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Stochastic Liouville Equations for Coherent Multidimensional Spectroscopy of Excitons

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Abstract

Signatures of chemical exchange and spectral diffusion in 2D photon-echo lineshapes of molecular aggregates are studied using model calculations for a dimer whose Hamiltonian parameters are stochastically modulated. Cross peaks induced by chemical exchange and by exciton transport has different dynamics, and distinguish two models which have the same absorption spectrum (a two-state-jump bath modulation model of a dimer and a four state jump bath model of a single chromophore). Slow Gaussian-Markovian spectral diffusion of a symmetric dimer induces new peaks which are damped as the dipole moment is equilibrated. These effects require an explicit treatment of the bath and may not be described by lower-level theories such as the Redfield equations, which eliminate the bath.

1 Introduction

Exciton models are widely used in the description of the coherent nonlinear optical response of complex systems.¹ Vibrational spectra of proteins,^{2–6} liquid water,⁷ and electronic spectra of photosynthetic antennae⁸ are a few examples. Bath-induced fluctuations of transition frequencies and couplings affect the electronic and transport properties of aggregates (e.g. photosynthetic antennae).

A broad arsenal of techniques has been developed towards the simulation of two dimensional coherent spectroscopy (2DCS) signals.¹ Direct simulation of the optical response requires repeated diagonalizations of the system Hamiltonian at many time points. The response is then given by a path integral over the trajectories of the time dependent eigenvalues and the overlap factors of the instantaneous eigenstates at different times.^{9,10}

The fluctuating time-dependent Hamiltonian $H(t)$ defines the instantaneous (adiabatic) basis $|\varphi_j(t)\rangle$ and energies $\varepsilon_j(t)$ (we set $\hbar = 1$)

$$H(t)|\varphi_j(t)\rangle = \varepsilon_j(t)|\varphi_j(t)\rangle$$

Direct evaluation of the time evolution operator, when the time t is divided into $N \rightarrow \infty$ short segments $\Delta t \equiv t/N$ gives

$$U \equiv T \exp \left[-i \int_0^t d\tau H(\tau) \right] = T \prod_{n=1}^N \exp[-i H(t_n) \Delta t]_{t_n = n \Delta t} \quad (1)$$

Adopting the matrix representation $\tilde{U}_{jk} \equiv \langle \phi_j(t) | U | \phi_k(0) \rangle$ we get

$$\tilde{U} = T \prod_{n=1}^N U_n S_n; \quad (2)$$

Here

$$(U_n)_{jj'} = \exp[-i\varepsilon_j(t_n)\Delta t]\delta_{jj'}$$

is the adiabatic propagator, and the nonadiabatic coupling matrix

$$(S_n)_{jj'} = \langle \phi_j(t_n) | \phi_{j'}(t_n - 1) \rangle,$$

represents the overlap of the adiabatic states at two adjacent points.

Implementing Eq. (1) is numerically expensive. Moreover, one must typically account for various fluctuation scenarios and average over sufficiently long trajectories (or, equivalently by ergodic hypothesis, over possible paths) of the fluctuating Hamiltonian.

More affordable simulations are feasible when the fluctuations are small and fast. The response can then be calculated by sums over delocalized eigenstates of the average Hamiltonian, where dephasing rates are introduced phenomenologically.¹¹ Exciton transport may be accounted for by using the Redfield equations^{1,12,13} for the reduced Liouville space dynamics of the chromophores. A quasiparticle approach based on the nonlinear exciton equations allows the interpretation of signals in terms of exciton scattering.¹ Very slow fluctuations can be readily incorporated by static averaging of the signals over their realizations.¹⁴

The stochastic Liouville equations (SLE)^{15–17} allow the modelling of strong fluctuations with arbitrary time scales provided they can be described by a few classical collective coordinates, which satisfy a Markovian master equation. The path integrals of Eq.(2) and the final averaging are avoided by calculating the density distributions in the joint system + bath space. The SLE generalize the Redfield equations, that are limited to fast fluctuations where the bath degrees of freedom can be eliminated. We have recently applied the SLE to calculate 2D lineshapes of a single chromophore whose transition frequency undergoes a stochastic modulation due to hydrogen bonding in water^{18,19} or organic solvents.^{20,21} Excitonic spectra of a multichromophoric system (trialanine) were described by the SLE approach for a limited class of models and delay times.¹⁰

In this paper we apply the SLE to a model dimer interacting with a classical bath. We predict the complete delay time evolution of 2D signals, and show new effects of interchromophore coupling, as well as spectral diffusion characteristics of the finite fluctuations time. Two types of stochastic models are considered: discrete chemical-exchange will be described by a two state jump model for the bath, and continuous spectral diffusion accounted for using a Gaussian-Markovian coordinate (high temperature limit of a Brownian overdamped oscillator). We show how the 2D signals may distinguish the model from a non excitonic system which has the same linear response. Some effects which are missed in the simpler Redfield treatment are pointed out.

2 Stochastic Liouville equations for molecular dimer

We consider a dimer with two one-exciton states $|e_1=B_1^\dagger|g$, and $|e_2=B_2^\dagger|g$, and one doubly excited state $|f_1 \equiv B_1^\dagger B_2^\dagger|g$, described by the Frenkel-exciton Hamiltonian.^{1,22–24}

$$H=\varepsilon_1(t)B_1^\dagger B_1+\varepsilon_2(t)B_2^\dagger B_2+J(t)(B_2^\dagger B_1+B_1^\dagger B_2)+\Delta B_1^\dagger B_2^\dagger B_1 B_2 \quad (3)$$

Both the coupling J and energies ε_j undergo stochastic fluctuations. We will assume that the doubly-excited state is strongly shifted $\Delta \rightarrow \infty$ so that it does not contribute to the optical signals near the single exciton frequency $\omega \approx \varepsilon$.

A discrete fluctuation model is introduced by an additional bath degree of freedom with two states u (up) and d (down), representing e.g. two conformers of the molecule or solvent configurations. We assume that the Hamiltonian parameters jump stochastically between two values $J_u, \varepsilon_{1u}, \varepsilon_{2u}$ and $J_d, \varepsilon_{1d}, \varepsilon_{2d}$ corresponding to the two configurations. The transitions between these states are described by a Markovian Pauli master equation²⁵ with down (k_d) and up (k_u) jump rates, respectively.

$$\begin{aligned} \left(\frac{d\rho_u}{dt}\right)_M &= -k_d\rho_u + k_u\rho_d \\ \left(\frac{d\rho_d}{dt}\right)_M &= k_d\rho_u - k_u\rho_d \end{aligned} \quad (4)$$

The entire density matrix, defined in the joint system + bath space, is described by the stochastic Liouville equation.^{15,16}

$$\frac{d\rho}{dt} = -i[H, \rho] + \left(\frac{d\rho}{dt}\right)_M \equiv \mathcal{L}_\rho$$

ρ carries three indices representing bra, and ket variable of the system Liouville space and one index denoting the state of bath.

