INFLUENCE OF A PHONON BATH ON ELECTRONIC CORRELATIONS AND OPTICAL RESPONSE IN MOLECULAR AGGREGATES

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Abstract. A generating function algorithm that allows the calculation of the optical response of coupled exciton-phonon systems is developed. For a model of assemblies of three-level molecules coupled via dipole interaction and interacting linearly with nuclear degrees of freedom, we derive a closed set of equations of motion for five generating functions representing the exact response to third order in the external field. These are equivalent to an infinite hierarchy of equations of motion for phonon-assisted variables. Starting with the equations for the generating functions, several reduction schemes are derived. By eliminating the phonon degrees of freedom in favor of self-energies, the Haken-Strobl model of relaxation is recovered as a limiting case. A set of time-local equations is presented extending the Haken-Strobl treatment by keeping the temperature dependence as well as the excitonic signatures of the phonon self-energies. Finally, we derive equations that interpolate between the coherent and incoherent limits of exciton propagation and properly include the two exciton dynamics.

1. Introduction. Optical properties of molecular aggregates have been the focus of intensive recent experimental [1,2,3,4] as well as theoretical [5,6] investigations, because of their importance for many technological applications (e.g. J-aggregates) [7,8,9,10] and for biological systems (photosynthetic antenna complexes and the reaction center) [11,12,13,14]. A further stimulation for theoretical studies comes from the fact that the nonlinear optical response of these systems is known to exhibit characteristic signatures of electronic correlation effects [15,16,17,18,19]. The calculation of this response therefore provides a nontrivial testing ground for theories which go beyond the mean field description, known as local field approximation (LFA). In the idealized limiting case, where interactions of the electronic system with a bath (phonons or impurities) can be neglected, these correlations show up in the nonlinear optical response functions only via the two exciton scattering matrix [19,20]. The coupling to a phonon bath adds new degrees of freedom which in turn can affect the excitonic dynamics in a variety of ways. The most obvious effect of the exciton phonon coupling is that it contributes to the dephasing of excitonic variables and thus introduces characteristic relaxation timescales in the electronic subsystem. For many experimental situations this is the dominant influence of the exciton phonon coupling and simplified descriptions are appropriate; The well known Haken-Strobl model [24] is an examples for such a simplified scheme. It describes coherent and incoherent exciton dynamics in a unified framework. Its main deficiency is that it is an infinite temperature approximation and does not contain the proper detailed balance relation, that is essential for the description of incoherent motion, as is the case

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when using the Förster rate equations [21,22,23]. Some aspects of the coupling to phonons can however only be understood when also the phonon system is treated explicitly. Examples are memory effects like the Urbach tail [25,26,27] or phonon-assisted beat phenomena which have recently been observed in structured semiconductor samples [27,28]. Another interesting aspect of exciton-phonon coupling is that it can lead to new resonances known as dephasing-induced resonances [29,30,31].

The purpose of the present article is to analyze the influence of phonons on optically generated electronic correlations in molecular aggregates. In section 2 we specify our model Hamiltonian and relate the optical polarization to the relevant dynamical variables. In section 3 we derive a closed set of equations of motion for five generating functions representing phonon-assisted variables. As they stand, these equations are still exact up to third order in the optical field and thus provide a compact rigorous starting point for further analysis. A direct numerical solution of these equations will however in general only be feasible for very simple exciton phonon coupling schemes. In sections 4 and 5 we therefore use the generating function approach as a unified starting point to derive several levels of reduced descriptions relevant for various limiting cases.

2. The multilevel-Frenkel-Exciton model. Molecular aggregates are adequately described by the Frenkel-exciton model in Heitler-London approximation [19]. Many applications consider only a few excited states on each molecule. Often a model with only one excited state per molecule gives realistic results [17,18,19]. Here, we treat explicitly the case with two excited states per site. This is usually sufficient for the description of pump-probe spectra; a generalization to an arbitrary number of site excitations is formally straightforward [32,39]. A convenient formulation of this molecular three level model is provided by the *deformed Boson representation* [39,40]. The material part of the Hamiltonian reads (cf. Fig.1):

$$H_{mat} \equiv \hbar \sum_n \Omega_n B_n^\dagger B_n + \sum_{m \neq n} J_{nm}\, B_n^\dagger B_m + \sum_n \frac{g_n}{2} (B_n^\dagger)^2 (B_n)^2 , \tag{1}$$

Ω_n is the fundamental electronic transition frequency of isolated molecules. The energy of the second level is given by

$$\hbar\Omega_n^{(2)} = 2\hbar\Omega_n + \Delta_n , \tag{2}$$

with the anharmonicity parameter

$$\Delta_n = \kappa_n^2\, g_n/2 + (\kappa_n^2 - 2)\,\hbar\Omega_n , \tag{3}$$

and $\kappa_n \equiv \mu_n^{(21)}/\mu_n^{(10)}$ is the ratio between the dipole moments for the transitions $|1\rangle \rightarrow |2\rangle$ ($\mu_n^{(21)}$) and $|0\rangle \rightarrow |1\rangle$ ($\mu_n^{(10)} \equiv \mu_n$). We assume that

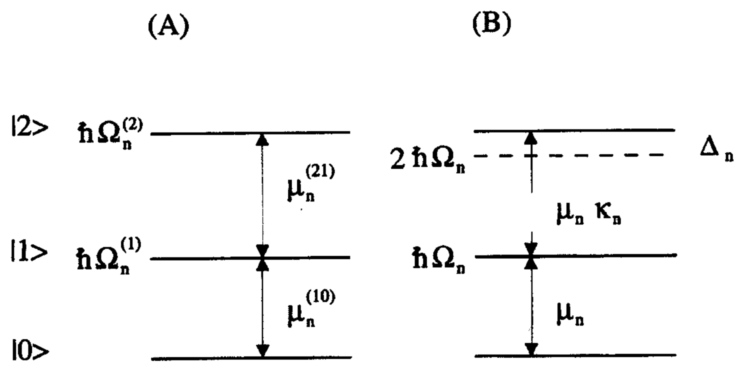

FIG. 1. *(A) Basic parameters (energies and transition dipole moments) of a three level molecule, (B) anharmonic oscillator parameters representing the same system.*

both transition dipoles of each molecule are oriented along the direction of the unit vector $\hat{\mu}_n$. J_{nm} accounts for the dipole-dipole interaction as well as for short-range exchange exciton couplings. $B_n^\dagger$ (B_n) are operators for the creation (annihilation) of excitations on site n. For a three-level model they obey the following commutation rules

$$[B_n, B_m] = [B_n^\dagger, B_m^\dagger] = 0\,, \tag{4}$$

$$[B_n, B_m^\dagger] = \delta_{nm}\{1 - q_n B_n^\dagger B_n + q_n'(B_n^\dagger)^2(B_n)^2\}\,, \tag{5}$$

with $q_n = 2 - \kappa_n^2$ and $q_n' = (\kappa_n^2 - \kappa_n^4 - 1)/\kappa_n^2$. Note that when $\Delta_n = 0$ and $\kappa_n = \sqrt{2}$ this results in a harmonic level scheme. For $\kappa_n = 0$ the third level is decoupled and we recover the usual (two-level) Frenkel-exciton model.

The nuclear degrees of freedom enter via the corresponding phonon modes. This leads to two additional contributions to our model Hamiltonian [25,41,42]. The first represents the noninteracting phonon system:

$$H_{ph} \equiv \sum_\lambda \hbar\omega_\lambda b_\lambda^\dagger b_\lambda\,, \tag{6}$$

while the second accounts for the exciton-phonon coupling:

$$H_{ep} \equiv \sum_{nm\lambda} \gamma_{nm}^\lambda B_n^\dagger B_m\,(b_\lambda^\dagger + b_\lambda)\,. \tag{7}$$

The operators $b_\lambda^\dagger$ (b_λ) in (6) and (7) are boson operators describing the creation (annihilation) of a phonon with frequency ω_λ in mode λ. They obey the commutation relations

$$[b_\lambda, b_{\lambda'}^\dagger] = \delta_{\lambda\lambda'}\,. \tag{8}$$

In (7) we kept only terms linear in the phonon amplitudes. Our present formulation of the phonon coupling is equivalent to equation (2.1) in [32] when we make the identification: $\gamma^{\lambda}_{nm} = -m_\lambda \omega_\lambda^2 \left(\frac{\hbar}{2m_\lambda\omega_\lambda}\right)^{1/2} d_{\lambda,nm}$, where m_λ is the mass of oscillator λ and $d_{\lambda,nm}$ is the corresponding displacement induced by molecular populations ($n = m$) and intermolecular coherences ($n \neq m$) respectively. Similar parameterizations of the interaction with phonons have been widely used [33,34,35,36,37,38].

Finally, the interaction with the optical field is given in dipole approximation by

$$H_{opt} \equiv -\sum_n \mu_n \, E_n \, (B_n + B_n^\dagger) \, , \tag{9}$$

where E_n is the component of the optical field in the direction $\hat{\mu}_n$ of the molecular dipole at site n.

The total Hamiltonian is

$$H = H_{mat} + H_{ph} + H_{ep} + H_{opt} \, . \tag{10}$$

Optical properties are derived from the optical polarization, which is given by [39,40]

$$P(t) = \sum_n \vec{\mu}_n \, \langle B_n \rangle(t) + c.c. \, . \tag{11}$$

3. Generating functions and their equations of motion. In this section we will derive closed equations of motion necessary for calculating the optical polarization up to third order in the optical field. We first note, that due to the Heitler-London approximation the expectation value of a product of p operators $B_n^\dagger$ and q operators B_n and an arbitrary number of phonon operators $b_\lambda^\dagger$,b_λ is at least of order $p + q$ in the external field, provided the product is in normal order (i.e. all operators $B^\dagger$ stand to the left of the operators B). Physically this is clear, because the only part of our Hamiltonian that does not conserve the number of excitations in the system is the dipole coupling to the optical field [18,19]. A more formal derivation of this statement can be made along the lines presented in [43] for the case of direct gap semiconductors.

We now consider the following five operators:

$$\hat{A}_{n\alpha\beta} = B_n \hat{F}_{\alpha\beta} \, , \tag{12}$$

$$\hat{B}_{nm\alpha\beta} = B_n B_m \hat{F}_{\alpha\beta} \, , \tag{13}$$

$$\hat{C}_{nm\alpha\beta} = B_n^\dagger B_m \hat{F}_{\alpha\beta} \, , \tag{14}$$

$$\hat{D}_{lnm\alpha\beta} = B_l^\dagger B_n B_m \hat{F}_{\alpha\beta} \, , \tag{15}$$

$$\hat{F}_{\alpha\beta} = \hat{F}(\{\alpha_\lambda\},\{\beta_\lambda\}) = \left(\prod_\lambda \exp(\alpha_\lambda b_\lambda^\dagger)\right) \left(\prod_\lambda \exp(\beta_\lambda b_\lambda)\right) \, , \tag{16}$$

where the sets $\{\alpha_\lambda\}$ and $\{\beta_\lambda\}$ represent arbitrary real parameters. The shorthand notation α, β in the arguments of these functions denotes the respective sets of parameters. The expectation values of these operators are generating functions for phonon-assisted dynamic variables; e.g. in the case of $A_{n\alpha\beta} = \langle \hat{A}_{n\alpha\beta} \rangle$ this means that

$$\frac{\partial^k}{\partial_{\alpha_{\lambda_1}} \cdots \partial_{\alpha_{\lambda_k}}} \frac{\partial^l}{\partial_{\beta_{\Lambda_1}} \cdots \partial_{\beta_{\Lambda_l}}} A_{n\alpha\beta}|_{\alpha=\beta=0} = \langle B_n b^\dagger_{\lambda_1} \cdots b^\dagger_{\lambda_k} b_{\Lambda_1} \cdots b_{\Lambda_l} \rangle . \tag{17}$$

Of particular interest is the case $k = l = 0$ yielding $\langle B_n \rangle = A_{n\alpha\beta}|_{\alpha=\beta=0}$, because according to (11) $\langle B_n \rangle$ is directly related to the polarization. This means that once we calculate the generating function A the polarization can be obtained from its values at $\alpha = \beta = 0$.

