Optimizing hierarchical equations of motion for quantum dissipation and quantifying quantum bath effects on quantum transfer mechanisms

Jin-Jin Ding,1 Rui-Xue Xu,1,a) and YiJing Yan1,2
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

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We present an optimized hierarchical equations of motion theory for quantum dissipation in multiple Brownian oscillators bath environment, followed by a mechanistic study on a model donor-bridge-acceptor system. We show that the optimal hierarchy construction, via the memory-frequency decomposition for any specified Brownian oscillators bath, is generally achievable through a universal pre-screening search. The algorithm goes by identifying the candidates for the best be just some selected Padé spectrum decomposition based schemes, together with a priori accuracy control criterions on the sole approximation, the white-noise residue ansatz, involved in the hierarchical construction. Beside the universal screening search, we also analytically identify the best for the case of Drude dissipation and that for the Brownian oscillators environment without strongly underdamped bath vibrations. For the mechanistic study, we quantify the quantum nature of bath influence and further address the issue of localization versus delocalization. Proposed are a reduced system entropy measure and a state-resolved constructive versus destructive interference measure. Their performances on quantifying the correlated system-environment coherence are exemplified in conjunction with the optimized hierarchical equations of motion evaluation of the model system dynamics, at some representing bath parameters and temperatures. Analysis also reveals the localization to delocalization transition as temperature decreases. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4724193]

I. INTRODUCTION

Hierarchical equations of motion (HEOM) theory for quantum open systems is emerging as a fundamental formalism in quantum statistical mechanics.1–7 It is exact and nonperturbative, assuming only the Gaussian statistics for interacting environment influence. HEOM is equivalent to Feynman-Vernon influence functional path integral theory,8,9 but much more operationally friendly and numerically efficient in applications. It has been applied to various systems, such as electron transfer,10–12 transient quantum transport,13–15 and nonlinear optical spectroscopy,16–20 including coherent two-dimensional electronic spectra on a model of light-harvesting Fenna-Matthews-Olson proteins.21,22

Efficient HEOM methods are needed not just for simulating such as multidimensional spectroscopic signals but also for analyzing the underlying mechanisms in the functions of complex molecular systems. There has been much effort on developing efficient HEOM methods. In particular, Shi and co-workers developed the on-the-fly numerical filtering algorithm, implemented with a properly scaled HEOM.23 This algorithm can dramatically reduce the effective number of HEOM dynamics variables and meanwhile also automatically truncate the level of hierarchy. Ding et al. proposed for Drude dissipation an optimized HEOM theory,16 constructed on the basis of the Padé spectrum decomposition (PSD) of Bose function.24,25 To advance HEOM as a standard tool in computational nonlinear spectroscopy, we have also put forward a mixed Heisenberg-Schrödinger scheme with block-matrix implementation on efficient HEOM evaluation of third-order optical response function.20 It is also worth to mention that the HEOM propagator is suited perfectly for the usage of graphics processing units, which has been recently implemented by Kramer and co-workers.22,26 Nevertheless, efficient HEOM methods developed by now are almost limited with the Drude dissipation case, where the influence of bath assumes purely diffusive. Although there have been a few applications,12,27–29 existing machineries for efficient HEOM dynamics in non-Drude environment remain far from satisfactory.

In this work, we develop an optimized HEOM theory for a class of non-Drude environment, followed by a mechanistic study to address some issues on correlated system-bath coherence and locality versus nonlocality. For the optimized HEOM theory, we consider multiple Brownian oscillators (BOs) environment that covers a broad range of reality. Individual BO can be either underdamped or overdamped or strongly overdamped (diffusive). We examine a total of 13 HEOM constructions. One is the conventional Matsubara spectrum decomposition (MSD) based formalism, while others are stemmed from three PSD approximants of Bose function.24,25 Actually, the search for the best or numerically most efficient HEOM formalism, among all sum-over-poles schemes, needs only be carried out with those 12 PSD-based constructions and some of their combinations if needed. We propose a priori accuracy control

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1Electronic mail: rxxu@ustc.edu.cn.
criterions for computer-aided search for the best. Beside this universal approach, we also identify analytically that the \([N/N]\) scheme be the best for the case of Drude dissipation\(^{19}\) and the \([N + 1/N]\) be the best for the Brownian oscillators dissipation in the absence of strongly underdamped bath vibrations.

The mechanistic study, in conjunction with the optimized HEOM evaluation, will be illustrated on the population transfer dynamics in a model donor-bridge-acceptor (D-B-A) system. We concern about the quantum versus classical nature of bath influence and the locality versus nonlocality of reduced system. Proposed are a reduced system entropy measure and a state-resolved constructive versus destructive interference measure, for quantifying the correlated system-environment coherence. Their performances are exemplified with the model system, at some representing bath parameters and temperatures. Revealed is also the underlying localization to delocalization transition as temperature decreases.

The paper is organized as follows. We overview the related background in Sec. II, covering the HEOM formalism (see also the Appendix), the BO model, and the PSD schemes. In Sec. III, we present the details about the universal screening search for the optimal hierarchy construction, via the memory-frequency decomposition for any specified Brownian oscillators bath. In Sec. IV, we analytically identify the best for the Drude dissipation and that for the Brownian oscillators environment in the absence of strongly underdamped bath vibrations. Numerical demonstrations in Sec. V are carried out in conjunction with a mechanistic study for the population transfer dynamics in a model donor-bridge-acceptor system. Finally, we conclude in Sec. VI.

II. BACKGROUND

A. Hierarchical equations of motion formalism

HEOM describes the correlated system-environment dynamics,\(^{2-7}\) through a set of linearly coupled auxiliary density operators (ADOs), in which the reduced system density operator, \(\rho(t) \equiv \text{tr}_B \rho_{\text{BO}}(t) \equiv \rho_{\text{BO=0}}(t)\), is just the zeroth-tier one. The system Liouvillian \(\mathcal{L}(t) \equiv [H(t), \cdot]\) can be time dependent, for example, in the presence of laser field. The system-bath coupling assumes the form of \(H'(t) = -\tilde{Q} \hat{F}_B(t)\) (or a sum of such terms), with \(\tilde{Q}\) being a system operator and \(\hat{F}_B(t)\) a bath operator. The latter is given in the bath Hamiltonian \(h_B\)-interaction picture, \(\hat{F}_B(t) \equiv e^{i\hbar \tilde{Q} t} \hat{F}_B e^{-i\hbar \tilde{Q} t}\), to specify its stochastic nature. We set \(\hbar = 1\) and \(\beta = 1/(k_B T)\) hereafter. Assuming \(\hat{F}_B(t)\) a Gaussian stochastic thermodynamics process, the effect of bath environment on system is completely determined by the bath correlation function \(C(t) \equiv \langle \hat{F}_B(t) \hat{F}_B(0) \rangle\). It is related to the environment spectral density \(J(\omega)\) via the fluctuation-dissipation theorem:\(^{30,31}\)

\[
C(t) = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \frac{e^{-i\omega t} J(\omega)}{1 - e^{-\beta \omega}} = \sum_{k=1}^{N+1} C_k e^{-\gamma_k t} + \delta C_N(t). \tag{1}
\]

The second identity above is evaluated via the Cauchy’s residue theorem in contour integration. It includes \(N\) poles from Bose function \(f(\omega) = \frac{1}{e^{\beta \omega} - 1}\) and \(N'\) poles from spectral density \(J(\omega)\), in the lower-half plane. We treat \(J(\omega)\) by the BOs bath model (Sec. II B), so that the unexpanded residue is written as \(\delta C_N(t)\), with \(\delta C_N \to \infty(0) = 0\). An individual pole from the bath spectral density can be complex in general; thus, Eq. (1) represents physically a memory-frequency decomposition of the bath correlation.