Since the Hamiltonian (Eq.(3)) conserves the number of excitons, the Liouville operator $\mathcal{L}$ is block-diagonal, with separate blocks corresponding to the gg , ee , ge , and eg manifolds. We define the basis set for ground state evolution ($|gg; u\rangle\rangle$, $|gg; d\rangle\rangle$), with the block

$$\mathcal{L}_{gg,gg} = \begin{pmatrix} -k_d & k_u \\ k_d & -k_u \end{pmatrix}$$

The coherence (eg) evolution is described in the following basis set $|e_1g; u\rangle\rangle$, $|e_1g; d\rangle\rangle$, $|e_2g; u\rangle\rangle$, and $|e_2g; d\rangle\rangle$ by the Liouvillean

$$\mathcal{L}_{eg,eg} = \begin{pmatrix} -k_d - i\varepsilon_{1u} & k_u & -iJ_u & 0 \\ k_d & -k_u - i\varepsilon_{1d} & 0 & -iJ_d \\ -iJ_u & 0 & -k_d - i\varepsilon_{2u} & k_u \\ 0 & -iJ_d & k_d & -k_u - i\varepsilon_{2d} \end{pmatrix}$$

Finally, the excited state block $|e_1e_1; u\rangle\rangle$, $|e_1e_1; d\rangle\rangle$, $|e_1e_2; u\rangle\rangle$, $|e_1e_2; d\rangle\rangle$, $|e_2e_1; u\rangle\rangle$, $|e_2e_1; d\rangle\rangle$, $|e_2e_2; u\rangle\rangle$, $|e_2e_2; d\rangle\rangle$ is represented by

$$\mathcal{L}_{ee',ee'} = \begin{pmatrix} -k_d & k_u & iJ_u & 0 & -iJ_u & 0 & 0 & 0 \\ k_d & -k_u & 0 & iJ_d & 0 & -iJ_d & 0 & 0 \\ iJ_u & 0 & -k_d - i\Delta\epsilon_u & k_u & 0 & 0 & -iJ_u & 0 \\ 0 & iJ_d & k_d & -k_u - i\Delta\epsilon_d & 0 & 0 & 0 & -iJ_d \\ -iJ_u & 0 & 0 & 0 & -k_d + i\Delta\epsilon_u & k_u & iJ_u & 0 \\ 0 & -iJ_d & 0 & 0 & k_d & -k_u + i\Delta\epsilon_d & 0 & iJ_d \\ 0 & 0 & -iJ_u & 0 & iJ_u & 0 & -k_d & k_u \\ 0 & 0 & 0 & -iJ_d & 0 & iJ_d & k_d & -k_u \end{pmatrix}$$

where we have denoted $\Delta\epsilon_d \equiv \epsilon_{1d} - \epsilon_{2d}$, $\Delta\epsilon_u \equiv \epsilon_{1u} - \epsilon_{2u}$. With $\mathcal{L}_{ge,ge} = \mathcal{L}_{eg,eg}^*$ the description is complete.

The Green's function solution of the Liouville equation is

$$\mathcal{G}(t) \equiv \theta(t) \exp \mathcal{L}t$$

In the frequency-domain $\mathcal{G}(\omega) = \int e^{i\omega t} \mathcal{G}(t) dt$ we have

$$\mathcal{G}(\omega) = -[i\omega + \mathcal{L}]^{-1} \quad (5)$$

Like $\mathcal{L}$, the Green's function is block diagonal as well. For instance, the time domain Green's function for the gg block reads

$$\mathcal{G}_{gg,gg}(t) = \frac{1}{k_d + k_u} \begin{pmatrix} k_u & k_u \\ k_d & k_d \end{pmatrix} + \frac{e^{-(k_d + k_u)t}}{k_d + k_u} \begin{pmatrix} k_d & -k_u \\ -k_d & k_u \end{pmatrix}$$

In the other manifolds the time domain Green's functions will be calculated numerically by spectral decomposition of the Liouville operator. In the frequency domain, all the block matrix inversions (Eq. 5) can be performed analytically in closed, though somewhat lengthy, form.

Averaging over bath variable is made with respect to the equilibrium bath density

$$\rho^{(eq)} = \frac{1}{k_d + k_u} \begin{pmatrix} k_u \\ k_d \end{pmatrix}$$

and the summation over final states is represented by the scalar product with the vector $\langle I | = (1, 1)$.

3 The two- dimensional signals

We shall calculate in the response of the system to three laser pulses. The interaction is given by $H_{int} = -E(t)D_{int}$ where

$$D_{int} = [\mu_1(B_1^\dagger + B_1) + \mu_2(B_2^\dagger + B_2)]$$

is the dipole operator. We consider impulsive experiments performed with short laser pulses. The linear response function is

$$S(t_1)=i\left\langle\left\langle\mu|\mathcal{G}(t_1)\mu^{(-)}|\rho(0)\right\rangle\right\rangle$$

and the third-order response function²⁶

$$S(t_3, t_2, t_1)=i^3\left\langle\left\langle\mu|\mathcal{G}(t_3)\mu^{(-)}\mathcal{G}(t_2)\mu^{(-)}\mathcal{G}(t_1)\mu^{(-)}|\rho(0)\right\rangle\right\rangle$$

where $\mu^{(-)} \equiv [D_{int}, \dots]$ is the dipole superoperator, and $\langle\langle\mu|\dots\rangle = \langle I|Tr D_{int}\dots$ provides the mean value of dipole moment. Initially the system is in the ground state and the bath is at equilibrium

$$|\rho(0)\rangle = |gg\rangle \rho^{(eq)}$$

The dipole moment is independent of the bath variables so that $\mu^{(-)}$ is represented by the diagonal matrices in bath space

$$\hat{\mu}_1 = \begin{pmatrix} \mu_1 & 0 \\ 0 & \mu_1 \end{pmatrix}; \hat{\mu}_2 = \begin{pmatrix} \mu_2 & 0 \\ 0 & \mu_2 \end{pmatrix}.$$

In our basis set, $\mu^{(-)}$ is represented by the following matrices

$$\begin{aligned} \mu_{eg,gg}^{(-)} &= \begin{pmatrix} \hat{\mu}_1 \\ \hat{\mu}_2 \end{pmatrix} \\ \mu_{ee,gg}^{(-)} &= \begin{pmatrix} -\hat{\mu}_1 & 0 \\ -\hat{\mu}_2 & 0 \\ 0 & -\hat{\mu}_1 \\ 0 & -\hat{\mu}_2 \end{pmatrix} \\ \mu_{ee,ge}^{(-)} &= \begin{pmatrix} \hat{\mu}_1 & 0 \\ 0 & \hat{\mu}_1 \\ \hat{\mu}_2 & 0 \\ 0 & \hat{\mu}_2 \end{pmatrix} \end{aligned}$$

