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Non-Perturbative Calculation of Two-Dimensional Spectra Using the Stochastic Hierarchy of Pure States

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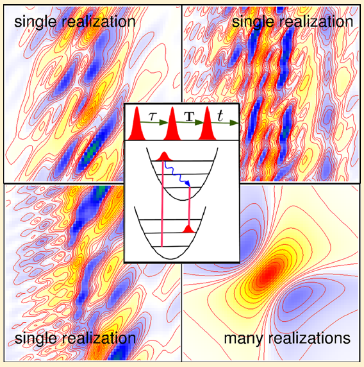
Supporting Information

ABSTRACT: Two-dimensional electronic spectroscopy has become an important experimental technique to obtain information on, for example, electronic coherences in large molecular complexes or vibronic couplings. For the correct interpretation of two-dimensional spectra, however, detailed theoretical calculations are required. Reliable theoretical calculations are impeded by large system sizes and large numbers of vibrational degrees of freedom that need to be explicitly taken into account. Here, we demonstrate that a numerical approach based on a stochastic hierarchy of pure states (HOPS) does allow the calculation of two-dimensional spectra, notwithstanding the stochasticity of the method. The number of coupled equations as well as the hierarchy depth shows a superior scaling with system size as compared to the previously developed hierarchical equations of motion (HEOM). Large systems thus become accessible for numerical calculation of two-dimensional spectra.



Two-dimensional (2D) electronic spectroscopy has become a popular tool to extract information about complex molecular systems.[1−4] It has been applied to study diverse systems and processes, such as coherence and excitation transfer in biological light harvesting systems,[5−7] J-aggregates,[8−10] conjugated polymers,[11] and nanotubes.[12,13] The basic principle of 2D electronic spectroscopy can be understood by considering three noncolinear femtosecond laser pulses that reach the sample at different times. The resulting time-dependent polarization of the system is then detected in a phase-matching direction, as a function of the delay-time between the pulses and the detection time. Two-dimensional Fourier transformation with respect to the detection time and one of the time delays of the pulses then gives a 2D spectrum.

Detailed theoretical calculations are necessary to correctly interpret the 2D spectra obtained in experiment. However, typical systems of interest are difficult to treat numerically, because of their size and complexity. A particular problem arises from strong coupling to many vibrational degrees of freedom. Because the 2D signal essentially stems from an operator that in many cases only depends on electronic degrees of freedom, open quantum system approaches are a possible way to treat such systems theoretically. Popular approaches are based on Lindblad or Redfield equations. However, the applicability of these approaches is very limited, which can lead to wrong conclusions. For example, they cannot capture the effect of strong coupling to weakly damped vibrational modes. To date, there have been only two numerically exact methods applied to calculate 2D spectra. One is the so-called QUAPI method;[19] the other is the so-called hierarchical equation of motion (HEOM) approach,[14−18] which will be of particular interest in the present work, since it is based on a similar hierarchy to that of our present method. In the HEOM method, the reduced density matrix of the system is obtained by solving a coupled system (hierarchy) of differential equations of density-matrix-like objects. The two main things that limit the applicability of this approach are (i) that the required number of differential equations (in the following denoted as the depth of the hierarchy) rapidly grows with the number of (weakly damped) vibrational modes and upon decreasing the temperature and (ii) that the size of the density-matrix-like objects grows quadratically with the system size.

To overcome the problems associated with the HEOM approach, in recent years numerically efficient approaches to calculate the reduced density matrix using stochastic wave functions within the non-Markovian quantum state diffusion (NMQSD) framework have been developed.[20,21] In particular, in ref 21, we developed a stochastic hierarchy of pure states (HOPS) with which one can recover the reduced density matrix exactly (for an infinite number of trajectories and an infinite depth). In the case of the excitation transfer in light harvesting systems, we have demonstrated that for typical parameters one has fast convergence with respect to the number of trajectories and the depth of the hierarchy. The HOPS is closely related to the HEOM: in ref 22, we have shown that HEOM can be directly derived from HOPS. HOPS provides reduced dimensionality (wave function versus density matrix), and furthermore, our studies indicate that it also converges faster with the number of equations involved in the hierarchies.[21]

