Optimized hierarchical equations of motion theory for Drude dissipation and efficient implementation to nonlinear spectroscopies

Jin-Jin Ding,1 Jian Xu,2 Jie Hu,2 Rui-Xue Xu,1,a) and YiJing Yan1,2,b)
1Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei, Anhui 230026, China
2Department of Chemistry, Hong Kong University of Science and Technology, Kowloon, Hong Kong, SAR, China

(Received 22 June 2011; accepted 30 September 2011; published online 31 October 2011)

Hierarchical equations of motion theory for Drude dissipation is optimized, with a convenient convergence criterion proposed in advance of numerical propagations. The theoretical construction is on the basis of a Padé spectrum decomposition that has been qualified to be the best sum-over-poles scheme for quantum distribution function. The resulting hierarchical dynamics under the a priori convergence criterion are exemplified with a benchmark spin-boson system, and also the transient absorption and related coherent two-dimensional spectroscopy of a model exciton dimer system. We combine the present theory with several advanced techniques such as the block hierarchical dynamics in mixed Heisenberg-Schrödinger picture and the on-the-fly filtering algorithm for the efficient evaluation of third-order optical response functions. © 2011 American Institute of Physics. [doi:10.1063/1.3653479]

I. INTRODUCTION

Quantum dissipation plays a pivotal role in many chemical, physical, and biological problems.1–5 Recent experiments on excitation energy transfer in photosynthesis systems6,7 show clearly the breakdown of conventional Markovian and perturbative quantum dissipation theories.8,9 The protein environment is nano-structured, with the time scale of modulation comparable to that of the excitation energy transfer. Also the protein-pigment coupling strength is about that between the pigments. Apparently, one needs a non-perturbative, non-Markovian, and also numerically implementable quantum dissipation theory. The demand is the same on the study of heating generation in quantum transport through mesoscopic systems10–13 and protection of qubits with the aid of photonic crystal environment.14–16

In this work we focus on the hierarchical equations of motion (HEOM) approach.17–23 We request the best HEOM construction, exemplified with Drude dissipation, together with a convenient criterion to estimate its convergence before propagations for general systems at any finite temperature. The HEOM approach was originally proposed in 1989 by Tanimura and Kubo for semi-classical dissipation.24 Formally exact HEOM formalism17–23 for Gaussian dissipation in general, including its second quantization,25 is now well established, with the aid of proper environment spectrum decomposition schemes. The HEOM describes how the reduced system density operator \( \rho(t) \equiv \text{tr}_B \rho_{\text{total}}(t) \), which is the bath subspace trace of the total system-and-bath composite density operator, couples to a set of auxiliary density operators (ADOs). The ADOs are also defined in the reduced system space, but resolve the influence of bath environment in a hierarchical manner. As a numerically efficient alternative to path integral influence functional,2,3,26 HEOM has been applied to such as electron transfer,27–31 nonlinear optical spectroscopy,32–39 and transient quantum transport.40–42

To have an explicit HEOM expression, one should exploit certain basis set spanning over the statistical bath space. This is equivalent to the choice of certain sum-over-pole scheme that decomposes individual bath correlation function into its multiple time scale memory spectrum components. The conventional scheme is the Matsubara expansion of quantum distribution function (i.e., Bose or Fermi function) involved in the bath correlation functions.2–4 However, Matsubara expansion is notorious for slow convergence. We have recently proposed three Padé spectrum decomposition (PSD) schemes be the candidates for the best sum-over-pole method.43,44 Mathematically, these three PSDs of Bose/Fermi function exploit \([N-1/N], [N/N], \) and \([N+1/N]\) Padé approximants, respectively. The resulting HEOM dynamics have been demonstrated in context of the transient quantum transport through a double quantum dots system and population transfer in a spin-boson system.44

Three closely related issues arise in the choice of statistical environment basis set (or sum-over-pole scheme) for efficient HEOM construction. The first one is to identify the best basis set spanning over the statistical bath space. The second one concerns the minimum basis set. It requests to have not only the smallest number of decomposition terms, but also a priori accuracy control criterion on the resulting HEOM dynamics for any given system under bath influence at finite temperature. The third issue is about the possibility of including at least partially the off-basis-set residue contribution in the HEOM dynamics.

In this work, we construct an optimized HEOM theory for Drude dissipation. We identify that \([N/N]\) PSD is the best and the minimum Drude dissipation basis set for the optimized HEOM construction. It leads naturally to an off-basis-
set white noise residue to approximate the difference between the expanded bath correlation function and the exact one. As it is the only approximation involved, the white noise residue ansatz renders a simple accuracy control criterion on the resulting HEOM dynamics. The present paper is a generalization of Refs. 28 and 29, where \( N = 0 \) and \( N = 1 \) cases were analyzed, respectively. We summarize the PSD-based HEOM for Drude dissipation in Sec. II, followed by proposing the accuracy control criterion. Numerical demonstrations are carried out in Sec. III. Included there are a benchmark spin-boson dynamics, studied before by Thoss, Wang, and Miller,\(^4\) and the dispersed transient absorption and the related coherent two-dimensional spectroscopy of a model dimer system. In the Appendix, we present some details of efficient evaluation of nonlinear spectroscopy via block-HEOM in mixed Heisenberg-Schrödinger picture.\(^3\) Finally, we conclude the paper in Sec. IV.