We further have

$\mu_{ge,gg}^{(-)} = -\mu_{eg,gg}^{(-)}$, $\mu_{gg,eg}^{(-)} = [\mu_{eg,gg}^{(-)}]^T$, $\mu_{gg,ge}^{(-)} = [\mu_{ge,gg}^{(-)}]^T$, $\mu_{eg,ee}^{(-)} = [\mu_{ee,eg}^{(-)}]^T$, $\mu_{ee,ge}^{(-)} = [\mu_{ge,ee}^{(-)}]^T$. We note that $\mu_{\alpha,\beta} = [\mu_{\beta,\alpha}]^T$, and $\mu_{ij,kl}^{(-)} = -\mu_{ji,lk}^{(-)}$ for $ij(kl) \neq ee$

The linear response is given by

$$S(t_1)=i\left\langle I|\mu_{gg,eg}\mathcal{G}_{eg,eg}(t_1)\mu_{eg,gg}^{(-)}|\rho^{(eq)}\right\rangle + c.c.$$

In frequency space $S(\omega_1) \equiv \int e^{i\omega_1 t_1} S(t_1)$. These represent a symmetric peak structure around ε and $-\varepsilon$, respectively ($S(\omega) = S^*(-\omega)$). We focus on the $\omega_1 \approx \varepsilon$ peaks. The absorption lineshape is given by

$$I(\omega_1) = \text{Im} S(\omega_1) = \text{Re} \left\langle I|\mu_{gg,eg}\mathcal{G}_{eg,eg}(\omega_1)\mu_{eg,gg}^{(-)}|\rho^{(eq)}\right\rangle \quad (6)$$

We next turn to the third order resonant signals generated in the $\mathbf{k}_I = -\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$ and $\mathbf{k}_{II} = \mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_3$ phase-matching directions. These will be displayed as ω_1, ω_3 frequency-frequency plots $S(\omega_3, t_2, \omega_1)$ for various time slices t_2 . As in the linear response (Eq. (6)), each contribution to the third order response has a complex conjugated counterpart giving peaks at opposite frequencies $S(\omega_3, t_2, \omega_1) = S^*(-\omega_3, t_2, -\omega_1)$.²⁷ We focus on the peak structure around $\omega_3 = \varepsilon$; The corresponding response function for the $\mathbf{k}_I$ signal is given by:

$$S_I(\omega_3, t_2, \omega_1) = (i)^3 [R_1(\omega_3, t_2, \omega_1) + R_2(\omega_3, t_2, \omega_1)],$$

and for $\mathbf{k}_{II}$

$$S_{II}(\omega_3, t_2, \omega_1) = (i)^3 [R_3(\omega_3, t_2, \omega_1) + R_4(\omega_3, t_2, \omega_1)]. \quad (7)$$

The various contributions R (Liouville space pathways) are represented by the 4 Feynman diagrams shown in Fig 1:

$$\begin{aligned} R_1(\omega_3, t_2, \omega_1) &= \left\langle I | \mu_{gg, eg} \mathcal{G}_{eg, eg}(\omega_3) \mu_{eg, gg}^{(-)} \mathcal{G}_{gg, gg}(t_2) \mu_{gg, ge}^{(-)} \mathcal{G}_{ge, ge}(\omega_1) \mu_{ge, gg}^{(-)} | \rho^{(eq)} \right\rangle \\ R_2(\omega_3, t_2, \omega_1) &= \left\langle I | \mu_{gg, eg} \mathcal{G}_{eg, eg}(\omega_3) \mu_{eg, ee}^{(-)} \mathcal{G}_{ee, ee}(t_2) \mu_{ee, ge}^{(-)} \mathcal{G}_{ge, ge}(\omega_1) \mu_{ge, gg}^{(-)} | \rho^{(eq)} \right\rangle \\ R_3(\omega_3, t_2, \omega_1) &= \left\langle I | \mu_{gg, eg} \mathcal{G}_{eg, eg}(\omega_3) \mu_{eg, gg}^{(-)} \mathcal{G}_{gg, gg}(t_2) \mu_{gg, eg}^{(-)} \mathcal{G}_{eg, eg}(\omega_1) \mu_{eg, gg}^{(-)} | \rho^{(eq)} \right\rangle \\ R_4(\omega_3, t_2, \omega_1) &= \left\langle I | \mu_{gg, eg} \mathcal{G}_{eg, eg}(\omega_3) \mu_{eg, ee}^{(-)} \mathcal{G}_{ee, ee}(t_2) \mu_{ee, eg}^{(-)} \mathcal{G}_{eg, eg}(\omega_1) \mu_{eg, gg}^{(-)} | \rho^{(eq)} \right\rangle \end{aligned} \quad (8)$$

We shall further display the following combination of signals which provide a clean absorptive signal²⁸

$$S_A(\omega_3, t_2, \omega_1) \equiv -\text{Im } S_I(\omega_3, t_2, -\omega_1) - \text{Im } S_{II}(\omega_3, t_2, \omega_1) \quad (9)$$

4 Slow fluctuations

The absorption spectrum (Fig 2) has four peaks, centered at two

$E_{1(2),u} = (\varepsilon_{1u} + \varepsilon_{2u})/2 \pm \sqrt{\Delta\varepsilon_u^2 + J_u^2}$ eigenvalues of H_u and two $E_{1(2),d} = (\varepsilon_{1d} + \varepsilon_{2d})/2 \pm \sqrt{\Delta\varepsilon_d^2 + J_d^2}$ eigenvalues of H_d , in the static limiting case $k_u, k_d \ll |E_{1(2),u} - E_{1(2),d}|$.

$$I(\omega) = \sum_{j=1}^2 \sum_{v=u,d} \frac{M_{j,v}^2 \Gamma_v \rho_{ggv}^{(eq)}}{\Gamma_v^2 + (\omega - E_{j,v})^2} \quad (10)$$

where

$$M_{j,v} = \langle E_{j,v} | \mu | g \rangle$$

is the transition dipole, and $\Gamma_d = k_u$, $\Gamma_u = k_v$ are the line broadening parameters.