In the present work, we demonstrate that HOPS is also suitable to calculate 2D spectra. To this end, we use a

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nonperturbative approach in the electric field strength. This technique depends sensitively on the phases of the laser-pulses,[23] and the signal of interest is constructed by phase sensitive summation of different contributions. Therefore, one might question the applicability of stochastic methods that lead to fluctuations in the time evolution. As an important result, we will show that HOPS provides sufficiently fast convergence with respect to the number of trajectories. We demonstrate this for the simple case of a single molecule with two one-dimensional harmonic Born−Oppenheimer surfaces coupled to a bosonic bath. We note that the real power of the approach will be for larger systems (e.g., several interacting molecules and more vibrational modes).

The paper is organized as follows: first, we introduce the general open quantum system model and review the HOPS approach. Then, we discuss how to apply HOPS within a nonperturbative treatment to calculate 2D spectra. The applicability of HOPS is demonstrated for our simple model system. Finally, we provide a summary and an outlook for this approach.

We consider the (total) Hamiltonian

$$H_{\mathrm{tot}} = H + V(t) + H_{\mathrm{env}} + H_{\mathrm{int}} \tag{1}$$

where H is the Hamiltonian of the "system" and

$$V(t) = -\hat{\vec{\mu}}\cdot\vec{E}(t) \tag{2}$$

describes the interaction with a time-dependent electro-magnetic field $\vec{E}(t)$ via the dipole operator $\hat{\vec{\mu}}$. The Hamiltonian of an environment consisting of harmonic oscillators is given by $H_{\mathrm{env}} = \sum_\lambda \omega_\lambda b_\lambda^\dagger b_\lambda$ with $[b_\lambda, b_{\lambda'}] = 0$ and $[b_\lambda, b_{\lambda'}^\dagger] = \delta_{\lambda\lambda'}$. The interaction of system and environment is modeled by a linear coupling Hamiltonian

$$H_{\mathrm{int}} = \sum_\lambda (g_\lambda^* L b_\lambda^\dagger + g_\lambda L^\dagger b_\lambda)$$

Here, L is a system operator and g_λ are complex numbers quantifying the coupling strength of the respective oscillator (λ) to the system. The extension to more than one system operator and coupling to several environments is straightforward.[21,22] Note that the form of H_{int} does not imply a rotating wave approximation. [This can be clearly seen for the case when $L = L^\dagger$.] It is convenient to encode the frequency dependence of the interaction strengths in the so-called spectral density

$$J(\omega) = \sum_\lambda |g_\lambda|^2 \delta(\omega - \omega_\lambda)$$

which is typically assumed to be a continuous function of frequency. The latter is related to the bath correlation function $\alpha(\tau)$ by[24]

$$\alpha(\tau) = \int_0^\infty \mathrm{d}\omega J(\omega)\left(\coth\left(\frac{\omega}{2k_{\mathrm{B}}T}\right)\cos(\omega\tau) - i\sin(\omega\tau)\right) \tag{3}$$

where T is the temperature. In many cases of interest, the bath correlation function can be well approximated by a finite sum of exponentials[25−27]

$$\alpha(\tau) = \sum_{j=1}^{J} p_j \exp(-w_j t) \qquad (t > 0) \tag{4}$$

with $w_j = i\Omega_j + \gamma_j$. We will use such a form throughout this work. For HOPS and HEOM, one typically wants to have as few exponentials as possible. One possibility is to directly fit the bath correlation function. We usually follow the procedure described in ref 27 by fitting the spectral density with suitable functions and handling the temperature dependent part via a Padé approximation. In this way one can, for example, efficiently treat superohmic spectral densities. The resulting errors are discussed in ref 27 explicitly for the case of linear spectra. Note that the error can be decreased by increasing J.

