Open quantum systems with nonlinear environmental backactions: Extended dissipaton theory versus core–system hierarchy construction

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In this paper, we present a comprehensive account of quantum dissipation theories with the quadratic environment couplings. The theoretical development includes the Brownian solvation mode embedded hierarchical quantum master equations, a core–system hierarchy construction that verifies the extended dissipaton equation of motion (DEOM) formalism [R. X. Xu et al., J. Chem. Phys. 148, 114103 (2018)]. Developed are also the quadratic imaginary–time DEOM for equilibrium and the \( \lambda (t) \)-DEOM for nonequilibrium thermodynamics problems. Both the celebrated Jarzynski equality and Crooks relation are accurately reproduced, which in turn confirms the rigorosity of the extended DEOM theories. While the extended DEOM is more numerically efficient, the core–system hierarchy quantum master equation is favorable for “visualizing” the correlated solvation dynamics.

I. INTRODUCTION

Quantum dissipation plays a crucial role in many fields of modern science, where irreversibility takes place during relaxation, dephasing, transport and thermodynamic processes. 1–12 In these studies, the environmental non-Markovian and non-perturbative quantum nature would be prominent if the system and bath are strongly correlated. Various exact methods, such as the Feynman–Vernon influence functional approach13 and its differential equivalence, the hierarchical equations of motion (HEOM) formalism,14–22 had been constructed. There are also quite a few studies that treat HEOM as quantum Fokker–Planck (FP) type equations, via transferring the involving degrees of freedom into the Wigner representation, such as the quantum hierarchical FP equation.23–28 Besides, transformations from HEOM to the low–temperature quantum FP or Smoluchowski equations are also suggested.29,30 However, most of these theories are exact only for Gaussian environments with linear couplings. This linearity intrinsically implies a weak backaction of the central system on the surroundings.

On the other hand, the nonlinear system–bath interactions are generally common and appealing in real physical systems.31–40 The quest of an exact treatment of quantum dissipation with nonlinear environment couplings remains a challenging task in recent years.41–46 In this account, we consider the total system–plus–bath composite Hamiltonian to take the form of

\[
H_t = H_s + h_n + \hat{Q}_s (\alpha_0 + \alpha_1 \hat{x}_n + \alpha_2 \hat{q}_n^2). \tag{1}
\]

Here, \( H_s \) is the system Hamiltonian and \( \hat{Q}_s \) is the dissipative mode which can be an arbitrary Hermitian system operator. The bath Hamiltonian and solvation coordinate are

\[
h_n = \frac{1}{2} \sum_j \alpha_1 (\hat{p}_j^2 + \hat{q}_j^2) \quad \text{and} \quad \hat{x}_n = \sum_j \hat{c}_j \hat{q}_j, \tag{2}
\]

respectively, where the Gaussian \( h_n \) is in line with the central limiting statistics description. The solvation coordinate \( \hat{x}_n \) is defined to be the linear part, but involved in both the \( \alpha_1 \) and \( \alpha_2 \) terms. In Eq. (1), \( \hat{Q}_s \) and \( \hat{x}_n \) are set to be dimensionless, while the \( \alpha \)–parameters are of energy unit. When \( \alpha_2 = 0 \), it is reduced to the linear bath coupling case. The nonlinearity is exemplified here with the quadratic coupling. The approaches presented later in this account can all be extended to higher orders. Throughout this paper we set \( \hbar = 1 \) and \( \beta = 1/(k_B T) \), with \( k_B \) being the Boltzmann constant and \( T \) the temperature.

To simulate the dynamics governed by the Hamiltonian in Eqs. (1) with (2), we had previously adopted the dissipaton theory. The dissipaton theory introduces statistical quasiparticles, dissipatons, to characterize the interacting bath statistical properties.47–51 The resulting dissipaton equation of motion (DEOM) is not only identical to the HEOM for the reduced system dynamics, but also convenient to treat the hybridized bath dynamics.51–53 Based on the DEOM, we had proposed two distinct approaches for the nonlinear bath coupling, namely, the extended DEOM and the stochastic–fields–dressed DEOM (SFD–DEOM).

In this work, an exact core–system hierarchy construction is developed. It explicitly treats the solvation phase space, including the nonlinear coupling term (\( \alpha_2 \) term). We name it as the Brownian solvation mode embedded hierarchical quantum master equations (BSM-HQME), with the standard FP algebra being exploited. We further scrutinize the extended DEOM and the SFD–DEOM with the newly developed BSM-HQME. All of them agree with each other, as inferred from their theoretical constructions and also evident from numerical simulations. This implies the extended DEOM and the underlying generalized Wick’s theorem (GWT-2)41,42 are universally correct.