Furthermore, we note that the leading order in the optical field of these functions can be read off from the number of $B^\dagger$ and B operators involved, e.g. $A_{n\alpha\beta} = \mathcal{O}(E)$.

Using the Hamiltonian introduced in the last section we can readily set up the Heisenberg equations of motion for the operators in (12)-(16). Neglecting terms which according to the above considerations do not contribute to the third order polarization, we obtain the following closed set of equations

$$\begin{aligned} i\hbar\partial_t A_{j\alpha\beta} = & \sum_n \{\bar{J}_{jn} + \hat{\Lambda}^b_{jn}\} (A_{n\alpha\beta} - q_j D_{jjn\alpha\beta}) + \frac{g_j}{2}\kappa_j^2 D_{jjj\alpha\beta} \\ & + \sum_{nm\lambda} \gamma^\lambda_{nm} (\beta_\lambda - \alpha_\lambda) D_{nmj\alpha\beta} - \mu_j E_j (F_{\alpha\beta} - q_j C_{jj\alpha\beta}) + \hbar\hat{\omega} A_{j\alpha\beta} , \end{aligned} \tag{18}$$

$$\begin{aligned} i\hbar\partial_t B_{ij\alpha\beta} = \xi_{ij} & \left\{ \sum_n (\bar{J}_{jn} + \hat{\Lambda}^b_{jn}) B_{in\alpha\beta} + \sum_n (\bar{J}_{in} + \hat{\Lambda}^b_{in}) B_{nj\alpha\beta} \right\} \\ & + \delta_{ij} \left\{ \kappa_j^2 \left[\sum_n (J_{jn} + \hat{\Lambda}^b_{jn}) B_{jn\alpha\beta} - \mu_j E_j A_{j\alpha\beta} \right] \right. \\ & \left. \qquad + (\Delta_j + 2\hbar\Omega_j) B_{jj\alpha\beta} \right\} \\ & - \xi_{ij} \{\mu_j E_j A_{i\alpha\beta} + \mu_i E_i A_{j\alpha\beta}\} + \hbar\hat{\omega} B_{ij\alpha\beta} + \mathcal{O}(E^4) , \end{aligned} \tag{19}$$

$$\begin{aligned} i\hbar\partial_t C_{ij\alpha\beta} = & \sum_n \{\bar{J}_{jn} + \hat{\Lambda}^b_{jn}\} C_{in\alpha\beta} - \sum_n \{\bar{J}_{ni} + \hat{\Lambda}^a_{ni}\} C_{nj\alpha\beta} \\ & + \mu_i E_i A_{j\alpha\beta} - \mu_j E_j A^*_{i\beta\alpha} + \hbar\hat{\omega} C_{ij\alpha\beta} + \mathcal{O}(E^4) , \end{aligned} \tag{20}$$

$$i\hbar\partial_t D_{kij\alpha\beta} = \xi_{ij} \left\{ \sum_n (\bar{J}_{jn} + \hat{\Lambda}^b_{jn}) D_{kin\alpha\beta} + \sum_n (\bar{J}_{in} + \hat{\Lambda}^b_{in}) D_{knj\alpha\beta} \right\}$$

$$- \sum_n (\bar{J}_{nk} + \hat{\Lambda}^a_{nk})\, D_{nij\alpha\beta} + \mu_k\, E_k\, B_{ij\alpha\beta}$$
$$-\xi_{ij}\{\mu_j\, E_j\, C_{ki\alpha\beta} + \mu_i\, E_i\, C_{kj\alpha\beta}\}$$
$$+\delta_{ij}\left\{ \kappa_j^2 \left[\sum_n (J_{jn} + \hat{\Lambda}^b_{jn}) D_{knj\alpha\beta} - \mu_j E_j C_{kj\alpha\beta} \right] \right.$$
$$\left. +(\Delta_j + 2\hbar\Omega_j)\, D_{kjj\alpha\beta} \right\}$$
$$+\hbar\hat{\omega}\, D_{kij\alpha\beta} + \mathcal{O}(E^5)\,, \tag{21}$$

$$i\hbar\partial_t F_{\alpha\beta} = \sum_{nm\lambda} \gamma^\lambda_{nm}\,(\beta_\lambda - \alpha_\lambda)\, C_{nm\alpha\beta} + \hbar\hat{\omega}\, F_{\alpha\beta}\,, \tag{22}$$

with

$$\bar{J}_{jm} \equiv \delta_{jm}\,\Omega_j + J_{jm} \quad , \quad \xi_{ij} = 1 - \delta_{ij}\,, \tag{23}$$

$$\hat{\omega} \equiv \sum_\lambda \omega_\lambda\,(\beta_\lambda\,\partial_{\beta_\lambda} - \alpha_\lambda\,\partial_{\alpha_\lambda})\,, \tag{24}$$

$$\hat{\Lambda}^a_{jm} = \sum_\lambda \gamma^\lambda_{jm}\,(\alpha_\lambda + \partial_{\alpha_\lambda} + \partial_{\beta_\lambda}) \;,\; \hat{\Lambda}^b_{jm} = \sum_\lambda \gamma^\lambda_{jm}\,(\beta_\lambda + \partial_{\alpha_\lambda} + \partial_{\beta_\lambda}). \tag{25}$$

Throughout this article we write time arguments only to avoid misinterpretations. All functions without explicit time arguments are understood to be taken at time t.

A calculation of the third order polarization based on these equations consists of the following steps. First one has to calculate the generating function $F_{\alpha\beta}$ for phonon correlations in thermal equilibrium. Here is the point where the temperature enters the equations. F is the only of the five functions that has non zero temperature-dependent values before the optical excitation. The linear response can be derived from the linearized equation for A, while the other functions are needed in order to calculate nonlinear optical signals. This procedure is illustrated in appendix A, where we explicitly treat a simple solvable case [44].

Although the above equations provide a compact way to formulate the dynamics rigorously up to third order in the exciting field, they obviously still represent a complicated many-body problem. A direct numerical scheme based on these equations is therefore only reasonable in limiting cases with either simplified electron phonon couplings (see appendix A) or when only a very limited set of phonons is dominantly coupled; e.g. when the system contains a few high frequency Raman active modes or when the effect of the phonon bath can be represented using a few collective oscillators. A theory on the same level of sophistication of equations (18)-(22) that puts particular emphasis on the latter aspect has recently been worked out in [32]. In all other cases a less demanding reduced description is needed.

4. Reduced dynamics expanded perturbatively in exciton-phonon coupling.

4.1. Truncating the hierarchy of phonon-assisted variables. One way to derive systematically a reduced computational scheme is to expand the equations (18)-(22) in a Tayler series around $\alpha_\lambda = \beta_\lambda = 0$. The result is an infinite hierarchy of equations of motion for the set of all derivatives of the functions $A - F$ with respect to α_λ and β_λ taken at the point $\alpha_\lambda = \beta_\lambda = 0$. From the generating function property of $A - F$ it is clear that these derivatives are nothing but the set of all phonon-assisted variables $\langle B_n \rangle$, $\langle B_n b_\lambda \rangle$, $\langle B_n b_\lambda^\dagger \rangle \cdots$. The scheme most often used to close this hierarchy is to keep only those variables with zero or one phonon assistance [43,45,46]; doubly assisted variables like $\langle B_n b_\lambda^\dagger b_{\lambda'} \rangle$ are then factorized according to the recipe $\langle B_n b_\lambda^\dagger b_\lambda \rangle \approx \langle B_n \rangle \, n_\lambda \, \delta_{\lambda\lambda'}$, where $n_\lambda = 1/(\exp(\hbar\omega_\lambda/kT) - 1)$ is the equilibrium phonon occupation. This factorization leads to a closed set of equations, because there are only four purely excitonic variables that contribute to the third order nonlinear response, namely $\langle B_n \rangle$, $\langle B_m B_n \rangle$, $\langle B_m^\dagger B_n \rangle$ and $\langle B_l^\dagger B_m B_n \rangle$. Thus, one would have to solve for these four excitonic variables and for the corresponding phonon (single) assisted variables. As these equations are still numerically quite demanding, there is a need for further reduction. Our goal is to eliminate the phonon-assisted variables in order to obtain a closed set of equations involving only the excitonic variables. To this end we next analyze a typical equation for a phonon-assisted variable emerging from the above scheme. We have chosen $\langle B_j b^\dagger \rangle$ to be our example. The corresponding equation of motion reads:

$$
\begin{aligned}
i\hbar\partial_t \langle B_j b_\lambda^\dagger \rangle &= \sum_n \bar{J}_{jn} \langle B_n b_\lambda^\dagger \rangle - \hbar\omega_\lambda \langle B_j b_\lambda^\dagger \rangle + n_\lambda \sum_n \gamma_{jn}^\lambda \langle B_n \rangle \\
&- \sum_{nm} \gamma_{nm}^\lambda \langle B_n^\dagger B_m B_j \rangle - n_\lambda \sum_n q_j \langle B_j^\dagger B_j B_n \rangle - q_j \sum_n \bar{J}_{jn} \langle B_j^\dagger B_j B_n b_\lambda^\dagger \rangle \\
&+ \Delta_j \langle B_j^\dagger B_j B_j b_\lambda^\dagger \rangle + \mu_j E_j q_j \langle B_j^\dagger B_j b_\lambda^\dagger \rangle \,. \qquad (26)
\end{aligned}
$$

Inversion of (26) leads to two types of terms: (i) Terms leading to contributions of self-energy-type (these are given by the first three terms of (26)); (ii) Additional source terms arising from the combined action of the phonon coupling and the electric field due to deviations from Bose statistics of the excitations generated by B_n. These additional terms are referred to in the literature as *cross terms* and are usually neglected [46].