Now that we have specified our open quantum system model, we discuss how HOPS can be applied to calculate the 2D signal. Expectation values of an operator A in the system space can be obtained via

$$\langle A\rangle = \mathcal{M}_z\{\langle\psi^{(\vec{0})}(t;z)|A|\psi^{(\vec{0})}(t;z)\rangle\} \tag{5}$$

where $\mathcal{M}_z$ denotes an average over the stochastic wave functions $|\psi^{(\vec{0})}(t;z)\rangle$ obtained by using the following hierarchy of pure states (HOPS)[21,22] (here and in the following, we use $\psi_t = \psi(t)$ interchangeably)

$$\begin{aligned}\partial_t\psi_t^{(\vec{\kappa})} &= \left(-i(H + V(t)) - \vec{\kappa}\cdot\vec{w} + \sum_j z_j^*(t)L_j\right)\psi_t^{(\vec{\kappa})} \\ &\quad + \sum_j \kappa_j\, p_j L_j \psi_t^{(\vec{\kappa}-\vec{e}_j)} - \sum_j L_j^\dagger \psi_t^{(\vec{\kappa}+\vec{e}_j)}\end{aligned} \tag{6}$$

with initial conditions $\psi_{t=0}^{(\vec{0})} = \psi_{t=0}$ and $\psi_{t=0}^{(\vec{\kappa})} = 0$ for $\vec{\kappa} \neq \vec{0}$. The $z = z_t$ are a set of complex stochastic processes with $\mathcal{M}_z\{z\} = 0$ and $\mathcal{M}_z\{z_t z_s^*\} = \alpha(t-s)$. Here, $\vec{w} = \{w_1, ..., w_J\}$, where J is the number of exponentials in eq 4 and $\vec{\kappa} = \{\kappa_1, ..., \kappa_J\}$, with κ_j integers ≥ 0. Furthermore, $\vec{e}_j = \{0, ..., 1, ..., 0\}$ is a vector that has a one at the jth position and the rest of the elements are zero. For numerical calculations, one has to truncate the hierarchy (6). There are many possibilities to do so. In the present work, we take a particular simple truncation scheme where we take only terms with $\sum_j \kappa_j \leq \mathcal{K}$ into account. We refer to $\mathcal{K}$ as the depth (order) of the hierarchy.

Equation 6 generates non-Hermitian, stochastic dynamics which can result in large fluctuations of the norm, which in turn can lead to problems in the convergence with respect to the number of realizations (one example can be found in ref 21). Therefore, in practice we use the corresponding normalizable evolution equation (see eq 15 of ref 21).

To obtain the 2D spectrum we use a nonperturbative approach based on phase cycling.[23,28−30] In this approach, the signal of interest (e.g., the one that is observed in a certain *phase-matching direction*) is obtain by the (weighted) sum of several signals. Each individual signal is obtained from the interaction with three pulses that have well-defined phases. How to choose the phases and the corresponding weights has been discussed in several publications (e.g., refs 23 and 28−30). Here, we choose the convention of ref 30 (see also eq 8 below, and the Supporting Information).

We express the electric field, consisting of three short pulses with specific phases, as

$$\vec{E}(t) = \sum_{n=1}^{3} \vec{\epsilon}_n f_n(t - t_n)\cos[\omega_n(t - t_n) - \phi_{s,n}] \tag{7}$$

In this expression the index n labels the three pulses. The polarization of each pulse is given by $\vec{\epsilon}_n$. The envelope functions are taken as $f_n(t - t_n) = \frac{a}{\sqrt{2\pi}\tau_n}\exp[-(t - t_n)^2/2\tau_n^2]$, that is, they are Gaussians with standard deviation τ_n, centered at t_n. The amplitude of the pulse is denoted by a, the carrier-frequency is denoted by ω_n, and $\phi_{s,n}$ denotes its phase. Here, the subscript s is used to label different combinations of the three phases $\vec{\phi}_s = (\phi_{s,1}, \phi_{s,2}, \phi_{s,3})$. For such a pulse we calculate the resulting time-dependent polarization $P_{\vec{\phi}_s}(t; \{t_1, t_2, t_3\}) = \mathrm{Tr}\{\rho_{\vec{\phi}_s}(t)\ \hat{\mu}\}$, where the electronic dipole operator of the system is denoted by $\hat{\mu}$ (independent of nuclear coordinates) and $\rho_{\vec{\phi}_s}(t)$ is the reduced density matrix in the electronic subspace. Note that here and in the following, we do not indicate the dependence on the pulse-times explicitly. This pulse sequence is sketched in Figure 1.