Some features of these methods are as follows. (i) The SFD-DEOM is exact in principle, constructed on the basis of SFD total Hamiltonian with only linear bath coupling terms, while the nonlinear terms are resolved via the stochastic fields. However, the SFD-DEOM approach is numerically available only for short–time evolutions, but subject to long–time instability. (ii) The BSM-HQME explicitly treats the solvation coordinate and momentum. Its phase space dynamics

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can be directly computed using this approach. Taking the electron transfer process, for example, this approach provides the exact reaction coordinate evolutions. (iii) The extended DEOM is mostly numerically efficient among those three methods. It can be readily extended to imaginary–time (i-DEOM) formulations\textsuperscript{31,58,59} to compute the hybridization free energy. (iv) We can also develop the nonequilibrium $\lambda$-DEOM (neq-$\lambda$-DEOM)\textsuperscript{51,60} to investigate the fluctuation theorems, such as Jarzynski equality and Crooks relation. The results here in turn confirm the rigorousness of the extended DEOM theories.

The remainder of this paper is organized as follows. Section II comprises a complete description of extended DEOM. In Sec. III A, the BSM-HQME is developed in detail. The FP algebra is outlined in Appendix. The numerical cross-check is extended DEOM mostly numerically efficient among those dissipations decomposition form,\textsuperscript{21,47} to investigate the fluctuation thermodynamics. (iv) The ex-

II. THE EXTENDED DEOM FORMALISM

In this section, we briefly review the extended DEOM formalism in Refs. 41 and 42 for nonlinear bath couplings. Before that, we first introduce the associated bath statistics. With the bath Hamiltonian and coupling in the form of Eqs. (1) and (2), the bath influence is completely described via the bath spectral density,

$$J(\omega \geq 0) = \frac{\pi}{2} \sum_{\gamma} \omega^2 \delta(\omega - \omega_{\gamma}) = -J(-\omega).$$

(3)

It is expressed in terms of $J(\omega) \equiv \Im\chi_0(\omega)$, with $1,4$

$$\chi_0(\omega) = i \int_0^\infty dt e^{i\omega t} \langle \hat{x}_0(t)\hat{x}_0(0) \rangle .$$

(4)

Here, $\langle \cdot \cdot \cdot \rangle$ denotes a commutator, $\hat{x}_0(t) = e^{i\omega t} \hat{x}_0 e^{-i\omega t}$ and $\langle \hat{O} \rangle_0 = tr\hat{O}e^{-\beta h_0}/tr e^{-\beta h_0}$. The fluctuation–dissipation theorem in relation to Eq. (4) reads\textsuperscript{1,4}

$$\langle \hat{x}_0(t)\hat{x}_0(0) \rangle_0 = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \frac{e^{-i\omega t} J(\omega)}{1 - e^{-\beta \omega}} .$$

(5)

This bare–bath subspace relation holds in general, regardless of the nature of bare bath Hamiltonian and also independent of the system–bath couplings involved in Eq. (1).

The DEOM formalism is established by expressing the influence of environment with a finite number of statistically independent quasi–particles, the dissipations.\textsuperscript{21,47} We expand Eq. (5) in an exponential series,\textsuperscript{4,61,62}

$$\langle \hat{x}_0(t)\hat{x}_0(0) \rangle_n = \sum_{k=1}^K \eta_k e^{-\gamma_k t} .$$

(6)

Its time reversal is expressed in the form of\textsuperscript{4,63}

$$\langle \hat{x}_n(0)\hat{x}_n(t) \rangle_n = \sum_{k=1}^K \eta_k e^{-\gamma_k t} ,$$

(7)

with $\gamma_k$ being defined via $\gamma_k = \gamma_k^\ast$, which must also appear in Eq. (6). The solvation coordinate can then be recast in the dissipations decomposition form,\textsuperscript{21,47}

$$\hat{x}_n = \sum_{k=1}^K \hat{f}_k ,$$

(8)

with

$$\langle \hat{f}_k(t)\hat{f}_0(0) \rangle_n = \langle \hat{f}_k\hat{f}_0 \rangle_n e^{-\gamma_k t} = \delta_{nk} \eta_k e^{-\gamma_k t} ,$$

(9a)

$$\langle \hat{f}_0(0)\hat{f}_k(t) \rangle_n = \langle \hat{f}_0\hat{f}_k \rangle_n e^{-\gamma_k t} = \delta_{nk} \eta_k e^{-\gamma_k t} .$$

(9b)

Apparently, both Eqs. (6) and (7) are reproduced.

Dynamical variables in DEOM are the dissipaton density operators (DDOs):\textsuperscript{21,47}

$$\rho_n^{(n)}(t) = \rho_{n_1\cdots n_k}(t) = \text{tr}_n\left[ \hat{f}_k^{n_k} \cdots \hat{f}_1^{n_1} \rho_n(t) \right] .$$

(10)

The reduced system density operator is just $\rho_n(t) = \rho_0^{(n)}(t)$. The indexes $n = n_1\cdots n_k$ and $n = n_1 + \cdots + n_k$ specify the occupations and the total number of dissipations, respectively. The notation, $(\cdots)^y$, denotes the irreducible representation. We have $\langle \hat{f}_k\hat{f}_0 \rangle_n = \langle \hat{f}_0\hat{f}_k \rangle_n$ for bosonic dissipations.