The exponential expansion of bath correlation function dictates HEOM,\(^{5-7}\)

\[
\rho_n(t) = -[i \mathcal{L}(t) + \gamma_n + \delta R_n] \rho_n(t) + \rho_n^{(-1)}(t) + \rho_n^{(+1)}(t). \tag{2}
\]

an explicit form (see the Appendix). In other words, the bath memory-frequency decomposition scheme serves effectively as a statistical environment basis set of size \(K = N + N'\) for HEOM construction. The resulting ADO \(\rho_n \equiv \rho_{n_1 \ldots n_K}\) is of the leading \(n_K\)th-order dependence\(^{5}\) on individual exponential component of \(C(t)\) and goes by the complex damping parameter \(\gamma_n = \sum_{k=1}^{K} n_k \gamma_k\). Let \(n = n_1 + \ldots + n_K\) be the tier of \(\rho_n\). In general, an \(n\)-th-tier ADO, \(\rho_n\), couples to its associated \((n + 1)\)th-tier ADOs, as symbolically described by \(\rho_n^{(\pm)}\) in Eq. (2), whose explicit expression is given in the Appendix. The total number of ADOs amounts to \(\sum_{n=0}^{L} \frac{(n+K-1)!}{n!(K-1)!} = \frac{L+K}{K!}\), where \(L\) denotes the highest tier level being considered. At this level, the system-bath coupling is accounted for at least to the \((2L)\)th order.\(^{5}\) As a result, HEOM resembles a configuration interaction formalism in many-particle quantum mechanics. In particular, the \(n\)-th-tier ADO \(\rho_n\) accounts for the specified \(n\)-“dissipaton” configuration in the HEOM dynamics of correlated system-bath coherence. In Eq. (2), \(\delta R_n\) denotes the residue dissipation superoperator due to the off-basis-set residue \(\delta C_N(t)\). In general it has to be treated with certain approximations.\(^{5,6}\) Among those tested to date the white-noise-residue ansatz is the only generally controllable and often is also the best.\(^{5,6,19,32}\) Thereby the quest of optimizing HEOM, as illustrated in Sec. III, is to search for the minimum-\(K\) memory-frequency decomposition scheme, altogether with an accuracy control over the white-noise-residue ansatz.

B. Brownian oscillators bath

The decomposition scheme for environment spectral density function is made in contact with molecular reality through BOs decomposition of \(J(\omega) = \sum_\alpha J_\alpha(\omega)\), where\(^{30,31}\)

\[
J_\alpha(\omega) = \text{Im} \left( \frac{2\lambda_\alpha \omega_\alpha^2}{\omega_\alpha^2 - \omega^2 - i \zeta_\alpha \omega} \right). \tag{3}
\]

Here \(\lambda_\alpha = \int d\omega J_\alpha(\omega)/2(\pi \omega)\) is contribution to the overall reorganization energy, \(\lambda = \sum_\alpha \lambda_\alpha\), and proportional to the system-bath coupling strength.\(^{30,31}\) The Huang-Rhys factor is given by \(S_\alpha = \lambda_\alpha/\omega_\alpha\) in the damping-free oscillator limit. Each BO (specified by \(\omega_\alpha\) and \(\zeta_\alpha\) hereafter) has two poles in the lower-half plane, and thus contributes in general two exponential terms to \(C(t)\) in Eq. (1), with \(\gamma_\alpha^{\pm} \in \{\gamma\}\) and
C. Three PSD approximants of Bose function
Consider now the Bose function (denoting \( x \equiv \beta \omega \)):
\[
f(x) = \frac{1}{1 - e^{-x}} = \frac{1 + \coth(x/2)}{2} = \frac{1}{2} \left( 1 + \frac{x}{x^2 + (2\pi j)^2} \right).
\] (8)
The conventional MSD approach is
\[
f(x) \approx f_N^{\text{MSD}}(x) = \frac{1}{2} + \frac{1}{x} + \sum_{j=1}^{N} \frac{2x}{x^2 + (2\pi j)^2}.
\] (9)
It becomes exact in the limit of \( N \to \infty \). However, MSD is notorious for slow convergence. Apparently, any sum-over-poles scheme such as MSD amounts to a certain fraction form, \( \Phi(y) \approx \frac{P_M(y)}{Q_N(y)} \), with \( y = x^2 \), where \( P_M(y) \) and \( Q_N(y) \) are polynomials of order \( M \) and \( N \), respectively. However, it is well established \( ^{33} \) that the Padé approximant (denoted as \([M/N]\)) is the best for right the form and accurate up to the order of \( O(y^{M+N}) \).
Denote hereafter \( f^{[M/N]}(x) \) the resulting Padé approximant of Bose function. For a general \( M \), the poles of \( f^{[M/N]}(x) \) are complex. However, we have shown that the following three of them classified as PSD schemes are of only pure imaginary poles. \( ^{25} \)
\[
f^{[N-1/N]}(x) = \frac{1}{2} + \frac{1}{x} + \sum_{j=1}^{N} \frac{2\eta_j x}{x^2 + \xi_j^2},
\] (10)
\[
f^{[N/N]}(x) = \frac{1}{2} + \frac{1}{x} + \sum_{j=1}^{N} \frac{2\eta_j x}{x^2 + \xi_j^2} + R_N x,
\] (11)
and
\[
f^{[N+1/N]}(x) = \frac{1}{2} + \frac{1}{x} + \sum_{j=1}^{N} \frac{2\eta_j x}{x^2 + \xi_j^2} + \tilde{R}_N x + \tilde{R}_N x^3.
\] (12)
They are exact up to \( O(x^{4N-1}), O(x^{4N+1}), \) and \( O(x^{4N+3}) \), respectively. We have also shown \( ^{25} \) that the accuracy length of each individual PSD scales as \( N^2 \), while that of MSD is only of \( N \). The PSD pole \( \xi \)-parameters are all real and positive, and can therefore be used to define the PSD frequencies, in analogy with the Matsubara frequencies. The PSD \( \eta \)-coefficients are all real and positive. All these PSD parameters can be evaluated readily with high precision. \( ^{25} \) With a PSD approximant, Bose function contributes to the bath correlation function \( C(t) \) of Eq. (1) \( N \) exponential terms. The exponents are just the PSD frequencies, such as \( \{ \gamma_j = \xi_j/\beta; j = 1, \ldots, N \} \), in relation to the pole parameters. Note that a bosonic spectral density is an odd function, \( ^{31} \) i.e., \( J(-\omega) = -J(\omega) \). Therefore, the coefficients \( \{ \epsilon_j = -2\eta_j(\gamma_j) / \beta \} \) associating with PSD frequencies in Eq. (1) are all real.