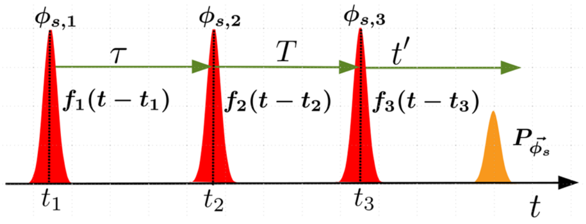

Figure 1. Sketch of the pulse sequence used in the phase-cycling scheme (cf. eq 7). The envelope functions of the three colinear pulses that interact with the sample and the emitted signal field are shown. The coherence, waiting, and detection times τ, T, and t' are defined in eq 10.

A phase-matching direction $P_{\vec{k}_r}$ can then be extracted via

$$P_{\vec{k}_r}(t) = \sum_s a_{r,s} P_{\vec{\phi}_s}(t) \tag{8}$$

using an appropriate choice of phase triples $\vec{\phi}_s$ and coefficients $a_{r,s}$. In the present work, we use the phase-triples as given in Table 1 of ref 30, and note that to obtain the $a_{r,s}$ of eq 8, one has to invert the coefficient matrix given in eq 40 of ref 30. For completeness we provide the phase triples and the coefficients $a_{r,s}$ in the Supporting Information.

Finally, within the HOPS formalism we calculate the polarization as

$$P_{\vec{\phi}_s}(t) = \mathcal{M}_z\{\langle\psi^{(\vec{0})}_{\vec{\phi}_s}(t, z)|\hat{\mu}|\psi^{(\vec{0})}_{\vec{\phi}_s}(t, z)\rangle\} \tag{9}$$

where we use a finite number M of stochastic trajectories.

To illustrate the formalism and to investigate the convergence with the number of trajectories, we will consider a particular simple model of a molecule. We consider two electronic states: the ground state $|g\rangle$ and the excited state $|e\rangle$. The "system" part of the Hamiltonian in eq 1 is chosen as $H = E_g|g\rangle\langle g| + E_e|e\rangle\langle e|$, which contains only the electronic degrees of freedom. The electronic part of the system-bath coupling is taken as $L = |e\rangle\langle e|$. Depending on the choice of the spectral density, this model can capture various situations ranging from internal molecular vibrations to relaxation and dephasing caused by the surroundings (see, for example, the discussions in refs 27 and 31). In the present work, our focus is on the convergence properties of the stochastic HOPS. To this end, we consider two bath-correlation functions that lead to quite different spectra. For a discussion of different forms of the bath correlation function and their representations as sums of exponentials, we refer to ref 27. The parameters that specify the bath correlation functions (BCF) in eq 4 are given in Table 1 for both cases studied in the present work.

Table 1. Parameters Used for the Two BCFs Discussed in the Text[a]

weakly damped BCF		
p	Ω	γ
1	1	0.05

strongly damped BCF			
j	p_j	Ω_j	γ_j
1	48 − 27i	0.89	0.82
2	−2.85 − 2.94i	3.42	2.23
3	69.3 + 18.5i	−0.89	0.82
4	−1.23 + 11.3i	−3.42	2.23
5	0.005	0.0	26.1

[a] Note that in general, p_j is a complex quantity.