When we keep only the former contributions, we obtain

$$
\langle B_j b_\lambda^\dagger \rangle (t) \approx n_\lambda \int_{-\infty}^{t} \sum_{nj'} G_{Aj}^{0\,j'}(t-t') \, e^{i\omega_\lambda (t-t')} \gamma_{j'n}^\lambda \langle B_n \rangle (t') \, dt'. \qquad (27)
$$

The one-exciton Green function $G^{0\,j'}_{Aj}(t)$ is given by:

$$G^{0\,j'}_{Aj}(t) = \frac{\theta(t)}{i\hbar}\exp(-i\bar{J}\frac{t}{\hbar})_{jj'}\,. \tag{28}$$

The same procedure can be applied to all relevant phonon-assisted variables. When the results are then inserted into the equations of motion for the corresponding excitonic variables, one finally obtains closed equations of motion for the excitonic degrees of freedom, where the phonons enter only via self-energies. This strategy results in the following set of equations:

$$\begin{aligned} i\hbar\partial_t\langle B_j\rangle &= \sum_n \bar{J}_{jn}\langle B_n\rangle - \mu_j E_j(1 - q_j\langle B_j^\dagger B_j\rangle) + \Delta_j\langle B_j^\dagger B_j B_j\rangle \\ &-q_j\sum_n J_{jn}\langle B_j^\dagger B_j B_n\rangle + \int_{-\infty}^{t}\sum_{j'}\hbar\Omega_B(t-t')_j^{j'}\langle B_{j'}\rangle(t')\,dt'\,, \end{aligned} \tag{29}$$

$$\begin{aligned} i\hbar\partial_t\langle B_i B_j\rangle &= \xi_{ij}\Big\{\sum_n(\bar{J}_{jn}\langle B_i B_n\rangle + \bar{J}_{in}\langle B_n B_j\rangle) \\ &\qquad -\mu_i E_i\langle B_j\rangle - \mu_j E_j\langle B_i\rangle\Big\} \\ &+\delta_{ij}\Big\{\kappa_j^2\Big(\sum_n J_{jn}\langle B_j B_n\rangle - \mu_j E_j\langle B_j\rangle\Big) \\ &\qquad +(\Delta_j + 2\hbar\Omega_j)\langle B_j B_j\rangle\Big\} \\ &+\int_{-\infty}^{t}\sum_{i'j'}\hbar\Omega_{BB}(t-t')_{i\,j}^{i'j'}\langle B_{i'}B_{j'}\rangle(t')\,dt', \end{aligned} \tag{30}$$

$$\begin{aligned} i\hbar\partial_t\langle B_i^\dagger B_j\rangle &= \sum_n(\bar{J}_{jn}\langle B_i^\dagger B_n\rangle \\ &\qquad -\bar{J}_{ni}\langle B_n^\dagger B_j\rangle) + \mu_i E_i\langle B_j\rangle - \mu_j E_j\langle B_i\rangle^* \\ &+\int_{-\infty}^{t}\sum_{i'j'}\hbar\Omega_{B^\dagger B}(t-t')_{i\,j}^{i'j'}\langle B_{i'}^\dagger B_{j'}\rangle(t')\,dt', \end{aligned} \tag{31}$$

$$\begin{aligned} i\hbar\partial_t\langle B_k^\dagger B_i B_j\rangle &= \mu_k E_k\langle B_i B_j\rangle - \sum_n \bar{J}_{nk}\langle B_n^\dagger B_i B_j\rangle \\ &+\xi_{ij}\Big\{\sum_n(\bar{J}_{in}\langle B_k^\dagger B_n B_j\rangle + \bar{J}_{jn}\langle B_k^\dagger B_i B_n\rangle) \end{aligned}$$

$$-\mu_i E_i \langle B_k^\dagger B_j \rangle - \mu_j E_j \langle B_k^\dagger B_i \rangle \Big\}$$

$$+\delta_{ij} \Big\{ \kappa_j^2 \Big(\sum_n J_{jn} \langle B_k^\dagger B_n B_j \rangle - \mu_j E_j \langle B_k^\dagger B_j \rangle \Big)$$

$$+(\Delta_j + 2\hbar\Omega_j) \langle B_k^\dagger B_j B_j \rangle \Big\}$$

$$+ \int_{-\infty}^{t} \sum_{k'i'j'} \hbar\Omega_{B^\dagger BB}(t-t')_{k\ i\ j}^{k'i'j'} \langle B_{k'}^\dagger B_{i'} B_{j'} \rangle (t')\, dt', \tag{32}$$

where the phonon induced self-energies are given by:

$$\hbar\Omega_B(t)_j^{j'} = \sum_{nm} \Gamma_{jnmj'}(t)\, G^{0\ m}_{An}(t), \tag{33}$$

$$\hbar\Omega_{BB}(t)_{i\ j}^{i'j'} =$$

$$(\xi_{ij} + \delta_{ij}\kappa_j^2) \Big\{ \sum_{nm} (\Gamma_{jnmj'}(t)\, \xi_{i'm}\, G^{0\ i'm}_{Bi\ n}(t) + \Gamma_{jnmi'}(t)\, \xi_{mj'}\, G^{0\ mj'}_{Bi\ n}(t))$$

$$+\kappa_{i'}^2 \sum_n \Gamma_{jni'j'}(t)\, G^{0\ i'i'}_{Bi\ n}(t) \Big\}$$

$$+\xi_{ij} \Big\{ \sum_{nm} (\Gamma_{inmj'}(t)\, \xi_{i'm}\, G^{0\ i'm}_{Bn\ j}(t) + \Gamma_{inmi'}(t)\, \xi_{mj'}\, G^{0\ mj'}_{Bn\ j}(t))$$

$$+\kappa_{i'}^2 \sum_n \Gamma_{ini'j'}(t)\, G^{0\ i'i'}_{Bn\ j}(t) \Big\}, \tag{34}$$

$$\hbar\Omega_{B^\dagger B}(t)_{i\ j}^{i'j'} = \sum_{nm} \{ \Gamma^*_{inmi'}(t)\, G^{0\ mj'}_{Cn\ j}(t) - \Gamma^*_{njmi'}(t)\, G^{0\ mj'}_{Ci\ n}(t)$$

$$+\Gamma_{jnmj'}(t)\, G^{0\ i'm}_{Ci\ n}(t) - \Gamma_{nimj'}(t)\, G^{0\ i'm}_{Cn\ j}(t) \}, \tag{35}$$

$$\hbar\Omega_{B^\dagger BB}(t)_{k\ i\ j}^{k'i'j'} =$$

$$\xi_{ij} \Big\{ \sum_{nm} (\Gamma_{inmj'}(t)\, \xi_{i'm}\, G^{0\ k'i'm}_{Dk\ n\ j}(t) + \Gamma_{inmi'}(t)\, \xi_{mj'}\, G^{0\ k'mj'}_{Dk\ n\ j}(t))$$

$$+\kappa_{i'}^2 \sum_n \Gamma_{ini'j'}(t)\, G^{0\ k'i'i'}_{Dk\ n\ j}(t) - \sum_{nm} \Gamma^*_{nimk'}(t)\, G^{0\ mi'j'}_{Dk\ n\ j}(t) \Big\}$$

$$+(\xi_{ij} + \delta_{ij}\kappa_j^2) \Big\{ \sum_{nm} (\Gamma_{jnmj'}(t)\, \xi_{i'm}\, G^{0\ k'i'm}_{Dk\ i\ n}(t)$$

$$+\Gamma_{jnmi'}(t)\, \xi_{mj'}\, G^{0\ k'mj'}_{Dk\ n\ i}(t))$$

$$
\left. + \kappa_{i'}^2 \sum_n \Gamma_{jni'j'}(t)\, G^{0\,k'i'i'}_{Dk\;i\;n}(t) - \sum_{nm} \Gamma^*_{njmk'}(t)\, G^{0\,mi'j'}_{Dk\;i\;n}(t) \right\}
$$

$$
- \sum_{nm} \Gamma_{nkmi'}(t)\, \xi_{mj'} G^{0\,k'mj'}_{Dn\;i\;j}(t) - \sum_{nm} \Gamma_{nkmj'}(t)\, \xi_{i'm} G^{0\,k'i'm}_{Dn\;i\;j}(t)
$$

$$
-\kappa_{i'}^2 \sum_n \Gamma_{nki'j'}(t)\, G^{0\,k'i'i'}_{Dn\;i\;j}(t) + \sum_{nm} \Gamma^*_{knmk'}(t)\, G^{0\,mi'j'}_{Dn\;i\;j}(t)\,, \tag{36}
$$

with:

$$
\Gamma_{mnij}(t) = \sum_\lambda \gamma^\lambda_{mn}\, \gamma^\lambda_{ij}\, \bar{g}_\lambda(t)\,, \tag{37}
$$

$$
\bar{g}_{\lambda_n}(t) = (n_{\lambda_n} + 1)\, e^{-i\omega_{\lambda_n} t} + n_{\lambda_n}\, e^{i\omega_{\lambda_n} t}\,. \tag{38}
$$

The Green functions entering the self-energies correspond to the respective phonon-free problems. The one exciton Green function G_A has been defined in (28). It has been shown previously [19,39,40] that the two exciton Green function G_B can be constructed from G_A by explicit calculation of the two exciton scattering matrix. The two remaining Green functions are given by

$$
G^{0\,i'j'}_{Ci\;j}(t) = \frac{\hbar}{i} G^{0\,i'}_{Ai}(t)^*\, G^{0\,j'}_{Aj}(t)\,, \tag{39}
$$

$$
G^{0\,k'i'j'}_{Dk\;i\;j}(t) = \frac{\hbar}{i} G^{0\,k'}_{Ak}(t)^*\, G^{0\,i'j'}_{Bi\;j}(t)\,. \tag{40}
$$

Thus, all quantities needed to calculate the phonon self-energies from (33)-(36) are explicitly known.

The procedure described above to deal with the coupling of nuclear degrees of freedom has lead to many successful applications in the theory of semiconductor optics [43,45,46,48,49,50]. Furthermore, it has been recognized [46,51] that the results are identical to those obtained from diagrammatic Green function approaches. In contrast to our approach, Green function methods keep track of multitime expectation values such as $\langle B_i^\dagger(t) B_j(t') \rangle$ e.g. by solving the Bethe Salpeter equation [6]. Among the problems that can be addressed on this level of sophistication are the microscopic modeling of pure dephasing [43,45,46], memory effects like the Urbach tail absorption [26,27,52], collisional broadening and retardation [46] as well as beats with the phonon-assisted variables [27,51]. Several authors, however, have pointed out [27,46,53] that the truncation scheme that factorizes double assisted variables might under certain circumstances lead to unphysical predictions when the resulting memory kernel is fully kept. This deficiency can be overcome when the hierarchy of equations for phonon-assisted variables is closed on the next higher level [46]. The main effect of this extended scheme is that the equations of motion for variables with a single phonon assistance are supplemented by a self-energy resulting from the coupling to higher levels of the hierarchy. Also the coupling to additional bath degrees of freedom is expected to have a similar effect. In many cases a simple yet reasonable modeling is obtained by allowing the phonon frequencies ω_λ to be complex valued [46,27,51]. Another suggestion [53] to remedy this shortcoming amounts to the introduction of quasiparticle corrections depending on the phonon density based on an analysis of the exactly solvable Jaynes Cummings model.

Most of the worked out examples have treated electronic correlations resulting from exciton exciton interactions only on a mean field level. However, the question how the combined action of excitonic interactions and bath couplings affects the observed signals is of great importance. A particular interesting aspect is that the gradual loss of coherence brought about by the phonon coupling not only leads to dephasing of excitonic transitions; at the same time it builds up new dynamic variables. To illustrate the latter point consider the variable $\langle B_i^\dagger B_j\rangle$ representing exciton coherences ($i \neq j$) and populations ($i = j$). It can be shown that $\langle B_i^\dagger B_j\rangle$ factorizes in the phonon-free case as

$$\langle B_i^\dagger B_j\rangle \to \langle B_i\rangle^* \langle B_j\rangle + \mathcal{O}(E^4)\,. \tag{41}$$

For Boson fields, like the electromagnetic field, it is customary to take factorization properties like (41), where intensities are factorized into transition amplitudes, as a definition of the coherence of these fields. Excitons behave like Bosons only in the low density regime. Therefore even without phonons the factorization (41) does no longer hold when higher order optical excitations are considered. The corrections to (41) brought in by the phonons already in order $\mathcal{O}(E^2)$ are not related to the non bosonic nature of excitons; rather they account for the gradual loss of coherence of the excitonic system after optical excitation due to the exchange of energy and momentum with the phonon bath. Analogous considerations apply to $\langle B_k^\dagger B_i B_j\rangle$, which in the phonon-free case factorizes like

$$\langle B_k^\dagger B_i B_j\rangle \to \langle B_k\rangle^* \langle B_i B_j\rangle + \mathcal{O}(E^5)\,. \tag{42}$$

Thus $\langle B_i^\dagger B_j\rangle$ and $\langle B_k^\dagger B_i B_j\rangle$ become dynamic variables in their own right only due to the dephasing action of the phonons.

