

## ARTICLE

**Dissipaton Equation of Motion with Controlled Truncation<sup>†</sup>**Yuan Kong<sup>a</sup>, Hou-dao Zhang<sup>b\*</sup>, Yi-meng Wang<sup>a</sup>, Rui-xue Xu<sup>a,c\*</sup>, YiJing Yan<sup>a,b</sup>*a. Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei 230026, China**b. Department of Chemistry, Hong Kong University of Science and Technology, Hong Kong, China**c. Synergetic Innovation Center of Quantum Information and Quantum Physics, University of Science and Technology of China, Hefei 230026, China*

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This work aims at *a priori* accuracy controlled truncation to the dissipaton equation of motion formalism for non-perturbative quantum dissipative dynamics. A new truncation scheme is proposed by adopting the Markovian and high-temperature approximation similar to the Caldeira-Leggett master equation made at the termination level. An accuracy criterion to determine the truncation level is put forward via a Markovianicity analysis. Performances of both the new truncation scheme and the control criterion are illustrated via dynamics simulation of electron transfer systems.

**Key words:** Dissipaton, Equation of motion, Controlled truncation**I. INTRODUCTION**

The central interest of quantum dissipation theory is the dynamics of open quantum systems embedded in thermal environments. Its importance has been manifested in diversified physical and chemical research fields together with its developments of theoretical methods and their applications. Nevertheless, universal methods both reliable and practical for realistic molecular systems still remain a challenging task for theoretical studies nowadays.

Approximate methods, such as quantum master equation approaches, which are on the basis of perturbative and Markovian treatments of system-bath couplings, are numerically efficient and easy to be implemented [1]. However, due to the perturbative and Markovian nature, they are often found to be inadequate and fail in simulating certain experimental results, for instance, the long-lived quantum coherence of excitation energy transfer in light-harvesting pigment-protein complex [2]. Thus, their validity and applicability are often questioned, and need to be verified.

One formally exact solution is the Feynman-Vernon influence functional path integral formalism [3–5]. However, this method is numerically too expensive hence practically limited to small size of systems with relatively short memory of baths [6]. On the other hand, the dissipaton equation of motion (DEOM), as a non-perturbative and non-Markovian approach equivalent

to the influence functional path integral for the reduced system dynamics, has the numerical advantage due to its linearly coupled differential equation of motion construction [7]. In recent years, this approach, formerly as hierarchical equation of motion [8–10], has been successfully applied to study quantum transport, electron/energy transfer, and coherent two-dimensional spectroscopies, *etc.* [11–17]. Besides, the DEOM describes naturally the environment dynamics and polarization [18] and provides potentially the methodology to study non-Gaussian bath effects.

The DEOM involves a number of dynamical quantities that are hierarchically coupled with each other, called the dissipaton density operators (DDOs). In practice its numerical cost for given size of system is linearly scaled with the number of DDOs that is determined by both the number of exponential terms in the decomposition of bath correlation functions (denoted as  $K$ ) and the truncation level of the hierarchy (denoted as  $L$ ). While the optimal control over the bath decomposition or the  $K$ -space expansion has been developed for the minimum exponential terms at given accuracy [14, 15], the  $L$ -space control is still unsatisfied. Although the previously proposed on-the-fly filtering algorithm [19] can greatly reduce the DDOs' number thus improve the efficiency, its implementation still costs numerically redundant resources.

In this work, we develop *a priori* accuracy controlled truncation of DEOM. The idea is similar to that of the optimized bath decomposition scheme [14, 15, 20], based on a Markovianicity analysis. A Caldeira-Leggett master equation form of termination is adopted, assuming the wide-band approximation of bath spectrum at the level of truncation. Performance of the proposed scheme will be illustrated with electron transfer sys-

<sup>†</sup>Dedicated to Professor Qing-shi Zhu on the occasion of his 70th birthday.

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tems. We introduce the hybridizing dissipaton decomposition and the generic construction of DEOM formalism, followed by the derivation of Caldeira-Leggett form of truncation. We analyze the control criterion and demonstrate its performance.