For the first case, the BCF consists of only one exponential, that is, $\alpha(t) = p\exp(-i\Omega t - \gamma t)$. We set $\hbar = 1$ and use Ω as the unit of energy. For the applied value $\gamma = 0.05$, one has $\Omega \gg \gamma$ and can roughly interpret this BCF as stemming from a molecule with two one-dimensional harmonic potential surfaces that are shifted with respect to each other, where Ω describes the vibrational frequency and γ is the vibrational damping (at low (zero) temperature).[27,31] In the following, we refer to this BCF as *weakly damped BCF*. The BCF and the underlying SD are shown in Figure 2A, together with the resulting linear absorption spectrum (Figure 2C). The absorption spectrum is calculated as described in ref 32 and clearly shows a weakly broadened vibrational progression. The ability to treat such weakly damped modes at low temperature is an important issue, see refs 33−36, for example.

As a second example, we use a BCF that appears in the context of bacteriochlorophyll molecules in a protein environment at room temperature.[37] The representation of this BCF in the form of eq 4 has been discussed in ref 27. We represent this BCF as a sum of five exponentials (cf. Table 1) and it is displayed in Figure 2B. The corresponding SD and absorption spectrum can be seen in Figure 2B (inset) and Figure 2D, respectively. The absorption spectrum now shows only a single broad peak. We will refer to this BCF as *strongly damped BCF*.

For the electromagnetic field used to calculate the 2D spectra, we consider the following parameters: we choose the amplitude a such that the resulting interaction $\mu_n a = 0.24$. The carrier frequencies are chosen to coincide with the bare electronic transition $\omega_{eg} = E_e - E_g$. The width of the pulses in the time domain is $\tau_n = 0.6$ and the first pulse peaks at $t_1 = 8$. Time is in units of $1/\Omega$, where Ω is the maximum of the SD. In the following, we will consider signals that correspond to the phase-matching direction $-\vec{k}_1 + \vec{k}_2 + \vec{k}_3$. We will also restrict the time ordering of the pulses $t_1 \le t_2 \le t_3$. It is convenient to define the following time intervals, denoted as coherence, waiting, and detection time, respectively (see Figure 1)

$$\tau = t_2 - t_1 \qquad T = t_3 - t_2 \qquad t' = t - t_3 \tag{10}$$

For a given waiting time T, the final 2D spectrum is then obtained from a two-dimensional Fourier transform with respect to τ and t' as $S(T;\omega_\tau,\omega_{t'}) = i\int_0^\infty \mathrm{d}\tau \int_0^\infty \mathrm{d}t' S(\tau, T, t')\, e^{-i\omega_\tau\tau} e^{i\omega_{t'}t'}$. In our case, $S(\tau, T, t') = P_{-\vec{k}_1+\vec{k}_2+\vec{k}_3}(\tau, T, t')$.