II. FORMALISM

A. Optimal hierarchy for Drude dissipation

In this subsection, we exploit the \([N/N]\) PSD scheme\(^4\) to construct HEOM for Drude dissipation cases. The HEOM has the following generic form:\(^{23}\)

\[
\dot{\rho}_n(t) = -i [\mathcal{L}(t) + \gamma_n + \delta \mathcal{R}_n] \rho_n(t) + \rho_n(0) \rho_n(t) + \rho_{n\downarrow}(0) \rho_{n\downarrow}(t).
\]  

(1)

It describes how an \( n \)-th-tier ADO \( \rho_n \) depends on its associated \((n \pm 1)\)-th-tier ADOS in \( \rho_{n\uparrow} \) and \( \rho_{n\downarrow} \). The ADO's index \( n \) is, in general, a collection of indices; i.e., \( n = \{n_1, \ldots, n_K\} \), with \( n_k \geq 0 \) for bosonic bath. Here \( n_1 + \cdots + n_K = n \) for \( \rho_n = \rho_{n_1, \ldots, n_K} \) being called an \( n \)-th-tier ADO. The reduced system density operator \( \rho(t) \equiv \text{tr}_B \rho(t) \) is just the zeroth-tier ADO. In Eq. (1), the reduced system Liouvillean \( \mathcal{L}(t) \) \( \equiv [H(t), \cdot] \) can be time dependent, e.g., in the presence of driving fields. Throughout this paper, we set \( \hbar = 1 \) and \( \beta = 1/(k_B T) \), with \( k_B \) being the Boltzmann constant and \( T \) being the temperature.

A specific HEOM construction, including the ADO labeling index \( n = \{n_1, \ldots, n_K\} \), depends on the way of decomposing bath correlation function into its memory-frequency components. For clarity, let the system-bath interaction be \( H(t) = -\mathcal{Q} \mathcal{F}_B(t), \) with \( \mathcal{Q} \) and \( \mathcal{F}_B(t) \) being operators in the reduced system and the stochastic bath subspaces, respectively. The influence of bath on system is completely determined by the correlation function \( \mathcal{C}(t) \equiv \mathcal{F}_B(0) \mathcal{F}_B(t) \). It is in turn related to the bath spectral density \( J(\omega) \) via the fluctuation-dissipation theorem:\(^{2,4}\)

\[
C(t) = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \frac{e^{-\omega t} J(\omega)}{1 - e^{-\beta \omega}}.
\]  

(2)

To have a HEOM construction,\(^{23}\) we expand \( C(t) \) in a finite exponential series, on the basis of certain sum-over-pole scheme, together with the Cauchy residue theorem of contour integration.

In this work we focus on the Drude model,

\[
J(\omega) = \frac{2\lambda \gamma \omega}{\omega^2 + \gamma^2}.
\]  

(3)

It has one pole, \( z = -i\gamma \equiv -i\gamma_D, \) in the lower-half plane. The exponential series of bath correlation function assumes then

\[
C(t) = \sum_{k=D,1}^{N} c_k e^{-\gamma_D t} + \delta C_N(t).
\]  

(4)

The index \( k = D \) denotes for the term contributed from the Drude spectral density pole, and \( k = 1, \ldots, N \) are for those from the poles of Bose function. In general the off-basis-set residue \( \delta C_N(t) \neq 0, \) as only finite \( N \) poles for the Bose function are exploited. The conventional scheme is the Matsubara expansion which is however notorious for slow convergence.\(^2,3\)

For Drude dissipation it has been suggested\(^{39}\) that \([N/N]\) PSD be the best sum-over-pole scheme of Bose function. It is accurate up to \( \mathcal{O}(x^{N+1}) \), in the order of \( x = \beta \omega, \) and reads as\(^{44}\)

\[
\frac{1}{1 - e^{-x}} \approx f^{[N/N]}(x) = \frac{1}{x} + \frac{1}{2} + \sum_{k=1}^{N} \frac{2\eta_k x}{x^2 + \xi_k^2} + R_N x,
\]  

(5)

with

\[
R_N = \frac{1}{4(N + 1)(2N + 3)}.
\]  

(6)

The PSD poles and coefficients, \( \{\xi_k, \eta_k; k = 1, \ldots, N\} \), are all positive and can be evaluated with high precision via the eigenvalues of real symmetric triangle matrices.\(^{44}\)

The corresponding exponential series expansion of Eq. (4) can now be obtained via the standard contour integration technique. We obtain (setting \( \gamma \equiv \xi/i\beta \))

\[
c_D = -2i \lambda \gamma f^{[N/N]}(\beta z) \bigg|_{z = -i\gamma},
\]

\[
c_k = \frac{2\eta_k}{i\beta} f(z) \bigg|_{z = -i\gamma}; \ k = 1, \ldots, N,
\]  

(7)

and

\[
\delta C_N(t) \equiv 4\beta \gamma R_N \delta(t) \equiv 2\Delta_N \delta(t).
\]  

(8)

Note that \( \{c_k; k = 1, \ldots, N\} \) are all real. On the other hand, \( c_D \) associating with the Drude exponent \( \gamma_D \) is complex and is evaluated by using the \([N/N]\) Bose function \( f^{[N/N]}(x) \), as given by Eq. (5).

The sum-over-pole scheme resembles a statistical environment basis set for HEOM construction. It dictates not only the exponential expansion of \( C(t) \) as Eq. (4), but also HEOM. The ADO reads now \( \rho_n \equiv \rho_{n_1, n_2, \ldots, n_K} \). The only approximation involved is the white noise residue treatment of the off-basis-set \( \delta C_N(t) \) by Eq. (8). It results in the white noise residue of \( \delta \mathcal{R}_n \) in Eq. (1) without further approximation.\(^{18,23}\)

\[
\delta \mathcal{R}_n \rho_n = \Delta_N [\mathcal{Q}, [\mathcal{Q}, \mathcal{R}_n]].
\]  

(9)

The damping parameter in Eq. (1) collects all relevant exponents,\(^{23}\)

\[
\gamma_n = \sum_{k=D,1}^{N} n_k \gamma_k.
\]  