## II. FORMALISM

### A. Bath statistics

We start from the total system-plus-bath Hamiltonian assuming the following form

$$H_T = H_S + h_B + \sum_a \hat{Q}_a \hat{F}_a \quad (1)$$

where the last term describes the system-bath coupling, with  $\{\hat{Q}_a\}$  and  $\{\hat{F}_a\}$  being the hybridizing system and bath operators, respectively. Hereafter, we set  $\hbar=1$  for the Planck constant and  $\beta \equiv 1/(k_B T)$  with  $T$  the temperature and  $k_B$  the Boltzmann constant. All hybridizing system operators  $\{\hat{Q}_a\}$  are Hermitian and dimensionless. The reduced system Liouvillian is denoted as  $\mathcal{L}_S \equiv [H_S, \cdot]$ .

The bath is modelled as noninteracting harmonic oscillators,  $h_B = \sum_j \frac{\omega_j}{2} (p_j^2 + x_j^2)$ , and the hybridizing

bath operators are linear,  $\hat{F}_a = \sum_j c_{aj} x_j$ , whose influences are completely described by the hybridizing bath spectral densities,  $J_{ab}(\omega) = \frac{\pi}{2} \sum_j c_{aj} c_{bj} \delta(\omega - \omega_j)$ . In

this model, the bath interaction spectral densities are all odd real functions. The above presents the microscopic description of a Gaussian bath interaction. Its thermodynamical equivalence is given by

$$J_{ab}(\omega) = \frac{1}{2} \int_{-\infty}^{\infty} d\omega' e^{i\omega(t-\tau)} \langle [\hat{F}_a(t), \hat{F}_b(\tau)] \rangle_B \quad (2)$$

Here,  $\hat{F}_a(t) = e^{ih_B t} \hat{F}_a e^{-ih_B t}$  and  $\langle \hat{O} \rangle_B \equiv \text{tr}_B(\hat{O} \rho_B^{\text{eq}})$  with  $\rho_B^{\text{eq}} = e^{-\beta h_B} / \text{tr}_B e^{-\beta h_B}$  being the canonical thermal equilibrium bath ensemble density operator. The underlying detailed-balance relation leads to the bath correlation functions [21, 22],

$$\begin{aligned} C_{ab}(t) &\equiv \langle F_a(t) F_b(0) \rangle_B \\ &= \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \frac{e^{-i\omega t} J_{ab}(\omega)}{1 - e^{-\beta\omega}} \end{aligned} \quad (3)$$

This is the bosonic fluctuation-dissipation theorem. Note the Bose function can be recast as:

$$\frac{1}{1 - e^{-\beta\omega}} = \frac{1}{2} \coth\left(\frac{\beta\omega}{2}\right) + \frac{1}{2} \quad (4)$$

Denoting

$$C_{ab}^S(\omega) = \frac{1}{2} J_{ab}(\omega) \coth\left(\frac{\beta\omega}{2}\right) \quad (5)$$

$$C_{ab}^A(\omega) = \frac{1}{2} J_{ab}(\omega) \quad (6)$$

The symmetric versus anti-symmetric (in this model equivalent to the real versus imaginary) parts of bath correlation functions are then given as

$$C_{ab}^S(t) = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \cos(\omega t) C_{ab}^S(\omega) \quad (7)$$

$$C_{ab}^A(t) = -\frac{i}{\pi} \int_{-\infty}^{\infty} d\omega \sin(\omega t) C_{ab}^A(\omega) \quad (8)$$

In high-temperature ( $\beta\omega \ll 1$ ) limit, we have

$$C_{ab}^A(t) \approx \frac{1}{2} i \beta \dot{C}_{ab}^S(t) \quad (9)$$

In this work, we adopt the Drude model for the bath spectral densities in diffusive limit, characterized by the reorganization energies  $\lambda_{ab}$  and a unified parameter of inversed timescale  $\gamma_D$ ,

$$J_{ab}(\omega) = \frac{2\lambda_{ab}\gamma_D\omega}{\omega^2 + \gamma_D^2} \quad (10)$$