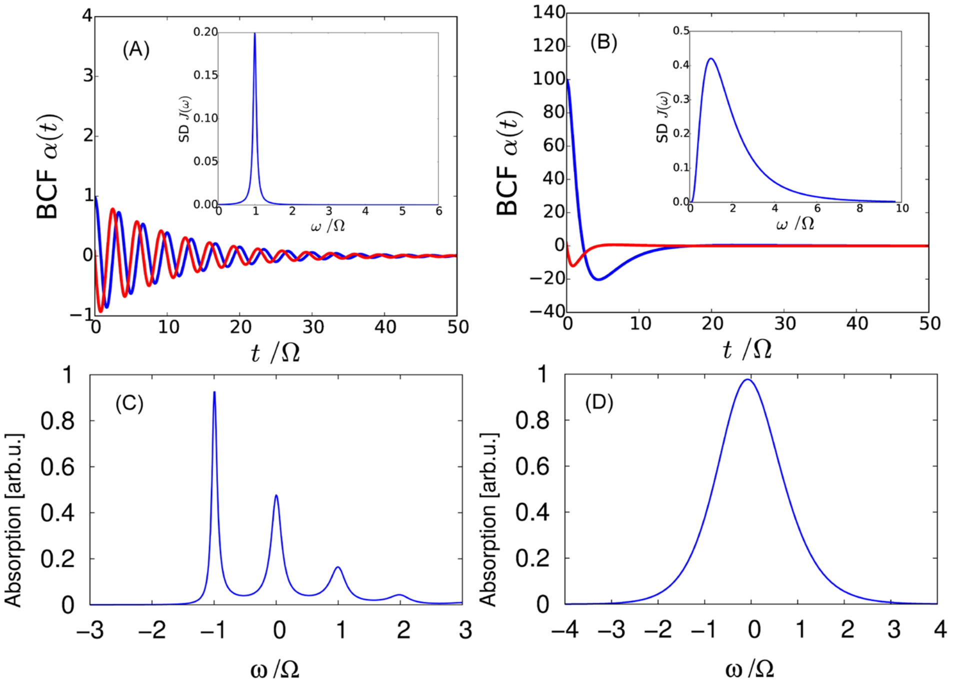

Figure 2. (A) and (B) Plots of the two bath correlation functions (BCFs) used in the present work. The corresponding spectral densities (SDs) are displayed in the inset. In (C) and (D), the absorption spectra corresponding to the two spectral densities are shown. The zero of frequency is chosen as the purely electronic transition energy $\omega_{eg} = E_e - E_g$.

