will be the derivation of a closed set of equations of motion which allows the determination of the polarization.

III. EQUATIONS OF MOTION

A. General

The calculation of the nonlinear optical response according to Eq. 2.16 requires establishing equations of motion for the oscillator operator B_n, i.e., we need to obtain a closed expression for

$$\frac{dB_n}{dt} = -\frac{i}{\hbar}[B_n, H_{\text{ex}} + H_{\text{field}}(t) + H_{\text{IC}} + H_{\text{ex-vib}}]$$
$$= \frac{dB_n}{dt}\Big|_{\text{ex}} + \frac{dB_n}{dt}\Big|_{\text{field}} + \frac{dB_n}{dt}\Big|_{\text{IC}} + \frac{dB_n}{dt}\Big|_{\text{ex-vib}} \tag{3.1}$$

Let us first consider the free evolution of the electronic system. In order to simplify the notation we will assume for the following that the ratio (Eq. 2.3) of the $S_1 \to S_N$ and the $S_0 \to S_1$ dipole moment is independent of the site index, i.e., we take $\kappa_n = \kappa$, $q_n^{(1)} = q_1$, and $q_n^{(2)} = q_2$. Further we will substitute $\gamma_n = \gamma$. We then have

$$\frac{dB_n}{dt}\Big|_{\text{ex}} = -\frac{i}{\hbar}\sum_k \Big[(\delta_{nk}\hbar\Omega_n + J_{nk})B_k$$
$$-(q_1 J_{nk} - \delta_{nk}\hbar\Delta_n)B_n^\dagger B_n B_k \tag{3.2}$$
$$+q_2 J_{nk}(B_n^\dagger)^2 B_n^2 B_k\Big]$$

Eq. 3.2 already indicates the challenges one faces with the equation of motion approach. The right-hand side couples the time evolution of the one-exciton oscillator variable B_n to other variables like $B_n^\dagger B_n B_k$ and $(B_n^\dagger)^2(B_n)^2 B_k$. The accumulation of oscillator variables continues if we look at the field dependent contribution to Eq. 3.1 which reads

$$\frac{dB_n}{dt}\Big|_{\text{field}} = \frac{i}{\hbar}\mathcal{E}(t)\mu_n\left[1 - q_1 B_n^\dagger B_n + q_2(B_n^\dagger)^2(B_n)^2\right] \tag{3.3}$$

Thus the field drives the one-exciton polarization by acting on the ground state but also on the populations of the one- and two-exciton oscillator states. The respective population operators enter as new variables. For the internal conversion contribution to Eq. 3.1 we get

$$\frac{dB_n}{dt}\Big|_{\text{IC}} = -\frac{i}{\hbar}V^{(\text{IC})}(R)\left[(B_n)^2 + \kappa^2 B_n^\dagger B_n\right.$$
$$\left. -(1+\kappa^2)(B_n^\dagger)^2(B_n)^2\right] \tag{3.4}$$

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i.e., the internal conversion connects not only the one-exciton polarization variable B_n to the population variables of the one- and two-exciton oscillator states but also introduces the two-exciton variable $(B_n)^2$.

Finally, we give the contribution due to the exciton-vibrational interaction. It reads

$$\left.\frac{dB_n}{dt}\right|_{ex-vib} = -\frac{i}{\hbar}\delta E_n(t)\left[B_n + (\gamma - 2)B_n^\dagger(B_n)^2)\right]$$

$$(3.5)$$

and does not introduce new excitonic variables.

As an additional complication in the equations of motion (3.4) new operator products appear which contain the nuclear degrees of freedom (so-called vibrational assisted operators); for example, we have $V^{(IC)}(R)(B_n)^2$ for which a separate equation of motion exists. Further, in Eq. 3.5 the stochastic process enters, for example, in the product $\delta E_n(t)B_n$ whose evaluation requires solving an additional equation of motion. Below we will show how the effects of internal conversion and exciton-vibrational coupling can be incorporated into respective relaxation and dephasing rates. Since these dissipative processes basically affect the coherences between different oscillator variables it is reasonable to assume that upon taking the expectation value of operator products not all types of coherences between different molecular sites have to be accounted for. In fact there are various approximation schemes for factorization of operator product expectation values which are suited to describe the spectroscopy of different physical processes (for a discussion see Refs. 29,32).

As has been pointed out in several places[27,28,32] the different operator products can be classified according to the order of the external field they correspond to, i.e., a product like $(B_n^\dagger)^a(B_n)^b$ is of order $a + b$ in the field. In the following we are interested in calculating the nonlinear optical polarization for rather strong pump fields, i.e., the above type of classification is not appropriate. The alternative which we provide is based on the assumption of weak inter-site dipole-dipole interaction and strong dephasing due to the exciton-vibrational interaction introduced via the stochastic fluctuations of electronic energies. Under these conditions the expectation values can be factorized into products of dynamical variables at different sites. This results in a Master Equation for the on-site excitonic variables which is exact in second order with respect to the dipole-dipole interaction. Coherences between different sites which are of higher than second order in the dipole-dipole interaction will be neglected. It should be noted, however, that the present treatment goes beyond the standard description of EEA and exciton transfer for it takes into account all on-site coher-

ences created by the external field. Inspecting Eqs. 3.2-3.5 we notice that this requires calculating the quantities $\langle B_n \rangle$, $\langle (B_n)^2 \rangle$, $\langle B_n^\dagger(B_n)^2 \rangle$, $\langle B_n^\dagger B_n \rangle$ and $\langle (B_n^\dagger)^2(B_n)^2 \rangle$, where the brackets indicate two averaging procedures, one stochastical and one quantum statistical.