On the other hand, calculations that include variables like $\langle B_i^\dagger B_j\rangle$ and $\langle B_k^\dagger B_i B_j\rangle$ can easily become time demanding. Keeping the treatment of phonons simple is therefore a must in these cases. Memory effects of the phonon system are not essential for studies of the questions as to how the interrelations between the various excitonic variables are affected by the coupling to nuclear degrees of freedom. Thus, it is worthwhile to work out in detail a time local version of the equations in order to provide a suitable starting point for numerical investigations. Such a treatment neglecting memory effects is in the literature often referred to as Markovian theory [45,48,54,55]. It should be pointed out, that this name does not imply, that the dynamics represents a Markov process in the sence of the theory of stochastic processes [56]. We will present the relevant equations in subsection 4.3 after we have shown in the next subsection how the well known Haken-Strobl model for relaxation is recovered as a limiting case of our equations.

4.2. The Haken-Strobl limit. The Haken-Strobl model of exciton-dephasing [24,19] marks the extreme case of a relaxation theory without bath induced memory effects. In order to derive it from our expressions for the phonon self-energies (equations (33)-(36)) we assume that each molecule has its own phonon bath coupled locally only to the corresponding site. The exciton-phonon coupling then assumes the form:

$$\gamma_{ij}^{\lambda} = \gamma^{\lambda_l}\, \delta_{ij}\, \delta_{il}\,,\, , \tag{43}$$

where λ_l labels the phonon modes coupled to site l. In this case the self-energies simplify to:

$$\hbar\Omega_B(t)_j^{j'} = \delta_{jj'}\Gamma_j(t)\, G_{A\,j}^{0\,j}(t) =: \delta_{jj'}\hbar\Omega_B(t)_j\,, \tag{44}$$

$$\begin{aligned} \hbar\Omega_{BB}(t)_{i\,j}^{i'j'} &= G_{B\,i\,j}^{0\,i'j'}(t)\,\times \\ &\times\{(\xi_{ij}+\delta_{ij}\kappa_j^2)\,[\xi_{i'j'}\,(\delta_{ji'}+\delta_{jj'})+\kappa_{i'}^2\,\delta_{i'j'}\,\delta_{jj'}]\Gamma_j(t) \\ &+\xi_{ij}\,[\xi_{i'j'}\,(\delta_{ii'}+\delta_{ij'})+\kappa_{i'}^2\,\delta_{i'j'}\,\delta_{ii'}]\Gamma_i(t)\}\,, \end{aligned} \tag{45}$$

$$\begin{aligned} \hbar\Omega_{B^\dagger B}(t)_{i\,j}^{i'j'} &= G_{C\,i\,j}^{0\,i'j'}(t)\,\times \\ &\times\{\Gamma_i^*(t)\,\delta_{ii'}-\Gamma_j^*(t)\,\delta_{ji'}+\Gamma_j(t)\,\delta_{jj'}-\Gamma_i(t)\,\delta_{ij'}\}\,, \end{aligned} \tag{46}$$

$$\begin{aligned} \hbar\Omega_{B^\dagger BB}(t)_{k\,i\,j}^{k'i'j'} &= G_{D\,k\,i\,j}^{0\,k'i'j'}(t)\,\times \\ &\times\{\xi_{ij}[\Gamma_i(t)\,(\xi_{i'j'}\,(\delta_{ii'}+\delta_{ij'}))+\kappa_{i'}^2\,\delta_{i'j'}\,\delta_{ii'})-\Gamma_i^*(t)\,\delta_{ik'}] \\ &+(\xi_{ij}+\delta_{ij}\kappa_j^2)[\Gamma_j(t)\,(\xi_{i'j'}\,(\delta_{ji'}+\delta_{jj'})+\kappa_{i'}^2\,\delta_{i'j'}\,\delta_{jj'})-\Gamma_j^*(t)\,\delta_{jk'}] \\ &-\Gamma_k(t)\,[\xi_{i'j'}\,(\delta_{ki'}+\delta_{kj'})+\kappa_{i'}^2\,\delta_{i'j'}\,\delta_{ki'}]+\Gamma_k^*(t)\,\delta_{kk'}\}\,, \end{aligned} \tag{47}$$

with:

$$\Gamma_j(t) = \sum_{\lambda_j} |\gamma^{\lambda_j}|^2\, \bar{g}_{\lambda_j}(t)\,. \tag{48}$$

From these equations, the Haken-Strobl model is easily recovered in the limit of a short bath relaxation time, where $\Gamma_j(t)$ approaches the form $\Gamma_j(t) \to \hat{\Gamma}\,\delta(t)$. The Greens functions entering (44)-(47) then have to be invoked at time $t = 0^+$, where by definition they become δ-functions, e.g. $G_{A\,j'}^{0\,j}(t=0^+) = \frac{-i}{\hbar}\delta_{jj'}$. Physically this means that the phonon bath is so fast that the excitonic excitations have no time to impose their spatial and temporal structure on the relaxation kernel. The self-energies (44)-(47) therefore assume the form:

$$\hbar\Omega_B(t)_j^{j'} = \delta_{jj'}\frac{\hat{\Gamma}}{i\hbar}\,\delta(t)\,, \tag{49}$$

$$\hbar\Omega_{BB}(t)_{i\ j}^{i'j'} = \frac{\hat{\Gamma}}{i\hbar}\,\delta(t)\,\delta_{ii'}\,\delta_{jj'}\,\{2\xi_{ij} + \delta_{ij}\kappa_j^4\}\,, \tag{50}$$

$$\hbar\Omega_{B^\dagger B}(t)_{i\ j}^{i'j'} = \frac{\hat{\Gamma}}{i\hbar}\,\delta(t)\,\delta_{ii'}\,\delta_{jj'}\,2\xi_{ij}\,, \tag{51}$$

$$\begin{aligned}\hbar\Omega_{B^\dagger BB}(t)_{k\ i\ j}^{k'i'j'} &= \frac{\hat{\Gamma}}{i\hbar}\,\delta(t)\,\delta_{kk'}\,\delta_{ii'}\,\delta_{jj'}\,\times\\ &\times\{\xi_{ij}\,(3-2\delta_{ki}-2\delta_{kj}) + \delta_{ij}(1+\kappa_j^4 - 2\delta_{kj}\,\kappa_j^2)\}\,.\end{aligned} \tag{52}$$

Equations (49)-(52) have previously been derived [19] for the case $\kappa_j = 0$, i.e. the case of Frenkel excitons with only one excitation per site (two-level molecules). Finally we note, that it immediately follows from the definition (48) of $\Gamma_j(t)$ that the limit $\Gamma_j(t) \to \hat{\Gamma}\,\delta(t)$ corresponds to a broad distribution of phonon frequencies and high temperatures. In addition it has to be assumed that the coupling strength to the bath is independent of the site, thereby excluding the possibility that different sites might be exposed to different environments. The limit $\Gamma_j(t) \to \hat{\Gamma}\,\delta(t)$ can also be reached, when the phonon-assisted variables are strongly damped due to the coupling either to higher order assisted variables or to additional bath degrees of freedom.

4.3. Finite Temperature theory with time-local bath influence. Although the Haken-Strobl model already allows the qualitative discussion of many aspects related to exciton bath interactions, it obviously represents an extreme limiting case. To address questions like the temperature dependence of the bath interaction, a less restrictive scheme is needed. Furthermore, we have seen that an ultrafast bath leads to δ-like spatial behavior, while in less extreme situations excitonic structures can be imposed on the relaxation kernel thereby opening otherwise forbidden relaxation channels. In this subsection we derive an approximation scheme that keeps the temperature dependence as well as the excitonic structure of the relaxation kernel, while still providing equations where the coupling to the phonons is local in time.

We will take equations (29)-(32) as our starting point. Our goal is to calculate the third order optical response. To be specific we consider the three electric fields generating this response to be of the form

$$\vec{E}^{(a)}(t) = \bar{E}^{(a)}(t)\,\vec{e}_{(a)}\,e^{-i\omega_a t} + c.c. \quad , \quad a = 1,2,3 \tag{53}$$

i.e. we assume that the fields are polarized in directions $\vec{e}_{(a)}$ and have well defined central frequencies ω_a, which implies that the pulse envelopes $\bar{E}^{(a)}(t)$ should be slowly varying on the timescale defined by the optical frequencies. We also neglect the spatial dependence of the fields, which is justified when their wavelengths are long compared to the extend of the sample. In this limit the dependence on the wavevectors $\vec{k}_a$ is only needed for bookkeeping purposes in order to determine in which phase matching direction a certain component is emitted. As this dependence is trivial we suppressed it in our notation.

The third order optical response predicted by equations (29)- (32) can be constructed using an iterative procedure: first solving for the linear response, than inserting the result of the first step to derive the sources for second order contributions and finally using the first and second order results to determine the third order response. For example, the relevant equation which determines the linear response generated by the pulse $\bar{E}^{(a)}(t)\, e^{-i\omega_a t}$ according to (29) reads in frequency space

$$\begin{aligned} \hbar\omega \langle B_j \rangle^{(a)}(\omega) &= \sum_n \bar{J}_{jn} \langle B_n \rangle^{(a)}(\omega) - \mu_j \bar{E}^{(a)}(\omega - \omega_a) \\ &+ \sum_{j'} \hbar\Omega_B(\omega)_j^{j'} \langle B_{j'} \rangle^{(a)}(\omega)\,. \end{aligned} \tag{54}$$

For the Fourier transformation connecting time domain functions to their frequency domain representations we use the convention

$$f(t) = \int_{-\infty}^{\infty} \frac{1}{2\pi}\, e^{-i\omega t}\, f(\omega)\, d\omega\,. \tag{55}$$

The source term $\bar{E}^{(a)}(\omega - \omega_a)$ in equation (54) is under the conditions stated above a function that has non zero values only in a finite frequency range centered at ω_a. If the self-energy $\hbar\Omega_B(\omega)_j^{j'}$ is slowly varying in this frequency range it can be replaced by its value $\hbar\Omega_B(\omega_a)_j^{j'}$ taken at $\omega = \omega_a$. Transforming back to the time domain we obtain an equation with a phonon coupling local in time

$$\begin{aligned} i\hbar\partial_t \langle B_j \rangle^{(a)} &= \sum_n \bar{J}_{jn} \langle B_n \rangle^{(a)} - \mu_j \bar{E}^{(a)}\, e^{-i\omega_a t} \\ &+ \sum_{j'} i\hbar \Im m(\Omega_B)(\omega_a)_j^{j'} \langle B_{j'} \rangle^{(a)}\,. \end{aligned} \tag{56}$$

As is common we keep only the imaginary part of the self-energy, because the energy shifts brought forth by the real part can be accounted for by using renormalized values of the material parameters. Obviously, the conditions under which (56) has been derived are less restrictive than the conditions required by the Haken-Strobl model. The case that the phonons are coupled as a sufficiently broad distribution in frequency is not the only case where $\hbar\Omega_B(\omega_a)_j^{j'}$ can be a slowly varying function in the frequency range covered by the laser pulse. To give an example one can think of a single LO phonon with frequency ω_{LO} in a semiconductor. In this case the line shape of $\hbar\Omega_B(\omega_a)_j^{j'}$ is a linear superposition of the phonon-free absorption spectrum shifted by $\pm\omega_{LO}$ [43]. The self-energy $\hbar\Omega_B(\omega_a)_j^{j'}$ will be a flat function in the relevant frequency range when the semiconductor is resonantly excited at the exciton frequency as long as the laser bandwidth is smaller than the phonon frequency, which is a typical situation [43].