It has one pole,  $z = -i\gamma_D$ , in the lower-half plane. The wide-band limit is reached when  $\gamma_D \gg \omega$  of the relevant frequency, resulting in  $J_{\text{WBL}}(\omega) \propto \omega$ . By certain sum-over-pole scheme, we can decompose  $C_{ab}(t)$  into a series of exponential terms with a residue part,

$$C_{ab}(t) = \sum_k \eta_{abk} e^{-\gamma_k t} + \delta C_{ab}(t) \quad (11)$$

The exponential terms here include one from the Drude spectral density with a complex pre-exponential coefficient and a real exponential decay factor  $\gamma_D$ . The other terms come from the Bose function, for which the optimized scheme has been developed on the basis of Padé spectrum decomposition (PSD) [23, 24], to minimize the number of exponential terms with controlled accuracy [14, 15], resulting in real coefficients and exponents.

### B. Dissipaton decomposition and equations of motion

Dissipaton operators,  $\{\hat{f}_{ak}\}$ , are introduced with respect to the exponential terms in Eq.(11), such that [7]

$$\langle \hat{f}_{ak}(t) \hat{f}_{bk'}(0) \rangle_B^> = \delta_{kk'} \eta_{abk} e^{-\gamma_k t} \quad (12)$$

The dissipaton correlation function, Eq.(12), is defined in  $t > 0$  region. Its backward counterpart is defined via  $\langle \hat{f}_{bk'}(0) \hat{f}_{ak}(t) \rangle_B^< = \delta_{kk'} (\eta_{ab\bar{k}} e^{-\gamma_{\bar{k}} t})^*$ , where  $\eta_{ab\bar{k}}$  denotes the pre-exponential coefficient of the complex

conjugate counterpart with  $\gamma_{\bar{k}} = \gamma_k^*$ , such that the forward and backward correlations share the same exponent. For those terms with  $\gamma_k^* = \gamma_k$ , we have simply  $\eta_{ab\bar{k}}^* = \eta_{abk}^*$  and  $\langle \hat{f}_{bk'}(0) \hat{f}_{ak}(t) \rangle_{\text{B}}^{\leq} = \delta_{kk'} \eta_{abk}^* e^{-\gamma_k t}$ . Introduce also  $\{\delta \hat{F}_a\}$  for the residue term in Eq.(11), such that  $\langle \delta \hat{F}_a(t) \hat{f}_{bk}(0) \rangle_{\text{B}} = 0$  and  $\langle \delta \hat{F}_a(t) \delta \hat{F}_b(0) \rangle_{\text{B}} = \delta C_{ab}(t)$  [7]. It is easy to verify that Eq.(11) can now be recast in terms of the dissipaton decomposition of

$$\hat{F}_a = \sum_k \hat{f}_{ak} + \delta \hat{F}_a \quad (13)$$

DDOs involved in DEOM for bosonic bath are defined as [7],

$$\rho_{\mathbf{n}}^{(n)}(t) \equiv \text{tr}_{\text{B}} \left[ \left( \prod_{ak} \hat{f}_{ak}^{n_{ak}} \right)^{\circ} \rho_{\text{T}}(t) \right] \quad (14)$$

Dissipaton inside the circled parentheses,  $(\dots)^{\circ}$ , are irreducible, satisfying the bosonic permutation relation,

$$(\hat{f}_{ak} \hat{f}_{bk'})^{\circ} = (\hat{f}_{bk'} \hat{f}_{ak})^{\circ} \quad (15)$$

$n_{ak} \geq 0$  is the occupation number of each  $\hat{f}_{ak}$ -dissipaton.

$$n = \sum_{ak} n_{ak} \quad \text{and} \quad \mathbf{n} \equiv \{n_{ak}\} \quad (16)$$

They specify the composites of the  $n$ -dissipaton cluster,  $\rho_{\mathbf{n}}^{(n)}$  of Eq.(14). Obviously,  $n=0$  indicates zero dissipaton occupation and  $\rho^{(0)} = \rho$  gives the reduced density operator of system.