B. Internal Conversion

Since our focus is on the process of EEA we start with a detailed derivation of the internal conversion contribution to Eq. 3.1. According to Eq. 3.4 the dynamics of the polarization variable B_n is coupled to operators which contain the nuclear degrees of freedom via $V^{(IC)}(R)$. Let A_n be the electronic part of these operator products. Our aim is to obtain an expression for $(V^{(IC)}(R)A_n)(t)$ by using perturbation theory. In lowest order with respect to $V^{(IC)}(R)$ we get

$$(V^{(IC)}(R)A_n)(t) = \frac{i}{\hbar}\int_0^t dt' H_{IC}(t - t')$$
$$U_0^\dagger(t)\,V^{(IC)}(R)A_nU_0(t)$$
$$-\frac{i}{\hbar}\int_0^t dt'\,U_0^\dagger(t)V^{(IC)}(R)$$
$$A_nU_0(t)H_{IC}(t - t')$$

$$(3.6)$$

Here, the time evolution operator $U_0(t)$ contains the electronic Hamiltonian H_{ex} and the vibrational Hamiltonian $H_{vib}(R)$ which is not further specified. In the above expression $H_{IC}(t)$ has been formulated in the interaction picture, i.e., it reads

$$H_{IC}(t) = V^{(IC)}(R; t)B_n^\dagger(B_n)^2\exp\{-i\tilde{\Omega}_n t\} + \text{h.c.} \quad (3.7)$$

where the time dependence of the operator $V^{(IC)}(R; t)$ is due to the free evolution with respect to $H_{vib}(R)$. Hence it follows that

$$-\frac{i}{\hbar}V^{(IC)}(R)A_n = \gamma_-^*(\tilde{\Omega}_n)\,B_n^\dagger(B_n)^2A_n$$
$$+\gamma_+^*(\tilde{\Omega}_n)\,(B_n^\dagger)^2B_nA_n$$
$$-\gamma_+(\tilde{\Omega}_n)\,A_nB_n^\dagger(B_n)^2$$
$$-\gamma_-(\tilde{\Omega}_n)\,A_n(B_n^\dagger)^2B_n$$

$$(3.8)$$

Here, the Markov approximation has been introduced, i.e., the correlation function of the vibrational degrees of freedom is assumed to decay fast compared to the dissipative dynamics of the system. In this limit the half-sided Fourier transforms of the correlation function of the vibrational degrees of freedom,

$$\gamma_\pm(\omega) = \frac{1}{\hbar^2}\int_0^\infty dt\,e^{\pm i\omega t}\langle V^{(IC)}(R, t)V^{(IC)}(R, 0)\rangle\,,$$

$$(3.9)$$

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enter the equation of motion. In the following these damping functions will be considered as real quantities, i.e., a renormalization of the electronic energies by the internal conversion processes will be neglected. The functions γ_+ (γ_-) are the internal conversion rates for downward (upward) non-radiative transitions between the second and the first excited oscillator electronic state. The ratio of upward and downward rates fulfills detailed balance, i.e., for reasonable temperatures the upward rate can be neglected. Hence we will set $\gamma_- \approx 0$ in the following.

At this point we introduce a secular approximation which can be justified as follows: Consider the case $A_n \equiv B_n$ in Eq. 3.8. Inserting this expression into Eq. 3.4 gives contributions like $(B_n^\dagger)^2 (B_n)^2$ etc. Now the free time evolution of B_n will contain a factor $\exp(-i\Omega_n t)$ while we have a constant contribution from $(B_n^\dagger)^2(B_n)^2$ (which, however, will give rise to an oscillating integrand in the solution for B_n). In the spirit of a coarse graining of the time axis the latter term can be neglected and only those terms on the right-hand side of Eq. 3.4 which also oscillate as $\exp(-i\Omega_n t)$ need to be considered. Neglecting all so-called non-secular terms we have

$$\frac{d\langle B_n\rangle}{dt}\bigg|_{IC} = -\kappa^2\gamma_+(\tilde{\Omega}_n)\langle B_n^\dagger(B_n)^2\rangle \tag{3.10}$$

For the remaining exciton variables of interest we obtain using Eq. 3.8 together with the secular approximation

$$\frac{d\langle (B_n)^2\rangle}{dt}\bigg|_{IC} = -\kappa^2\gamma_+(\tilde{\Omega}_n)\langle (B_n)^2\rangle \tag{3.11}$$

$$\frac{d\langle B_n^\dagger(B_n)^2\rangle}{dt}\bigg|_{IC} = -\kappa^2\gamma_+(\tilde{\Omega}_n)\langle B_n^\dagger(B_n)^2\rangle \tag{3.12}$$

$$\frac{d\langle B_n^\dagger B_n\rangle}{dt}\bigg|_{IC} = -2(\kappa^2 - 1)\gamma_+(\tilde{\Omega}_n)\langle (B_n^\dagger)^2(B_n)^2\rangle \tag{3.13}$$

and

$$\frac{d\langle (B_n^\dagger)^2(B_n)^2\rangle}{dt}\bigg|_{IC} = -2\kappa^2\gamma_+(\tilde{\Omega}_n)\langle (B_n^\dagger)^2(B_n)^2\rangle \tag{3.14}$$