Unlike the Matsubara counterparts, the PSD frequencies and coefficients are both scheme- and \( N \)-dependent. Below is an example of the \([N+1/N]\) PSD frequencies and coefficients for Bose function with \( N = 6 \)
\[
\begin{align*}
\tilde{\xi}_j & = 1.000, 1.000, 1.000, 1.003, 1.069, 1.447, \\
\tilde{\eta}_j & = 1.000, 1.000, 1.000, 1.055, 1.842, 6.006.
\end{align*}
\] (13)
We see that PSD tails primarily those poles and coefficients close to $N$ from the MSD counterparts. Thus in a sense PSD can be viewed as an optimally corrected finite Matsubara expansion.\(^{24,25}\)

Both $[N/N]$ and $[N + 1/N]$ of Bose function $[\text{Eqs. (11) and (12)}]$ diverge at large $x$, while $[N − 1/N]$ [Eq. (10)] approaches to $x^{−1}$. The divergence parameter $R_N$ in $[N/N]$ has the expression $R_N = [4(N + 1)(2N + 3)]^{−1}$, but those for $\tilde{R}_N$ and $\tilde{T}_N$ in $[N + 1/N]$ are rather complicated\(^{25}\) and thus plotted in Fig. 2 for visualization. We observe that $\tilde{R}_N$ and $\tilde{T}_N$ behave similarly, while $\tilde{T}_N$ that is negative\(^{25}\) scales approximately as $\tilde{T}_N \propto N^{−α}$, for large $N$. Note that we may make use of the divergence of the given Bose function approximant to achieve the white-noise residue limit, i.e., $\delta C_N(t) \propto δ(t)$ in Eq. (1). It would lead to an optimized HEOM, as elaborated in Sec. III.

III. OPTIMIZING HEOM WITH ACCURACY CONTROL: GENERAL CONSIDERATIONS

A. The bath decomposition schemes

As mentioned earlier the memory-frequency decomposition of bath correlation function in Eq. (1) serves as a statistical environment basis set of size $K = N + N'$ for HEOM construction. We request for the minimum-$K$ memory-frequency decomposition scheme, together with an accuracy control over the white-noise-residue ansatz (see Sec. III B) for a partial resum of the off-basis-set contribution. With given BO bath parameters, the best bath memory-frequency decomposition scheme that leads to the most efficient HEOM construction is therefore of the smallest $N$. Evidently, the best will go to one of the PSD-based bath decompositions. In general, a computer-aided search can be readily carried out among a total of 12 PSD-based schemes to be specified soon, together with the standard MSD approach for the sake of completeness. We will also show in Sec. IV that for BO bath with $r_{BO} \geq 0.5$, the best can be identified analytically.

To proceed, we recast the second identity of Eq. (1) as

$$C(t) = C_N^{\text{Bose}}(t) + C_J(t) + δC_N(t).$$

(14)

Here $C_N^{\text{Bose}}(t)$ in exponential series arises from the $N$ poles of a given Bose function approximant. For the exponential series $C_J(t) \sim e^{-\gamma_{\text{BO}}t}$ arising from the poles of spectral density $J(\omega)$, there are two options for the Bose function $f_{\text{Bose}}(z)$ in determining the coefficients by Eq. (5): the exact one versus the same approximant for $C_N^{\text{Bose}}(t)$. The latter is often (but not always) the choice. We will discuss this issue in Sec. IV. Once the approximant for $C_N^{\text{Bose}}(t)$ and the way of treating $C_J(t)$ are decided, the corresponding residue follows as $δC_N(t) \equiv (C(t) - C_N^{\text{Bose}}(t)) - C_J(t)$.

For the 12 PSD-based memory-frequency decomposition schemes in total, six of them are labeled by

$$[M/N]_X$$

and $[M/N]_Y$, with $M = N − 1, N, N + 1$.\(^{15}\)

Adopted for $C_J(t)$ in $[M/N]_X$ is the exact Bose function, while that in $[M/N]$ is the same PSD approximant as in $C_N^{\text{Bose}}(t)$. Another six PSD-based schemes are labeled by

$$[M/N]'_X$$

and $[M/N]'_Y$, with $M = N − 1, N, N + 1$.\(^{16}\)

They exploit $[M + 1/N + 1]$ PSD of Bose function, but retaining only the first $N$ poles explicitly in the exponential expansion of $C_N^{\text{Bose}}(t)$, while including the $(N + 1)$th pole contribution into the residue $δC_N(t)$.\(^{29}\) This treatment arises from the observation [cf. Eq. (13)] that the last contributed exponential term of a PSD scheme for Bose function to $C(t)$ may be well approximated by a Markovian $δ$-function and therefore be included into the residue. Moreover, the $C_J(t)$ in $[M/N]'_X$ goes with the exact Bose function, while that in $[M/N]'_Y$ goes with $C_N^{\text{Bose}}(t)$ of $[M + 1/N + 1]$ PSD counterpart.

Note that the above 12 PSD-based schemes are often used in a combined manner, as a complex dissipative system in reality has many $Q$-modes and the bath coupling with each of them has multiple BO components. While independent $Q$-modes are treated individually, the combined PSD-based schemes for multiple BOs in each $Q$ should have common PSD poles for the involving Bose function approximant (except for those particular BO modes that need no PSD poles at all). For completeness we may also consider the commonly adopted MSD scheme, in which $C_J(t)$ goes with the exact Bose function. This is often the best in the MSD family.

B. Accuracy control on white noise residue ansatz

The optimized HEOM to be developed in this work goes with the white-noise-residue ansatz,

$$δC_N(t) \approx 2DA_Nδ(t).$$

(17)

It leads to $δR_N = \Delta_N[Q, [Q, .]]$ for HEOM (2), at all tiers. This is by far the only generally controllable and also often the best among various tested methods of residue treatment.\(^{6,19,29}\)

The accuracy control can then be analyzed in principle by considering the fact that the only approximation involved in HEOM is the white noise residue of $δC_N(t)$ by Eq. (17). The criterion on the applicability of HEOM comprises therefore the conditions under which $δC_N(t)$ and its effect on the reduced system dynamics can be treated as Markovian white.
noise.\textsuperscript{11, 19, 34} We demand \textit{a priori} accuracy control or estimation on the resulting HEOM dynamics for general systems at finite temperatures. Apparently, the unapproximated $\delta C_N(t)$ is a real and even function. The residue spectrum $\delta C_N(\omega) \equiv \frac{1}{\Omega_0} \int dt \, e^{\omega t} \delta C_N(t)$ is symmetric.

The validation of white-noise-residue ansatz goes as follows: (i) \textit{Prerequisite of line shape}: Residue spectrum $\delta C_N(\omega)$ be monotonic in $\omega \in [0, \infty)$, varying from $\delta C_N(\omega = 0) = \Delta_N \neq 0$ to $\delta C_N(\omega \rightarrow \infty) = 0$; (ii) \textit{Control parameters} $\{\Gamma_N, \kappa_N\}$: Define the residue modulation parameter:\textsuperscript{19, 35, 36}

$$\kappa_N \equiv |\Gamma_N / \Delta_N|^{1/2},$$

with $\Gamma_N$ being the residue spectrum width, at which $\delta C_N(\omega = \Gamma_N) = \delta C_N(\omega = 0)/2 = \Delta_N/2$. Denote the characteristic system frequency as $\Omega_c$. The white-noise-residue ansatz becomes exact when $\Gamma_N \gg \Omega_c$, and $\kappa_N \gg 1$. In practice it is found that the HEOM dynamics is numerically accurate when\textsuperscript{11, 19, 34}

$$\min(\Gamma_N / \Omega_c, \kappa_N) \gtrsim 5.$$  \hspace{1cm} (19)

It can be used as the accuracy control criterion, upon the residue line shape prerequisite is satisfied.