Following

$$\dot{\rho}_{\text{T}}(t) = -i[H_{\text{T}}(t), \rho_{\text{T}}(t)] \quad (17)$$

proceeded by exploiting the single exponent property of dissipaton correlation functions,

$$\begin{aligned} & -i \text{tr}_{\text{B}} \left[ \left( \prod_{ak} \hat{f}_{ak}^{n_{ak}} \right)^{\circ} [h_{\text{B}}, \rho_{\text{T}}] \right] \\ &= -i \text{tr}_{\text{B}} \left\{ \left[ \left( \prod_{ak} \hat{f}_{ak}^{n_{ak}} \right)^{\circ}, h_{\text{B}} \right] \rho_{\text{T}} \right\} \\ &= \text{tr}_{\text{B}} \left\{ \left[ \frac{\partial}{\partial t} \left( \prod_{ak} \hat{f}_{ak}^{n_{ak}} \right)^{\circ} \right]_{\text{B}} \rho_{\text{T}} \right\} \\ &= - \left( \sum_{ak} n_{ak} \gamma_{ak} \right) \rho_{\mathbf{n}}^{(n)} \end{aligned} \quad (18)$$

and the Wick's type of contraction [7],

$$\begin{aligned} \rho_{\mathbf{n};ak}^{\gt} &\equiv \text{tr}_{\text{B}} \left[ \left( \prod_{bk'} \hat{f}_{bk'}^{n_{bk'}} \right)^{\circ} f_{ak} \rho_{\text{T}}(t) \right] \\ &= \rho_{\mathbf{n}_{ak}^+}^{(n+1)} + \sum_{bk'} n_{bk'} \langle \hat{f}_{bk'} \hat{f}_{ak} \rangle_{\text{B}}^{\gt} \rho_{\mathbf{n}_{bk'}^-}^{(n-1)} \\ &= \rho_{\mathbf{n}_{ak}^+}^{(n+1)} + \sum_b n_{bk} \eta_{bak} \rho_{\mathbf{n}_{bk}^-}^{(n-1)} \end{aligned} \quad (19)$$

$$\begin{aligned} \rho_{\mathbf{n};ak}^{\lt} &\equiv \text{tr}_{\text{B}} \left[ \left( \prod_{bk'} \hat{f}_{bk'}^{n_{bk'}} \right)^{\circ} \rho_{\text{T}}(t) f_{ak} \right] \\ &= \rho_{\mathbf{n}_{ak}^+}^{(n+1)} + \sum_{bk'} n_{bk'} \langle \hat{f}_{ak} \hat{f}_{bk'} \rangle_{\text{B}}^{\lt} \rho_{\mathbf{n}_{bk'}^-}^{(n-1)} \\ &= \rho_{\mathbf{n}_{ak}^+}^{(n+1)} + \sum_b n_{bk} \eta_{bak}^* \rho_{\mathbf{n}_{bk}^-}^{(n-1)} \end{aligned} \quad (20)$$

we obtain

$$\begin{aligned} \dot{\rho}_{\mathbf{n}}^{(n)} &= -(i\mathcal{L}_{\text{S}} + \Gamma_{\mathbf{n}}^{(n)}) \rho_{\mathbf{n}}^{(n)} - i \sum_{ak} n_{ak} C_{ak} \rho_{\mathbf{n}_{ak}^-}^{(n-1)} \\ &\quad - i \sum_{ak} \mathcal{A}_a \rho_{\mathbf{n}_{ak}^+}^{(n+1)} - i \sum_a \mathcal{A}_a \varrho_{\mathbf{n};a}^{(n)} \end{aligned} \quad (21)$$

where

$$\begin{aligned} \Gamma_{\mathbf{n}}^{(n)} &= \sum_{ak} n_{ak} \gamma_k, \quad \mathcal{A}_a \hat{O} \equiv [\hat{Q}_a, \hat{O}] \\ C_{ak} \hat{O} &\equiv \sum_b (\eta_{abk} \hat{Q}_b \hat{O} - \eta_{ab\bar{k}}^* \hat{O} \hat{Q}_b) \end{aligned}$$