The construction of DEOM starts from

$$\rho_n^{(n)}(t) = \rho_{n_1\cdots n_k}(t) = \text{tr}_n\left[ \hat{f}_k^{n_k} \cdots \hat{f}_1^{n_1} \rho_n(t) \right] ,$$

(11)

with the total composite density operator satisfying

$$\rho_n(t) = -i[H, \rho_n(t)] .$$

(12)

The dissipaton formalism consists of the generalized diffusion equation and the generalized Wick’s theorems (GWTs). The former reads

$$\text{tr}_n\left[ \left( \frac{\partial \hat{f}_k}{\partial t} \right) \rho_n(t) \right] = -\gamma_k \text{tr}_n\left[ \hat{f}_k \rho_n(t) \right] .$$

(13)

It together with $\left( \frac{\partial \hat{f}_k}{\partial t} \right) = -\gamma_k$ will give rise to

$$i\text{tr}_n\left[ \left( \hat{f}_k^{n_k} \cdots \hat{f}_1^{n_1} \right)^\ast [\hat{h}_n, \rho_n(t)] \right] = \left( \sum_{k=1}^K \eta_k \gamma_k \right) \rho_n^{(n)}(t) .$$

(14)

The GWT-1 evaluates the linear bath coupling with one dissipaton added each time. It reads\textsuperscript{21,47}

$$\text{tr}_n\left[ \left( \hat{f}_k^{n_k} \cdots \hat{f}_1^{n_1} \right)^\ast \rho_n^{(n)}(t) \right]$$

$$= \rho_{n_k}^{(n+1)}(t) + \left( \sum_{k=1}^K \eta_k \langle \hat{f}_k \rangle_n^\ast \right) \rho_{n_k}^{(n-1)}(t) .$$

(15)

The expression of $\text{tr}_n\left[ \left( \hat{f}_k^{n_k} \cdots \hat{f}_1^{n_1} \right)^\ast \rho_n(t) \right]$ is similar, but with $\langle \hat{f}_k \rangle_n^\ast$ being replaced by $\langle \hat{f}_k \hat{f}_k \rangle_n^\ast$. The associated index $n_k$ differs from $n = n_1\cdots n_k$ by replacing the specified $n_k$ with $n_k \pm 1$. This specifies the (n ± 1)–particle DDO.
\[ \rho_{n_k}^{(n \pm 1)}(t), \text{ in Eq. (15). In comparison, we may recall some} \]

properties about the “normal order” in textbooks, which arranges creation operators before annihilation operators. Denote this also with \((\cdot)^o\), such that \((\hat{a} \hat{a}^\dagger)^o = (\hat{a} \hat{a}^\dagger)^o = \hat{a}^\dagger \hat{a}\). Assume \(\hat{f} = \sqrt{\eta} (\hat{a} + \hat{a}^\dagger)\), with \(\eta\) being an arbitrary real parameter. It is easy to obtain \((\hat{p}^{n+1})^o = n! (\hat{p}^{n-1})^o = \hat{f} (\hat{p})^o\), in line with the standard normal ordering.\(^{54}\) The GWT-1 is just the generalization of this result, which has been already verified analytically in the linear environmental coupling scenarios.\(^{51,65}\)

The GWT-2 is related to the quadratic bath coupling, where a pair of dissipatons are added each time. It was validated under the minimum–dissipaton ansatz,\(^{57,66}\) via the Zussman or the Fokker–Planck equation.\(^{31}\) One of the purposes of this work is to confirm the GWT-2 beyond these limitations. More precisely, we will first assume the correctness of the GWT-2 in more general scenarios, and then scrutinize it numerically by comparing with the exact results from the SFD–DEOM\(^{54}\) and the newly developed BSM-HQME (cf. Sec. III). In this sense, the GWT-2 is a validated “theorem” that is generally correct. However, a rigorous proof of GWT-2 within the canonical Feynman–Vernon influence formalism is absent so far. The GWT-2 is evaluated as\(^{41,42}\)

\[
\text{tr}_{\mu} \left[ (\hat{p}^{n}_{kk} \cdots \hat{p}^{n}_{1})^o (\hat{f}_k \hat{f}^\dagger_k) \rho_{\mu}(t) \right] = \rho^{(n+2)}_{\mu+\hat{n}^+} + \sum_{k} n_k \langle \hat{f}_k \hat{f}^\dagger_k \rangle_{\mu}^o \rho^{(n)}_{\mu k} + \sum_{k<k'} \langle \hat{f}_k \hat{f}^\dagger_k \rangle_{\mu}^o \rho^{(n)}_{\mu k} + \sum_{k} n_k (n_k - \delta_{kk'}) \langle \hat{f}_k \hat{f}^\dagger_k \rangle_{\mu}^o \rho^{(n-2)}_{\mu k}. \tag{16}
\]