\section*{C. Search for the best HEOM construction}

The established criterions above guide the universal, computer-aided screening search for the best, case by case (except for those the best can be identified analytically; see Sec. IV). In general, given the BO bath parameters, one can always screen by the criteria, over all those 12 PSD-based and the MSD-based bath decomposition schemes, together with their proper combinations as detailed in Sec. IIIA, identify the best one, and then construct the most efficient HEOM. The results of screening are reported in terms of the control parameters $\{\Gamma_N, \kappa_N\}$, whenever the prerequisite of residue line shape is satisfied. As a small token it is worth to mention that the prerequisite failure by $\delta C_N(\omega = 0) = 0$ occurs for any pure $[N - 1/N]$-based scheme in all cases. The same failure occurs also for the $[N/N]$-based scheme in the absence of Drude bath mode. This is also the reason why the MSD-based scheme adopts the exact Bose function to evaluate its $C(t)$ part.

It turns out the dummy search needs only for the cases involving strongly underdamped ($r_{BO} < 0.5$) BO bath modes. The reason behind is the friction spectrum $J(\omega)/\omega$ in this region does not peak at $\omega = 0$, leading to some seemingly advanced PSD-based scheme failure on the prerequisite of residue line shape. For example, for $\{r_{BO}, \beta_0/\omega_{BO}\} = \{0.04, 1\}$, the $[N + 1/N]$ scheme does not satisfy the prerequisite, while $[N + 1/N]_{1x}$ serves as the best scheme, as seen from Fig. 3, provided $N = 1$ is sufficient for the given system and temperature at study. On the other hand, for $\{r_{BO}, \beta_0/\omega_{BO}\} = \{0.01, 50\}$, $[N/N]_{1x}$ turns out to be the best (not depicted here). Note also that when Drude modes and BO modes coexist, dummy search may also be needed.

\section*{IV. TWO SPECIAL CASES: ANALYTICAL IDENTIFICATIONS}

There are two special cases where the best can be identified analytically. The first one is the pure Drude dissipation (all $r_{BO} \gg 1$), for which the best scheme is $[N/N]$. The second case is the pure BO dissipation with all $r_{BO} \geq 0.5$, for which the best scheme is $[N + 1/N]$. The common feature for these two special cases is that their friction spectrum $\omega J(\omega)/\omega$ has only one peak centered at $\omega = 0$. This feature is closely related to the residue spectrum line shape requirement for the subsequent white-noise-residue treatment. Identifying the best for these two cases follows the same analysis, as illustrated with the Drude dissipation case here.

\subsection*{A. $[N/N]$ the best for Drude dissipation}

 Apparently, for the pure Drude dissipation [Eq. (6)] case, the best scheme can be analyzed with $[N/N]$ versus $[N/N]_{1x}$ only, comparing their resultant approximations in the bath spectrum $C(\omega) = J_D(\omega)/\beta_0$ in $[N/N]$ versus $[N/N]_{1x}$ only, comparing their resultant approximations in the bath spectrum $C(\omega) = J_D(\omega)/\beta_0$ in $[N/N]_{1x}$, which is accurate up to $\mathcal{O}(0.01)$. On the other hand, the $[N/N]_{1x}$ scheme assumes an effective BO function approximant, i.e., $C_{[N/N]_{1x}}(\omega)/J_D(\omega) = 1/[\omega^2 + \beta_0^2/2\kappa^2]$, which will be verified below be accurate only at the zeroth order of $\beta_0$. In fact we have [cf. Eq. (24)]

$$f_{\text{eff}}^{[N/N]_{1x}}(\omega) = \frac{(\Delta_N^X - \Delta_N^\beta) \omega}{2\kappa^2} + f^{[N/N]}(\omega),$$

where $\Delta_N^X$ and $\Delta_N^\beta$ are the white-noise amplitudes of the $[N/N]_{1x}$ and $[N/N]$ schemes, respectively. The above observation highlights the fact that the $[N/N]$ scheme is the best for Drude dissipation. It fully utilizes the high precision of the Padé approximation of Bose function and meanwhile results in automatically a white noise residue for Drude dissipation.
The proof of Eq. (20) below will go along with the evaluation of the related parameters in the two captioned schemes. $C_{[N/N]}(t) = C_{N}^{\text{Bose}}(t) + c e^{-\gamma t} + 2\Delta_N \delta(t)$ versus $C_{[N/N \lambda]}(t) = C_{N}^{\text{Bose}}(t) + c e^{-\gamma t} + 2\Delta_N \delta(t)$. They share the same $C_{N}^{\text{Bose}}(t) = \sum_{j=1}^{N} c_j e^{-\gamma_j t}$ associated with the [N/N]-Bose function poles; see Eq. (25) for the $c_j$ coefficients. Let us start with the [N/N] scheme. Its bath spectrum $C_{[N/N]}(\omega) = J_D(\omega)\sqrt{\kappa_N}(\omega)$ has a constant term that corresponds also to white noise residue amplitude, i.e., $C_{[N/N]}(\omega \to \infty) = 2\beta \gamma_D \kappa_N N = \Delta_N$. We obtain

$$c_D = -2i \lim_{\xi \to -i\gamma_D} \{ (z + i\gamma_D)[C_{[N/N]}(z) - C_{[N/N]}(\infty)] \} = \left( \frac{2\lambda}{\beta} - \gamma_D \Delta_N - \gamma_D \sum_{j=1}^{N} \frac{c_j}{\gamma_j} \right) - i\lambda \gamma_D. \quad (21)$$

Turn now to the [N/N\lambda] scheme. It uses the exact Bose function to evaluate $C_{J}(t) = c e^{-\gamma t}$, i.e.,

$$C_X = -2i \gamma_D f(z)|_{z=-i\gamma_D} = \lambda \gamma_D \cot(\beta \gamma_D/2) - i\lambda \gamma_D,$$

and consequently

$$\Delta_X^N = \frac{2\lambda}{\beta \gamma_D} - \lambda \cot(\beta \gamma_D/2) - \sum_{j=1}^{N} \frac{c_j}{\gamma_j}. \quad (23)$$

It is now easy to verify that $c_X - c_D = -\lambda \gamma_D(\Delta_X^N - \Delta_N)$. Consequently,

$$C_{[N/N\lambda]}(\omega) - C_{[N/N]}(\omega) = \frac{\gamma_D(c_X - c_D)}{\omega^2 + \gamma_D^2} + \left( \frac{\Delta_X^N - \Delta_N}{\omega^2 + \gamma_D^2} \right) = \left( \frac{\Delta_X^N - \Delta_N}{\omega^2 + \gamma_D^2} \right) \omega \lambda \gamma_D(t)/2(\lambda \gamma_D). \quad (24)$$

We have thus proved Eq. (20). It states that $C_{[N/N\lambda]}(\omega)$ has an effective Bose function approximant inaccurate even at $O(\beta \omega)$. In fact, [N/N\lambda] could even be worse than the conventional MSD-based scheme in some parameter range. It is also noticed that the difference in Eq. (24) may be practically insignificant in the high temperature limit. Nevertheless, the [N/N] is the best for Drude dissipation, in the full range of its parameters.