The subscript  $\mathbf{n}_{ak}^{\pm}$  differs from  $\mathbf{n}$  only by changing the specified  $n_{ak}$  to  $n_{ak} \pm 1$ . The last term of Eq.(20) arises from the residue related part  $\delta \hat{F}_a$ ,

$$\varrho_{\mathbf{n};a}^{(n)} = \text{tr}_{\text{B}} \left[ \left( \delta \hat{F}_a \prod_{ak} \hat{f}_{ak}^{n_{ak}} \right)^{\circ} \rho_{\text{T}} \right] \quad (22)$$

For the white-noise approximation  $\delta C_{ab}(t) \approx 2\Delta_{ab} \delta(t)$ , the residue correction term has a simple form [7]:

$$\varrho_{\mathbf{n};a}^{(n)} = -i \sum_b \Delta_{ab} \mathcal{A}_b \rho_{\mathbf{n}}^{(n)} \quad (23)$$

This is obtained by setting

$$\langle \delta \hat{F}_a(t) \delta \hat{F}_b(0) \rangle = \lim_{\zeta \rightarrow \infty} \Delta_{ab} \zeta e^{-\zeta t} \quad (24)$$

while the equation of  $\varrho_{\mathbf{n};a}^{(n)}$  is independent of  $\zeta$  together with the ansatz, there are no more than single-irreducible white-noise dissipatons [7].

### C. Truncation of DEOM

Denote  $K$  the number of exponential terms in Eq.(11). There will then be  $K$  distinct dissipatons for each coupling bath force constituting the so-called  $K$ -space. Truncating the hierarchy at certain level  $L$ , *i.e.*, the maximum occupation number of dissipatons, the total number of involved DDOs is given by

$$\mathcal{N} = \frac{(K+L)!}{K!L!} \quad (25)$$

Obviously, the hierarchy space will explode rapidly as  $K$  and/or  $L$  increase, which is often encountered in cases

of low temperature, intensive system-bath coupling, and strong non-Markovian environment.

The  $K$ -space truncation has been optimized to be both efficient and accuracy controllable on basis of PSD scheme of Bose function [14, 15]. On the other hand, the  $L$ -space truncation has not been well settled, from the closure form of terminator to the quantitative control protocol. So far the widely adopted terminator sets  $\rho_{\mathbf{n}}^{(n>L)}=0$ , *i.e.*, the higher level DDOs do not participate, and the resulting formalism for  $\rho_{\mathbf{n}}^{(n\leq L)}$  is in closed form. This is also called the chronological ordering prescription (COP) scheme [8]. The conventional second-order time non-local master equation is recovered when  $L=1$ .

In the rest of this section, we like to introduce another scheme, the Caldeira-Leggett (CL) master equation form of truncation. In this scheme, the DDOs' equation of motion at the terminated level  $L$  is expressed as

$$\dot{\rho}_{\mathbf{n}}^{(L)} = -(i\mathcal{L}_S + \Gamma_{\mathbf{n}}^{(n)})\rho_{\mathbf{n}}^{(L)} - i \sum_{ak} n_{ak} \mathcal{C}_{ak} \rho_{\mathbf{n}_{ak}}^{(L-1)} - i \sum_a \mathcal{A}_a \bar{\varrho}_{\mathbf{n};a}^{(L+1)} \quad (26)$$

where

$$\bar{\varrho}_{\mathbf{n};a}^{(L+1)} \equiv \varrho_{\mathbf{n};a}^{(L)} + \sum_k \rho_{\mathbf{n}_{ak}}^{(L+1)} = \text{tr}_{\text{B}} \left[ \left( \hat{F}_a \prod_{a'k'} \hat{f}_{a'k'}^{n_{a'k'}} \right) \rho_{\text{T}} \right] \quad (27)$$