The associated DDO index, \(n_{kk}^{\pm}\), differs from \(n = n_1 \cdots n_K\) on the specified subindexes, \(n_k\) and \(n_k\), that are replaced by \(n_k \pm 1\) and \(n_k \pm 1\), respectively. Together with Eqs. (8) and (9), we obtain

\[
\text{tr}_{\mu} \left[ (\hat{p}^{n}_{kk} \cdots \hat{p}^{n}_{1})^o (\hat{f}_k \hat{f}^\dagger_k) \rho_{\mu}(t) \right] = \sum_{kk'} \rho^{(n+2)}_{\mu k} + \sum_{k} n_k \langle \hat{f}_k \hat{f}^\dagger_k \rangle_{\mu}^o \rho^{(n)}_{\mu k} + \sum_{k} n_k (n_k - \delta_{kk'}) \langle \hat{f}_k \hat{f}^\dagger_k \rangle_{\mu}^o \rho^{(n-2)}_{\mu k}. \tag{17}
\]

The expression of \(\text{tr}_{\mu} \left[ (\hat{p}^{n}_{kk} \cdots \hat{p}^{n}_{1})^o \rho_{\mu}(t) \right] \) is similar, but with \(\eta_k\) and \(\eta_k\) being replaced by \(\eta_{\mu k}\) and \(\eta_{\mu k}\), respectively. Combining Eqs. (11)–(17), the extended DEOM is finally constructed\(^{41,42}\)

\[
\rho_{\mu}^{(n)} = - \left( i \mathcal{L}_{\mu} + \sum_{k} n_k \eta_k \right) \rho_{\mu}^{(n)} - i \left( \alpha_0 + \alpha_2 \langle \tilde{\zeta}^{(n)}_{\mu} \rangle \right) \rho_{\mu}^{(n)} - 2 i \alpha_2 \sum_{kk'} \rho_{\mu k}^{(n+1)} \rho_{\mu k'}^{(n-1)} + \sum_{k} n_k (n_k - \delta_{kk'}) \rho_{\mu k}^{(n-2)}, \tag{18}
\]

with \(\mathcal{L}_{\mu} \equiv [H_{\mu}, \hat{O}]\) and other involved superoperators defined as

\[
\mathcal{S} \hat{O} \equiv [\hat{O}_s, \hat{O}], \tag{19a}
\]
\[
\mathcal{B}_{kk'} \hat{O} \equiv \eta_k \eta_{k'} \hat{O}_s - \eta_k \eta_{k'} \hat{O}, \tag{19b}
\]
\[
\mathcal{C}_{k} \hat{O} \equiv \eta_k \hat{O}_s - \eta_k \hat{O}. \tag{19c}
\]

III. BSM-HQME: A CORE-SYSTEM HIERARCHY CONSTRUCTION

In this section, we propose a new exact core–system hierarchy method, named as BSM-HQME. In the core–system description, the bath Hamiltonian of Eq. (2) is divided into two parts, the solvation mode and the secondary bath coupled to it. The FP algebra is used to provide a basis set for describing the solvation mode inside the core system.\(^{55–57}\) The details of BSM-HQME construction are given in Sec. III A. In Sec. III B, we carry out the numerical cross check among BSM-HQME, extended DEOM, and SFD-DEOM. Both dynamics and spectroscopies are simulated, together with the explicit solvation mode dynamics obtained from the BSM-HQME.

A. The construction of BSM-HQME

In the core–system description, the bath Hamiltonian of Eq. (2) is divided into the solvation modes and secondary bath parts with the Caldeira–Leggett model, which reads

\[
h_b = \frac{1}{2} \omega_b (\hat{p}^2 + \hat{x}^2) + \frac{1}{2} \sum_j \tilde{\alpha}_j [\hat{p}^2_j + (\tilde{x}_j - \tilde{\xi}_j)^2]. \tag{20}
\]

The solvation mode behaves as a Brownian oscillator, with the correlation function, \(\langle \tilde{x}_b(t), \tilde{x}_b(0) \rangle_b\), given by Eq. (5) in which\(^{56,57}\)

\[
J(\omega) = \text{Im} \left[ \frac{\omega_b}{\omega_b^2 - \omega^2 - i \omega \zeta_b(\omega)} \right]. \tag{21}
\]

Here, \(\zeta_b(\omega) \equiv \int_0^\infty dt e^{i \omega t} \tilde{z}_b(t)\), with the classical friction function reading

\[
\tilde{z}_b(t) = \omega_b \sum_j (\tilde{\xi}_j / \tilde{\alpha}_j) \cos(\tilde{\alpha}_j t). \tag{22}
\]

The spectral density of the secondary bath, \(\tilde{h}_b = \frac{1}{2} \sum_j \tilde{\alpha}_j (\hat{p}^2_j + \tilde{x}^2_j)\), is then\(^{56,57}\)

\[
\tilde{J}(\omega) = \frac{\theta}{\omega_b} \text{Re} \zeta_b(\omega), \tag{23}
\]

and the secondary bath fluctuation–dissipation theorem reads

\[
\langle F(i) F(i) \rangle_b = \frac{1}{\pi} \int_{-\infty}^\infty d\omega \frac{|\tilde{J}(\omega)| e^{-i\omega t}}{1 - e^{-\beta \omega}} \tag{24}
\]

where \(\langle \hat{O} \rangle_b \equiv \text{tr}_b (\hat{O} e^{-\beta h_b}) / \text{tr}_b e^{-\beta h_b}\).
Using Eq. (24) with Eq. (23), we can write down the HEOM/DEOM where the primary system and solvation mode compose the core system,

\[ H_{\text{core}} = H_\text{c} + \hat{Q}_c F(\hat{x}_u) + \frac{\omega_0}{2} (\hat{p}_u^2 + \hat{x}_u^2) + \tilde{\lambda} \hat{x}_u^2 \]  

where

\[ F(\hat{x}_u) = \alpha_0 + \alpha_1 \hat{x}_u + \alpha_2 \hat{x}_u^2 \]  

and

\[ \tilde{\lambda} \equiv \frac{1}{2} \sum_j \tilde{c}_j^2 = \bar{\tilde{\rho}}(0) / 2 \omega_0 \]  