(10)
The tier-down and tier-up terms are\textsuperscript{23,46}
\begin{align*}
\rho_N^{\downarrow} &= -i \sum_{k=1}^{N} \frac{k}{c_k} \left( c_k Q \rho_N - c_k^* \rho_N^* Q \right), \\
\rho_N^{\uparrow} &= -i \sum_{k=1}^{N} \sqrt{(n_k + 1)c_k} \left[ Q, \rho_N^* \right], \quad (11)
\end{align*}
with $\rho_N^*$ being the associated $(n \pm 1)$th-tier ADO, respectively. The labeling index $n_k^\pm$ differs from $n$ only by changing the specified $n_k$ to $n_k \pm 1$. All ADOs here are dimensionless and scaled properly for implementing the efficient HEOM propagator method, i.e., the recently developed on-the-fly filtering algorithm, which also automatically truncates the level of hierarchy.\textsuperscript{46}

Apparently, HEOM defines a linear space. Related algebra will be detailed in the Appendix. Included there are also block-HEOM dynamics in mixed Heisenberg-Schrödinger picture for efficient evaluation of third-order optical response functions and coherent two-dimensional spectroscopy.\textsuperscript{39}

**B. Accuracy control criterion**

As mentioned earlier, the only approximation involved is the white noise residue treatment of the off-basis-set $\delta C_N(t)$ by Eq. (8). Its validity dictates, therefore, the accuracy of the resulted HEOM. The exact residue $\delta C_N(t)$, which is a real and even function, is defined via Eq. (4), together with Eq. (7) for the Drude model. Its spectrum $\delta C_N(\omega)$ is a symmetric and bell-shaped function, being positive and monotonically decreasing in $\omega > 0$ from $\delta C_N(\omega = 0) = \Delta_N$ to $\delta C_N(\omega \rightarrow \infty) = 0$, where $\Delta_N = 2\lambda \beta \gamma R_N$ was defined in Eq. (8). The half-width-at-half-maximum $\Gamma_N(\gamma)$ that characterizes the inverse time scale of $\delta C_N(t)$ is determined via $\delta C_N(\omega)|_{\omega = \Gamma_N(\gamma) = \Delta_N/2}$. It is found that $\Gamma_N(\gamma)$ can be well approximated by (within 0.6% of relative error for $N \leq 15$ as tested)
\begin{equation}
\Gamma_N(\gamma) \approx \frac{1}{\beta} \left[ r_N + \sqrt{(\beta \gamma)^2 + 0.34r_N^2} \right], \quad (12)
\end{equation}
where $r_N = 1/(2R_N) = (N + 1)(2N + 3)$ [cf. Eq. (6)].

Figure 1 depicts the residue spectrum $\delta C_N(\omega)$, plotted in terms of $\delta C_N(\omega)/\Delta_N$ versus $\omega/\Gamma_N(\gamma)$ for some selected values of $\{N, \beta \gamma\}$. Used here for scaling the x-axis is the approximated $\Gamma_N(\gamma)$ value of Eq. (12). Thus, this figure shows also the excellent quality of Eq. (12).

To validate the $\delta$-function approximation of $\delta C_N(t)$ [Eq. (8)], we examine the Kubo’s motional narrowing line shape parameter,\textsuperscript{47}
\begin{equation}
\kappa_N(\gamma, \lambda) = \sqrt{\Gamma_N(\gamma)/\Delta_N} = \sqrt{r_N \Gamma_N(\gamma)/(\beta \lambda \gamma)}. \quad (13)
\end{equation}
The evaluated $\beta \Gamma_N(\gamma)$ and $\tilde{\kappa}_N(\gamma) \equiv (\beta \lambda)^{1/2}\kappa_N(\gamma, \lambda)$, as functions of $\beta \gamma$, are depicted in Figs. 2(a) and 2(b), respectively.

The accuracy control criterion on the HEOM in Sec. II A comprises, therefore, the conditions under which $\delta C_N(t)$ and its effect on the reduced system dynamics can be treated as Markovian white noise. Apparently, it is valid when $\Gamma_N(\gamma) \gg \Omega_N$, and $\kappa_N(\gamma, \lambda) \gg 1$, with $\Omega_N$ denoting the characteristic frequency of system. We have found\textsuperscript{28,29} that HEOM assumes numerically accurate (if not exact) when
\begin{equation}
\min\{\Gamma_N(\gamma)/\Omega_N, \kappa_N(\gamma, \lambda)\} \geq 5, \quad (14)
\end{equation}
while semi-quantitative when
\begin{equation}
2 \lesssim \min\{\Gamma_N(\gamma)/\Omega_N, \kappa_N(\gamma, \lambda)\} \lesssim 5. \quad (15)
\end{equation}
The above accuracy control criterion facilitates the choice of minimum $N$ for the desired quality of HEOM; see Refs. 28 and 29 for the cases of $N = 0$ and 1, respectively.

**III. NUMERICAL DEMONSTRATIONS**

**A. Spin-boson dynamics**

To demonstrate the efficiency of HEOM and also the proposed accuracy control criterion, consider a benchmark spin-boson system, studied earlier by Thoss, Wang, and Miller via their numerically exact self-consistent hybrid approach.\textsuperscript{35} The system Hamiltonian is $H = \epsilon \sigma_z + V \sigma_x$, with the dissipative mode of $Q = \sigma_z$, subject to Drude dissipation. Here, $\sigma_z$ and $\sigma_x$ are the Pauli matrices and $\epsilon$ is the energy level of the spin. The coupling constant $V$ determines the strength of the interaction between the spin and the bath. The Drude model is characterized by the Drude frequency $\Gamma_0$ and the Drude damping constant $\kappa_0$. The system is initially prepared in the ground state $|\psi_0\rangle = |\uparrow\rangle$.