To exemplify the validity of the involving white noise residue ansatz, we demonstrate in Fig. 4 the evaluated $\delta C_N(\omega)$, with $N = 1$, comparing between the [N/N] (solid black), [N/N\lambda] (red dash), and MSD (blue dot) schemes. The four panels are for four different regimes: (a) $\beta \gamma_D = 1$ representing for the moderate or high-temperature regime; (b) $\beta \gamma_D = 6.2$ for the Drude frequency $\gamma_D$ near the Matsubara frequency $2\pi n \beta$; (c) $\beta \gamma_D = 6.5$ near the [1/1]-PSD pole of $\xi_l = \sqrt{2}\xi_1$; and (d) $\beta \gamma_D = 10$ for low-temperature. The corresponding accuracy control parameters in terms of $[\Gamma_N \equiv \beta \Gamma_N, \xi_N \equiv \sqrt{\beta \kappa_N}]$ are reported in Table I. They clearly demonstrate that the [N/N] scheme is the best in all regimes. Although the [N/N\lambda] is similar to the [N/N] scheme in the moderate or high-temperature condition, it does not perform well and can even be worse than MSD in the low-temperature region, due to its low-order precision, as analyzed earlier. Moreover, [N/N\lambda] performs notoriously when the bath parameter is close to its divergent points, as seen from Figs. 4(b) and 4(c).

The [N/N] scheme is the best for the Drude dissipation, enjoying the following properties. (i) Its residue spectrum $\delta C_N(\omega)$ always has the proper line shape. (ii) Both the accuracy control parameters $\Gamma_N$ and $\xi_N$ increase about quadratically with $N$. Criterion analysis on the [N/N] scheme for Drude dissipation were detailed in Ref. 19, together with the simple expressions of $\Gamma_N$ and $\kappa_N$. (iii) It converges uniformly in the full range of Drude parameters. To complete this statement, let us consider the special value, $\gamma_D = \gamma_j = \xi_j/\beta$, coinciding with one of the [N/N] Bose function poles. The corresponding $c_j e^{-\gamma_j t}$ term in $C_{N}^{\text{Bose}}(t)$ will diverge, as the coefficient is given by

$$c_j = -2i \lambda \gamma_j J_D(z = -i\gamma_j)/\beta = \frac{4\lambda \gamma_j \eta_j \gamma_j/\beta}{\gamma_j^2 - \gamma_D^2}. \quad (25)$$

This coefficient involves however also in $c_D$ of Eq. (21), as the [N/N] scheme exploits the same Bose function approximant for both $C_J(t)$ and $C_{N}^{\text{Bose}}(t)$. We shall therefore treat the related two terms together, resulting in

$$\lim_{\gamma_D \to \gamma_j} \left( c_j e^{-\gamma_j t} - \gamma_D \frac{c_j}{\gamma_j} e^{-\gamma_D t} \right) = 2\eta_j \lambda \beta (e^{-\gamma_j t} - \gamma_D e^{-\gamma_D t}).$$

**TABLE I.** The scaled accuracy control parameters $[\Gamma_N, \xi_N]$, corresponding to each residue function in Fig. 4.

<table>
<thead>
<tr>
<th>Panel</th>
<th>[1/1]</th>
<th>[1/1]x</th>
<th>MSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>[31.5, 25.1]</td>
<td>[31.5, 25.1]</td>
<td>[29.9, 18.7]</td>
</tr>
<tr>
<td>(b)</td>
<td>[33.0, 10.3]</td>
<td>[6.3, 0.6]</td>
<td>[21.2, 6.7]</td>
</tr>
<tr>
<td>(c)</td>
<td>[33.2, 10.1]</td>
<td>[6.5, 0.2]</td>
<td>[21.0, 6.5]</td>
</tr>
<tr>
<td>(d)</td>
<td>[35.2, 8.4]</td>
<td>[15.4, 3.4]</td>
<td>[17.5, 3.9]</td>
</tr>
</tbody>
</table>
It removes the divergence in the \([N/N]\) scheme expansion of bath correlation function. The construction of HEOM is then similar to that in the critically damped BO case, see the Appendix. Together with the normal Drude case,\(^{19}\) we complete the HEOM formalism for Drude dissipation. The \([N/N]\) leads to the best HEOM among all sum-over-poles based constructions for Drude dissipation.

**B. \([N + 1/N]\) the best for BO dissipation of \(r_{\text{BO}} \geq 0.5\)**

Following the same analysis one can immediately identify that \([N + 1/N]\) is the best for BO dissipation with \(r_{\text{BO}} \geq 0.5\). In this region, the friction spectrum \(J(\omega)/\omega\) of BO bath has only one peak centered at \(\omega = 0\). This feature guarantees the resulting residue spectrum function \(\delta C_N(\omega)\) a proper line shape for the white-noise-residue ansatz treatment that appears naturally in \([N + 1/N]\) for BO dissipation. The \([N + 1/N]\) is ruled out here, by the same reasons as the case of \([N/N]\) for Drude dissipation considered earlier. It suffers also the low-order approximation and possibility of divergence, when the white-noise-residue ansatz is employed.

As the best of all sum-over-poles schemes for BO dissipation in the \(r_{\text{BO}} \geq 0.5\) region, \([N + 1/N]\) always meet the line shape requirement for the white-noise-residue treatment of \(\delta C_N(\omega)\). As exemplified in Fig. 5, it is also observed that \(\delta C_N(\omega)/\Delta_N\) as functions of \(\omega/\Gamma_N\) all look similar with different BO parameters when \(N \geq 1\). Here \(\Delta_N \equiv \delta C(\omega = 0) = 2\beta^2 \omega_{\text{BO}}^2 \xi_N \Gamma_N < 0\). The half-width-at-half-maximum \(\Gamma_N\) is evaluated numerically. Figure 6 demonstrates the scaled accuracy control parameters, \([\Gamma_N, \xi_N]\equiv [\sqrt{\beta/\kappa_N}]\), as functions of \(\beta \omega_{\text{BO}}\) for three selected values of \(r_{\text{BO}}\). Apparently, both criterion parameters increase monotonically with \(N\).

**V. QUANTIFYING QUANTUM BATH EFFECTS ON QUANTUM TRANSFER MECHANISMS**

In conjunction of demonstrating the HEOM dynamics, we shed some light on the quantum nature of bath influence and its related mechanisms such as the localization to delocalization transition with the varying of bath parameters such as \(r_{\text{BO}}\) and temperature. The classical bath analogue of HEOM goes with a real bath correlation function \(C_C(t) = \text{Re}\, C(t)\) only, by setting the imaginary part to be zero. This classical limit is considered with the situation that \(C_C(t)\) comes from such as classical molecular dynamics or classical Fokker-Planck equation. The underlying classical fluctuation-dissipation theorem at finite temperature reproducing \(\text{Re}\, C(t) = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \, e^{-i\omega t} \bar{f}(\omega) \coth(\gamma/2)\) is not just the high-temperature limit of Eq. (1). The present choice of \(C_C(t) = \text{Re}\, C(t)\) would be more relevant to the difference between the quantum and the classical bath influence at finite temperature of study. Let \(\rho(t)\) be the classical bath counterpart of the reduced system density operator \(\rho(t)\). As a measure of the correlated system-bath coherence, consider the relative entropy related quantity,

\[
\varphi(t) \equiv 1 - \frac{S(t)}{S(\infty)} = 1 - \frac{\text{Tr}[\rho(t) \ln \rho(t)]}{\text{Tr}[\rho(0) \ln \rho(0)]} .
\] (26)

It is anticipated that \(S(t) \geq S(\infty)\), as the information loss in the classical bath simplification; thus \(0 \leq \varphi(t) \leq 1\). Proposed is also a *state-resolved interference measure* on the quantum nature of bath influence via

\[
\phi_\alpha(t) \equiv \frac{\rho_{\alpha\alpha}(t) - \rho_{\alpha\alpha}(0)}{\rho_{\alpha\alpha}(t) + \rho_{\alpha\alpha}(0)} .
\] (27)

It quantifies the constructive \((\phi_\alpha(t) > 0)\) or destructive \((\phi_\alpha(t) < 0)\) interference between the bath and system coherences on the specified state \(\alpha\) at time \(t\), in a certain physically relevant representation. Apparently, \(|\phi_\alpha| \leq 1\).