The secondary bath is treated as the environment. According to Eq. (24), followed by applying the exponential decomposition scheme,\(^{61,62}\) we obtain

\[ \langle F(t)F(0) \rangle_\tilde{\rho} = \sum_{k=1}^K \tilde{\eta}_k e^{-\tilde{\lambda} t} \]  

The HEOM for the core system can be then constructed as

\[ \dot{\tilde{\rho}}_\tilde{n} = -(i\mathcal{L}_{\text{core}} + \gamma_\tilde{n})\tilde{\rho}_\tilde{n} - i \sum_k \tilde{\lambda} \tilde{\eta}_k \tilde{\rho}_n \tilde{\eta}^*_k \]

\[ -i \sum_k \tilde{\lambda} \tilde{\eta}_k \left( \tilde{\eta}_k \tilde{x}_u - \tilde{\eta}^*_k \bar{\tilde{\rho}}(0) / 2 \omega_0 \right) \tilde{\rho}_n \tilde{\eta}^*_k , \]  

where \( \mathcal{L}_{\text{core}} \tilde{\rho} \equiv \{ H_{\text{core}}, \tilde{\rho} \} \) and \( \gamma_\tilde{n} = \sum_k \tilde{\eta}_k \tilde{\eta}^*_k \). The \( \tilde{n} \) is the array of dissipaton occupation numbers; see comments after Eq. (10). Hereafter, we denote \( A^\dagger = A^\dagger - A^\dagger \) and \( A^\dagger \tilde{O} = \tilde{O} A \). In Eq. (29), \( \{ \rho_\tilde{n} \} \) are the DDOs of the core system, i.e. the primary system plus the solvation mode degrees of freedom. Let \( \tilde{W}_\tilde{n}(x_u, p_u) \equiv \{ \rho_\tilde{n} \} \) be the Wigner representation of the solvation subspace. Moreover, we expand \( \{ \tilde{W}_\tilde{n}(x_u, p_u) \} \) by the FP basis set as [cf. Eq. (A.18)]

\[ \tilde{W}_\tilde{n}(x_u, p_u, t) = \left( \frac{\beta \omega_0}{2\pi} \right)^{1/2} \sum_{n_1, n_2} \frac{s_{n_1, n_2}}{\sqrt{n_1! n_2!}} \rho_{n_1, n_2, \tilde{n}}(t) \times e^{-\beta \omega_0 \left( x^2_u + p^2_u \right) / 2} \psi_{n_1, n_2}(x_u, p_u) . \]  

Here, \( \{ \rho_{n_1, n_2, \tilde{n}} \} \) are operators in the original system subspace, and \( \rho_{00, \tilde{n}} \) is just the reduced system operator. The scaling parameters, \( \{ s_{n_1, n_2} \} \) and the functions \( \{ \Psi_{n_1, n_2} \} \) are detailed in Appendix. After some simple algebra, we obtain

\[ \dot{\rho}_{n, \tilde{n}} = -(i\mathcal{L}_{\text{core}} + \gamma_{n, \tilde{n}})\rho_{n, \tilde{n}} - i \sum_{k=1}^{N_k} \tilde{\lambda} \tilde{\eta}^*_k \rho_{n, \eta} \tilde{\eta}_k \]

\[ -i \sum_{k=1}^{N_k} \tilde{\lambda} \tilde{\eta}^*_k \left( \tilde{\eta}_k \tilde{x}_u - \tilde{\eta}^*_k \bar{\rho}(0) / 2 \omega_0 \right) \rho_{n, \eta} \tilde{\eta}^*_k . \]  

The solvation mode actions, \( x^u_\tilde{n} \) and \( \tilde{x}^u_\tilde{n} \) are considered in the Wigner representation; see Eqs. (A.24a)–(A.24d). Moreover,

\[ \mathcal{L}_{\text{core}} \rho_{n, \tilde{n}} = \mathcal{L}_c \rho_{n, \tilde{n}} + \hat{Q}_c F(\hat{x}_u) \rho_{n, \tilde{n}} - F(\hat{x}_u) \rho_{n, \tilde{n}} \tilde{Q}_s \]

\[ + \frac{\omega_0}{2} (\tilde{p}^2_u + \tilde{x}^2_u - \tilde{p}^2_u - \tilde{x}^2_u) \rho_{n, \tilde{n}} \]

\[ + \tilde{\lambda} (\tilde{x}^2_u - \tilde{x}^2_u) \rho_{n, \tilde{n}}. \]  