will be approximately treated as

$$\bar{\varrho}_{\mathbf{n};a}^{(L+1)} \approx \text{tr}_{\text{B}} \left[ \left( \bar{F}_a \prod_{a'k'} \hat{f}_{a'k'}^{n_{a'k'}} \right) \rho_{\text{T}} \right] \quad (28)$$

here  $\bar{F}_a$  denotes the white-noise approximation of  $\hat{F}_a$  with bath correlations

$$\langle \bar{F}_a(t) \bar{F}_b(0) \rangle_{\text{B}} = 2[\Delta'_{ab} \delta(t) + i\tilde{\Delta}_{ab} \dot{\delta}(t)] \quad (29)$$

where

$$\Delta'_{ab} = C_{ab}^S(\omega)|_{\omega=0}, \quad \tilde{\Delta}_{ab} = \frac{C_{ab}^A(\omega)}{\omega}|_{\omega=0}$$

satisfying the high-temperature fluctuation-dissipation relation, Eq.(9). For example, for the Drude model of Eq.(10), we get  $\Delta'_{ab}=2\lambda_{ab}/(\beta\gamma_{\text{D}})$  and  $\tilde{\Delta}_{ab}=\lambda_{ab}/\gamma_{\text{D}}$ .

Following the white-noise dissipaton algebra briefed above and detailed in Ref.[7], we can evaluate Eq.(28) as

$$i\bar{\varrho}_{\mathbf{n};a}^{(L+1)} = \sum_b \text{tr}_{\text{B}} \left[ \left( \prod_{a'k'} \hat{f}_{a'k'}^{n_{a'k'}} \right) \cdot (X_{ab}^> \rho_{\text{T}} - \rho_{\text{T}} X_{ab}^<) \right] \quad (30)$$

where

$$X_{ab}^>(t) = \bar{\Delta}_{ab} \hat{Q}_b + i\tilde{\Delta}_{ab} \dot{\hat{Q}}_b \quad (31)$$

$$X_{ab}^<(t) = \bar{\Delta}_{ab}^* \hat{Q}_b - i\tilde{\Delta}_{ab}^* \dot{\hat{Q}}_b \quad (32)$$

here

$$\begin{aligned} \bar{\Delta}_{ab} &= \Delta'_{ab} - \frac{i}{2\pi} \int_{-\infty}^{\infty} d\omega \frac{J_{ab}(\omega)}{\omega} \\ &= \Delta'_{ab} - i\lambda_{ab} \end{aligned} \quad (33)$$

where  $\lambda_{ab}$  is the reorganization energy. Consider the Heisenberg equation for dissipative modes,

$$\begin{aligned} \dot{\hat{Q}}_b &= i \left[ H_{\text{S}} + h_{\text{B}} + \sum_{b'} \hat{Q}_{b'} \bar{F}_{b'}, \hat{Q}_b \right] \\ &= i[H_{\text{S}}, \hat{Q}_b] + i \sum_{b'}' [\hat{Q}_{b'}, \hat{Q}_b] \bar{F}_{b'} \end{aligned} \quad (34)$$

We have

$$X_{ab}^>(t) = \bar{\Delta}_{ab} \hat{Q}_b - \tilde{\Delta}_{ab} \left( [H_{\text{S}}, \hat{Q}_b] + \sum_{b'}' [\hat{Q}_{b'}, \hat{Q}_b] \bar{F}_{b'} \right) \quad (35)$$

$$X_{ab}^<(t) = \bar{\Delta}_{ab}^* \hat{Q}_b + \tilde{\Delta}_{ab}^* \left( [H_{\text{S}}, \hat{Q}_b] + \sum_{b'}' [\hat{Q}_{b'}, \hat{Q}_b] \bar{F}_{b'} \right) \quad (36)$$

here the notation  $\sum_{b'}'$  sums over all coupling modes except  $b'=b$ . Consequently, we get