![FIG. 1. The deviation spectrum function $\delta C_N(\gamma)$ of Drude bath, plotted in terms of $\delta C_N(\omega)/\Delta_N$ versus $\omega/\Gamma_N(\gamma)$ for some selected values of $\{N, \beta \gamma\}$, where $\Delta_N$ is given via Eq. (8) and $\Gamma_N(\gamma)$ is by the approximate of Eq. (12).](image1)

![FIG. 2. $\beta \Gamma_N(\gamma)$ and $\tilde{\kappa}_N(\gamma) \equiv (\beta \lambda)^{1/2}\kappa_N(\gamma, \lambda)$ versus $\beta \gamma$.](image2)
are identical to that of the dimer system \( N \). Nonlinear spectroscopy of a model exciton \( \sigma \) system with \( \frac{\gamma}{\Omega_1} = 2.6, 3.6 \) for \( N = 4 \) and \( \frac{\gamma}{\Omega_1} = 6.3, 12.0 \).}

\[ H = \epsilon (\hat{b}_1 \hat{b}_1 + \hat{b}_2 \hat{b}_2) + V (\hat{b}_1 \hat{b}_2 + \hat{b}_2 \hat{b}_1) + U \hat{b}_1 \hat{b}_1 \hat{b}_2 \hat{b}_2, \]

where \( \hat{b}_j \) and \( \hat{b}_j^\dagger \) denote, respectively, the exciton annihilation and creation operators on the molecular site. In the following we examine the \([N/N]\) PSD-based HEOM with its accuracy control criterion [Eqs. (14) and (15)] in evaluating nonlinear spectroscopic signals. We consider the dispersed transient absorption spectroscopy \( \alpha_\omega, t_\delta \) signals, due to a careless mistake in the excitation field configuration used there. The correct signals (in rotating wave approximation) are now depicted in Figs. 4 and 5, respectively. Demonstrated are the different components of the dispersed transient absorption coefficient of a model exciton dimer.

**B. Nonlinear spectroscopy of a model exciton dimer system**

Nonlinear spectroscopic techniques have been developed to be a powerful tool to probe excitation energies, molecular interactions, transfer and relaxation processes, and so on. To analyze experimental results and extract molecular structure and dynamic information, theoretical investigations are indispensable, especially for complex molecular systems. For this purpose, HEOM has been adopted to reveal the non-Markovian, nonperturbative, and even coherent influences of system-environment interactions. In the Appendix, we present the details of efficient HEOM evaluation of nonlinear optical signals including coherent two-dimensional spectroscopy. Highlighted are the block-HEOM dynamics and the mixed Heisenberg–Schrödinger picture, constructed recently for efficient evaluation of third-order optical response functions.

FIG. 3. Evolution of the reduced spin system density matrix elements, with the same parameters as Fig. 8 of Ref. 45, i.e., \( \epsilon/V = 1, \lambda/V = 0.25, \gamma/V = 5, \) and \( \beta V = 50 \). The accuracy control parameters \{\( \Gamma_N/\Omega_1, \kappa_N \)\} = \{2.6, 3.6\} for \( N = 4 \) and \{4.7, 8.5\} for \( N = 8 \), as indicated. The converged dynamics are identical to that of \( N = 10 \) whose \{\( \Gamma_N/\Omega_1, \kappa_N \)\} = \{6.3, 12.0\}.

FIG. 4. Dispersed transient absorption coefficient signals of the model dimer system (see text): (a) Linear absorption (A) and emission (E) signals; (b) Nonlinear absorptive \( \alpha^N_{\omega, t_\delta} \) component; (c) Nonlinear emissive \( \alpha^E_{\omega, t_\delta} \) component. The pump field is a transform-limited 50 fs-pulse of finite intensity (see text), centered at \( \omega = \epsilon \); i.e., \( \Delta \omega = \omega - \epsilon = 0 \), as indicated by the arrow in panel (a). At \( T = 298 \) K, \( N = 1 \) is in the numerically accurate range, with \{\( \Gamma_N/\Omega_1, \kappa_N \)\} = \{8.3, 8.7\} as indicated.
system at two representing temperatures. Here, \( t_d \) denotes the probe delay time with respect to the pump pulse. Denote also \( \Delta \omega = \omega - \epsilon \), where \( \epsilon = \epsilon_1 = \epsilon_2 \) is the on-site excitonic energy. The dimer system parameters\(^{29}\) are \( V = -400 \text{ cm}^{-1} \) for exciton transfer, \( U = 200 \text{ cm}^{-1} \) for exciton Coulomb interaction, and \( \mu_2/\mu_1 = 0.35 \) for the dimer transition dipoles orientation asymmetry. The characteristic frequency of the system is \( \Omega_s = (\epsilon_1 - \epsilon_2)^2 + 4V^2 = 2V \). The on-site Drude fluctuation parameters are \( \gamma = \gamma_1 = \gamma_2 = 600 \text{ cm}^{-1} \) and \( \lambda = \lambda_1 = \lambda_2 = 600 \text{ cm}^{-1} \).

The pump field is a transform-limited Gaussian pulse with 50 fs at the full width at half maximum, centered at \( \omega = \epsilon \), i.e., \( \Delta \omega \equiv \omega - \epsilon = 0 \), as indicated by the arrow in panel (a) of each Figs. 4 and 5. The peak intensity is \( \mu_1E_{\text{max}} = 100 \text{ cm}^{-1} \). At \( t_d = 100 \text{ fs} \), the pump-transferred occupations in the single on-site exciton \([1] \) and \([2] \) states, and the double-exciton \([f] \) state are 6.5\%, 6.5\%, and 1.7\%, respectively, at \( T = 298 \text{ K} \); while they are 6.3\%, 6.1\%, and 1.9\%, respectively, at \( T = 77 \text{ K} \). The probe field assumes in the weak and impulsive limit. Apparently, the dips appearing in the nonlinear absorptive \( \alpha_{\text{NL}}^E(\omega, t_d) \) components in the (b) panels of Figs. 4 and 5 arise mainly from the excited state absorption to the doubly excited state. The linear emission signal (dashed curves in Fig. 4(a) and Fig. 5(a)) involves the transition from the lower-lying single exciton eigenstate to ground state, without involving the double-exciton \([f] \) state. However, as the moderately strong pump field is used, the nonlinear emissive \( \alpha_{\text{NL}}^E(\omega, t_d) \) component [(c) panels] contains (in the blue side) also the contribution of the \([f] \) state emission.