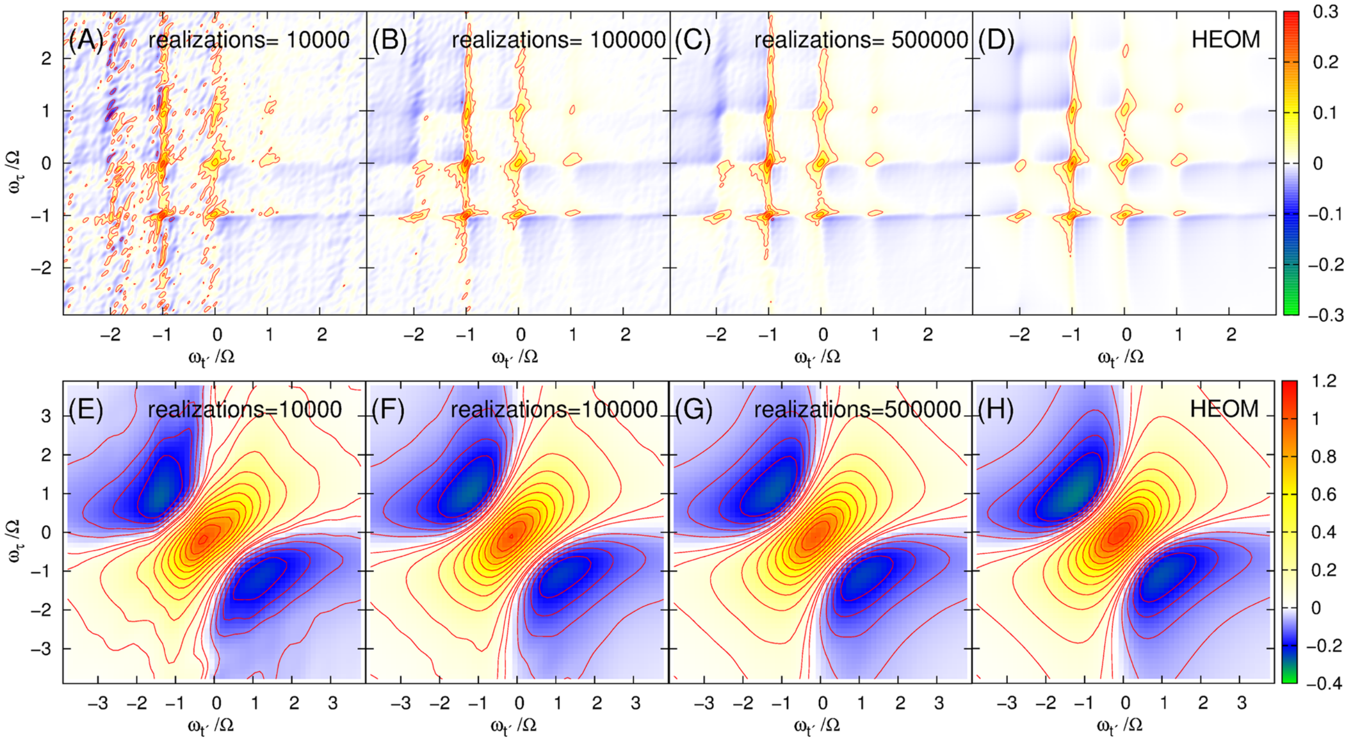

Figure 3. Convergence of the 2D spectra with respect to the number of realizations. Upper row: *weakly damped BCF* with depth $\mathcal{K} = 8$. Lower row: *strongly damped BCF* with depth $\mathcal{K} = 5$.

In Figure 3, we show such 2D spectra for waiting time $T = 0$. From left to right, we increase the number of realizations of the HOPS calculations. For comparison, in the rightmost panel we show the result of the corresponding HEOM calculation. For both BCFs, we have used a large depth of the hierarchy to ensure convergence. Because the hierarchy used for HEOM is equivalent to the corresponding HOPS equations (see ref 22), for a given depth of HOPS, the number of auxiliary vectors in HEOM is the square of the number of auxiliary matrices in HOPS. [For HEOM, each auxiliary matrix $\rho^{\vec{\kappa},\vec{\kappa}'}$ has two labels $\vec{\kappa}$ and $\vec{\kappa}'$ (see, e.g., refs 22, 38, and 39).]

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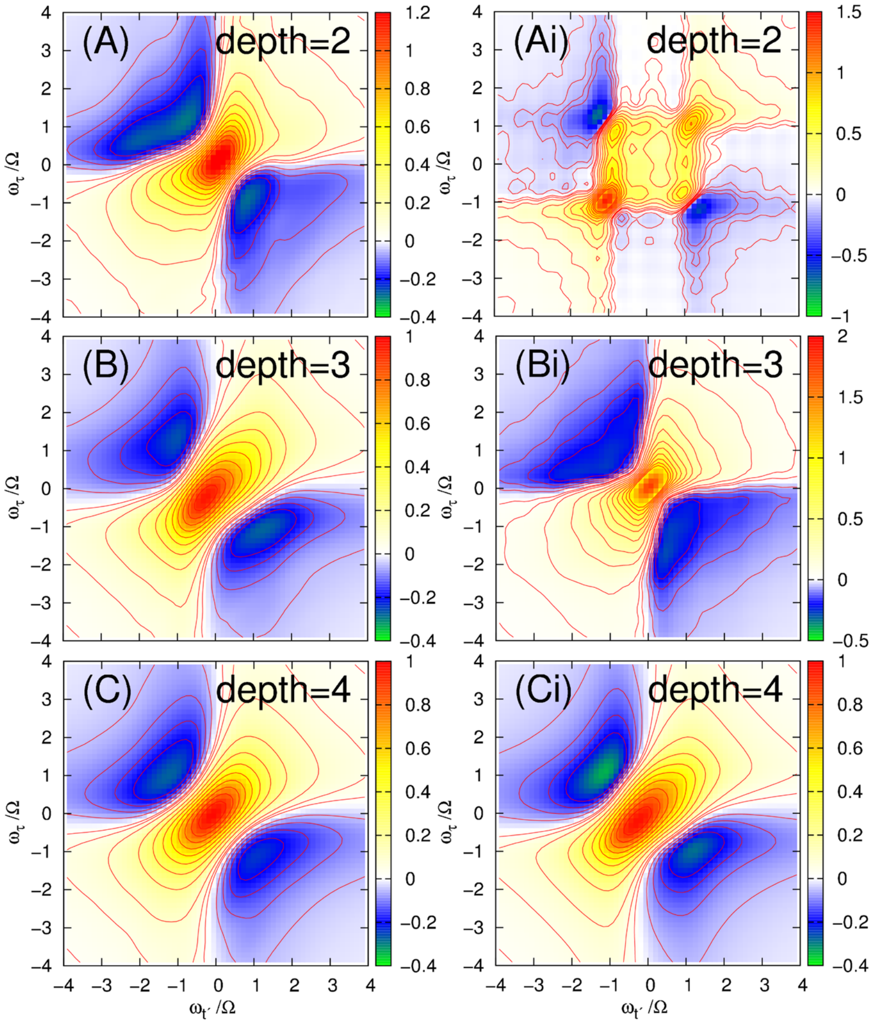