To second order in the laser field, two functions have to be calculated: (i) the two exciton transition density $\langle B_i B_j\rangle$ and (ii) the function $\langle B_i^\dagger B_j\rangle$ describing excitonic coherences and occupation densities. Inserting the results of the calculation of the linear response into equations (30) and (31) it can be seen that the total sources leading to second order contributions can be split into components with well defined central frequencies. For each frequency component, the same procedure outlined above can be applied. In this way we obtain for the component $\langle B_i B_j\rangle^{(a,b)}$ of the two exciton transition density with central frequency $\omega_a+\omega_b$ generated by the pulses a and b the following equation

$$
\begin{aligned}
i\hbar\partial_t\langle B_iB_j\rangle^{(a,b)} = \xi_{ij}\Bigg\{ &\sum_n(\bar{J}_{jn}\langle B_iB_n\rangle^{(a,b)} + \bar{J}_{in}\langle B_nB_j\rangle^{(a,b)}) \\
&-\bar{E}^{(a)}e^{-i\omega_a t}[\mu_i\langle B_j\rangle^{(b)} + \mu_j\langle B_i\rangle^{(b)}] \\
&-\bar{E}^{(b)}e^{-i\omega_b t}[\mu_i\langle B_j\rangle^{(a)} + \mu_j\langle B_i\rangle^{(a)}]\Bigg\} \\
+\delta_{ij}\Bigg\{\kappa_j^2\Bigg(&\sum_n J_{jn}\langle B_jB_n\rangle^{(a,b)} - \mu_j[\bar{E}^{(a)}e^{-i\omega_a t}\langle B_j\rangle^{(b)} \\
&+\bar{E}^{(b)}e^{-i\omega_b t}\langle B_j\rangle^{(a)}]\Bigg) + (\Delta_j + 2\hbar\Omega_j)\langle B_jB_j\rangle^{(a,b)}\Bigg\} \\
+\sum_{i'j'} i\hbar\Im m&(\Omega_{BB})(\omega_a+\omega_b)_{i\ j}^{i'j'}\langle B_{i'}B_{j'}\rangle^{(a,b)}\,,
\end{aligned}
\tag{57}
$$

while the component $\langle B_i^\dagger B_j\rangle^{(-a,b)}$ with central frequency $\omega_b-\omega_a$ resulting from pulses a and b has to be calculated from

$$
\begin{aligned}
i\hbar\partial_t\langle B_i^\dagger B_j\rangle^{(-a,b)} = &\sum_n(\bar{J}_{jn}\langle B_i^\dagger B_n\rangle^{(-a,b)} - \bar{J}_{ni}\langle B_n^\dagger B_j\rangle^{(-a,b)}) \\
&+\mu_i(\bar{E}^{(a)*}e^{i\omega_a t}\langle B_j\rangle^{(b)} + \bar{E}^{(b)}e^{-i\omega_b t}\langle B_j\rangle^{(-a)}) - \mu_j(\bar{E}^{(b)}e^{-i\omega_b t}\langle B_i\rangle^{(a)*} \\
&+\bar{E}^{(a)*}e^{i\omega_a t}\langle B_i\rangle^{(-b)*}) + \sum_{i'j'} i\hbar\Im m(\Omega_{B^\dagger B})(\omega_b-\omega_a)_{i\ j}^{i'j'}\langle B_{i'}^\dagger B_{j'}\rangle^{(-a,b)}\,.
\end{aligned}
\tag{58}
$$

When the laser frequencies are tuned in resonance with the excitonic transition, it is possible to neglect the source terms proportional to $\langle B_j\rangle^{(-a)}$ and $\langle B_i\rangle^{(-b)*}$ in (58), because in this case they are small compared to the contributions proportional to $\langle B_i\rangle^{(a)*}$ or $\langle B_j\rangle^{(b)}$. This is known as the rotating wave approximation (RWA).

Proceeding along the same lines, we find the following equations for the third order variables

$$
\begin{aligned}
i\hbar\partial_t\langle B_k^\dagger B_i B_j\rangle^{(-a,b,c)} &= \mu_k \bar{E}^{(a)*}\, e^{i\omega_a t}\langle B_i B_j\rangle^{(b,c)} \\
&- \sum_n \bar{J}_{nk}\langle B_n^\dagger B_i B_j\rangle^{(-a,b,c)} \\
&+\xi_{ij}\Bigg\{\sum_n(\bar{J}_{in}\langle B_k^\dagger B_n B_j\rangle^{(-a,b,c)} + \bar{J}_{jn}\langle B_k^\dagger B_i B_n\rangle^{(-a,b,c)}) \\
&-\mu_i \bar{E}^{(b)}\, e^{-i\omega_b t}\langle B_k^\dagger B_j\rangle^{(-a,c)} - \mu_i \bar{E}^{(c)}\, e^{-i\omega_c t}\langle B_k^\dagger B_j\rangle^{(-a,b)} \\
&-\mu_j \bar{E}^{(b)}\, e^{-i\omega_b t}\langle B_k^\dagger B_i\rangle^{(-a,c)} - \mu_j \bar{E}^{(c)}\, e^{-i\omega_c t}\langle B_k^\dagger B_i\rangle^{(-a,b)}\Bigg\} \\
&+\delta_{ij}\Bigg\{\kappa_j^2\Bigg(\sum_n J_{jn}\langle B_k^\dagger B_n B_j\rangle^{(-a,b,c)} - \mu_j \bar{E}^{(b)}\, e^{-i\omega_b t}\langle B_k^\dagger B_j\rangle^{(-a,c)} \\
&-\mu_j \bar{E}^{(c)}\, e^{-i\omega_c t}\langle B_k^\dagger B_j\rangle^{(-a,b)}\Bigg) + (\Delta_j + 2\hbar\Omega_j)\langle B_k^\dagger B_j B_j\rangle^{(-a,b,c)}\Bigg\} \\
&+ \sum_{k'i'j'} i\hbar\Im m(\Omega_{B^\dagger BB})(\omega_c+\omega_b-\omega_a)_{k\ i\ j}^{k'i'j'}\langle B_{k'}^\dagger B_{i'} B_{j'}\rangle^{(-a,b,c)}\,,
\end{aligned}
\tag{59}
$$

$$
\begin{aligned}
i\hbar\partial_t\langle B_j\rangle^{(-a,b,c)} &= \sum_n \bar{J}_{jn}\langle B_n\rangle^{(-a,b,c)} \\
&+\mu_j\, q_j\left\{\bar{E}^{(b)}\, e^{-i\omega_b t}\langle B_j^\dagger B_j\rangle^{(-a,c)} + \bar{E}^{(c)}\, e^{-i\omega_c t}\langle B_j^\dagger B_j\rangle^{(-a,b)}\right\} \\
&+\Delta_j\langle B_j^\dagger B_j B_j\rangle^{(-a,b,c)} - q_j\sum_n J_{jn}\langle B_j^\dagger B_j B_n\rangle^{(-a,b,c)} \\
&+\sum_{j'} i\hbar\Im m(\Omega_B)(\omega_c+\omega_b-\omega_a)_j^{j'}\langle B_{j'}\rangle^{(-a,b,c)}\,,
\end{aligned}
\tag{60}
$$

where we have written in (59) and (60) only the resonant contributions according to the RWA.

When $\langle B_j\rangle^{(-a,b,c)}$ has been calculated for a given combination of the pulses a, b, c it can be inserted into (11) resulting in a contribution to the third order polarization that is radiated in direction $\vec{k}_c + \vec{k}_b - \vec{k}_a$ with central frequency $\omega_c + \omega_b - \omega_a$. Depending on the experimental setup, only a subset of all possible contributions to the third order polarization is registered. This subset is selected by a choice of directions (wavevectors) and/or a choice of a suitable frequency window to be detected. Equations (56)-(60) can be used to follow the time evolution of all relevant dynamic variables. The self-energies entering these equations are the Fourier transforms of (33)-(36). However, for many applications the simpler form (44)-(47) is appropriate. Finally the signal is obtained by summing over all contributions to the third order polarization with the desired wavevectors.

5. Unified description of coherent and incoherent exciton dynamics. So far we did not make any distinction between coherent and incoherent exciton dynamics. Therefore, the respective contributions are mixed in our formulation. In many situations it is desirable to separate these contributions, thus allowing for a greater flexibility in developing appropriate approximations. The goal of this section is to derive equations that correctly reproduce both the limit of fully coherent dynamics (i.e. dynamics without bath coupling) and the incoherent transport limit.

To identify coherent and incoherent contributions we recall that in the coherent case only the transition densities $\langle B_j \rangle$ and $\langle B_i B_j \rangle$ are independent dynamical variables. The partial density-like quantities $\langle B_i^\dagger B_j \rangle$ and $\langle B_k^\dagger B_i B_j \rangle$ factorize according to (41) and (42) respectively. We will first concentrate on $\langle B_i^\dagger B_j \rangle$. In order to isolate the incoherent part we consider the function

$$\bar{C}_{ij\alpha\beta} \equiv C_{ij\alpha\beta} - A^*_{i\beta\alpha} A_{j\alpha\beta} \, . \tag{61}$$

According to (20) and (18) $\bar{C}$ obeys the equation of motion

$$\begin{aligned} i\hbar\partial_t \bar{C}_{ij\alpha\beta} &= \sum_n \{\bar{J}_{jn} + \Lambda^b_{jn}\} \bar{C}_{in\alpha\beta} - \sum_n \{\bar{J}_{ni} + \Lambda^a_{ni}\} \bar{C}_{nj\alpha\beta} \\ &+ \hbar\hat{\omega} \, \bar{C}_{ij\alpha\beta} + Q_{\bar{C}ij\alpha\beta} \, , \end{aligned} \tag{62}$$

where the source $Q_{\bar{C}}$ is given by

$$\begin{aligned} Q_{\bar{C}ij\alpha\beta} &\equiv \sum_n \{A_{n\alpha\beta} \, \Lambda_{jn} \, A^*_{i\beta\alpha} - A^*_{n\beta\alpha} \, \Lambda_{ni} A_{j\alpha\beta}\} \\ &+ \mu_i \, E_i \, (1 - F_{\beta\alpha}) - \mu_j \, E_j \, (1 - F_{\alpha\beta}) \, , \end{aligned} \tag{63}$$

with

$$\Lambda_{jn} = \sum_\lambda \gamma^\lambda_{jn} (\partial_{\alpha_\lambda} + \partial_{\beta_\lambda}) \, .$$

We find that, taken at the point $\alpha = \beta = 0$, $\bar{C}_{ij\alpha=\beta=0} = \langle B_i^\dagger B_j \rangle - \langle B_i \rangle^* \langle B_j \rangle$ represents the deviation of $\langle B_i^\dagger B_j \rangle$ from its coherent part. Of particular interest are the diagonal elements $N_j = \bar{C}_{jj\alpha=\beta=0}$, because these are the only components that directly couple to the transition $\langle B_j \rangle$ which finally determines the polarization. As the coherent contribution is split off, N_j

represents the incoherent population on site j. In many cases it is therefore appropriate to describe the propagation of this variable in configuration space by a Förster type rate equation. When we again adopt the coupling scheme (43) the relevant equation reads

$$\hbar\partial_t N_j = \sum_m (R_{jm} N_m - R_{mj} N_j) + Q_{N_j} \,. \tag{64}$$

Within our model, the rates R_{mj} are readily expressed through the parameters of the Hamiltonian as shown in appendix B. When phonon-assisted variables are eliminated as discussed before, the source Q_{N_j} turns out to be

$$\begin{aligned} Q_{N_j}(t) = -iQ_{\bar{C}_{jj\alpha=\beta=0}} &= -i\{\langle B_j\rangle(t) \int_{-\infty}^{t} (\hbar\Omega_B(t-t')_j \langle B_j\rangle(t'))^* \, dt' \\ &-\langle B_j\rangle(t)^* \int_{-\infty}^{t} \hbar\Omega_B(t-t')_j \langle B_j\rangle(t')\} \, dt', \end{aligned} \tag{65}$$

where $\hbar\Omega_B$ is given by (44).