Figure 6 shows the coherent two-dimensional spectroscopy \( S_{k+k}(\omega_3, t_d, \omega_1) \) of the same dimer system at \( T = 298 \text{ K} \); see third part of the Appendix for the details of technique. Both the excitation and the \( t_d \)-delayed detection

![Graph](image.png)
fields are now operated in the weak and impulsive limit, so that \( t_2 \approx t_d \) the delay time. The frequencies of excitation and detection are dispersed as \( \omega_1 \) and \( \omega_3 \), respectively. Denote also \( \Delta \omega_0 = \omega_3 - \epsilon \). As inferred from Fig. 4, the \([1/1]\) PSD-based HEOM is sufficient to give the numerically accurate results here. For demonstration, we examine again the absorptive (upper panels) and the emissive (middle panels) components of the experimentally measurable \( S_{k_1 k_2} (\omega_3, t_2, \omega_1) \) (bottom panels) that amounts to the total pump-probe absorption signal; see third part of the Appendix for the details. Evidently, the dips appearing in the absorptive components are due to the excited state absorption, while the emissive pathways do not include the \([f]/\) state emission, as the pump field is now in the weak response regime.

Figure 7 depicts the \( \Delta \omega_0 = 0 \) slices of the absorptive and emissive panels of Fig. 6. It, thus, resembles the impulsive pump counterpart of Fig. 4, except for the emissive control parameter of Fig. 6. It, thus, resembles the impulsive pump counterpart of Fig. 4.

IV. SUMMARY

In summary, we have constructed the \([N/N]\) PSD-based HEOM, which is qualified to be the best hierarchical theory for Drude dissipation. The present work generalizes the previous \([0/0]\) and \([1/1]\) PSD-based hierarchical constructions.\(^{28, 29}\) The proposed accuracy control criterion [Eqs. (14) and (15)] is confirmed not only through the reduced system density matrix dynamics, but also through the nonlinear optical spectroscopy calculations. No expensive convergence check would thus be needed for HEOM dynamics of complex open systems. The criterion proposed here is brought into force by estimating the accuracy of white noise residue ansatz for the residue of bath correlation function. The analysis made in Sec. II B and the resulting accuracy control parameters can be generalized to other bath spectral models. However, HEOM for non-Drude environments may need to be optimized case by case. This will be considered in the future paper.

ACKNOWLEDGMENTS

Support from the NNSF of China (21033008 & 21073169), the National Basic Research Program of China (2010CB923300 & 2011CB921400), and the Hong Kong RGC (604709) and UGC (AoE/P-04/08-2) is gratefully acknowledged.

APPENDIX: HEOM EVALUATION OF NONLINEAR OPTICAL SPECTROSCOPIES

1. HEOM in Heisenberg picture and algebra

In the evaluation of coherent two-dimensional spectroscopy, we have applied several advanced numerical techniques. These included the block-HEOM dynamics, the mixed Heisenberg-Schrödinger picture,\(^ {39} \) and the on-the-fly filtering algorithm;\(^ {36} \) see third part of the Appendix. These advanced techniques are used together with the optimized HEOM theory constructed in this work, on basis of PSD scheme with the accuracy control criterion. We have therefore dramatically improved the capability of evaluating multi-dimensional optical spectroscopy, involving non-Markovian and strong system-bath coupling dynamics. For example, the calculations of \( t_2 = 0 \) and 100 fs panels of Fig. 6 take the CPU time 20 s and 47 s, respectively; see Sec. III A for the specifications of the processor. The filtering error tolerance is chosen to be \( 2 \times 10^{-5} \), the standard value. Its convergence is confirmed by decreasing it to \( 1 \times 10^{-7} \), with which the calculations of those two panels take 63 s and 187 s, respectively. Results with these two filtering control parameters are found indistinguishable.
In the absence of time-dependent external field, $\tilde{A}(t) = \Lambda$ and $\mathcal{G}(t, \tau) = \exp[-\Lambda(t - \tau)] \mathcal{G}(t - \tau)$. The time-independent generator $\Lambda$ and its associated Green’s function $\mathcal{G}(t)$ will be used soon to define the HEOM in Heisenberg picture. It will be exploited further together with the HEOM in Schrödinger picture for efficient evaluation of third-order optical response functions in third part of the Appendix.

The inner product in HEOM space is made in contact with the expectation value of an arbitrary system variable through the following identities:

$$\tilde{A} \equiv \text{tr}(A\rho) \equiv \langle A | \rho \rangle = \sum_n \langle A_n | \rho_n \rangle. \quad (A2)$$

The introduced tetradic notion is now extended to the HEOM space in the last identity of Eq. (A2), where $\langle A_n | \rho_n \rangle \equiv \text{tr}(A_n \rho_n)$. The HEOM space equivalence, $\langle A | \rho \rangle = \langle A | \rho \rangle$, implies also that

$$A \equiv \{A_{n=0} = A, A_{n\neq 0} = 0\} = (t = 0). \quad (A3)$$

The last identity takes the form of initial value to HEOM in Heisenberg picture. Introduce also

$$\tilde{\mathcal{A}} \rho \equiv \{A_{t\rho_{n=0} = 0}, A_{t\rho_{n\neq 0} = 0}\}, \quad \tilde{\mathcal{A}} \rho \equiv \{\rho_{t=0} A, \rho_{t\neq 0} = A\}. \quad (A4)$$

They will be used in the HEOM formulation of optical response functions to be presented in the next two subsections.