$$\begin{aligned} i\bar{\varrho}_{\mathbf{n};a}^{(L+1)} &= \sum_b \left\{ \left( \bar{\Delta}_{ab} \hat{Q}_b - \tilde{\Delta}_{ab} [H_{\text{S}}, \hat{Q}_b] \right) \rho_{\mathbf{n}}^{(L)} - \rho_{\mathbf{n}}^{(L)} \left( \bar{\Delta}_{ab}^* \hat{Q}_b + \tilde{\Delta}_{ab}^* [H_{\text{S}}, \hat{Q}_b] \right) - \sum_{b'}' \left( \Delta_{ab} [\hat{Q}_{b'}, \hat{Q}_b] \bar{\varrho}_{\mathbf{n};b'}^{(L+1)} + \tilde{\Delta}_{ab}^* \bar{\varrho}_{\mathbf{n};b'}^{(L+1)} [\hat{Q}_{b'}, \hat{Q}_b] \right) \right\} \quad (37) \end{aligned}$$

Eq.(26) and Eq.(37) are now in closed form, which truncates the DEOM at level  $L$ , counting partially in the higher levels' effects. Obviously, the single-mode zeroth-level truncation recovers the conventional Caldeira-Leggett master equation [4].

### III. NUMERICAL VALIDATION

In this section, we analyze the control criterion for the above DEOM level truncation, followed by numerical illustrations comparing the performances between CL and COP truncation schemes. The criterion is made by comparing the damping factor  $\Gamma_{\mathbf{n}}^{(n)}$  associated with each

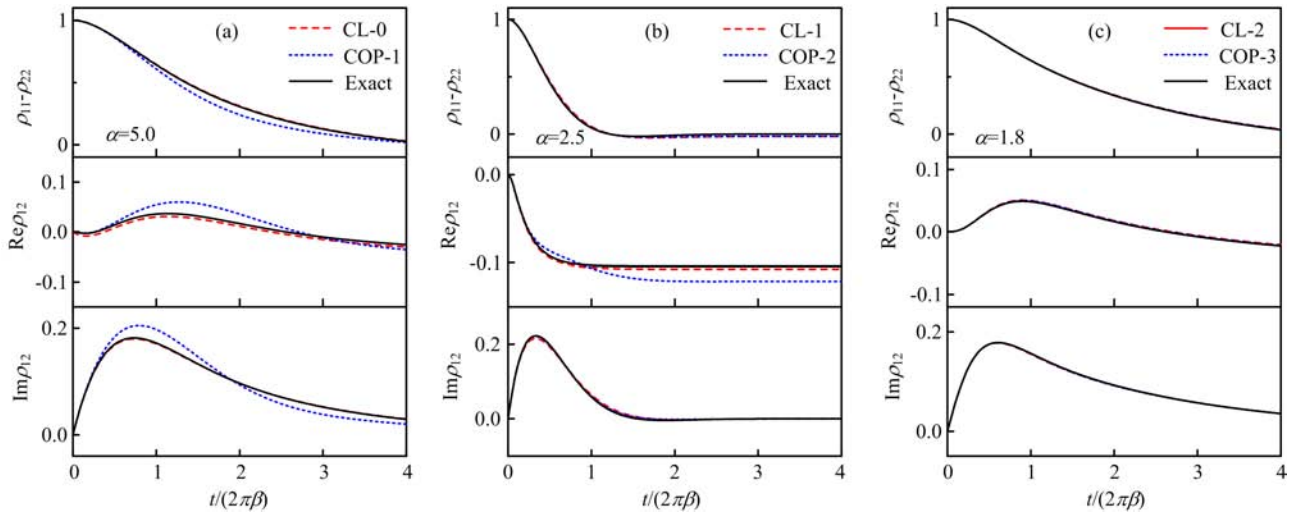


FIG. 1 Dynamics of  $\rho(t)$  for the electron transfer systems: (a)  $\alpha=5.0$ ,  $\beta\lambda=0.6$ ,  $\beta\gamma_D=3$ ,  $\beta\epsilon=-0.2$ ,  $\beta V=0.1$ , (b)  $\alpha=2.5$ ,  $\beta\lambda=1.0$ ,  $\beta\gamma_D=2.5$ ,  $\beta\epsilon=0.0$ ,  $\beta V=0.25$ , (c)  $\alpha=1.8$ ,  $\beta\lambda=0.3$ ,  $\beta\gamma_D=1.0$ ,  $\beta\epsilon=-0.3$ ,  $\beta V=0.1$ .