C. Exciton-Vibrational Coupling

In Section IIC the model of stochastic dichotomic noise for the description of the dynamical fluctuations of the environment has been introduced. This resulted in Eq. 3.5 which we will discuss in more detail now. According to the theorem of Shapiro and Loginow[39] the equation of motion

for the stochastic average of a product of type $\delta E_n(t)B_n$ reads in the Heisenberg representation

$$\frac{d}{dt}\langle \delta E_n(t)B_n(t)\rangle = -\tau_{cor}^{-1}\langle \delta E_n(t)B_n(t)\rangle$$
$$+\langle \delta E_n(t)\frac{d}{dt}B_n(t)\rangle \tag{3.15}$$

Here τ_{cor} is the correlation time of the stochastic process introduced in Eq. 2.13. Using the property $(\delta E_n(t))^2 = \hbar^2\eta^2$ and Eq. 2.13 (neglect of site-site correlations) the system of differential Eqs. 3.15 can be closed and no higher correlation functions of the fluctuation term are generated. In principle the model of dichotomic noise allows inclusion of non-Markovian effects into the dynamics, i.e., arbitrary correlation times τ_{cor}. For simplicity we will assume for the following that $\tau_{cor} \ll \tau_{system}$ where τ_{system} is some characteristic time of the system dynamics. Thus a perturbative treatment of the noise within the Markov limit becomes possible. To this end we write down the equation of motion for $\langle \delta E_n B_n\rangle(t) \equiv \langle \delta E_n(t)B_n(t)\rangle$ using Eq. 3.15,

$$\frac{d}{dt}\langle \delta E_n B_n\rangle(t) = -i(\Omega_n - i\tau_{corr}^{-1})\langle \delta E_n B_n\rangle(t)$$
$$-i\Delta_n\langle \delta E_n B_n^\dagger(B_n)^2\rangle(t)$$
$$-i\eta^2(\langle B_n\rangle(t) + (\gamma - 2)\langle B_n^\dagger(B_n)^2\rangle(t)) \tag{3.16}$$

Here we have neglected the influence of the external field, the Coulomb interaction and the internal conversion processes (so-called cross terms). The formal solution of Eq. 3.16 reads

$$\langle \delta E_n B_n\rangle(t) = -i\int_0^t dt'\, e^{-i(\Omega_n - i\tau_{cor}^{-1})t'}$$
$$\left(\Delta_n\langle \delta E_n B_n^\dagger(B_n)^2\rangle(t - t')\right.$$
$$+\eta^2(\langle B_n\rangle(t - t')$$
$$\left.+(\gamma - 2)\langle B_n^\dagger(B_n)^2\rangle(t - t'))\right). \tag{3.17}$$

Next we evaluate $\langle \delta E_n B_n^\dagger(B_n)^2\rangle(t)$ along the same lines which gives

$$\langle \delta E_n B_n^\dagger(B_n)^2\rangle(t) = -i\int_0^t dt\, e^{-i(\tilde{\Omega}_n - i\tau_{cor}^{-1})t'}$$
$$\eta^2(\gamma - 1)\langle B_n^\dagger(B_n)^2\rangle(t - t') \tag{3.18}$$

Using the Markov approximation we can shift the upper integration limit to infinity and replace the time argument $t - t'$ by t by taking into account the free evolution in terms of the site energies (the diagonal term of H_{ex}), i.e.,

$B_n^\dagger(B_n)^2(t - t') \approx e^{i\tilde{\Omega}_n t'} B_n^\dagger(B_n)^2(t)$. Such a replacement is justified if the system dynamics is dominated by the diagonal term of H_{ex} on the time scale of the correlation time of the bath degrees of freedom, i.e., we assume an ultrashort correlation time of the bath. This gives

$$\langle \delta E_n B_n^\dagger(B_n)^2 \rangle(t) = -i\eta^2 \tau_{\text{cor}}(\gamma - 1)\langle B_n^\dagger(B_n)^2 \rangle(t)$$
(3.19)

Applying this result to Eq. 3.17 gives in the limit where $\tau_{\text{cor}}^{-1} \gg \Delta_n = \tilde{\Omega}_n - \Omega_n$, i.e., assuming a small detuning of the S_N-state

$$\langle \delta E_n B_n \rangle(t) = -i\eta^2 \tau_{\text{cor}}(\langle B_n \rangle(t) + (\gamma - 2)\langle B_n^\dagger(B_n)^2 \rangle(t))$$
(3.20)

Inserting the above two expressions into Eq. 3.5 we finally obtain the following dephasing contribution

$$i\hbar \frac{d}{dt}\langle B_n \rangle \bigg|_{\text{ex-vib}} = -\Gamma\left[\langle B_n \rangle + \gamma(\gamma - 2)\langle B_n^\dagger(B_n)^2 \rangle\right]$$
(3.21)

where the dephasing rate constant Γ is given in terms of the amplitude and correlation time of the stochastic noise as

$$\Gamma = \eta^2 \tau_{\text{cor}}$$
(3.22)

In complete analogy we get for the remaining dephasing terms

$$\frac{d}{dt}\langle B_n^\dagger(B_n)^2 \rangle \bigg|_{\text{ex-vib}} = -\Gamma(\gamma - 1)^2\langle B_n^\dagger(B_n)^2 \rangle$$
(3.23)

and for the two-exciton variable

$$\frac{d}{dt}\langle(B_n)^2 \rangle \bigg|_{\text{ex-vib}} = -\Gamma\gamma^2\langle(B_n)^2 \rangle$$
(3.24)

The relaxation dynamics of the population variables for the first and second excited oscillator state $B_n^\dagger B_n$ and $(B_n^\dagger)^2 (B_n)^2$, respectively, is intimately connected to the population transfer between different sites.[3,33] Therefore they will be treated separately in the following section.