Similar to $\langle B_i^\dagger B_j\rangle$ we can decompose $\langle B_k^\dagger B_i B_j\rangle$ into a coherent and an incoherent part, where the former is according to (42) given by $\langle B_k\rangle^* \langle B_i B_j\rangle$. In order to calculate the transition $\langle B_j\rangle$ only the components $Z_{ij} = \langle B_i^\dagger B_i B_j\rangle - \langle B_i\rangle^* \langle B_i B_j\rangle$ are needed. In appendix B we further show that in analogy to the incoherent part of $\langle B_i^\dagger B_j\rangle$, a rate-like equation can be derived for Z_{ij}. But for most purposes it is sufficient to determine Z_{ij} from the factorization ansatz proposed in [17] on the basis of a maximum entropy argument

$$Z_{ij} \approx N_i \langle B_j\rangle + \{\langle B_i^\dagger B_j\rangle - \langle B_i\rangle^* \langle B_j\rangle\} \langle B_i\rangle \,. \tag{66}$$

When the factorization (66) is used to approximate Z_{ij} we see that besides the incoherent population N_j also the deviation $\langle B_i^\dagger B_j\rangle - \langle B_i\rangle^* \langle B_j\rangle$, $i \neq j$ of the off-diagonal elements of $\langle B_i^\dagger B_j\rangle$ from their coherent values are needed. These off-diagonal elements can be eliminated using the same perturbative procedure with respect to the dipole couplings that lead to the rates R_{ij} in (64) (cf. appendix B).

Collecting the results of this subsection on the incoherent propagation of N_j and using the factorization (66) for Z_{ij}, these results can be combined with the coherent time evolution of the transitions $\langle B_j\rangle$ and $\langle B_i B_j\rangle$ found in subsection 4.1. Thus, we finally arrive at the following set of dynamic equations which describe the third order material response

$$i\hbar\partial_t \langle B_j\rangle = \sum_n \bar{J}_{jn} \langle B_n\rangle - \mu_j E_j \{1 - q_j (\langle B_j\rangle^* \langle B_j\rangle + N_j)\}$$

$$-q_j \sum_n \{J_{jn}(\langle B_j\rangle^* \langle B_j B_n\rangle + N_j \langle B_n\rangle) + i(\bar{R}_{jn} N_n - \bar{R}^*_{nj} N_j)\langle B_j\rangle\}$$

$$+\Delta_j \{\langle B_j\rangle^* \langle B_j B_j\rangle + 2\, N_j \langle B_j\rangle\} + \int_{-\infty}^{t} \hbar\Omega_B(t-t')_j \langle B_j\rangle(t')\, dt', \tag{67}$$

$$i\hbar\partial_t \langle B_i B_j\rangle = \xi_{ij} \left\{ \sum_n (\bar{J}_{jn} \langle B_i B_n\rangle + \bar{J}_{in} \langle B_n B_j\rangle) - \mu_i E_i \langle B_j\rangle - \mu_j E_j \langle B_i\rangle \right\}$$

$$+\delta_{ij} \left\{ \kappa_j^2 \left(\sum_n J_{jn} \langle B_j B_n\rangle - \mu_j E_j \langle B_j\rangle \right) + (\Delta_j + 2\hbar\Omega_j)\langle B_j B_j\rangle \right\}$$

$$+ \int_{-\infty}^{t} \sum_{i'j'} \hbar\Omega_{BB}(t-t')_{i\,j}^{i'j'} \langle B_{i'} B_{j'}\rangle(t')\, dt', \tag{68}$$

$$\hbar\partial_t N_j = \sum_m (R_{jm} N_m - R_{mj} N_j) - i\left\{ \langle B_j\rangle(t) \int_{-\infty}^{t} (\hbar\Omega_B(t-t')_j \right.$$

$$\left. \langle B_j\rangle(t'))^*\, dt' - \langle B_j\rangle(t)^* \int_{-\infty}^{t} \hbar\Omega_B(t-t')_j \langle B_j\rangle(t') \right\} dt', \tag{69}$$

where the self-energies $\hbar\Omega_B$ and $\hbar\Omega_{BB}$ are given by (44) and (45). The transfer-rates $\bar{R}_{nj}$ in equation (67) are related to the transport rates R_{nj} in equation (69) by $R_{nj} = 2\Re e(\bar{R}_{nj})$. Explicit formulas relating these rates to the parameters of our model can be found in appendix B. After decomposition into components corresponding to well defined central frequencies as before, time local equations can be obtained by replacing the memory kernels according to the scheme discussed in subsection 4.3. The resulting equations are listed in appendix C.

Clearly these equations correctly reproduce the coherent dynamics in the limiting case of vanishing phonon interaction, because in this limit there are no sources for N_j or Z_{ij}. Thus, these quantities stay zero in this case. On the other hand, when the bath influence is strong, the transitions $\langle B_j\rangle$ and $\langle B_i B_j\rangle$ will be strongly damped and the dynamics will be dominated by the incoherent transport described by N_j. Treating coherent and incoherent dynamics together on a common footing, equations (67)-(69)

therefore interpolate between these extreme limiting cases.

6. Discussion. Starting from rigorous equations of motion for five generating functions in the joint phase-space of excitons and nuclei, we obtained reduced descriptions of the coupled exciton phonon dynamics on various levels of sophistication. A treatment keeping memory effects (see section 4.1) is needed for a description of phenomena such as beats of the phonon-assisted variables. Simpler time-local models can be used to investigate the influence of the bath on the interplay between the excitonic variables. Such models are a good compromise between the need to keep the numerical effort on a reasonable level and the desire to realistically model the relevant interactions in the system. In the present paper we presented three time-local models. The simplest of these is the Haken-Strobl model of relaxation. It has been shown that this model naturally emerges as a limiting case of the treatment introduced in section 4.3. However, a treatment on the level of section 4.3 is required when one intends to address questions like the temperature dependence of pure dephasing. Finally, we have shown in section 5 that separating the incoherent and coherent parts of the dynamics leads to a compact formulation of their combined dynamics. The distinction between coherent and incoherent parts of the dynamics is in our formulation intimately related to the distinction between the fast transition-like variables $\langle B_j \rangle$ and $\langle B_i B_j \rangle$ and the slow population density N_j. Thus identifying different variables with coherent or incoherent dynamics makes this distinction particularly transparent. Equations (67)-(69) pinpoint the respective roles of coherent and incoherent contributions in the extreme limiting cases. In intermediate cases they allow for studies of the interplay between these contributions on a numerically feasible level. Unlike the Haken-Strobl model, which also interpolates between these extremes in the infinite temperature limit, our formulation in section 5 correctly obeys the detailed balance relation.

A. Green functions for a simple exciton-phonon coupling scheme. In this appendix we study a simple solvable model [44] for the phonon coupling using equations (18)-(22) for the relevant generating functions. The purpose of the following calculations is twofold: (i) we wish to provide an illustration as to how the generating functions can be used to calculate optical signals and (ii) the explicit solutions in this simple case give further insight into the physical significance of the dynamic variables involved.

Our model is defined by the following choice for the exciton-phonon coupling

$$\gamma_{ij}^{\lambda} = \gamma^{\lambda}\, \delta_{ij}\, . \tag{A1}$$

As far as the phonon part is concerned, this problem is equivalent to the *independent Boson model* discussed in [44]. The model can also be thought of as a limiting case of the standard coupling for periodic systems given by [25,41]

$$\gamma_{ij}^{\lambda} = \gamma^{\lambda}\, e^{-iR_j q_\lambda} \delta_{ij}\,, \tag{A2}$$

where q_λ is the wavevector of the phonon labeled λ. From the point of view of equation (A2), the approximation (A1) is justified when the coupling γ^λ is strongly peaked around $q_\lambda \approx 0$, which is e.g. the case for LO phonons coupled via the Fröhlich mechanism. More precisely it is required that the spatial extent of the relevant excitonic excitations is small compared to the wavelengths of all dominantly coupled phonon modes. In such a case the exchange of energy with the phonon bath is more important than the exchange of momentum described by the factor $e^{-iR_j q_\lambda}$ in (A2).

For simplicity we will only deal with the case $\kappa_j = 0$ in this appendix; i.e. a system of coupled two level Frenkel excitons.

As explained in section 3, we first have to calculate the 0-th order, i.e. the value of the generating function for phonon correlations $F^0_{\alpha\beta}$ in thermal equilibrium (cf. (16)). This can be done along the lines described in [44], finally yielding

$$F^0_{\alpha\beta} = \exp\left(\sum_\mu n_\mu \alpha_\mu \beta_\mu\right)\,, \tag{A3}$$

where $n_\mu = 1/(\exp(\hbar\omega_\mu/kT) - 1)$ is the Bose distribution.

Next we calculate the linear response from equation (18). To this end we construct the corresponding Green function defined as the solution of

$$\begin{aligned} i\hbar\partial_t G_{A_j}{}^{j'}{}_{\alpha}{}^{\alpha'}{}_{\beta}{}^{\beta'}(t) &= \sum_n \bar{J}_{jn} G_{A_n}{}^{j'}{}_{\alpha}{}^{\alpha'}{}_{\beta}{}^{\beta'}(t) \\ &+ \sum_\lambda \{\gamma^\lambda (\beta_\lambda + \partial_{\alpha_\lambda} + \partial_{\beta_\lambda}) + \hbar\omega_\lambda (\beta_\lambda \partial_{\beta_\lambda} - \alpha_\lambda \partial_{\alpha_\lambda})\}\, G_{A_j}{}^{j'}{}_{\alpha}{}^{\alpha'}{}_{\beta}{}^{\beta'}(t) \\ &+ \delta(t)\, \delta_\alpha^{\alpha'}\, \delta_\beta^{\beta'}\, \delta_j^{j'}\,. \end{aligned} \tag{A4}$$

For the solution of (A4) we make an ansatz in the form of a phonon wavepackage with time dependent wavevectors

$$G_{A_j}{}^{j'}{}_{\alpha}{}^{\alpha'}{}_{\beta}{}^{\beta'}(t) = \frac{\theta(t)}{i\hbar} \int_k g^k_{jj'}(t) \prod_\mu \left(e^{-i(\alpha_\mu\, a^k_\mu(t) - k_{\alpha_\mu}\, \alpha'_\mu + \beta_\mu\, b^k_\mu(t) - \beta'_\mu\, k_{\beta_\mu})} \frac{1}{(2\pi)^2} \right)\,, \tag{A5}$$

where the shorthand notation k has been used to represent the set of wavevectors $k = \{k_{\alpha_\mu}, k_{\beta_\mu}\}$ and the integration over k runs over all members of the set each from $-\infty$ to ∞. Insertion into (A4) reveals that the ansatz (A5) is the solution of (A4) provided the amplitude function $g^k_{jj'}(t)$ and the time dependent wavevectors $a^k_\mu(t)$ and $b^k_\mu(t)$ for $t > 0$ solve the equations

$$\dot{g}^k_{jj'} = \sum_n \frac{1}{i\hbar} \bar{J}_{jn}\, g^k_{nj'} - g^k_{jj'} \sum_\mu \frac{\gamma^\mu}{\hbar}(a^k_\mu + b^k_\mu)\,, \tag{A6}$$

$$\dot{a}^k_\mu = i\omega_\mu\, a^k_\mu\,, \tag{A7}$$

$$\dot{b}^k_\mu = \frac{\gamma^\mu}{\hbar} - i\omega_\mu\, b^k_\mu\,, \tag{A8}$$

with the initial conditions

$$g^k_{jj'}(t=0^+) = \delta_{jj'}\ ; \quad a^k_\mu(t=0^+) = k_{\alpha_\mu}\ ; \quad a^k_\mu(t=0^+) = k_{\beta_\mu}\,. \tag{A9}$$