Demonstrations are carried out with quantum transfer in a three-level system, referred as a D-B-A system hereafter. The reduced system Hamiltonian assumes \(H = \sum_\alpha \epsilon_\alpha \rho_\alpha + \lambda_\alpha |\alpha\rangle\langle\alpha| + V_{DA}(|\text{D}\rangle\langle\text{B}| + |\text{B}\text{D}\rangle + V_{BA}(|\text{B}\rangle\langle\text{A}| + |\text{A}\rangle\langle\text{B}|),\) where \(\lambda_\alpha\) denotes the reorganization energy due to the environment induced on-site energy fluctuation.\(^{11,37}\) This

![](image-url) FIG. 6. The scaled accuracy control parameters \([\Gamma_N, \xi_N]\) using the \([N + 1/N]\) scheme, as functions of \(\beta \omega_{\text{BO}}\) for \(r_{\text{BO}} = 0.5\) (black), \(1\) (red), and \(2\) (blue).
model system can describe electron transfer, excitation energy transfer, or proton transfer, involving three local states. For example, it had been used in context of electron transfer in Ref. 12, where the transfer evolutions and rates were studied for their dependence on the model parameters. In the following, we focus on the quantum bath effects on quantum transfer and demonstrate the performance of the proposed measures, \(\varphi(t)\) and \(\phi_\alpha(t)\) [Eqs. (26) and (27)], on the mechanistic study.

We set the transfer couplings \(V_{DB} = V_{BA} = -140\,\text{cm}^{-1}\), and the on-site energies \(\epsilon_D = \epsilon_A = 0\) and \(\epsilon_B = 200\,\text{cm}^{-1}\), with \(\lambda_0 = 0\). Taking the donor site as initial state for the total system and bath composite, the effective dissipative modes become \(Q_\alpha = |\alpha\rangle\langle\alpha|\), with \(\alpha = B\) and \(A\), for the bridge and acceptor sites. The bath interactions with these two modes are assumed uncorrelated and each has the fixed \(\lambda_{BO} = \zeta_{BO} = 100\,\text{cm}^{-1}\).

In the following, we demonstrate the effect of bath on population transfer through comparison between \(r_{BO} = 0.25\), \(1\), and \(3\). They represent the underdamped (black curves), critically damped (red curves), and overdamped (blue curves) BO bath cases, respectively. Also note that the bath coherence decreases as \(r_{BO}\) increases. The optimized HEOM constructions for the above three cases are identified to be of [2/1, 2/1], and [2/1] when \(T = 298\,\text{K}\) (Fig. 7), and [3/2, X], [3/2], and [3/2] when \(T = 77\,\text{K}\) (Fig. 8), respectively.

Figures 7 and 8 depict the time evolutions of the relative entropy related quantity \(\varphi(t)\) (a panels), the population evolution (b panels), and the state-resolved interference measure \(\phi_\alpha(t)\) (c panels), at 298 K and 77 K, respectively. Note that \(\varphi(t)\) is a representation-independent measure, which would be zero if the bath were treated as classical. Evidently as shown in Figs. 7(a) and 8(a), \(\varphi(t)\) quantifies the regular trends as anticipated. (i) The quantum nature of bath influence is more prominent in the case of underdamped BO bath and at low temperatures. The overdamped BO bath influence at the high temperature in study, i.e., the blue curve in Fig. 7(a), is close to the classical behavior with \(\varphi(t) \approx 0\). While the same regular trend is also observed in Fig. 7(c) at 298 K, for the \(r_{BO}\)-dependence of the state-resolved constructive versus destructive interference measure \(\phi_\alpha(t)\), a certain “irregularity” occurs in Fig. 8(c) where \(T = 77\,\text{K}\). We will elaborate the physical origin behind the irregular appearance later.

Consider the population evolutions, as in the (b) panels of both figures. We have the following observations and comments. (ii) The BO bath coherence tends to facilitate the tunneling transfer. As the population on the acceptor site (thick curves) is concerned, the smaller \(r_{BO}\) is, the faster the transfer would be. This observation may be understood in view of the fact that the donor and acceptor are degenerate in the system of study. The resulting effective coupling or overlap between the donor and the acceptor waves increases as the BO environment varies from the overdamped (\(r_{BO} > 1\)) to the underdamped (\(r_{BO} < 1\)) case. (iii) The population on the bridge site (thin curves) is relatively insensitive to the variation of \(r_{BO}\), due to both its off-resonant configuration and its two-channel connections to the donor and to the acceptor that are symmetric in the present study. (iv) The observed oscillatory features in both acceptor and bridge population dynamics are enhanced as temperature decreases. (v) For the symmetric D-B-A system studied here, the bridge state involves about a single beating frequency, which is, however, subject to a dynamic Stokes shift, along the transfer evolution, and the more diffusive the bath is (larger \(r_{BO}\)), the more Stokes shift will be. (vi) The beating of acceptor state has two frequency components, showing certain interference between the superexchange...
tunneling and sequential hopping pathways. (vii) The complexity in the observed beatings reflects interferences not just within the system but also with the bath coherence. The observed effective coherent time appears to have a varying trend for its dependence on the parameter $r_{BO}$ as the temperature varies.

The aforementioned complicity is also reflected in examining the state-resolved interference measures $[\phi_0(t)$ of Eq. (27)] in Fig. 7(c) at 298 K versus those in Fig. 8(c) at 77 K. Observed at high temperature are a sort of regular behaviors. (viii) The quantum bath interference with the acceptor site is largely constructive, while it with the bridge site is largely destructive. (ix) Both the constructive and destructive interferences are strengthened as the quantum nature of bath increases along $r_{BO}$ decreases. However, what observed at low temperature [Fig. 8(c)], are rather “irregular”, especially the large amplitude alternation between constructive and destructive interference when $r_{BO} = 0.25$.

The physical origin behind the irregular appearance in Figs. 8(b) and 8(c), in comparing to their Fig. 7 counterparts, is rather the dynamic delocalization at low temperature. Recall that all state-resolved quantities are representation or basis-set dependent. To reveal the delocalization mechanism, we recast Figs. 8(b) and 8(c) in Fig. 9, for the delocalized populations, $\{P_j\}$ in the left panels, and state-resolved interference measures, $\{\phi_j\}$ in the right panels, respectively. They are defined by the eigenstate representation of the system Hamiltonian after reorganization. We have $|1\rangle = 0.83|D\rangle + 0.44|B\rangle + 0.35|A\rangle$, $|2\rangle = -0.48|D\rangle + 0.22|B\rangle + 0.85|A\rangle$, and $|3\rangle = -0.30|D\rangle + 0.87|B\rangle - 0.39|A\rangle$, with the eigenenergies of $\{E_1, E_2, E_3\}/(\text{cm}^{-1}) = \{-75, 64, 411\}$, respectively. Exhibited in the right panels of Fig. 9 are the constructive environment interference with the ground system state and the destructive interferences with the two excited states. All the right panels of Fig. 9 have the aforementioned regular $r_{BO}$-dependence trend, completely in line with the results of Fig. 8(a) and also those in Figs. 7(a) and 7(c). We have thus concluded the localization to delocalization transition mechanism, as the temperature decreases from 298 K to 77 K.