D. Exciton Transfer

Exciton transfer initiated by the dipole-dipole interaction (J_{mn}) will be treated within the second order of perturbation theory.[33] In particular this implies that the dephasing of the site-site coherences due to the stochastic fluctuations of the site energies is rapid as compared to typical transfer times. This allows us to derive a closed set of equations of motion for the on-site exciton variables employing a certain factorization scheme for the stochastical and quantum statistical expectation values. This is illustrated for the occupation

variable of the higher excited state in the following, whose equation of motion is found as

$$\frac{d}{dt}\langle(B_n^\dagger)^2(B_n)^2 \rangle \bigg|_{\text{ex}} = \frac{2}{\hbar}\text{Im}\sum_n J_{kn}\kappa^2\langle(B_n^\dagger)^2 B_n B_k \rangle$$
(3.25)

To obtain a transfer rate a separate equation of motion for the operator $\langle(B_n^\dagger)^2 B_n B_k \rangle$ on the right-hand side has to be solved. This can be achieved by formal integration and the restriction to first order in the dipole-dipole coupling. Further, the stochastic exciton-vibrational coupling is included in the second order. The details of the calculation are given in Appendix A. Here we only quote the result:

$$\frac{d}{dt}\langle(B_n^\dagger)^2(B_n)^2 \rangle \bigg|_{\text{ex}} = -\frac{2}{\hbar}\sum_k \kappa^2|J_{nk}|^2 \frac{\tilde{\Gamma}}{(\Omega_n - \Omega_k)^2 + \tilde{\Gamma}^2}$$
$$\times \left[\langle(B_n^\dagger)^2(B_n)^2 \rangle(1 + (2\kappa^2 - 1)\langle B_k^\dagger B_k \rangle\right.$$
$$+ q_2\langle(B_k^\dagger)^2(B_k)^2 \rangle)$$
$$\left. - \kappa^2\langle B_k^\dagger B_k \rangle\langle B_n^\dagger B_n \rangle\right]$$
(3.26)

where the broadening parameter is determined as $\tilde{\Gamma} = \Gamma(1 + (\gamma-1)^2)$. In deriving Eq. 3.26 we assumed that the detuning of the higher excited state Δ_n is small compared to the dephasing rate $\tilde{\Gamma}$. Therefore, in the Lorentzian prefactor $\tilde{\Omega}_n$ does not appear. Note, however, that the effect of different transition frequencies due to static disorder, for instance, is fully included, i.e., we can have $\Omega_k - \Omega_n \gg \tilde{\Gamma}$.

In complete analogy the exciton transfer contribution to the equation of motion for $\langle B_n^\dagger B_n \rangle$ is obtained as

$$i\hbar \frac{d}{dt}\langle B_n^\dagger B_n \rangle \bigg|_{\text{ex}} = (1 - 2\kappa^{-2})\left(\frac{d}{dt}\langle(B_n^\dagger)^2(B_n)^2 \rangle\bigg|_{\text{ex}}\right)$$
$$+ \frac{2}{\hbar^2}\sum_k \kappa^2|J_{nk}|^2 \frac{\Gamma}{(\Omega_n - \Omega_k)^2 + \Gamma^2}$$
$$\times ([\langle B_n^\dagger B_n \rangle(1 + q_2\langle(B_k^\dagger)^2(B_k)^2 \rangle)]$$
$$- \{k \leftrightarrow n\})$$
(3.27)

Note that from Eqs. 3.26 and 3.27 we can derive the equation of motion for the electronic state populations; details are given in Appendix B.

To complete the second order treatment of the dipole-dipole coupling we need in principle equations of motion for the operator products corresponding to polarization terms, i.e., $\langle B_n \rangle$, $\langle(B_n)^2 \rangle$, and $\langle B_n^\dagger(B_n)^2 \rangle$. These equations lead to a transfer of coherences between different sites. However, coherence transfer has to compete with the intra-site dephasing of coherences described by Eqs. 3.21, 3.23 and 3.24 and

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characterized by the rate constant Γ (Eq. 3.22). One finds in complete analogy to Eqs. 3.26 and 3.27 that the coherence transfer scales with the rate constant $|J_{nk}/\hbar|^2/\Gamma$. Assuming strong intra-site dephasing and weak dipole-dipole coupling, i.e., $\Gamma^2 \gg |J_{nk}/\hbar|^2$, coherence transfer can be neglected. Note that there is no influence of the exciton-vibrational coupling on the level populations. This justifies to take into account the influence of the dipole-dipole interaction on the level populations but neglect it for the transfer of coherences. For stronger dipole-dipole coupling the latter may contribute as well. However, in this case a more sophisticated factorization scheme than applied here would be necessary (see, e.g., Refs. 29,32,40).