Equations (A6)-(A8) clearly demonstrate that the parameters α,β of the generating functions are related to simple harmonic oscillator degrees of freedom. After the elementary solution of these equations is inserted in (A5), it is easy to perform the integrations over the wavevectors $k_{\alpha_\mu}, k_{\beta_\mu}$ leading to

$$\begin{aligned} G_{A\,j\ \alpha\ \beta}^{\ \,j'\alpha'\beta'}(t) &= G_{A\,j}^{0\,j'}(t)\, f(t)\, \exp\left(\sum_\mu \beta_\mu \frac{\gamma^\mu}{\hbar\omega_\mu}[e^{-i\omega_\mu t}-1]\right) \times \\ &\times \prod_\mu \delta\left(\alpha_\mu e^{i\omega_\mu t} - \alpha'_\mu - \frac{\gamma^\mu}{\hbar\omega_\mu}[e^{i\omega_\mu t}-1]\right) \times \\ &\times \prod_\mu \delta\left(\beta_\mu e^{-i\omega_\mu t} - \beta'_\mu + \frac{\gamma^\mu}{\hbar\omega_\mu}[e^{-i\omega_\mu t}-1]\right)\,, \end{aligned} \tag{A10}$$

$$f(t) = \exp\left(\sum_\mu -i\frac{\gamma^{\mu\,2}}{\hbar^2\omega_\mu}\left\{\frac{i}{\omega_\mu}(e^{-i\omega_\mu t}-1) - t\right\}\right)\,. \tag{A11}$$

According to (18), and with the help of the Green function (A10) we can write the linear part of the generating function A as

$$A^{(1)}_{j\alpha\beta}(t) = -\int_{-\infty}^{t}\int_{\alpha'\beta'}\sum_{j'} G_{A\,j\ \alpha\ \beta}^{\ \,j'\alpha'\beta'}(t-t')\,\mu_{j'}\,E_{j'}(t')\,F^0_{\alpha'\beta'}\,dt' \tag{A12}$$

The α',β' integrations in (A12) run over the whole set $\{\alpha'_\lambda, \beta'_\lambda\}$ each from $-\infty$ to ∞. They are trivial due to the δ-functions in the Green function. The linear response is therefore given by

$$\langle B_j\rangle^{(1)}(t) = A^{(1)}_{j\,\alpha=\beta=0}(t) =$$

$$G_{C\,i\;j\;\alpha\;\beta}^{\;i'j'\alpha'\beta'}(t) = G_{C\,i\;j}^{0\,i'j'}(t)\,\exp\Bigg(\sum_\mu \frac{\gamma^\mu}{\hbar\omega_\mu}\{\alpha_\mu(e^{i\omega_\mu t}-1)$$
$$+\beta_\mu(e^{-i\omega_\mu t}-1)\}\Bigg)\times$$
$$\times\prod_\mu \delta(\alpha_\mu e^{i\omega_\mu t}-\alpha'_\mu)\prod_\mu \delta(\beta_\mu e^{-i\omega_\mu t}-\beta'_\mu)\,, \tag{A19}$$

$$G_{D\,k\;i\;j\;\alpha\;\beta}^{\;k'i'j'\alpha'\beta'}(t) = G_{D\,k\;i\;j}^{0\,k'i'j'}(t)\,f_D(t)\,\times$$
$$\times\exp\left(\sum_\mu \frac{\gamma^\mu}{\hbar\omega_\mu}\{\alpha_\mu(e^{i\omega_\mu t}-1)+2\beta_\mu(e^{-i\omega_\mu t}-1)\}\right)\times$$
$$\times\prod_\mu \delta\left(\alpha_\mu e^{i\omega_\mu t}-\alpha'_\mu-\frac{\gamma^\mu}{\hbar\omega_\mu}[e^{i\omega_\mu t}-1]\right)\times$$
$$\times\prod_\mu \delta\left(\beta_\mu e^{-i\omega_\mu t}-\beta'_\mu+\frac{\gamma^\mu}{\hbar\omega_\mu}[e^{-i\omega_\mu t}-1]\right)\,, \tag{A20}$$

$$f_D(t) = \exp\Bigg(-i\sum_\mu \frac{\gamma^{\mu 2}}{\hbar^2\omega_\mu}\Bigg\{\frac{1}{i\omega_\mu}(e^{i\omega_\mu t}-1)$$
$$-\frac{2}{i\omega_\mu}(e^{-i\omega_\mu t}-1)-3t\Bigg\}\Bigg) \tag{A21}$$

$$G_{F\,\alpha\;\beta}^{\;\alpha'\beta'}(t) = \frac{\theta(t)}{i\hbar}\prod_\mu \delta(\alpha_\mu e^{i\omega_\mu t}-\alpha'_\mu)\prod_\mu \delta(\beta_\mu e^{-i\omega_\mu t}-\beta'_\mu)\,. \tag{A22}$$

Thus, equations (A18)-(A22) and (A10) explicitly express the Green functions of the equations of motion for the generating functions $A-F$ in terms of the known Green functions for the corresponding phonon-free problems. In principle, these Green functions can be used to invert the equations for the generating functions and thus would provide explicit but rather lengthy Green function expressions for the generating functions, from which the optical response can then be derived setting $\alpha=\beta=0$.

Finally we will discuss one further example, namely the second order result for the excitonic population variable $\langle B_i^\dagger B_j\rangle$. Using the Green function (A19) and equation (20) we find

$$\langle B_i^\dagger B_j\rangle^{(2)}(t) = C^{(2)}_{ij\,\alpha=\beta=0}(t) = \sum_{i'j'}\int_{-\infty}^{\infty} G_{C\,i\;j}^{0\,i'j'}(t-t')\times$$
$$\times\{\mu_{i'}E_{i'}(t')\langle B_{j'}\rangle(t')-\mu_{j'}E_{j'}(t')\langle B_{i'}\rangle^*(t')\}\,dt'$$

$$= \sum_{i'j'} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} G_{Ai}^{0\,i'}(t-t')^* \, G_{Aj}^{0\,j'}(t-t'') \, \mu_{i'} E_{i'}(t') \, \mu_{j'} E_{j'}(t'') \times$$

$$\times \{\theta(t'-t'')\, f^0(t'-t'') + \theta(t''-t')\, f^{0*}(t''-t')\} \, dt' dt''. \tag{A23}$$

It is interesting to note that according to (A23) the propagation in configuration space of the excitonic populations and coherences represented by $\langle B_i^\dagger B_j \rangle$ is totally unaffected by the interaction with the phonons once the generation process is completed (i.e. once the driving field E has vanished). Phonons affect this variable only via the modification of the sources $\langle B \rangle$. This means that no matter on which timescale the excitonic transition density $\langle B \rangle$ decays due to the pure dephasing provided by the phonons, the variable $\langle B_i^\dagger B_j \rangle$ remains long-lived. The decay of $\langle B_i^\dagger B_j \rangle$ is governed by the homogeneous lifetime broadening (not included in our present description). The fact that the influence of the phonons on the configuration space propagation of $\langle B_i^\dagger B_j \rangle$ is completely missing, is of course a consequence of our oversimplified coupling scheme. However, it illustrates as an extreme example the expectation that population-like variables are less affected by pure dephasing processes than transition-like quantities. Furthermore, we see from the explicit representations (A13) and (A23) that in general $\langle B_i^\dagger B_j \rangle \neq \langle B_i^\dagger \rangle \langle B_j \rangle$. We therefore have to conclude that the gradual loss of coherence due to the coupling to phonons manifests itself in the deviation from the factorization properties of variables like $\langle B_i^\dagger B_j \rangle$ even in our simple model, where there is only exchange of energy (without exchange of momentum).

B. Derivation of transfer rates. In this appendix we compute the rates for the incoherent transfer of excitations between different sites as predicted by our model. These quantities are needed in equations (67) and (69) describing the combined influence of coherent and incoherent exciton dynamics. To this end, we assume that the system is at an initial time t_0 represented by the density matrix for a state where site j is excited and the phonons are in thermal equilibrium

$$\rho_0 = B_j^\dagger |0\rangle\langle 0| B_j \exp\left\{ \frac{-1}{KT} \sum_{l\lambda} \left(\hbar\omega_{\lambda_l} b_{\lambda_l}^\dagger b_{\lambda_l} + \gamma_l^{\lambda_l} B_l^\dagger B_l (b_{\lambda_l}^\dagger + b_{\lambda_l}) \right) \right\} / \bar{Z}, \tag{B1}$$

$$\bar{Z} = \mathrm{Tr}\left[B_j^\dagger |0\rangle\langle 0| B_j \exp\left\{ \frac{-1}{KT} \sum_{l\lambda} \left(\hbar\omega_{\lambda_l} b_{\lambda_l}^\dagger b_{\lambda_l} + \gamma_l^{\lambda_l} B_l^\dagger B_l (b_{\lambda_l}^\dagger + b_{\lambda_l}) \right) \right\} \right]. \tag{B2}$$

From ρ_0 we find that the function $\bar{C}_{jj\alpha\beta}$ initially has the value

$$\bar{C}_{jj\alpha\beta} = \exp\left(\sum_{l\lambda_l} \alpha_{\lambda_l} \beta_{\lambda_l} n_{\lambda_l} \right) \exp\left(- \sum_{\lambda_j} \frac{\gamma^{\lambda_j}}{\hbar\omega_{\lambda_j}} \{\alpha_{\lambda_j} + \beta_{\lambda_j}\} \right). \tag{B3}$$

Unlike the population N_j, the correlation Z_{ij} originates from off diagonal elements of the density matrix. In order to determine how an excitation, that initially gives a non zero value only to the the matrix element Z_{ij}, propagates in time, we consider an initial state given by the density matrix

$$\tilde{\rho}_0 = (a_j B_j^\dagger|0\rangle + \tilde{a}_{ij} B_i^\dagger B_j^\dagger|0\rangle)(\langle 0|B_j a_j^* + \langle 0|B_i B_j \tilde{a}_{ij}^*) \times$$

$$\times \exp\left\{-\frac{1}{KT}\sum_{l\lambda}(\hbar\omega_{\lambda_l} b_{\lambda_l}^\dagger b_{\lambda_l} + \gamma_l^{\lambda_l} B_l^\dagger B_l (b_{\lambda_l}^\dagger + b_{\lambda_l}))\right\}/\tilde{Z}, \tag{B8}$$

where a_j and $\tilde{a}_{ij}$ are arbitrary constants characterizing the initial state and $\tilde{Z}$ is a normalization factor. Starting from this initial condition, we can proceed in the same way as we did in the case of N_j; i.e. first, one sets up an equation of motion for the function $\bar{D}_{kij\alpha\beta} = D_{kij\alpha\beta} - A_{k\beta\alpha}^* B_{ij\alpha\beta}$ and determines the initial value of $\bar{D}_{iij\alpha\beta}$. Then one constructs the Green function for the propagation of $\bar{D}$ to zeroth order in the dipole coupling. Finally, one iterates the homogeneous part of the equation for $\bar{D}$ up to second order in J. The above steps result in the following equation describing the generation and propagation of the function Z_{ij} defined in section 5.