The HEOM in Heisenberg picture can be readily obtained by considering $\tilde{A}(t) = \langle A | \rho(t) \rangle = \langle A | e^{-\Lambda t} | \rho(0) \rangle \equiv \langle A(t) | \rho(0) \rangle$. The action of $\mathcal{G}(t) = e^{-\Lambda t}$ from the right on a dynamic variable, $A(t) \equiv A\mathcal{G}(t)$ (also called the right action of $\mathcal{G}(t)$), defines the Heisenberg picture, in which HEOM reads $\tilde{A}(t) = -A(t) \Lambda$. The explicit form can be derived via the standard algebra. \(^{39,57}\) It explores the identities $\langle A | \rho(t) \rangle = \langle A | \rho \rangle$, where $\tilde{A} \equiv \Lambda A = -A$ and $\tilde{\rho} \equiv \Lambda \rho = -\rho$, together with the specified HEOM in Schrödinger picture, such as Eq. (A1). The corresponding HEOM in Heisenberg picture reads explicitly as \(^{39}\)

$$\tilde{A}_n = -A_n(n \mathcal{L} + \gamma_n + \Delta_n Q^2)$$

$$-i \sum_{k=0}^{N} \sqrt{n_k + 1} \left( \varepsilon_k A_{n_k}^\dagger Q - c_k^\dagger A_{n_k} Q \right)$$

$$-i \sum_{k=0}^{N} \sqrt{n_k} \varepsilon_k A_{n_k}^\dagger. \quad (A5)$$

Here, $\mathcal{L} = [O,H]$ and $\mathcal{Q} = [O,Q]$, following the identities of $\mathcal{L} \mathcal{Q} = [H, O]$ and $\mathcal{Q} \mathcal{Q} = [Q, O]$ defined earlier. Note that the Eq. (18) of Ref. 38 has mistakes and should be corrected similarly as Eq. (A5).

2. Pump-dressed optical response function

The dispersed transient probe absorption spectroscopy, as demonstrated in Figs. 4 and 5, is given by \(^{38,58}\)

$$\alpha(\omega, t_d) = -\text{Im} \int_0^\infty d\tau \: e^{i \Delta \omega \tau} \{R_+(\tau, t_d) + R_-^*(\tau, t_d)\}$$

$$\equiv \alpha_A(\omega, t_d) + \alpha_E(\omega, t_d), \quad (A6)$$

with $\Delta \omega = \omega - \omega_{eg}$ and the pump-dressed response functions

$$R_{\pm}(\tau, t) = i \: \langle D_{\pm} \mathcal{G}(\tau + t) \mathcal{D}_{\pm} \rho(t) \rangle. \quad (A7)$$

Notations of Eqs. (A3) and (A4) are used here. Equation (A7) is obtained by applying the linear response theory with respect to the weak probe field for HEOM dynamics in the presence of strong pump field. It is equivalent to Eq. of Ref. 58, the convention expression in the full system-and-bath composite matter space.

The pump field-dressed reduced system Hamiltonian under the rotating-wave-approximation reads as

$$H(t) = H - \left[ D_+ E(t) e^{-i \Delta \Omega t} + D_- E^*(t) e^{i \Delta \Omega t} \right]. \quad (A8)$$

We denote $\Delta \Omega = \Omega - \omega_{eg}$ as the detuning frequency of pump field. Its slowly varying amplitude $E(t)$ is set to be centered at $t = 0$. The field-free reduced system Hamiltonian $H$ assumes the block-diagonal form, in virtue of Born-Oppenheimer principle. Three electronic manifolds, the ground $|g\rangle$, the single-excited $|e\rangle$, and the doubly excited $|f\rangle$, are considered. Let $N_e$ be the number of levels in the electronic $|e\rangle$-manifold. The transition dipole is

$$D_{\pm} = \tilde{\mu}_{eg} |g\rangle + \tilde{\mu}_{ef} |f\rangle \equiv \mathbb{D}_{\pm}, \quad (A9)$$

where $\tilde{\mu}_{uv}$ is an $N_e \times N_e$ matrix in the off-diagonal $(uv)$-block. For an aggregates of size $M$ in the basic exciton model similar to Eq. (16), $N_e = 1, N_c = M, N_{fe} = M(M - 1)/2$.

The system is initially at equilibrium in the ground state $|g\rangle$-manifold, i.e., $\rho_{eq} = \rho_{eq}^{gg}$. For the basic exciton model system in consideration, the $|g\rangle$-manifold has only one level, so that all matrices reduce to c-numbers. The steady-state solution to the HEOM leads to $\rho_{eq}^{gg} = \rho_{eq}^{gg} = 1, \rho_{eq}^{gg} = 0$. It then propagates to $\rho(t)$ under the influence of pump pulse field centered at $t = 0$. The time $t$ in Eq. (A7) specifies when the weak probe pulse field interacts with the system. The resulting $\mathcal{D}_{\pm}(t) = \{D_{\pm} \rho_{eq}^{gg}(t), D_{\pm} \rho_{eq}^{gg}(t)\}$ propagates again under the influence of the pump pulse field from $t = 0$ to $t + \tau$, for the evaluation of the pump-dressed response functions as Eq. (A7).