The 2D S_A lineshape at short t_2 , displayed in Fig 3, top left panel, shows primarily four diagonal peaks and four selected cross peaks. Three consecutive interactions with laser pulses

(applications of $\mu^{(-)}$) for times $t_2 \ll k_{d,u}^{-1}$ induce cross-peaks between peaks belonging to the same bath state, but different excitons.

$$\begin{aligned}
S_A(\omega_3, t_2 \ll k_{d,u}^{-1}, \omega_1) \\
= \text{Re} \sum_{k=1}^2 \sum_{j=1}^2 \sum_{v=u,d} M_{kv}^2 M_{jv}^2 \rho_{gg}^{(eq)} \frac{1}{\Gamma_v - i(\omega_3 - E_{j,v})} \times \left[\frac{2\Gamma_v}{\Gamma_v^2 + (\omega_1 - E_{k,v})^2} + e^{-\Gamma_{v,kj}^e t_2 - i(E_{j,v} - E_{k,v})t_2} \left(\frac{1}{\Gamma_v + i(\omega_1 - E_{j,v})} + \frac{1}{\Gamma_v + i(\omega_1 - E_{k,v})} \right) \right]
\end{aligned}
\tag{11}$$

where exciton dephasing $\Gamma_{v,kj}^e$ is negligible in the slow limit (compare fast limit).

Additional cross-peaks induced by jumps among the u and d peaks (top left panel) appear for $t_2 \gg k_{d,u}^{-1}$. The dynamics is quite rich on these timescales, since the phase relation between u and d eigenstates $\langle E_{j,u} | E_{i,d} \rangle$ is important for ee evolution and may also induce fluctuations of the peaks magnitudes at $2\pi(E_{j,v} - E_{i,v})^{-1}$ period. We distinguish between two cases: If the u and d eigenstates are degenerate $|E_{j,u}\rangle = |E_{j,d}\rangle$ no exciton transport is allowed. This is shown in the top panels of Fig 3 where the delay time t_2 increases from the left to the right panel. The peaks gradually develop at all possible combinations of frequencies. However, peaks belonging to the same exciton are stronger even for very long times. When $|E_{j,u}\rangle \neq |E_{j,d}\rangle$, exciton transfer is allowed and asymptotically we have

$$\mathcal{G}_{E_j E_{kv}, E_l E_{mw}}(t_2 \rightarrow \infty) = \frac{1}{2} \delta_{jk} \delta_{lm} \frac{k_v}{k_u + k_d}$$

The absorptive lineshape can then be factorized as follows

$$S_A(\omega_3, t_2 \rightarrow \infty, \omega_1) = 3I(\omega_1)I(\omega_3). \tag{12}$$

This is similar to the asymptotic lineshape of the monomer (Eq.(21)).^{29,30} Eq. (12) holds for arbitrary timescale and for any type of stochastic modulation (once transport is allowed). Eq. (12) can be generalized beyond the stochastic model³¹ to include finite temperature effects, where the emission lineshape is red shifted with respect to the absorption (the Stokes shift).

Lineshapes of this simple spectra are qualitatively reminiscent of 2D NMR spectra³³ measured on systems obeying similar dynamical rules. The general relation between 2D NMR methods and their optical counterpart has been discussed in Ref.³² 2D NMR works on different timescales (with differences in models and approximations used), has no phase matching, but has a better control of the pulses. These differences and the rather weak fields applied in most optical experiments make the nonlinear response functions,²⁶ such as used here, particularly adequate for interpreting 2D optical and infrared experiments.

For a more detailed analysis of these lineshapes we display the four contributions R_i to S_A in Figure 4. At $t_2 = 0$ $R_1 = R_2$ (Fig 4, top panels) since these diagrams only differ by the second interval evolution in the ee or gg manifolds. The ket and the bra action of the dipole moment connects different exciton states in t_1 and t_3 intervals resulting in their cross peaks. A similar peak-pattern is seen in R_3 , but this nonrephasing contribution is elongated in the antidiagonal direction compared to the diagonal elongation of the rephasing contribution. R_4 only shows

diagonal peaks, because the eg state in the third interval is caused by interaction with the first pulse and represents the same exciton state.

Fig 5 repeats these calculations in the long delay tuime regime $k_u t_2, k_d t_2 \gg 1$. The ground state t_2 evolution for R_1 and R_3 mixes the u and d bath states, and their combination shows a complete peak structure. When the rephasing R_1 and nonrephasing R_3 contributions, characterized by the ground state (gg) evolution during t_2 , are summed over, the lineshape may be recast as the product of the two lineshapes $\sim 2I(\omega_1)I(\omega_3)$.

The ee evolution in the R_2 and R_4 diagrams is more complex. During t_2 coherences decay creating a statistical mixture of diagonal E_{jv} states. Since our parametrization does not allow exciton transport, we see decoherence. All contributions with different acting dipole moments at the first and second pulse decay. The only resulting cross peaks are connected with the u and d jumps. This explains why the peaks are stronger in the S_A lineshape. The features shown in Fig 5 are not universal. When exciton transport is allowed the other cross-peaks appear, approaching Eq. (12).

The complete peak structure described above is simplified when the dipole moment does not couple to all of the $|E_{jv}\rangle$ eigenstates, or when some levels are accidentally degenerate. The 2D lineshapes can distinguish between various dynamical models with a similar absorption (1D) spectrum. To illustrate this we compare the dimer with a two state bath with the four state jump bath model (FSJ) modulating single chromophore, given in Appendix B. Comparison of Eq. (10) with Eq. (20) or the lineshapes displayed in Fig 2 shows that the two models may have identical absorption lineshape in the static limit with the proper choice of the resonance frequencies and linewidth (as defined by Eqs. (10) and (20)).

2D lineshapes of the two models are markedly different at short times as shown in Fig 3. The slow fluctuation FSJ limit (bottom left) S_A lineshape at short t_2 jumps only reveals the diagonal peaks, because no change of bath state can occur in contrast to dimer. With increasing delay time the complete peak structure is developed, in contrast to the dimer, peak oscillations due to coherence dynamics (Eq. (11))³⁴ can not be observed. Asymptotically these two lineshape agree (compare Eqs.(12), (21), and (22)), except when exciton transfer is not allowed.

5 Fast and intermediate fluctuations timescale

In the motional narrowing $k_u, k_d \gg |E_{ju} - E_{kd}|$ limit fluctuations are averaged on the timescale of optical experiments. The averaged Hamiltonian

$$\bar{H} = \bar{\epsilon}_1 B_1^\dagger B_1 + \bar{\epsilon}_2 B_2^\dagger B_2 + \bar{J}(B_2^\dagger B_1 + B_1^\dagger B_2) \quad (13)$$

where

$$\bar{J} = \frac{k_u J_u + k_d J_d}{k_u + k_d}, \quad \bar{\epsilon}_j = \frac{k_u \epsilon_{ju} + k_d \epsilon_{jd}}{k_u + k_d},$$

may be used.