IV. CALCULATION OF NONLINEAR OPTICAL SIGNALS

In the following we will show how to incorporate the interaction with the external field into the equations of motion derived so far. This will put us into the position to calculate nonlinear optical spectra taking into account the effect of intense pump fields which are known to provide information about EEA. For strong pump fields a perturbation expansion with respect to the field strength is no longer feasible and a nonperturbative theory is required. For this purpose it is necessary keep track of the phase of the polarization, i.e., to distinguish the different propagation directions of the nonlinear polarization wave in the sample. This is conveniently done using an expansion of excitonic oscillator expectation values with respect to the carrier waves of the external fields[26,27,41]

$$\langle (B_m^\dagger)^a (B_n)^b \rangle = \sum_{n_1,n_2=-\infty}^{\infty} e^{i\sum_{s=1,2} n_s(\mathbf{k}_s \mathbf{r} - \omega_s t)} \sigma_{ab}^{(n_1,n_2)}(m,n;t) \tag{4.1}$$

Here, we assumed two external fields with wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$. The equation of motion for the expansion coefficients then reads

$$\frac{d}{dt} \sigma_{ab}^{(n_1,n_2)}(m,n;t) = \int d^3\mathbf{r} \, e^{-i\sum_{s=1,2} n_s(\mathbf{k}_s \mathbf{r} - \omega_s t)}$$

$$\frac{d}{dt} \langle (B_m^\dagger)^a (B_n)^b \rangle$$

$$+i \sum_s \omega_s \sigma_{ab}^{(n_1,n_2)}(m,n;t) \tag{4.2}$$

Introducing the expansion 4.1 does not alter the equations of motion derived in Section III. The contributions due to

internal conversion, exciton-vibrational coupling and exciton motion leave the indices n_1 and n_2 unchanged. The field-dependent contribution to the right-hand side in Eq.3.1, however, mixes different expansion coefficients as will be shown subsequently. Since the interaction Hamiltonian 2.14 is diagonal in the site index we will drop this index for brevity. The external field contributions for the related expansion coefficients of the exciton variables discussed in Section III are obtained as

$$i\hbar \frac{d}{dt} \sigma_{01}^{(n_1,n_2)}\Big|_{\text{field}} = \frac{i}{\hbar}\mu \sum_{s=1,2} \mathcal{E}_{\omega_s}(t)$$

$$\left(\delta_{n_s,1} - q_1\sigma_{11}^{(n_s-1,n_{\bar{s}})} + q_2\sigma_{22}^{(n_s-1,n_{\bar{s}})} \right) \tag{4.3}$$

where $\bar{s} = 1(2)$ if $s = 2(1)$,

$$i\hbar \frac{d}{dt} \sigma_{02}^{(n_1,n_2)}\Big|_{\text{field}} = \frac{i}{\hbar}\mu \sum_{s=1,2} \mathcal{E}_{\omega_s}(t)$$

$$\left((\kappa^2 + 1)\sigma_{12}^{(n_s-1,n_{\bar{s}})} + \kappa^2\sigma_{01}^{(n_s-1,n_{\bar{s}})} \right) \tag{4.4}$$

$$i\hbar \frac{d}{dt} \sigma_{12}^{(n_1,n_2)}\Big|_{\text{field}} = -\frac{i}{\hbar}\mu \sum_{s=1,2}$$

$$\left\{ \mathcal{E}_{\omega_s}^*(t)\sigma_{02}^{(n_s+1,n_{\bar{s}})} - \mathcal{E}_{\omega_s}(t)\left(\kappa^2\sigma_{11}^{(n_s-1,n_{\bar{s}})} - (1+\kappa^2)\sigma_{22}^{(n_s-1,n_{\bar{s}})}\right) \right\} \tag{4.5}$$

$$\frac{d}{dt} \sigma_{11}^{(n_1,n_2)}\Big|_{\text{field}} = \frac{2}{\hbar}\mu \sum_{s=1,2} \text{Im}$$

$$\left\{ \mathcal{E}_{\Omega_s}^*(t)\left(\sigma_{01}^{(n_s+1,n_{\bar{s}})} - q_1\sigma_{12}^{(n_s+1,n_{\bar{s}})}\right) \right\} \tag{4.6}$$

and

$$\frac{d}{dt} \sigma_{22}^{(n_1,n_2)}\Big|_{\text{field}} = \frac{2}{\hbar}\mu\kappa^2 \sum_{s=1,2} \text{Im}$$

$$\left(\mathcal{E}_{\Omega_s}^*(t)q_1\sigma_{12}^{(n_s+1,n_{\bar{s}})} \right) \tag{4.7}$$

The action of the external fields changes the indices n_1 and n_2 of the expansion coefficients, i.e., different contributions to Eq. 4.1 are mixed. However, due to the rotating wave approximation the sum of excitations of the field and the aggregate is conserved and the relation

$$n_1 + n_2 + a - b = 0 \tag{4.8}$$

holds for the indices of the expansion coefficients. Eq. 4.8 remains valid also for the remaining contributions to Eq.