As indicated in Eq. (A6), $R_\pm(t, \tau)$ is responsible for the absorption/emissive component of the transient probe absorption signal, respectively. Apparently, the emissive component is pure nonlinear, $\alpha_E(\omega, t_d) = \alpha_{NL}^{\alpha}(\omega, t_d)$. The absorptive contribution contains both linear and nonlinear components, $\alpha_A(\omega, t_d) = \alpha_A^{(1)}(\omega) + \alpha_{NL}^{\alpha}(\omega, t_d)$. Experimentally, the nonlinear pump-probe spectroscopy is obtained as the difference signal between pump-on and pump-off measurements. In the absence of pump field, the $\rho(t)$ and $\mathcal{G}(t + \tau, t)$ in Eq. (A7) reduces to $\rho_{eq}^{gg} \otimes gg$ and $\mathcal{G}(t)$, respectively, resulting in $R_+(t, \tau) \rightarrow R_{NL}^{(1)}(\tau)$ and $R_-(t, \tau) \rightarrow 0$, and the associating $\alpha(\omega, t_d)$ of Eq. (A6) reduces to the linear absorption $\alpha_A^{(1)}(\omega)$ expression.

The steady-state emission spectrum is also linear and can be formulated via $R_{\pm}^{(1)}(\tau) = i \: \langle D_{\pm} \mathcal{G}(t) \mathcal{D}_{\pm} \rho_{eq}^{gg} \rangle$, with $\rho_{eq}^{gg} = \rho_{eq}^{gg}(\omega)$. Unlike the ground state that consists of only one level, the excited state manifold consists of $M$ single-excitative levels. Each individual ADO in $\rho_{eq}^{gg}$ is an $M \times M$ matrix, and should be evaluated numerically via the corre-
sponding steady-state solution of the HEOM. The steady-state emission spectrum is then \( S_{\text{eq}}(\omega) = -\text{Im} \int_0^\infty dt e^{i\Delta \omega \tau} \left[ R^a(t) \right]^{*} \), in consistent with Eq. (A6).

### 3. Coherent two-dimensional spectroscopy

The coherent two-dimensional spectroscopy studied in Fig. 6 is formally the sum signals of two basic four-wave-mixing configurations: \(^{59}\)

\[
S_{k_1+k_2}(\omega_3, t_2, \omega_1) = S_{k_1}(\omega_3, t_2, \omega_1) + S_{k_2}(\omega_3, t_2, \omega_1).
\]

(A10)

The \( S_{k_1} \) signal goes with \( k_1 = k_3 + k_2 - k_1 \), the stimulated photon echo or rephasing configuration. \(^{60}\) The \( S_{k_2} \) signal goes with \( k_{11} = k_3 - k_2 + k_1 \), a non-rephasing configuration. In these two basic four-wave-mixing configurations, the three pulsed-fields are separated in time, interacting with the system in the sequential order, first with \( k_1 \)-field, then \( k_2 \)-field, and finally \( k_3 \)-field. Experiments are also performed with the pulsed \( k_2 \)-field applied continuously not only after, but also before the pulsed \( k_1 \)-fields. This amounts to the sum signal as Eq. (A10), which is actually the coherent two-dimensional pump-probe absorption. All three incoming fields are operated in the weak response regime and impulsive limit. Under the rotating wave approximation, \( \text{we have} \)

\[
S_{k_{11}}(\omega_3, t_2, \omega_1) = \text{Re} \int_0^\infty \! dt_3 \int_0^\infty \! dt_1 e^{i(\Delta \omega_1 t_1 + \Delta \omega_3 t_3)} \times R_{k_{11}}(t_1, t_2, t_3),
\]

(A11)

with \( \Delta \omega_k = \omega_k - \omega_{eq} \) and

\[
R_{k_1} = R_2 + R_3 + R_5, \quad R_{k_2} = R_1 + R_4 + R_6.
\]

(A12)

The Liouville-space pathway contributions \( \{ R_{\alpha}; \alpha = 1, \ldots, 6 \} \) to the third-order optical response function are specified by standard \(^{5,48,59}\) Now with the HEOM, the third-order perturbation pathways analysis results in \(^{50}\)

\[
\begin{align*}
R_1(t_1, t_2, t_1) &= \langle \hat{\mu}_{ge} | \mathcal{G}_{eg}(t_1) \hat{\mu}_{ge} \mathcal{G}_{eg}(t_2) \hat{\mu}_{ge} \mathcal{G}_{eg}(t_1) \hat{\mu}_{ge} | \rho_{eq}^{\text{sg}} \rangle, \\
R_2(t_1, t_2, t_1) &= \langle \hat{\mu}_{ge} | \mathcal{G}_{eg}(t_1) \hat{\mu}_{eg} \mathcal{G}_{ge}(t_2) \hat{\mu}_{ge} \mathcal{G}_{eg}(t_1) \hat{\mu}_{ge} | \rho_{eq}^{\text{sg}} \rangle, \\
R_3(t_1, t_2, t_1) &= \langle \hat{\mu}_{ge} | \mathcal{G}_{eg}(t_1) \hat{\mu}_{eg} \mathcal{G}_{ge}(t_2) \hat{\mu}_{eg} \mathcal{G}_{eg}(t_1) \hat{\mu}_{ge} | \rho_{eq}^{\text{sg}} \rangle, \\
R_4(t_1, t_2, t_1) &= \langle \hat{\mu}_{ge} | \mathcal{G}_{eg}(t_1) \hat{\mu}_{ge} \mathcal{G}_{eg}(t_2) \hat{\mu}_{ge} \mathcal{G}_{eg}(t_1) \hat{\mu}_{ge} | \rho_{eq}^{\text{sg}} \rangle, \\
R_5(t_1, t_2, t_1) &= -\langle \hat{\mu}_{ge} | \mathcal{G}_{ge}(t_1) \hat{\mu}_{ge} \mathcal{G}_{eg}(t_2) \hat{\mu}_{ge} \mathcal{G}_{eg}(t_1) \hat{\mu}_{ge} | \rho_{eq}^{\text{sg}} \rangle, \\
R_6(t_1, t_2, t_1) &= -\langle \hat{\mu}_{ge} | \mathcal{G}_{ge}(t_1) \hat{\mu}_{ge} \mathcal{G}_{eg}(t_2) \hat{\mu}_{ge} \mathcal{G}_{eg}(t_1) \hat{\mu}_{ge} | \rho_{eq}^{\text{sg}} \rangle.
\end{align*}
\]