The dynamics is however different from the isolated dimer, which follows the Hamiltonian Eq. (13) since the fluctuations lead to an additional population relaxation rate (the exciton transfer) $\Gamma^T \sim \langle |\bar{E}_1| (H - \bar{H}) |\bar{E}_2\rangle|^2 \rangle / k$ and dephasing rates

$$\Gamma^e \sim \Gamma^T + \sum_{i=1}^2 \langle \bar{E}_i | \langle (H - \bar{H})^2 | \bar{E}_i \rangle \rangle / k \text{ and dephasing between ground and excited states } \Gamma_i \sim$$

$\Gamma^T/2 + \langle \bar{E}_i | \langle (H - \bar{H})^2 | \bar{E}_i \rangle / k + \langle g | \langle (H - \bar{H})^2 | g \rangle / k$. The averaged density matrix is approximately described by the Redfield master equations in the secular approximation in the high temperature limit

$$\begin{aligned}\frac{d\rho_{\bar{E}_1\bar{E}_1}}{dt} &= -\Gamma^T \rho_{\bar{E}_1\bar{E}_1} + \Gamma^T \rho_{\bar{E}_2\bar{E}_2} \\ \frac{d\rho_{\bar{E}_2\bar{E}_2}}{dt} &= -\Gamma^T \rho_{\bar{E}_2\bar{E}_2} + \Gamma^T \rho_{\bar{E}_1\bar{E}_1} \\ \frac{d\rho_{\bar{E}_1\bar{E}_2}}{dt} &= [-i(E_1 - E_2) - \Gamma^e] \rho_{\bar{E}_1\bar{E}_2} \\ \frac{d\rho_{\bar{E}_jg}}{dt} &= [-i\bar{E}_j - \Gamma_j] \rho_{\bar{E}_jg}\end{aligned}$$

The dynamics may be described in the reduced system Liouville space. Signatures of the fluctuations are present in the relaxation and dephasing rates, which may not be described in the Hilbert space. The corresponding Green's functions in system Liouville space are

$$\begin{aligned}\mathcal{G}_{\bar{E}_1\bar{E}_1, \bar{E}_1\bar{E}_1}(t) &= \mathcal{G}_{\bar{E}_2\bar{E}_2, \bar{E}_2\bar{E}_2}(t) = \frac{1+e^{-2\Gamma^T t}}{2} \\ \mathcal{G}_{\bar{E}_1\bar{E}_1, \bar{E}_2\bar{E}_2}(t) &= \mathcal{G}_{\bar{E}_2\bar{E}_2, \bar{E}_1\bar{E}_1}(t) = \frac{1-e^{-2\Gamma^T t}}{2} \\ \mathcal{G}_{\bar{E}_1\bar{E}_2, \bar{E}_1\bar{E}_2}(t) &= \mathcal{G}_{\bar{E}_2\bar{E}_1, \bar{E}_2\bar{E}_1}^*(t) = e^{[-i(\bar{E}_1 - \bar{E}_2) - \Gamma^e]t} \\ \mathcal{G}_{\bar{E}_jg, \bar{E}_jg}(t) &= \mathcal{G}_{g\bar{E}_j, g\bar{E}_j}^*(t) = e^{[-i\bar{E}_j - \Gamma_j]t}\end{aligned}$$

Note that the SLE provides an exact representation of stochastic Markovian fluctuations of Hamiltonian dynamics. Both Liouville equation, and the averaging over bath paths preserve the positive semidefiniteness of the density matrix, so does the SLE. The positivity issue of master equations,³⁵ which is a major problem for the Redfield equations when the secular approximation is not invoked, is avoided.

The absorption spectrum has two peaks centered at the eigenvalues $\bar{E}_1$ and $\bar{E}_2$ of the averaged dimer Hamiltonian

$$I(\omega) = \sum_{i=1}^2 \frac{M_i^2 \Gamma_i}{(\Gamma_i)^2 + (\omega - \bar{E}_i)^2}$$

If $\Gamma_1 + \Gamma_2 > \bar{E}_1 - \bar{E}_2$ these can eventually overlap and merge into a single peak. The 2D lineshape (Fig 6, bottom line) has two cross peaks induced by the annihilation of one excitation by the second pulse and the creation of different excitation by the third pulse also for short t_2 .

$$S_A(\omega_3, t_2, \omega_1) = \sum_{i=1}^2 \sum_{j=1}^2 2M_i^2 M_j^2 \frac{\Gamma_i}{(\Gamma_i)^2 + (\omega_1 - \bar{E}_i)^2} \frac{\Gamma_j}{(\Gamma_j)^2 + (\omega_3 - \bar{E}_j)^2} + \text{Re} \sum_{i,j,k,l=1}^2 \frac{M_i M_j M_k M_l G_{\bar{E}_i \bar{E}_k, \bar{E}_j \bar{E}_l}(t_2)}{\Gamma_l - i(\omega_3 - \bar{E}_l)} \times \left[\frac{1}{\Gamma_j - i(\omega_1 - \bar{E}_j)} + \frac{1}{\Gamma_i + i(\omega_1 - \bar{E}_i)} \right]$$

This is different from two state jump model lineshapes in the slow modulation limit.²⁰ The cross peaks have intensities comparable with the diagonal peaks at long times.

The limiting cases of slow or fast fluctuations can be treated by a simpler methods, the stochastic approach is however essential for the intermediate regime.

Fig 6 compares the intermediate (top) and fast (bottom) fluctuation limit. The separated peaks of the static case overlap and merge into a single peak. In the intermediate regime, however, the memory of two bath states can still be tracked by the diagonal elongation of peaks at short

times. In the fast limit the peaks become narrower and all signatures of memory are erased. Panel B shows the corresponding absorption lineshapes.

At longer delay times (right panels) the decoherence and exciton transport erase all memory and lineshapes approach Eq. (12). The t_2 dependence follows from the ee t_2 evolution of R_2 and R_4 , while the R_1 and R_3 contributions give half of the product (Eq.21). (not shown)

The intermediate timescale shows additional delicate effects caused by altering the eigenvectors (rather than merely eigenvalues) of Hamiltonian. These will be discussed in the next section using a Gaussian model for spectral diffusion.

We next examine more closely the R_3 , R_4 contributions (Fig 7). At short times $\mathcal{G}_{\bar{E}_l\bar{E}_k,\bar{E}_j\bar{E}_i} = \delta_{lj}\delta_{ik}$, and R_3 follows the four peak structure identical to R_1 , while R_4 is diagonal, from the same reason mentioned in Fig 4, At long times t_2 coherences are dumped. Asymptotically

$\mathcal{G}_{\bar{E}_l\bar{E}_k,\bar{E}_j\bar{E}_i} = \frac{1}{2}\delta_{lk}\delta_{ij}$ and the lineshape (Eq.12) is restored. This argument holds as long as exciton transfer is allowed $\delta J \neq 0$, otherwise the picture of Fig 5 is repeated and the cross peaks never show up in R_4 .