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3.1. For the dipole-dipole coupling this is a consequence of the applied Heitler-London approximation which conserves the number of molecular excitations during exciton transfer. Using Eq. 4.8 the index n_2, for example, can be dropped. In principle the remaining index n_1 still goes from $-\infty$ to $+\infty$. If, however, one of the two pulses is weak, as for example, in a pump-probe experiment, then the set of equations can be closed by restricting n_1 to $n_1 = \{-1, 0, 1\}$ assuming that pulse 1 is the weak probe pulse. Notice also that $(\sigma_{ab}^{(n_1, n_2)}(m, n; t))^{\dagger} = \sigma_{ba}^{(-n_1, -n_2)}(n, m; t)$ which relates the expansion coefficients for different exciton variables.

Next we discuss the issue of factorization of expectation values introduced in Section III in the present context. Following the reasoning of Section III we suggest the simple factorization scheme for the expansion coefficients

$$\sigma_{ab}^{(n_1)}(m, n; t) = \sum_{\tilde{n}} \sigma_{a0}^{(\tilde{n})}(m; t) \sigma_{0b}^{(n_1-\tilde{n})}(n; t) \qquad (4.9)$$

Applying this scheme, for example, to Eq. 3.26 leads to the following transfer equation for the population of the second excited molecular state at site n

$$
\begin{aligned}
\frac{d}{dt}\sigma_{22}^{(n_1)}(n, t)\bigg|_{\text{ex}} &= -\frac{2}{\hbar} \sum_k \kappa^2 |J_{nk}|^2 \frac{\tilde{\Gamma}}{(\Omega_n - \Omega_k)^2 + \tilde{\Gamma}^2} \\
&\quad \times \bigg[\sigma_{22}^{(n_1)}(n, t) + \sum_{\tilde{n}} \big\{\sigma_{22}^{(\tilde{n})}(n, t) \\
&\quad \big[(2\kappa^2 - 1)\sigma_{11}^{(n_1-\tilde{n})}(k, t) \\
&\quad + q_2\sigma_{22}^{(n_1-\tilde{n})}(k, t)\big] \\
&\quad - \kappa^2 \sigma_{11}^{(\tilde{n})}(n, t)\sigma_{11}^{(n_1-\tilde{n})}(k, t)\big\}
\end{aligned}
$$

(4.10)

Equations of motion for the expansion coefficients of the remaining variables are obtained in direct analogy.

Finally, we give the relation between the above defined expansion coefficients and the differential pump-probe absorption spectrum defined as

$$\frac{\Delta\alpha}{\alpha} = \frac{S_{\text{tot}}(\mathcal{E}_{\text{pu}}, \mathcal{E}_{\text{pr}}, \tau_d) - S_{\text{tot}}(\mathcal{E}_{\text{pu}} = 0, \mathcal{E}_{\text{pr}})}{S_{\text{tot}}(\mathcal{E}_{\text{pu}} = 0, \mathcal{E}_{\text{pr}})} \qquad (4.11)$$

Here $S_{\text{tot}}(\mathcal{E}_{\text{pu}}, \mathcal{E}_{\text{pr}}, \tau_d)$ is the energy loss that a weak probe pulse (wave vector $\mathbf{k}_{\text{pr}} = \mathbf{k}_1$) experiences when traveling through the probe. This quantity is investigated in dependence on the delay time τ_d to a strong pump pulse (wave vector $\mathbf{k}_{\text{pu}} = \mathbf{k}_2$). $S_{\text{tot}}(\mathcal{E}_{\text{pu}} = 0, \mathcal{E}_{\text{pr}})$ is the probe pulse energy loss in the linear optical regime, i.e., without the pump-pulse. For the calculation of S_{tot} we need the envelope of the spatial part of the nonlinear polarization wave $\mathcal{P}_{\omega_{\text{pr}}}^{(n_{\text{pu}}=0, n_{\text{pr}}=1)}(t)$ traveling in probe pulse direction. The

overall light induced polarization reads (cf. Eq. 2.16)

$$P(\mathbf{r}, t) = \sum_n \mu_n \sum_{n_{\text{pu}}, n_{\text{pr}}} e^{i \sum_{s=\text{pu,pr}} n_s(\mathbf{k}_s \mathbf{r} - \omega_s t)} \sigma_{10}^{(n_{\text{pu}}, n_{\text{pr}})}$$

(4.12)

The desired envelope of the polarization traveling along $\mathbf{k}_{\text{pr}}$ is obtained as

$$\mathcal{P}_{\omega_{\text{pr}}}^{(n_{\text{pu}}=0, n_{\text{pr}}=1)}(t) = \sum_n \mu_n \sigma_{10}^{(n_{\text{pu}}=0, n_{\text{pr}}=1)}(t) \qquad (4.13)$$

The integral energy loss experienced by the probe beam finally follows as

$$S_{\text{tot}} = 2\omega_{\text{pr}} \text{Im} \int_{-\infty}^{+\infty} dt\, \mathcal{E}_{\omega_{\text{pr}}}^*(t) \mathcal{P}_{\omega_{\text{pr}}}^{(n_{\text{pu}}=0, n_{\text{pr}}=1)}(t) \qquad (4.14)$$

Together with the discussed truncation scheme for the set of equations for the expansion coefficients this expression enables us to calculate pump-probe spectra for arbitrary strong pump fields. Of particular importance hereby is the intensity dependence of the spectra. As demonstrated in Ref. 26 EEA affect the global behavior of pump-probe spectra qualitatively and a nonperturbative inclusion of the pump field is required.