VI. CONCLUDING REMARKS

In summary, we have proposed an optimized HEOM theory, which maximizes the range of practical application of this exact method. Not just it acquires the minimum number of dynamics variables (i.e., the ADOs), the optimized HEOM theory goes also by a priori accuracy control over its numerical application to any given quantum dissipative system, embedded in multiple Brownian oscillators environment, at a finite temperature. We have justified that in general the best HEOM could be achieved case by case via a universal screen search algorithm, on the basis of the following two observations: (i) The white-noise residue ansatz is by far the most efficient while reliable method for the partial treatment of the off-basis-set bath space residue effect on the HEOM dynamics; (ii) The family of PSD-based schemes, as listed and analyzed in Sec. III, are where the best among all memory-frequency bath decompositions could be chosen from for different cases of application. Moreover, we have analytically identified the best for each of the two specific cases in Sec. IV.

We have also proposed the quantitative measures, in conjunction with the accurate HEOM evaluation, on the quantum versus classical nature of Brownian oscillators environment influence on the dissipative system dynamics. Revealed also is the localization to delocalization transition as temperature decreases. Apparently, a proper set of measures, which can be readily identified in a similar manner, would be needed for a comprehensive study of various mechanisms underlying complex quantum dissipative systems, such as photosynthesis pigments–proteins complexes. Work along this direction is under way.

ACKNOWLEDGMENTS

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APPENDIX: REVISIT OF HIERARCHICAL EQUATIONS OF MOTION CONSTRUCTION

This appendix highlights some details of HEOM construction, which results in fewer ADOs than the previous form,\(^5, 6\) provided the memory-frequency decomposition of bath correlation function in Eq. (1). As bath spectrum is a real function, the resulting exponents from the poles in the lower-half plane are either real or complex conjugates in pairs. It is well established that each real exponent term contributes one sub-index $n_k \in \{n_1, \ldots, n_K\}$ for ADOs. We will show soon that each pair of complex-conjugate-exponent terms can be accounted by two sub-indices, rather than four.\(^5, 6\) Thus, the number of memory-frequency bath components in decomposition constitutes the size of stochastic environment basis set for HEOM construction.
Let us start with the Feynman-Vernon influence functional expression,\textsuperscript{5,6}
\[
\mathcal{F}[\alpha] = \exp \left\{ -i \int_0^t d\tau \mathcal{A}[\alpha(\tau)] B(\tau; \alpha) \right\},
\] (A1)
with
\[
\mathcal{A}[\alpha(t)] = Q[\alpha(t)] - Q[\alpha'(t)],
\] (A2)
and
\[
iB(t; \alpha) = \int_0^t d\tau \left[ C(t - \tau) Q[\alpha(\tau)] - C^*(t - \tau) Q[\alpha'(\tau)] \right].
\] (A3)
Consider now a pair of complex-conjugate-exponent terms in bath correlation,
\[
C(t) \sim c_+ e^{-\gamma t} + c_- e^{-\gamma' t}, \quad \text{with } \gamma_+ = \gamma^*,-
\] (A4)
but \(c_+ \) and \(c_- \) are independent. We identity immediately the two generating functionals,
\[
iB_{+}(t; \alpha) \equiv c_+ B_{+}(t; \alpha(t)) - c_- B_{-}(t; \alpha'(t)),
\] (A5)
\[
iB_{-}(t; \alpha) \equiv c_- B_{+}(t; \alpha(t)) - c_+ B_{-}(t; \alpha'(t)),
\] (A6)
where
\[
B_{\pm}(t; \alpha) = \int_0^t d\tau e^{-\gamma \pm (t - \tau)} Q[\alpha(t)].
\] (A7)
We have
\[
B(t; \alpha) = B_{+}(t; \alpha) + B_{-}(t; \alpha),
\] (A8)
and
\[
\partial_t B_{\pm}(t; \alpha) = \gamma_{\pm} B_{\pm}(t; \alpha) - i C_{\pm}[\alpha(t)],
\] (A9)
with
\[
C_{\pm}[\alpha(t)] = c_{\pm} Q[\alpha(t)] - c_{\pm}^* Q[\alpha'(t)].
\] (A10)
The auxiliary influence functionals for ADOs can now be generated via\textsuperscript{5,6}
\[
\mathcal{F}_{n_+,n_-} \equiv (B_{\pm}^n B_{\pm}^\dagger)^F.
\] (A11)
Applying \(\partial_t \mathcal{F} = -iA(\mathcal{B}_{+} + \mathcal{B}_{-}) \) and Eq. (A8), we obtain
\[
\partial_t \mathcal{F}_{n_+,n_-} = -(n_+ \gamma_+ + n_- \gamma_-) \mathcal{F}_{n_+,n_-} - \gamma_{\pm} \mathcal{F}_{n_+,n_-} - \gamma_{\pm} \mathcal{F}_{n_-,n_+} - \gamma_{\pm} \mathcal{F}_{n_-,n_-} - i A \mathcal{F}_{n_+,n_-} + A \mathcal{F}_{n_-,n_+} + A \mathcal{F}_{n_-,n_-} + .
\] (A12)
The corresponding equation in terms of ADO \(\rho_n = \rho_{n_+,n_-} \), can be obtained immediately, as the involving functionals \(\mathcal{A} \) and \(\mathcal{C}_{\pm} \), defined in Eqs. (A2) and (A9), respectively, depend only on the ending points of path.

For numerical convenience, we like to have a scaled ADO \(\rho_n \) related rather with \(s_n \mathcal{F}_n \), where \(s_n \) is the scaling factor. We set it in analogy to the Drude case,\textsuperscript{10}
\[
s_n = \prod_{k=+,-} \frac{1}{\sqrt{n_k |c_k|^2}}, \quad \text{with } |\bar{c}_+| = |\bar{c}_-| = \sqrt{|c_+ c_-|}.
\] (A13)
The HEOM corresponding to Eq. (A11) will read then\textsuperscript{29}
\[
\dot{\rho}_n = -\left( i \mathcal{L} + \gamma_n \right) \rho_n - i \sum_k \sqrt{n_k} (c_k Q \rho_{n_k} - c_k^* \rho_{n_k}^* Q)
\]
\[
- i \sum_k \sqrt{(n_k + 1)|c_k|^2} \left[ Q, \rho_{n_k}^* \right],
\] (A14)
with \(\gamma_n = \sum_k n_k \gamma_k \). The last and the second last terms in Eq. (A12) describe the tier-up \((\rho_n^+)^{} \) and tier-down \((\rho_n^-)^{} \) dependence. The involving index set \(n_k^\pm \) differs from \(n \) at the specified sub-index \(n_k \) by \(+1 \).