\[ \text{FIG. 1. Comparison between extended DEOM (solid) and BSM-HQME (dashed) in terms of von Neumann entropy, } S_{\text{V}} = -tr(\rho \ln \rho), \text{ and the evolution of population, } \rho^{\text{ext}}_c - \rho^{\text{ext}}_c. \text{ Here, we set } \omega_0 = \sqrt{5} \omega_0. \text{ The Rabi frequency is } \Omega = \sqrt{5} \omega_0. \text{ The bath related parameters are selected as } (\theta_0, \lambda / \omega_0) = (1.125, 0.1) \text{ and } (1.333, 0.25), \text{ plotted in blue and red curves, respectively.} \]

\[ \text{The above solvation mode subspace Wigner representation also highlights the role of the FP formulation.}^{41,55,68,69} \]

\[ \text{B. Numerical demonstrations} \]

For demonstration, we select a two–state model system as in Ref. 42. In this model, the total Hamiltonian can be described by

\[ H_t = h_g |g\rangle \langle g| + (h_e + \omega_0) |e\rangle \langle e|, \]  

where

\[ h_e = \frac{1}{2} \omega_0 (\rho^2_n + \tilde{x}^2_n) + \frac{1}{2} \sum_k \tilde{\omega}_k \left[ \tilde{p}^2_k + (\tilde{x}_k - \tilde{c}_k / \tilde{\omega}_k)^2 \right], \]  

and

\[ h_g = \frac{1}{2} \omega_0 (\rho^2_n + \tilde{x}^2_n) + \frac{1}{2} \sum_k \tilde{\omega}_k \left[ \tilde{p}^2_k + (\tilde{x}_k - \tilde{c}_k / \tilde{\omega}_k)^2 \right], \]  

follow the Caldeira–Leggett’s interaction form.\(^{70}\) Then in the \( H_t \)-based description, \( H_t \) can be reformulated as

\[ H_t = \omega_0 |e\rangle \langle e| + h_g + (h_e - h_g) |e\rangle \langle e| \]

\[ = \Omega_t |e\rangle \langle e| + h_g + (\alpha_0 + \alpha_1 \tilde{x}_n + \alpha_2 \tilde{x}_n^2) |e\rangle \langle e|, \]  

with

\[ \alpha_0 = \lambda \theta_0^2, \quad \alpha_1 = -(2 \lambda \omega_0) \frac{1}{2} \theta_0^2, \quad \alpha_2 = \frac{\omega_0}{2} (\theta^2_0 - 1). \]
The SFD–DEOM encounters error accumulation in the long-time simulation, requiring a vast of trajectories to converge when \( \omega_s \) is relatively large. In the BSM-HQME simulations, we exploit the on–the–fly numerical filter technique,\(^1\) with the accuracy of \( 10^{-8} \) that effectively corresponds to the converged level of truncation at \( n_1 + n_2 = 8 \) and \( \sum_k \tilde{\omega}_k = 30 \).

Figure 2 reports the evaluated absorption spectra using the extended DEOM and the BSM-HQME, with three pairs of the specified bath related parameters \( (\theta_b, \lambda/\omega_b) \). The absorption spectrum is defined as

\[
S(\omega) = \text{Re} \int_0^\infty dt e^{-i\omega t} \langle \hat{\mu}_s(t) \hat{\mu}_s(0) \rangle
\]

with \( \hat{\mu}_s = |e\rangle \langle g| + |g\rangle \langle e| \). As shown in the figure, the extended DEOM and BSM-HQME agree with each other perfectly.

Figure 3 (Multimedia view) depicts the time evolution of the solvation mode phase–space distribution [cf. Eq. (30) with Eqs. (A.21) and (A.22)],

\[
\rho_n(x_n, p_n; t) = \text{tr}_s \left[ W_0(x_n, p_n; t) \right].
\]

We choose \( (\theta_b, \lambda/\omega_b) = (1, 0.25), (1.33, 0) \) and \( (1.33, 0.25) \) to represent the pure linear (L), the pure quadratic (Q) and the mixed (L+Q) coupling bath scenarios, respectively. The video shows the dynamic interplay between the nonadiabatic coupling \( V \), the linear bath coupling that contributes to the center displacement, and the quadratic bath coupling that causes the curvature change. Evidently, compared to the DEOM, the BSM-HQME is the choice to “visualize” the solvation mode dynamics.