$$\begin{aligned}
i\hbar\partial_t Z_{ij} = \xi_{ij}\Bigg\{&\sum_n \bar{J}_{jn} Z_{in} + 2\hbar\omega_j Z_{ij} - J_{ji} Z_{jj} \\
&-iJ_{ij}J_{ji}[\kappa_j^2\sigma_{ij}Z_{ij} - \bar{\sigma}_{ij}Z_{jj}] \\
&-i\sum_n (J_{in}J_{ji}[S_{ijn}(\bar{\Omega}_n)Z_{in} - \bar{S}_{ijn}(\bar{\Omega}_n)Z_{jn}] \\
&+J_{in}J_{ni}[S_{inj}(\bar{\Omega}_j)Z_{ij} - \bar{S}_{inj}(\bar{\Omega}_j)Z_{nj}])\Bigg\} \\
+\delta_{ij}\Bigg\{&[(\kappa_j^2 - 1)2\kappa_j^2\hbar\omega_j + \Delta_j + \hbar\Omega_j]Z_{jj} \\
&+i\sum_n J_{jn}J_{ni}[\kappa_j^2\sigma_{nj}Z_{nj} - \bar{\sigma}_{ni}Z_{jj}] + \kappa_j^2\sum_n J_{in}Z_{in}\Bigg\} \\
&+i\sum_n \{J_{ni}J_{jn}[S_{nji}(\bar{\Omega}_i)Z_{ni} - \bar{S}_{nji}(\bar{\Omega}_i)Z_{ji}] \\
&+J_{ni}J_{in}[S_{nij}(\bar{\Omega}_j)Z_{nj} - \bar{S}_{nij}(\bar{\Omega}_j)Z_{ij}]\} + Q_{Z_{ij}},
\end{aligned} \tag{B9}$$

where the source $Q_{Z_{ij}}$ is given by

$$\begin{aligned}
Q_{Z_{ij}} = &-\xi_{ij}\mu_j E_j N_i - \delta_{ij}\kappa_j^2\mu_j E_j N_j \\
&+\xi_{ij}\langle B_i B_j\rangle \int_{-\infty}^{t} \hbar\left(\bar{\Omega}_B(t-t')_i^j\langle B_j\rangle(t') + \bar{\Omega}_B(t-t')_i^i\langle B_i\rangle(t')\right)^* dt'
\end{aligned}$$

$$-\langle B_i\rangle(t)^* \sum_{i'j'} \int_{-\infty}^{t} \hbar\bar{\Omega}_{BB}(t-t')_{i\ j}^{i'j'} \langle B_{i'}B_{j'}\rangle(t')\,dt'$$

$$-\delta_{ij}\kappa_j^2\langle B_jB_j\rangle(t) \int_{-\infty}^{t} \left(\hbar\bar{\Omega}_B(t-t')_i^j \langle B_j\rangle(t')\right)^* dt', \tag{B10}$$

with

$$\hbar\bar{\Omega}_B(t)_i^j = \Gamma_j(t)G_{A\,i}^{0\,j}(t),$$
$$\hbar\bar{\Omega}_{BB}(t)_{i\ j}^{i'j'} = G_{B\,i\ j}^{0\,i'j'}(t)\Gamma_i(t)\{\xi_{i'j'}(\delta_{ij'}+\delta_{ii'})+\delta_{i'j'}\kappa_{j'}^2\delta_{ij'}\}.$$

The transfer rates in (B9) are

$$S_{ijn}(t) = S_{ijn}^0(t)\,\exp\left(-\sum_{\lambda_i} f_i^{\lambda_i}(e^{i\omega_{\lambda_i}t}-e^{-i\omega_{\lambda_i}t})\right), \tag{B11}$$

$$\bar{S}_{ijn}(t) = S_{ijn}^0(t)\,\exp\left(\sum_{\lambda_j} f_j^{\lambda_j}(e^{i\omega_{\lambda_j}t}-e^{-i\omega_{\lambda_j}t})\right), \tag{B12}$$

$$S_{ijn}^0(t) = \xi_{ij}\xi_{nj}\xi_{in}\frac{1}{\hbar}e^{-i(\bar{\Omega}_n+\bar{\Omega}_j-\bar{\Omega}_i)t}\times$$
$$\times\exp\left(\sum_{\lambda_j} f_j^{\lambda_j}\{(e^{-i\omega_{\lambda_j}t}-1)-n_{\lambda_j}|e^{i\omega_{\lambda_j}t}-1|^2\}\right)\times$$
$$\times\exp\left(\sum_{\lambda_i} f_i^{\lambda_i}\{(e^{i\omega_{\lambda_i}t}-1)-n_{\lambda_i}|e^{i\omega_{\lambda_i}t}-1|^2\}\right)\times$$
$$\times\exp\left(\sum_{\lambda_n} f_n^{\lambda_n}\{(e^{i\omega_{\lambda_n}t}-1)-n_{\lambda_n}|e^{i\omega_{\lambda_n}t}-1|^2\}\right), \tag{B13}$$

$$\sigma_{ij} = \int_0^\infty \frac{\xi_{ij}}{\hbar}e^{-\left(\frac{\Delta_j}{\hbar}+2\Omega_j+\omega_j\kappa_j^2-\bar{\Omega}_i-\bar{\Omega}_j\right)t}\times$$
$$\times\exp\left(\sum_{\lambda_j}\kappa_j^4 f_j^{\lambda_j}(e^{-i\omega_{\lambda_j}t}-1)\right)\,\exp\left(\sum_{\lambda_i} f_i^{\lambda_i}(e^{-i\omega_{\lambda_i}t}-1)\right)\times$$
$$\times\exp\left(\sum_{\lambda_j}\kappa_j^2 f_j^{\lambda_j}(e^{i\omega_{\lambda_j}t}-e^{-i\omega_{\lambda_j}t})\right)$$
$$\exp\left(-\sum_{\lambda_i} f_i^{\lambda_i}n_{\lambda_i}|e^{i\omega_{\lambda_i}t}-1|^2\right)\times$$

$$\times \exp\left(-\sum_{\lambda_j}\kappa_j^4 f_j^{\lambda_j} n_{\lambda_j}|e^{i\omega_{\lambda_j}t}-1|^2\right)\,dt\,, \tag{B14}$$

$$\bar{\sigma}_{ij} = \int_0^\infty \frac{\xi_{ij}}{\hbar} e^{-(\bar{\Omega}_j-\bar{\Omega}_i)t}\ \times$$

$$\times \exp\left(\sum_{\lambda_j}\kappa_j^4 f_j^{\lambda_j}(e^{-i\omega_{\lambda_j}t}-1)\right)\ \exp\left(\sum_{\lambda_i} f_i^{\lambda_i}(e^{i\omega_{\lambda_i}t}-1)\right)\times$$

$$\times \exp\left(-\sum_{\lambda_i} f_i^{\lambda_i} n_{\lambda_i}|e^{i\omega_{\lambda_i}t}-1|^2\right)$$

$$\exp\left(-\sum_{\lambda_j}\kappa_j^4 f_j^{\lambda_j} n_{\lambda_j}|e^{i\omega_{\lambda_j}t}-1|^2\right)\times$$

$$\times \exp\left(\sum_{\lambda_j}(\kappa_j^2-1) f_j^{\lambda_j}(e^{i\omega_{\lambda_j}t}-e^{-i\omega_{\lambda_j}t})\right)\,dt\,. \tag{B15}$$

and $S_{ijn}(\Omega)$ and $\bar{S}_{ijn}(\Omega)$ are the Fourier transforms of $S_{ijn}(t)$ and $\bar{S}_{ijn}(t)$.

C. Time-local version of the combined coherent and incoherent exciton dynamics. Starting from equations (67)-(69) time-local equations of motion can be obtained following the procedures of subsection 4.3. These equations read

$$i\hbar\partial_t\langle B_j\rangle^{(a)} = \sum_n \bar{J}_{jn}\langle B_n\rangle^{(a)} - \mu_j \bar{E}^{(a)}\,e^{-i\omega_a t}$$
$$+ i\hbar\Im m(\Omega_B)(\omega_a)_j\langle B_j\rangle^{(a)}\,, \tag{C1}$$

$$i\hbar\partial_t\langle B_iB_j\rangle^{(a,b)} = \xi_{ij}\left\{\sum_n(\bar{J}_{jn}\langle B_iB_n\rangle^{(a,b)} + \bar{J}_{in}\langle B_nB_j\rangle^{(a,b)})\right.$$
$$-\bar{E}^{(a)}\,e^{-i\omega_a t}\,[\mu_i\langle B_j\rangle^{(b)} + \mu_j\langle B_i\rangle^{(b)}]$$
$$\left.-\bar{E}^{(b)}\,e^{-i\omega_b t}\,[\mu_i\langle B_j\rangle^{(a)} + \mu_j\langle B_i\rangle^{(a)}]\right\}$$
$$+\delta_{ij}\left\{\kappa_j^2\left(\sum_n J_{jn}\langle B_jB_n\rangle^{(a,b)} - \mu_j[\bar{E}^{(a)}e^{-i\omega_a t}\langle B_j\rangle^{(b)}+\right.\right.$$
$$\left.\left.\bar{E}^{(b)}e^{-i\omega_b t}\langle B_j\rangle^{(a)}]\right) + (\Delta_j + 2\hbar\Omega_j)\langle B_jB_j\rangle^{(a,b)}\right\}$$
$$+\sum_{i'j'} i\hbar\Im m(\Omega_{BB})(\omega_a+\omega_b)_{i\ j}^{i'j'}\langle B_{i'}B_{j'}\rangle^{(a,b)}\,, \tag{C2}$$

$$\hbar\partial_t N_j^{(-a,b)} = \sum_m (R_{jm} N_m^{(-a,b)} - R_{mj} N_j^{(-a,b)})$$

$$-\langle B_j\rangle^{(a)*}\langle B_j\rangle^{(b)}\hbar\{\Im m(\Omega)(\omega_a)_j + \Im m(\Omega)(\omega_b)_j\}\ , \tag{C3}$$

$$i\hbar\partial_t\langle B_j\rangle^{(-a,b,c)} = \mu_j\, q_j\, \bar{E}^{(b)}\, e^{-i\omega_b t}\left\{\langle B_j\rangle^{(a)*}\langle B_j\rangle^{(c)} + N_j^{(-a,c)}\right\}$$

$$+\mu_j\, q_j\, \bar{E}^{(c)}\, e^{-i\omega_c t}\left\{\langle B_j\rangle^{(a)*}\langle B_j\rangle^{(b)} + N_j^{(-a,b)}\right\}$$

$$+\Delta_j\left\{\langle B_j\rangle^{(a)*}\langle B_j B_j\rangle^{(b,c)} + 2\,(N_j^{(-a,b)}\langle B_j\rangle^{(c)} + N_j^{(-a,c)}\langle B_j\rangle^{(b)})\right\}$$

$$-q_j\sum_n J_{jn}\left\{\langle B_j\rangle^{(a)*}\langle B_j B_n\rangle^{(b,c)} + N_j^{(-a,b)}\langle B_n\rangle^{(c)} + N_j^{(-a,c)}\langle B_n\rangle^{(b)}\right\}$$

$$-iq_j\sum_n\left\{(\bar{R}_{jn} N_n^{(-a,b)} - \bar{R}^*_{nj} N_j^{(-a,b)})\langle B_j\rangle^{(c)}\right.$$

$$\left.+(\bar{R}_{jn} N_n^{(-a,c)} - \bar{R}^*_{nj} N_j^{(-a,c)})\langle B_j\rangle^{(b)}\right\} + \sum_n \bar{J}_{jn}\langle B_n\rangle^{(-a,b,c)}$$

$$+i\hbar\Im m(\Omega_B)(\omega_c + \omega_b - \omega_a)_j\langle B_j\rangle^{(-a,b,c)}\ , \tag{C4}$$

where again the RWA has been invoked. The self-energies $\hbar\Omega_B$ and $\hbar\Omega_{BB}$ are the Fourier transforms of (44) and (45).

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