6 Spectral diffusion

We now turn to a different model representing the coupling to uncorrelated continuous diagonal frequency fluctuations. This situation, very common in molecular aggregates, is described by adding the following coupling term

$$H_{SQ} = f_1(Q_1(t))B_1^\dagger B_1 + f_2(Q_2(t))B_2^\dagger B_2$$

to the Hamiltonian, together with a Fokker-Planck master equation for the density evolution of the two collective coordinates Q_1 and Q_2 .

$$\left(\frac{d\rho(Q_1, Q_2)}{dt}\right)_Q = \sum_{w=1}^2 \Lambda_w \frac{\partial}{\partial Q_w} \left(Q_w + \sigma_w^2 \frac{\partial}{\partial Q_w} \right) \rho(Q_1, Q_2) = \mathcal{L}^Q \rho \quad (14)$$

This model assumes, that bath motions primarily alter (and in simple way) the local site frequencies. The resulting delocalized eigenenergy changes are secondary and more complicated. Standard simulations of aggregates rely on diagonalization of averaged Hamiltonian allowing arbitrary timescale for Gaussian diagonal fluctuations (diagonal in *the eigenbasis*), but only fast (if any) fluctuations off-diagonal. This make the problem numerically tractable, however it may not always hold. Our aim here is to treat arbitrary timescales for off-diagonal (in eigenbasis) fluctuations by using the SLE and show significant differences from the more approximate treatments. This may lead to the development of better approximations, that retain the reduced bath treatment (necessary for large aggregates), but properly includes effects of bath timescale. For smaller aggregates the SLE can be directly used to calculate 2D spectra.

The SLE assumes the form:

$$\frac{d\rho}{dt} = -i[H + H_{SQ}, \rho] + \left(\frac{d\rho}{dt}\right)_M + \left(\frac{d\rho}{dt}\right)_Q$$

The eigenvectors of the Fokker-Planck operator Eq. (14) are direct products of two single Fokker-Planck variables Q_1, Q_2

$$\varphi_{\alpha\beta} = \varphi_{\alpha}^1 \varphi_{\beta}^2 \quad (15)$$

The eigenvectors are given by

$$\varphi_{\alpha}^w = \frac{\exp[-(Q_w/\sigma_w)^2]}{2^{\alpha} \sqrt{2\pi} \alpha! \sigma_w} \mathcal{H}_{\alpha} \left(\frac{Q_w}{\sigma_w \sqrt{2}} \right)$$

where $\mathcal{H}_{\alpha}$ are Hermite polynomials

$$\mathcal{H}_{\alpha}(x) = (-1)^{\alpha} e^{x^2} \frac{d^{\alpha}}{dx^{\alpha}} e^{-x^2}.$$

$\{\phi_{\alpha\beta}\}$, $\alpha = 0, 1, 2, \dots$; $\beta = 0, 1, 2, \dots$; correspond to eigenvalues $-\alpha\Lambda_1 - \beta\Lambda_2$, and form the suitable basis for a matrix representation of bath densities.³⁶ The matrix elements of $\mathcal{L}^Q$ are

$$[\mathcal{L}^Q]_{\alpha\beta,\gamma\eta} = (-\alpha\Lambda_1 - \beta\Lambda_2) \delta_{\alpha,\gamma} \delta_{\beta,\eta} \quad (16)$$

The Q variable is represented by the following matrix

$$\begin{aligned} [Q_1]_{\alpha\beta,\gamma\eta} &= \left(\alpha\sigma_1 \sqrt{2} \delta_{\alpha-1,\gamma} + \frac{\sigma_1}{\sqrt{2}} \delta_{\alpha,\gamma-1} \right) \delta_{\beta\eta} \\ [Q_2]_{\alpha\beta,\gamma\eta} &= \left(\beta\sigma_2 \sqrt{2} \delta_{\beta-1,\eta} + \frac{\sigma_2}{\sqrt{2}} \delta_{\beta,\eta-1} \right) \delta_{\alpha\gamma} \end{aligned} \quad (17)$$

If H_{SQ} is a polynomial in Q_1, Q_2 it can be represented by the block-tridiagonal matrix, and the algorithm of Ref.^{10,20,36} may be employed to obtain the Green's function by inverting the block-tridiagonal matrices (Eq. (5)). For instance, the linear coupling $c_1 Q_1 + c_2 Q_2 + c_{12} Q_1 Q_2$ becomes tridiagonal in blocks $\{\phi_{00}\}, \{\phi_{10}, \phi_{11}, \phi_{01}\}, \{\phi_{20}, \phi_{21}, \phi_{22}, \phi_{12}, \phi_{02}\}, \dots$. However, the SLE approach is not limited to any particular form of the coupling; f can be arbitrary function.

The zero eigenvector $\rho^{Q;(eq)} = \phi_{00}$ (or in the matrix notation $[\rho^{eq}]_{\alpha\beta} = \delta_{\alpha 0} \delta_{\beta 0}$) gives the equilibrium distribution. Summation over the bath $\int dQ_1 dQ_2$ corresponds to zero left eigenvector in the eigenbasis $\{\phi_{\alpha}\}$ thus $\langle I^Q |_{\alpha\beta} = \delta_{\alpha 0} \delta_{\beta 0}$. The initial state is direct product of equilibrium densities of all the bath variables $|\rho^{(eq)}\rangle |\rho^{Q;(eq)}\rangle$ and similarly the final summation.

The various Liouville space exciton manifold blocks of the Liouville superoperator $\mathcal{L}^{SQ} = -i[H_{SQ}, \dots]$ are

$$\mathcal{L}_{eg, eg}^{SQ} = \begin{pmatrix} -if_1(Q_1) & 0 & 0 & 0 \\ 0 & -if_1(Q_1) & 0 & 0 \\ 0 & 0 & -if_2(Q_2) & 0 \\ 0 & 0 & 0 & -if_2(Q_2) \end{pmatrix} \quad \mathcal{L}_{gg, gg}^{SQ} = 0;$$

$$\mathcal{L}_{ee', ee'}^{SQ} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -i(f_1 - f_2) & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -i(f_1 - f_2) & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & i(f_1 - f_2) & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & i(f_1 - f_2) & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & i(f_1 - f_2) & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & i(f_1 - f_2) & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

Here $f_1 \equiv f_1(Q_1)$, $f_2 \equiv f_2(Q_2)$. The response can still be calculated using (Eq.(8)) but now in the higher space which combines Q with the u, d space.