**IV. THERMODYNAMIC MIXING**

In this section, we extend the present DEOM formalism to thermodynamics problems. Involved would be the imaginary–time DEOM (i-DEOM) and also nonequilibrium \( \lambda \)-DEOM (neq-\( \lambda \)-DEOM), to be detailed in Sec. IV A and Sec. IV B, respectively. The key quantities are the system–bath mixing, free–energy, nonequilibrium work and its distribution function. The numerical results in Sec. IV C reproduce the Jarzynski equality\(^72\) and the Crooks relation.\(^73\)

**A. Extended i-DEOM formalism**

The i-DEOM aims at the hybridization partition function,

\[
Z_{hyb} \equiv Z_{\text{hyb}}(T) / Z_0 \equiv \text{Tr} \ g_\text{t} (\beta),
\]

with \( Z_t \equiv \text{Tr} e^{-\beta H_t} \) and \( Z_0 \equiv \text{Tr} e^{-\beta H_0} \), where \( H_0 = H_s + h_\text{n} \) (cf. Eq. (1)). The hybridization free–energy before and after isotherm system–bath mixing, \( A_{hyb}(T) \equiv A_s(T) - A_\text{n}(T) \), is given by

\[
A_{hyb}(T) = -\beta^{-1} \ln Z_{hyb}(T).
\]

This is to be evaluated by using Eq. (42) via

\[
\varrho_\text{t} (\tau) = e^{-\tau H_t} e^{-(\beta - \tau) H_0} / Z_0,
\]

that satisfies

\[
\frac{d \varrho_\text{t} (\tau)}{d\tau} = -(H_s^\times + h_\text{n}^\times + H_\text{sa}^\times) \varrho_\text{t} (\tau),
\]

with 

\[
\varrho_\text{t} (\tau) = \left[ \begin{array}{c} \varrho_{1,1} (\tau) \\ \varrho_{1,2} (\tau) \\ \varrho_{2,1} (\tau) \\ \varrho_{2,2} (\tau) \end{array} \right],
\]

and

\[
\frac{d \varrho_{ij} (\tau)}{d\tau} = -\sum_{kl} \left( \varrho_{ik} (\tau) \varrho_{lj} (\tau) - \varrho_{ij} (\tau) \varrho_{kl} (\tau) \right) \left( H_s^\times + h_\text{n}^\times + H_\text{sa}^\times \right). \]
where $H_{\text{sb}} \equiv \hat{Q}_A (\alpha_0 + \alpha_1 \hat{x}_n + \alpha_2 \hat{x}_n^2)$. The i-DEOM–space mapping goes by\textsuperscript{51,58}

$$\quad \hat{\varrho}_n (\tau) \rightarrow \varrho (\tau) \equiv \{ \varrho_n^{(n)} (\tau) \}. \quad (46)$$

We obtain\textsuperscript{51,58}

$$\frac{d \varrho_n^{(n)} (\tau)}{d \tau} = - \varrho_n^{(n)} (\tau; H^x_{\text{sb}}) - \varrho_n^{(n)} (\tau; h^x_{\text{sb}}) - \varrho_n^{(n)} (\tau; H^z_{\text{sb}}) \quad (47)$$

with

$$\varrho_n^{(n)} (\tau; H^x_{\text{sb}}) = \alpha_0 \hat{Q}_A \varrho_n^{(n)} (\tau) + \alpha_1 \hat{Q}_A \varrho_n^{(n)} (\tau; \hat{x}_n^z) + \alpha_2 \hat{Q}_A \varrho_n^{(n)} (\tau; \hat{x}_n^{z2}). \quad (48)$$

In parallel to the dissipaton algebra introduced in Sec. II, especially Eq. (17) that deal with the quadratic coupling, we obtain the final i-DEOM formalism,

$$\hat{\varrho}_n^{(n)} \left( - \mathcal{L}_A + i \sum_k n_k \mathcal{H}_k \right) \varrho_n^{(n)} - (\alpha_0 + \alpha_2 \hat{Q}_A \varrho_n^{(n)} - \alpha_1 \hat{Q}_A \varrho_n^{(n)} - \alpha_2 \hat{Q}_A \varrho_n^{(n)} \tau - \alpha_2 \sum_{kk'} \hat{\varrho}_n^{(n+1)} - \eta_k \hat{Q}_A \varrho_n^{(n-1)} - 2 \alpha_2 \sum_{kk'} \hat{\varrho}_n^{(n+2)} - \eta_{k'} \varrho_n^{(n-1)} - \delta_{kk'} \hat{\varrho}_n^{(n+2)} - \eta_{k'} \varrho_n^{(n-2)} \right], \quad (49)$$

with

$$\hat{\varrho} \hat{\varrho} \equiv \hat{Q}_A \hat{\varrho}_A, \quad \hat{\varrho} \hat{\varrho}_A \equiv \eta_k \hat{Q}_A \hat{\varrho}_A. \quad (50a)$$

Evidently, when $\alpha_2 = 0$, Eq. (49) reduces to the conventional i-DEOM formalism.\textsuperscript{51,58} The solutions of $Z_{\text{hyb}} = \text{Tr} \varrho_0^{(0)} (\hat{\varrho})$ can be obtained by propagation of Eq. (49) from the initial values $\varrho_0^{(0)} (0) = e^{-\beta H_0 / Z_0}$ and $\varrho_0^{(n>0)} (0) = 0$.