individual DDO to the bath fluctuations denoted as  $\Lambda_{ab}$  and reorganizations  $\lambda_{ab}$ , as well as the characteristic system frequency  $\Omega_S$ . For the Drude model of this work, the bath fluctuation amplitudes are estimated via

$$\begin{aligned}\Lambda_{ab} &= \sum_k |\text{Re}(\eta_{abk})| \int_0^\infty dt e^{-\gamma_k t} \\ &= \sum_k \frac{|\text{Re}(\eta_{abk})|}{\gamma_k}\end{aligned}\quad (38)$$

The Markovianity parameter for DDOs at the  $n$ th level is then proposed as

$$\alpha^{(n)} = \frac{\min\{\Gamma_{\mathbf{n}}^{(n)}\}}{\max\{\{\Lambda_{ab}\}, \{\lambda_{ab}\}, \Omega_S\}}\quad (39)$$

where the numerator can also be recast as  $\min\{\Gamma_{\mathbf{n}}^{(n)}\} = n \min\{\gamma_k\}$  and the denominator is independent of  $n$ . Thus this Markovianity parameter can actually be expressed as  $\alpha^{(n)} = n\alpha$  where  $\alpha \equiv \alpha^{(1)}$ . The Markovian limit is reached when  $\alpha^{(n)} \gg 1$ . Based on our calculations so far, we find that  $\alpha^{(n)} \gtrsim 5$  would be roughly sufficient. The truncation level  $L$  for the COP scheme would be determined with  $\alpha^{(L)} \gtrsim 5$  and that for the CL scheme be with  $\alpha^{(L+1)} \gtrsim 5$ . With controlled truncations, the number of DDOs could be fixed before simulations, unlike the on-the-fly filtering algorithm [19].

We also illustrate the performances of proposed level control schemes. We take, for example, the two-level electron transfer systems, with the reduced system Hamiltonian given as

$$H_S = (\epsilon + \lambda)|b\rangle\langle b| + V(|a\rangle\langle b| + |b\rangle\langle a|)\quad (40)$$

and the dissipative mode being

$$\hat{Q} = |b\rangle\langle b|\quad (41)$$

here,  $\epsilon$  and  $\lambda$  represent the reaction endothermicity and solvation reorganization, respectively, while  $V$  denotes the transfer coupling strength. The characteristic system frequency is then  $\Omega_S = \sqrt{\epsilon^2 + 4V^2}$ .

Figure 1 shows the results calculated with the [0/0]-PSD scheme [14] by the following equation [20]

$$C(t) \simeq (\eta_D^r - i\eta_D^i)e^{-\gamma_D t} + 2\Delta\delta(t)\quad (42)$$

with

$$\eta_D^r = \frac{2\lambda}{\beta} - \Delta\gamma_D, \quad \eta_D^i = \lambda\gamma_D, \quad \Delta = \frac{1}{6}\beta\lambda\gamma_D\quad (43)$$

The accuracy for this selected  $K$ -space expansion has been verified with its related criterion [20].

Figure 1 reports the electron transfer dynamics where the truncation scheme plus level adopted in each calculation are indicated. The performance of the criterion parameter for control of truncation is clearly demonstrated. It is also found that the results from CL truncation are comparable to or even better than those from COP truncation at one more level, for the systems studied here.

#### IV. CONCLUSION

The Caldeira-Leggett master equation form of truncation is derived for general multi-mode system-bath couplings to close the DEOM formalism in this work. Proposed also is *a priori* accuracy control criterion; to determine the terminated level for both the CL and the conventional COP truncation schemes. Performances of the criterion and the CL truncation scheme are illustrated with simple electron transfer systems. Based on the idea of this work, more generalized, extensively applicable and efficient accuracy-controlled DEOM meth-

ods for more complicated system-bath couplings are carrying on and will be published elsewhere.

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