V. SUMMARY

A closed set of equations of motion for expectation values of excitonic oscillator variables (operator products) has been derived. They include contributions from exciton transfer, Eqs. 3.26-3.27, stochastic exciton-vibrational coupling, Eqs. 3.21-3.24, and internal conversion, Eqs. 3.10-3.14. This allows the calculation of the optical polarization according to Eqs. 3.1 and 2.16. A prescription of how to extract the nonlinear optical signal for a pump-probe setup in any order of perturbation theory with respect to the pump pulse has been given as well. The most important approximation has been the perturbative treatment of site-site correlations within second order with respect to the dipole-dipole coupling. This treatment is justified if the dipole-dipole interaction is small compared to the amplitude of the stochastic modulation of the transition energies. It should be noted that the present factorization scheme for multi-site correlation functions is not the only possible choice (cf. Ref. 32), but it gives a rather small number of coupled equations which allows treatment of large aggregates. Whether other factorizations would be superior for the description of a particular aspect of the nonlinear optical response remains to be investigated.

Our approach goes beyond the standard rate limit type description of exciton dynamics in the presence of annihilation since multi-exciton populations and coherences are taken into account. Further, the formulation in terms of driven anharmonic excitonic oscillators enables us to establish a direct connection to observables in nonlinear optical experiments.

In the Introduction we discussed the issue of energy transfer in photosynthesis. The present approach is suited to be applied to photosynthetic systems in two situations, First, we can study exciton dynamics in antenna complexes with weakly coupled pigment pools. A typical example would be the LHC-II of green plants. Second, one could take the broader point of view assuming that the dynamics inside a particular pigment protein antenna complex is not of importance. Instead, one is interested in the transfer and its spectroscopic signatures in a large domain of antennae (e.g., an array of LH2 complexes surrounding the LH1 which encircles the reaction center in purple bacteria). In this case individual antenna complexes would be modeled as electronic three level systems. The inclusion of the reaction center in terms of a particle trap into the existing theory is straightforward.

APPENDIX A: DERIVATION OF EQ. (3.26)

A second order transfer rate for the higher excited state populations can be obtained after writing down the equation of motion for the operator product on the right-hand side of Eq. 3.26. This equation will be formally solved and products of operators acting at different sites will be factorized. This factorization is therefore correct in the second order with respect to the dipole-dipole interaction. We start with the contribution from the dipole-dipole coupling to the equation of motion which reads

$$i\hbar \frac{d}{dt}(B_n^\dagger)^2 B_n B_m \bigg|_{ex} = \frac{i}{\hbar} \Big[J_{nk}(B_n^\dagger)^2 (B_n)^2$$
$$+ (2\kappa^2 - 1)(B_n^\dagger)^2 (B_n)^2 B_k^\dagger B_k$$
$$- \kappa^2 B_n^\dagger B_n B_k^\dagger B_k$$
$$+ q_2 (B_n^\dagger)^2 (B_n)^2 (B_k^\dagger)^2 (B_k)^2 \Big]$$

$$(A1)$$

The diagonal part of H_{ex} contributes according to

$$\frac{d}{dt}(B_n^\dagger)^2 B_n B_k \bigg|_{diag-ex} = i(\tilde{\Omega}_n - \Omega_k)(B_k^\dagger)^2 B_n B_k$$
$$- i\Delta_k (B_n^\dagger)^2 (B_n)^2 (B_k^\dagger)^2 (B_k)^2$$

$$(A2)$$

To obtain an expression for the dephasing rate, the contribution due to exciton vibrational coupling is examined. Since inter-site correlations of fluctuations are neglected, we can write the exciton vibrational coupling in terms of the intra-site dephasing terms derived in Section III. We have

$$\frac{d}{dt}(B_n^\dagger)^2 B_n B_k \bigg|_{ex-vib} \approx \left(\frac{d}{dt}(B_n^\dagger)^2 B_n \bigg|_{ex-vib} \right) B_k$$
$$+ (B_n^\dagger)^2 B_n \left(\frac{d}{dt} B_k \bigg|_{ex-vib} \right)$$
$$= -\Gamma((\gamma - 1)^2 + 1)\langle (B_n^\dagger)^2 B_n B_k \rangle$$
$$- \Gamma(\gamma - 2)^2 \langle (B_n^\dagger)^2 B_n B_k^\dagger (B_k)^2 \rangle$$

$$(A3)$$

By combining the diagonal parts of Eqs. A2 and A3 with the equation of motion containing the dipole-dipole interaction Eq. A1 we arrive at the following expression for the expectation value

$$\langle (B_n^\dagger)^2 B_n B_k(t) \rangle = -\frac{i}{\hbar} \int_0^t dt' \, e^{i(\Omega_n - \Omega_k + i\bar{\Gamma})t'}$$
$$J_{nk} \Big[\langle (B_n^\dagger)^2 (B_n)^2 \rangle (t - t')$$
$$+ (2\kappa^2 - 1)\langle (B_n^\dagger)^2 (B_n)^2 \rangle (t - t')\langle B_k^\dagger B_k \rangle (t - t')$$
$$- \kappa^2 \langle B_n^\dagger B_n \rangle (t - t')\langle B_k^\dagger B_k \rangle (t - t')$$
$$+ q_2 \langle (B_n^\dagger)^2 (B_n)^2 \rangle (t - t')\langle (B_k^\dagger)^2 (B_k)^2 \rangle (t - t') \Big]$$