Figure 4. Convergence with the depth $\mathcal{K}$ of the hierarchy for the case of the "strongly damped BCF". Left column: HOPS with 500 000 realizations. Right column: HEOM. The depth is indicated in each plot.

For the smallest number of realizations (10 000) in Figure 3, there is still a lot of noise in the spectra. Nevertheless, the main features are already clearly visible. Upon increasing the number of realizations by an order of magnitude the noise has decreased dramatically and the agreement with the HEOM result is quite good. For 500 000 realizations (panel C), HOPS has nearly converged.

As mentioned earlier, one expects that for HOPS one needs a smaller depth of the hierarchy than for HEOM. To demonstrate this, in Figure 4, we show HOPS and HEOM calculations for different depths of the hierarchy for the case of the "strongly damped BCF". Results for the "weakly damped BCF" can be found in the Supporting Information. Though for depth $\mathcal{K} = 2$, HOPS already shows reasonable agreement with the correct result, the HEOM spectrum suggests a totally wrong peak structure. Note that depth $\mathcal{K} = 2$ implies 20 auxiliary vectors in HOPS and already 400 auxiliary matrices in HEOM.

In the present work, we have shown that the HOPS method, which is based on the stochastic quantum state diffusion, is well suited to calculate 2D spectra. Here, we used a nonperturbative treatment based on the method suggested in ref 23. This approach is very closely related to experimental phase-cycling[40,41] and phase-modulation[42,43] techniques. These techniques can also be applied to individual molecules, using a fourth pulse to create a population that can then be detected, for example by fluorescence or by ionization. Our approach is easily extendable to this situation and has the flexibility to handle arbitrary pulse shapes and different carrier frequencies of the pulses; also in a nonperturbative regime. The extension to a larger number of pulses is also straightforward. Compared to the density-matrix-based HEOM, for the stochastic HOPS, quite a large number of trajectories has to be calculated. The detailed dependence of this number is difficult to assess beforehand. Fortunately, the convergence with respect to the number of trajectories is already easy to see for a small number of realizations. Note that within a perturbative treatment, the absorption spectra can be calculated using HOPS with a *single* trajectory.[32] This seems not to be possible for the 2D spectra. The advantages of HOPS compared to HEOM are that, in HOPS, one propagates vectors instead of matrices, and furthermore, that the convergence with respect to the hierarchy is usually faster.[21] Both aspects will become crucial if one considers larger systems with more complicated bath correlation functions. The dimension of the system of equation that one has to propagate is for HEOM roughly by a power two larger than that of HOPS, when using the same order of the hierarchy (and the same truncation scheme). In HOPS, it is straightforward to add external stochastic fluctuations (e.g., phase-noise or static disorder), without much additional cost. In the present work, the system only contained electronic degrees of freedom and the vibrational mode was shifted to the environment. This is not always possible (for example, if the potential surfaces are strongly anharmonic). For such situations, approximate stochastic methods have been proposed recently.[44,45] The approach in the present work can be easily adapted to this situation by including the respective nuclear degree of freedom in the system, coupling it to a "simpler" environment.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.6b02111.

> (1) We provide details on how we extract a certain phase-matching condition from our phase-cycling scheme. (2) We discuss convergence for the case of a "weakly damped" mode. (PDF)

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Notes

The authors declare no competing financial interest.

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