Several methods have been employed to describe the signatures of spectral diffusion in the nonlinear response of aggregates. Standard simulations use the Redfield equations for the evolution of the exciton density matrix during t_2 , Gaussian peak of arbitrary relaxation timescale for peaks can be added.¹ Static disorder in site frequencies can be easily incorporated. Slow fluctuations only account for peakshape, interlevel coupling fluctuation are fast, and dynamical effects on dipole moments are neglected.

The SLE framework is more general. Consider a symmetric dimer $J_u = J_d$, $\varepsilon_1 = \varepsilon_2$, $\mu_1 = \mu_2$ where only the symmetric eigenvector $|E_1\rangle = |1\rangle + |2\rangle$ is radiatively coupled to the ground state. For fast spectral diffusion the other peak $|E_2\rangle = |1\rangle - |2\rangle$ is dark. However when the slow coordinate nonequilibrium eigenstates $|E_2(Q_1, Q_2)\rangle$ couple to the dipole moment $\langle E_2(Q_1, Q_2) | \mu | g \rangle \neq 0$, the other peak may be observed (Fig 8, left panel). The SLE can consistently describe the fluctuation timescales where the additional diagonal peak vanishes (Fig 8, right panel). This is not properly described by simulations at the Redfield level, which do not account for the necessary correlations between Liouville space and bath coordinates during the transport. Additional static disorder can induce some oscillator strength to the dark state, but cannot describe its evolution.

At zero delay time the magnitude of the $(-1, -1)$ peak is proportional to the probability $\tilde{p}$ that bath coordinates shifts the site energies ε so that dipole moment $\langle E_2(Q_1, Q_2) | \mu | g \rangle$ is substantial. Such configurations are rather rare and far from equilibrium, so they disappear at relaxation timescale Λ^{-1} . For $t_2 \gg \Lambda^{-1}$ the $(-1, -1)$ peak can only be induced by two independent hits of the " $\tilde{p}$ " area, so its magnitude is quadratically proportional to $\tilde{p}$, in agreement with asymptotic formula Eq. (12).

These effects are illustrated in Fig 9, which depicts the magnitudes (normalized with respect to $t_2 = 0$) of all peaks at Fig 8 as they vary with the delay time t_2 . We see significant decay of the $(-1, -1)$ peak at the Λ^{-1} timescale as discussed. The $(1, 1)$ diagonal and the cross peak $(1, -1)$ (the other cross-peaks $(-1, 1)$ has the same magnitude) change less significantly, because the cross peak requires instantaneous dipole moment for dark state, only in the t_1 (peak $(1, -1)$) or t_3 interval (peak $(-1, 1)$). Its magnitude thus remains linear in p (for small p) for any delay times. In addition, we see oscillation of the peaks, caused by the coherent dynamics, as predicted by the Redfield level of theory³⁴⁻³⁷ and observed experimentally.³⁸ Such

oscillations require the interplay of both exciton states. The effect is thus most pronounced for $(-1, -1)$ and cross peak, and not for the $(1, 1)$ peak.

7 Conclusions

It is straightforward to extend the present model to other types of excitonic systems as long as the fluctuations are Markovian. In fact, the code developed for the present calculations can treat any number of ground, excited and doubly excited states, and multistate or Gaussian - Markovian fluctuations (coordinate linearly or quadratically coupled to Q coordinate). Since the computational time grows exponentially with the number of stochastic coordinates, applications to extended excitonic systems will require the identification of a few relevant coordinates.

We showed that the SLE approach is essential tool for describing intermediate timescale of fluctuations and may thus be used to test various approximate methods^{39,40} developed in order to avoid the numerically expensive explicit representation of stochastic coordinate.

The SLE assume that the stochastic process is independent on the state of the system. This is justified at high temperatures. Finite-temperature effects such as the Stokes-shift or nonuniform exciton distributions are missed. The Redfield equations in contrast, contain finite temperature effects. The high temperature $\hbar\Delta\epsilon < kT$ limit usually holds for infrared,^{19,21} but not in optical domain at room temperatures. Finite temperature corrections for linear coupling include system dependent bath dynamics.^{16,41–44} Provided the temperature is not too low, the equations of motion have the same complexity as the SLE and may be readily implemented, if necessary. This level was widely used to describe electron transfer processes (adiabatic and nonadiabatic). At very low temperatures, when the quantization of bath degrees of freedom is necessary, some additional oscillator modes with Matsubara frequencies has to be added increasing computation costs.¹⁶

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Appendix B

A The four-state-jump (FSJ) model

We consider a single two level chromophore described by the Hamiltonian

$$H = \epsilon(t) B^\dagger B \quad (18)$$

Where ϵ_s assumes four possible values $s = 1, 2, 3, 4$. The model has a four-peak linear spectrum indistinguishable from the TSJ dimer (Fig 2). This model has 12 rates k_{sr} for the transitions between r to s states. The time evolution is described by the master equation

$$\frac{d\rho_s}{dt} = - \sum_{r \neq s} k_{rs} \rho_s + \sum_{r \neq s} k_{sr} \rho_r \quad (19)$$

Eq. (19) further describes the evolution in the gg and ee manifolds because no coherence is connected with the ground (excited) state evolution.

The SLE for the coherence evolution is

$$\frac{d\rho_{egs}}{dt} = -i\varepsilon_j\rho_{egs} - \sum_{r \neq s} k_{rs}\rho_{egs} + \sum_{r \neq s} k_{sr}\rho_{egr}$$

The rates were chosen to yield the same linear spectrum as the TSJ dimer in the slow limit

$$I(\omega) = \mu^2 \sum_{v=1}^4 \frac{\Gamma_v \rho_{ggv}^{(eq)}}{[\Gamma_v^2 + (\omega_1 - \varepsilon_v)^2]} \quad (20)$$

with $\Gamma_v = \sum_{r \neq v} k_{rv}$.

Consider 2D lineshape in the slow jumps limit $k_{rs}/(\varepsilon_r - \varepsilon_s) \ll 1$. At short times $k_{rs}t_2 \ll 1$ lineshapes show only diagonal peaks at fundamental frequencies. Cross-peaks are absent (Fig 3 bottom left panel)

$$S_A(\omega_3, t_2=0, \omega_1) = \mu^4 \sum_{v=1}^4 \frac{\Gamma_v^2 \rho_{ggv}^{(eq)}}{[\Gamma_v^2 + (\omega_1 - \varepsilon_v)^2][\Gamma_v^2 + (\omega_3 - \varepsilon_v)^2]}$$

Since there is no coherence during t_2 , the S_A lineshape will only change at k^{-1} timescale, where the cross peaks appear. Asymptotically the lineshape approaches the factorized form

$$S_A(\omega_3, t_2 \rightarrow \infty, \omega_1) = 4I(\omega_1)I(\omega_3). \quad (21)$$