$$(A4)$$

Note that a site specific factorization of the expectation values on the right-hand side has been carried out. Further, we used $\bar{\Gamma} = \Gamma((\gamma - 1)^2 + 1)$ and replaced $\tilde{\Omega}_k$ by Ω_k assuming that the dephasing ($\bar{\Gamma}$) is much stronger than the detuning of the S_N state. For strong dephasing the Markov approximation is justified as discussed earlier. Thus we can replace in the integrand of Eq. A4 the time $t - t'$ by t and carry out the integration (setting the upper limit formally to infinity) resulting in a Lorentzian. After introducing the solution into Eq. 3.25 we finally arrive at Eq. 3.26.

APPENDIX B: MASTER EQUATION

It is instructive to make the connection between the dynamics of the excitonic oscillator variables and the populations of the different electronic states of each pigment. We have $N_{2n} = \langle |2_n\rangle\langle 2_n| \rangle = \kappa^{-2}\langle (B_n^\dagger)^2 (B_n)^2 \rangle$, $N_{1n} = \langle |1_n\rangle\langle 1_n| \rangle = \langle B_n^\dagger B_n \rangle - \langle (B_n^\dagger)^2 (B_n)^2 \rangle$, and $N_{0n} = 1 - N_{2n} - N_{1n}$. Eq. 3.26 expressed in terms of population

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variables then becomes

$$\frac{d}{dt}N_{2n}\,|_{\text{ex}} = -\frac{2}{\hbar}\sum_k \kappa^2 |J_{nk}|^2 \frac{\tilde{\Gamma}}{(\Omega_n - \Omega_k)^2 + \tilde{\Gamma}^2}$$
$$\times \left\{N_{2n}N_{0k} + \kappa^2 N_{2n}N_{1k} - \kappa^2 N_{1n}N_{2k} - N_{1k}N_{1n}\right\}$$
(B1)

The interpretation of the different terms on the right-hand side is straightforward. The first two terms couple the transition $|2_n\rangle \to |1_n\rangle$ at the n- site to the transitions $|0_k\rangle \to |1_k\rangle$ and $|1_k\rangle \to |2_k\rangle$ at the k-th site. The first process corresponds to exciton *fission* (see Fig. 3(A)), whereas the second process describes the transfer of a higher excited state excitation (see Fig. 3(B)). The third term is equivalent to the second one with interchanged site indices. The fourth term in Eq. (B1) describes the *fusion* of two single excited state excitons leading to a higher excited state exciton (see Fig. 3(C)). This process combined with internal conversion obtained from Eqs. 3.14 and 3.13 as

$$\frac{d}{dt}N_{2n}\bigg|_{\text{IC}} = -\frac{d}{dt}N_{1n}\bigg|_{\text{IC}} = -2\gamma_+(\tilde{\Omega}_n)\kappa^2 N_{2n}$$
(B2)

provides the microscopic picture for exciton-exciton annihilation in the considered aggregate.

Next we turn to the population of the first excited state. The respective equation of motion can be obtained from Eq. 3.27. We get
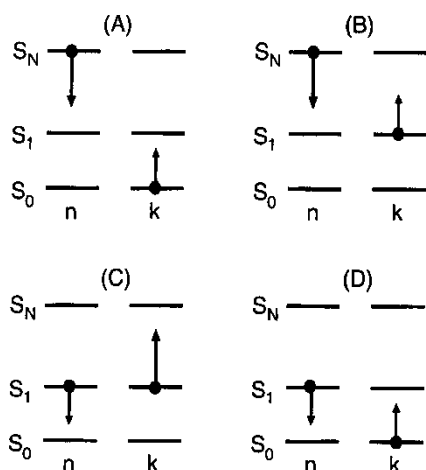

Fig. 3. Illustration of different contributions to Eqs. B1 and B3: (A) first term of Eq. B1 (exciton fission); (B) second term of Eq. B1 (S_N-state transfer); (C) fourth term of Eq. B1 (exciton fusion); (D) first term of Eq. B3 (S_1-state transfer).

$$\frac{d}{dt}(N_{1n} + 2N_{2n}) = \frac{2}{\hbar^2}\sum_k \kappa^2 |J_{nk}|^2 \frac{\Gamma}{(\Omega_n - \Omega_k)^2 + \Gamma^2}$$
$$\times \left(\{N_{1n}N_{0k} + \kappa^2 N_{2n}N_{0k} + \kappa^4 N_{2n}N_{1k}\} - \{k \leftrightarrow n\}\right)$$
(B3)

From this representation the physical origins of the single terms become obvious. The first term describes the motion of an exciton in first excited state manifold (see Fig. 3(D)) the second term is responsible for the fission of a higher excited state exciton into two first excited state excitons, whereas the third term describes the motion of a higher excited state exciton. Note that for the missing exciton fusion term it holds $\frac{d}{dt}N_{1n} = -2\frac{d}{dt}N_{2n})$ and therefore such a term does not appear explicitly on the right-hand side of Eq. B3.

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