In Eq. (A12), \(c_k \) and \(c_k^* \) denote the coefficients of the complex-conjugate-exponent pair in bath correlation. That is \(c_k = c_\mp \) if \(k = \pm, \) cf. Eq. (A9). For a real-exponent bath component, \(k = \pm \), so that Eq. (A12) has taken all exponential terms of Eq. (1) into account. In other words, Eq. (A12) is just the HEOM (2), for bath correlation function in pure exponential expansion. The off-exponential residue in Eq. (1) will be treated with the ansatz \(\delta C_N(t) \approx 2 \Delta_N \delta(t) \) [cf. Eq. (17)]. It results in \(\delta N \cdot \Delta_N \equiv \Delta_N \left[ \{ Q, \cdot \} \right] \) to the HEOM (2).

For completeness, we consider also the critically damped bath mode. It contributes a real exponent term and also an associated \((t e^{-\gamma t})\)-term that is not included in the bath correlation function exponential expansion of Eq. (1) and thus Eq. (A12). Focus on this component of bath correlation function,
\[
C(t) \sim c_y t e^{-\gamma t}.
\] (A15)
Introduce
\[
B(t; \alpha) \equiv \gamma \int_0^t d\tau (t - \tau) e^{-\gamma (t - \tau)} Q[\alpha(t)],
\] (A16)
\[
\tilde{B}(t; \alpha) \equiv \int_0^t d\tau e^{-\gamma (t - \tau)} Q[\alpha(t)],
\] (A17)
and \(B(t; \alpha') = B' \) for short and so on. Two generating functionals, \(B \equiv -i(c B - c^* B') \) and \(\tilde{B} \equiv -i(c \tilde{B} - c^* \tilde{B}') \), are identified for each term of Eq. (A13). The closed differential relations are
\[
\partial_t B = -\gamma B + \gamma \tilde{B} \quad \text{and} \quad \partial_t \tilde{B} = -\gamma B - i C,
\] (A18)
with \(C = c Q[\alpha(t)] - c^* Q[\alpha'(t)] \), whereas it for the influence functional is \(\partial \mathcal{F} = -i c \mathcal{B} \).

Auxiliary influence functionals are now
\[
\mathcal{F}_{v,\tilde{v}} \equiv (B' B^\dagger)^{\mathcal{F}}.
\] (A19)
We have then
\[
\partial_t \mathcal{F}_{v,\tilde{v}} = -(v + \tilde{v}) \gamma \mathcal{F}_{v,\tilde{v}} + v \mathcal{F}_{v-1,\tilde{v}+1}
\]
\[
- i \sqrt{v(v + 1)} \gamma \rho_{v-1,\tilde{v}+1}.
\] (A20)
Together with the scaling factor \((v!)^2 |c|^{v+\tilde{v}})^{-1/2} \), we obtain
\[
\dot{\rho}_{v,\tilde{v}} = -i \mathcal{L} \rho_{v,\tilde{v}} - (v + \tilde{v}) \gamma \rho_{v,\tilde{v}} + \sqrt{v(v + 1)} \gamma \mathcal{L} \rho_{v-1,\tilde{v}+1}
\]
\[
- i \sqrt{v} \mathcal{L} \rho_{v-1,\tilde{v}+1} - c^* \mathcal{L} \rho_{v-1,\tilde{v}+1} Q
\]
\[
- i \sqrt{v(v + 1)} \left[ \rho_{v,\tilde{v}}, \mathcal{L} \right].
\] (A21)
Note that $\rho_{n-1,\tilde{v}+1}$ is of the same tier order of $\rho_{n,\tilde{v}}$.

To conclude, we consider the generalized memory-frequency decomposition of the bath correlation function,

$$C(t) \approx \sum_{k=1}^{K} c_k e^{-\gamma_k t} + \sum_{k=1}^{K'} c_k' e^{-\gamma_k' t} + 2\Delta \delta(t).$$  \hspace{1cm} \text{(A19)}$$

The last term is the residue to be treated as white noise (or zero). This is the only approximation and generates the formalism below. The ADO is now $\rho_{n,\tilde{n}}$, labeled in relation to the two distinct types of contributions in Eq. (A19), respectively, with $n = [n_1, n_2, \ldots, n_K]$ and $\tilde{n} = [(v_1, \tilde{v}_1), (v_2, \tilde{v}_2), \ldots, (v_{K'}, \tilde{v}_{K'})]$.

Denote $\tilde{\rho}_{n,\tilde{n}}$, $\tilde{\rho}_{n,\tilde{n}}^{-}$, and $\tilde{\rho}_{n,\tilde{n}}^{+}$, such as

$$\tilde{\rho}_{n,\tilde{n}}^{-} \equiv \{(v_1 - 1, \tilde{v}_1 + 1), (v_2, \tilde{v}_2), \ldots, (v_{K'}, \tilde{v}_{K'})\},$$

$$\tilde{\rho}_{n,\tilde{n}}^{+} \equiv \{(v_1 + 1, \tilde{v}_1), (v_2, \tilde{v}_2), \ldots, (v_{K'}, \tilde{v}_{K'})\},$$

for the shift, tier-down, and tier-up hierarchical couplings, as described by Eq. (A18), for the $(e^{-\gamma t})$-components of bath correlation function. The final HEOM formalism, a combination of Eqs. (A12) and (A18), reads now

$$\rho_{n,\tilde{n}} = -(i\mathcal{L} + \gamma_{n,\tilde{n}} + \delta\mathcal{R})\rho_{n,\tilde{n}} + \rho_{n,\tilde{n}}^{-} + \rho_{n,\tilde{n}}^{+} + \rho_{n,\tilde{n}}^{-},$$  \hspace{1cm} \text{(A22)}$$

with

$$\gamma_{n,\tilde{n}} = \sum_{k=1}^{K} n_k y_k + \sum_{k=1}^{K'} (v_k + \tilde{v}_k) y_k'.$$  \hspace{1cm} \text{(A23)}$$

$$\rho_{n,\tilde{n}}^{-} = \sum_{k=1}^{K'} \sqrt{v_k (v_k + 1)} y_k' \rho_{n,\tilde{n}}^{-} + \rho_{n,\tilde{n}}^{-} \rho_{n,\tilde{n}}^{-},$$  \hspace{1cm} \text{(A24)}$$

$$\rho_{n,\tilde{n}}^{-} = -(i \sum_{k=1}^{K} \sqrt{n_k} \tilde{c}_k Q \rho_{n,\tilde{n}}^{-} - c_k Q \rho_{n,\tilde{n}}^{-} Q),$$  \hspace{1cm} \text{(A25)}$$

and

$$\rho_{n,\tilde{n}}^{+} = -i \sum_{k=1}^{K'} \sqrt{v_k} (v_k + 1) \rho_{n,\tilde{n}}^{+} \rho_{n,\tilde{n}}^{+}.$$  \hspace{1cm} \text{(A26)}$$

The above formalism is established for the system-bath coupling $H'(t) = -Q \tilde{F}_B(t)$. Extension to the general case of $H' = -Q F_B(t)$ is carried out readily.\(^6\) Note also that for the BOs bath (Sec. II B) having $N_D$ Drude modes, $N_c$ critically damped modes and $N_{BO}$ other BO modes, $K = N + N_D + N_c + 2N_{BO} + K' = N_c$, where $N$ denotes the number of Bose function poles in the lower-half plane being used in evaluating the bath correlation function $C(t)$.