(A13)

They are just the direct HEOM analogues to their full system- and-bath composite space expressions. \(^{51,59}\)

The \( t_1 \) and \( t_2 \) represents the time durations of excitation and detection, respectively. Therefore, the \( \omega_1 \) and \( \omega_3 \), which are expressed in terms of detunings in Eq. (A11), are the excitation and detection frequencies, respectively. The \( t_2 \) denotes the waiting time, during which the system is either in the excited or the ground state manifold, with underlying dynamics being governed by \( \mathcal{G}_{ge}(t_2) \) or \( \mathcal{G}_{eg}(t_2) \), respectively. As inferred from Eq. (A13), these six pathways can be classified into the excited-state emission \( (R_1, R_2) \), ground-state bleaching \( (R_3, R_4) \), and excited-state absorption \( (R_5, R_6) \) contributions. In terms of emissive and absorptive components, we have \( R_0 = R_1 + R_2 \) and \( R_A = R_3 + R_4 + R_5 + R_6 \).

Involved in Eq. (A13) are the block-HEOM propagator \( \mathcal{G}_{\alpha\beta}(t) \), with the ADOs in \((uv)\)-block being now all \( N_g \times N_e \) matrices. We have \( \tilde{\rho}_{uv}(t) = \mathcal{G}_{uv}(t) \tilde{\rho}_{uv}(0) \) in Schrödinger picture, while \( A_{uv}(t) = A_{uv}(0) \mathcal{G}_{uv}(t) \) in Heisenberg picture. The block-HEOM in these two pictures is similar to Eqs. (A1) and (A5), respectively, but with the following changes,

\[
\{ \mathcal{L} \rho_n, Q_n \rho_n \} \longrightarrow \{ \mathcal{L}_{uv} \rho_n^{\text{sg}}, Q_{uv} \rho_n^{\text{sg}} \}, \\
\{ A_n \mathcal{L}, A_n Q \} \longrightarrow \{ A_{uv}^\text{sg} \mathcal{L}_{uv}, A_{uv} Q_{uv} \},
\]

(A14)

where

\[
\begin{align*}
\mathcal{L}_{uv} &\equiv H_{uv} - \hat{O} - \hat{O} H_{uv}, \\
Q_{uv} &\equiv \hat{O} \mathcal{L}_{uv} - H_{uv} \hat{O} - \hat{O} Q_{uv}.
\end{align*}
\]

The block-matrix form follows the Born-Oppenheimer principle, where the excitonic manifolds are adiabatic and the relaxation between them is negligible. With this picture, both the system Hamiltonian and dissipative modes are block diagonalized (i.e., \( H_{uv} = 0 \) and \( Q_{uv} = 0 \), if \( u \neq v \)). The transition dipoles \( \tilde{\mu}_{uv} \) through which the external fields interrogate the system are in off-diagonal blocks.

The evaluation of Eq. (A13) exemplified with \( R_1 \) is as follows.

1. Determine the initial equilibrium \( \rho_{eq}^{\text{sg}} \) in the ground state manifold via the steady-state solution to the HEOM in the \((gg)\)-block. For the basic exciton model \( \text{cf. Eq. (16)} \), the ground state manifold has only one level, i.e., \( N_g = 1 \), so that all ADOs in \((gg)\)-block being \( N_g \times N_e \) matrices are just c-numbers. We obtain \( \rho_{eq}^{\text{sg}} = \{ \rho_{eq}^{\text{sg}}(0) = 1, \rho_{eq}^{\text{sg}}(n) = 0 \} \).
2. Evaluate \( \hat{\mu}_{ge}(t_1 = 0) \equiv \tilde{\mu}_{ge} \rho_{eq}^{\text{sg}} = \{ \tilde{\mu}_{ge} \rho_{eq}^{\text{sg},g}\} \), for the system being promoted upon the first interrogation.
3. Perform the \( t_1 \)-propagation \( \tilde{\mu}_{ge}(t_1) = \mathcal{G}_{ge}(t_1) \tilde{\mu}_{ge}(0) \) in Schrödinger picture.
4. Calculate \( \tilde{\mu}_{ge}(t_2 = 0; t_1) = \mathcal{G}_{ge}(t_2) \tilde{\mu}_{ge}(t_1) \rho_{eq}^{\text{sg}} \) for the system being promoted upon the second interrogation.
5. Carry out the nested \( t_2 \)-propagation \( \tilde{\mu}_{ge}(t_2; t_1) = \mathcal{G}_{ge}(t_2) \tilde{\mu}_{ge}(0; t_1) \) in Schrödinger picture. The \( t_2 \)-propagation can be unshielded from the nested loop by carrying it out in the Heisenberg picture on dynamic variables; i.e., \( \tilde{\mu}_{ge}(t_2) = \tilde{\mu}_{ge}(t_1) \) in \( R_1 \). Finally, we evaluate third-order optical response functions such as \( R_1(t_3, t_2; t_1) \)

\[
\{ \tilde{\mu}_{ge}(t_3) | \tilde{\mu}_{ge}^{\text{sg}}(t_2; t_1) \} \text{ via block-HEOM in mixed Heisenberg-Schrödinger picture.}^{39}\]