This limit holds for all one exciton stochastic lineshapes with finite memory; see 30 for some exceptions when the memory persists for arbitrary timescales. A similar relation can be generalized for the first manifold contribution of any excitonic system, that allows the excitonic transfer toward the thermodynamic high temperature uniform excitonic distribution

$$S_A(\omega_3, t_2 \rightarrow \infty, \omega_1) = 2 \frac{n+1}{n} I(\omega_1)I(\omega_3). \quad (22)$$

where n is the number of excitons.³¹

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31. As noted in³⁰ for single chromophore, Eq. (22) may be generalized beyond the stochastic model. For multiexcitonic, but exciton conserving Hamiltonian, the four diagrams of Fig 1 contributes $\hbar S_A(\omega_3, t_2 = \infty, \omega_1) = I(\omega_1)[I(\omega_3) + I_E(\omega_3)]$ where I_E is emission line-shape obtained from excited state equilibrium ρ_v , assuming that the asymptotic Green's function (of *gg* and *ee* manifold) approach $[G]_{vv'}(t \rightarrow \infty) = \rho_v Tr v'$ in some suitable representation, where *v* is multiindex (quantum or classical) completely describing the excited (ground) state of the system. Additional contribution to S_A could, however, come from the excited state absorption (involving the second exciton manifold).
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Fig 1. Double sided Feynman diagrams for the Liouville space pathways contributing to the third order response in the phase matching direction $\mathbf{k}_I = -\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$ and $\mathbf{k}_{II} = \mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_3$. (Eq. 7)

Fig 2.

Absorption lineshapes (Eq. (6)) of a dimer with two state bath fluctuations (Eqs. (3) and (4)) (solid line) and a monomer with four state bath fluctuations (Eqs. (18) and (19)) (dotted line) in static limit. The dimer peaks correspond to resonance with (from left to right) ε_{2u} , ε_{2d} , ε_{1d} , ε_{1u} levels. Parameters: Dimer: $\varepsilon_{1u} = 30\Gamma$, $\varepsilon_{1d} = 10\Gamma$, $\varepsilon_{2u} = -30\Gamma$, $\varepsilon_{2d} = -10\Gamma$, $J_u = J_d = 0$, $k_u = k_d = k = \Gamma$. Monomer: $\varepsilon_1 = 30\Gamma$, $\varepsilon_2 = 10\Gamma$, $\varepsilon_3 = -30\Gamma$, $\varepsilon_4 = -10\Gamma$, $k_{12}k_{21} = k_{13} = k_{31} = k_{14} = k_{41} = k_{23} = k_{32} = k_{24} = k_{42} = k_{34} = k_{43} = \Gamma/3$, $\mu_{4sj} = \sqrt{2}\mu_{dim}$. All the lineshapes shown at Figs 2–8 are calculated by solving the full SLE model, and not by using the various limiting approximations discussed in the main text.

Fig 3.

The S_A signal (Eq. 9) for a dimer with two state bath (top panels) and monomer with four state bath (bottom panels) corresponding to Fig 2. For delay times $\Gamma t_2 = 0, 0.1, 0.2, 1.0, 100$ increasing from left to right panels. Other parameters same as in Fig 2.

Fig 4. The $R_1(\omega_3, t_2, -\omega_1)$, $R_2(\omega_3, t_2, -\omega_1)$, $R_3(\omega_3, t_2, \omega_1)$, $R_4(\omega_3, t_2, \omega_1)$ (Eq.(8), real parts) contributions to S_A signal (from left to right, then top to bottom) for the dimer with two state bath for short delay times $t_2 = 0$, corresponding to the most left top panel of Fig. 2. Other parameters are same as in Fig 2.

Fig 5

Fig 5.

The same as Fig 4., but for long delay times $\Gamma t_2 = 100$, corresponding to the most right top panel of Fig 3.

Fig 6A

Fig 6B

Fig 6.

Fig 6A Top: The S_A (Eq.9) signal for dimer with two state bath (Eqs. (3) and (4)) for intermediate (top) and fast (bottom) fluctuations at short $t_2 = 0$ (left panels) and long $t_2 = 2000E_\Delta^{-1}$ (right panels) delay times. Measured in the peak splitting

$$E_\Delta = \frac{\varepsilon_{1u} + \varepsilon_{1d}}{4} - \frac{\varepsilon_{2u} + \varepsilon_{2d}}{4}. \text{ Parameters (top): } \varepsilon_{1u} = 1.5E_\Delta, \varepsilon_{1d} = 0.5E_\Delta, \varepsilon_{2u} = -1.5E_\Delta, \varepsilon_{2d} = 0.5E_\Delta, J_u = -J_d = 0.68E_\Delta, k_u = k_d = k = 0.5E_\Delta, \mu_1 = \mu_2 = 1.189\mu. \text{ Bottom: } \varepsilon_{1u} = 6.5E_\Delta, \varepsilon_{1d} = -0.45E_\Delta, \varepsilon_{2u} = -6.5E_\Delta, \varepsilon_{2d} = 4.5E_\Delta, J_u = -J_d = 0.75E_\Delta, k_u = k_d = k = 100E_\Delta, \mu_1 = \mu_2 = \mu.$$

Fig 6B Absorption lineshapes of the model of Fig 6A. Dashed line corresponds to fast limit (bottom of Fig 6A), solid line to the intermediate limit (top of Fig 6A).

Fig 7.
The R_3 (top panel) and R_4 (bottom panel) signal (Eq.(8, real parts)) for the dimer in fast modulation limit for short $t_2 = 0$ (left panels) and long $t_2 = 2000 E_\Delta^{-1}$ (right panels) delay times. Other parameters as in Fig 6A, bottom.

Fig 8.

The S_A lineshape of a dimer with spectral diffusion for short $\Lambda t_2 = 0$ (left panel) and long $\Lambda t_2 = 2$ (right panel) times. Other parameters $\mu_1 = \mu_2 = 1$, $J_u = J_d = J$, $f(Q) = Q$, $\sigma_1 = \sigma_2 = 0.3J$, $\Lambda_1 = \Lambda_2 = \Lambda = 0.1J$, $\varepsilon_{1d} = \varepsilon_{1u} = \varepsilon_{1d} = \varepsilon_{1u} = 0.0$.

Fig 9.

The relative intensities of peaks (against t_2 value) at $I_0(t_2) = S_A(\omega_3, t_2, \omega_1)/S_A(\omega_3, 0, \omega_1)$ lineshape of a dimer with spectral diffusion for varying delay times t_2 at diagonal peak $\omega_1 = \omega_3 = J$ (solid line), cross peak at $\omega_1 = -\omega_3 = J$ (dashed line), and transitory diagonal $\omega_1 = \omega_3 = -J$ (dotted line). Other parameters as in Fig. 8.