### B. Extended neq-$\lambda$–DEOM formalism

Turn to the neq-$\lambda$–DEOM formalism, aiming at the system–bath mixing nonequilibrium work and its distribution function.\textsuperscript{51,60} The involved $\lambda(t)$–augmented total composite Hamiltonian reads

$$H(t) = H_s + h_n + \lambda(t) H_{\text{sb}}. \quad (51)$$

A time–dependent mixing function $\lambda(t)$ is used subject to $\lambda(t = 0) = 0$ and $\lambda(t = t_f) = 1$. This represents a nonequilibrium scenario. In related studies, the work distribution $p(w)$ is the key quantity. There exists the Jarzynski equality\textsuperscript{72}

$$\langle e^{-\beta w} \rangle \equiv \int_{-\infty}^{\infty} dw e^{-\beta w} p(w) = e^{-\beta A_{\text{hyb}}} \quad (52)$$

and the Crooks relation\textsuperscript{73}

$$e^{-\beta w} p(w) = e^{-\beta A_{\text{hyb}}} \bar{p}(-w). \quad (53)$$

The latter is about a pair of conjugate processes, with the forward and backward processes being controlled by $\lambda(t)$.
and \( \tilde{\lambda}(t) \equiv \lambda(t_f - t) \), respectively.\textsuperscript{74} The forward work distribution \( p(w) \) and the backward \( \tilde{\beta}(-w) \) cross at \( w = \Delta_{ab} \) where \( A_{ab} \) can be obtained via the i-DEOM calculation with Eqs. (42) and (43).

The \( \text{neg}-\lambda \)-DEOM enables the accurate evaluation of \( p(w) \). To proceed, we start with \( H_0 |n \rangle = H_1(\lambda = 0) |n \rangle = \epsilon_n |n \rangle \) and \( H_1(\lambda = 1) |N \rangle = E_N |N \rangle \) before and after mixing. The distribution of mixing work is given by\textsuperscript{75}

\[
p(w) = \sum_{N,n} \delta(w - E_N + \epsilon_n) P_{N,n}(t_f, 0) e^{-\beta \epsilon_n} / Z_0.
\]

In Eq. (54), \( P_{N,n}(t, 0) = |\langle N | \hat{U}_1(t) |n \rangle |^2 \) is the transition probability with the propagator \( \hat{U}_1(t) \) being governed by the Hamiltonian \( H_1(t) = H_0 + \lambda(t) H_{ab} \).

Define then

\[
\Phi_1(t; \tau) = \hat{U}_1(t) \hat{V}_+ + (t; \tau) \rho_0^{eq}(T) \hat{V}_- (t; \tau) \hat{U}_1^\dagger(t),
\]

where

\[
\hat{V}_\pm (t; \tau) = \exp \left[ \frac{i {\tau}}{\hbar} \left( \hat{h}_1 \mp \frac{1}{2} \hat{\lambda}(t') H_{ab} \right) \right].
\]

It can be shown that\textsuperscript{75,76}

\[
p(w) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\tau e^{-\nu \tau} \text{Tr} \hat{\Phi}_1(t_f; \tau).
\]

This concludes that \( \hat{\Phi}_1(t; \tau) \), defined in Eq. (55), is the work generating operator, satisfying

\[
\frac{\partial \hat{\Phi}_1}{\partial \tau} = -i [\hat{h}^+_1 + \hat{h}^-_1 + \hat{\lambda}_-(t) H_{ab} - \hat{\lambda}_+(t) H_{ab}] \hat{\Phi}_1,
\]

with

\[
\hat{\lambda}_\pm(t) \equiv \hat{\lambda}(t) \pm (\tau/2) \hat{\lambda}(t).
\]

Initially, \( \hat{\Phi}_1(0; \tau) = \rho_0^{eq}(T) = e^{-\beta H_0} / Z_0 \), as inferred from Eq. (55).

Similar to Eq. (46), we obtain the dissipatis-
ons-augmented work generating operators (D-WGOs) mapping,

\[
\hat{\Phi}_1(t; \tau) \rightarrow \hat{\Phi}_1(t; \tau) \equiv \{ \hat{\Phi}_1^{(n)}(t; \tau) \}.
\]

Following the similar procedure from Eq. (12) to Eq. (18) applied to Eq. (58), we obtain the D-WGO correspondence\textsuperscript{51,60}

\[
\hat{\Phi}_1^{(n)} = - \left( i \hat{L}_1 + \sum_k n_k \gamma_k \right) \hat{\Phi}_1^{(n)} - i \left( \alpha_0 + \alpha_2 \hat{\lambda}^2 \right) \hat{\lambda} \hat{\Phi}_1^{(n)} - i \alpha_1 \sum_k \left[ \hat{\lambda} \hat{\Phi}_1^{(n+1)} + n_k \hat{\lambda} \hat{\Phi}_1^{(n-1)} \right] - i \alpha_2 \sum_{kk'} \left[ \hat{\lambda} \hat{\Phi}_1^{(n+2)} + n_{kk'} \hat{\lambda} \hat{\Phi}_1^{(n-2)} \right] - 2i \alpha_3 \sum_{kk'} n_{kk'} \hat{\lambda} \hat{\Phi}_1^{(n)}.
\]

where

\[
\begin{align*}
\hat{\lambda}'(t) &\equiv \lambda - (t) \hat{\Omega} \hat{\Omega} - \lambda_+(t) \hat{\Omega} \hat{\Omega}, \\
\hat{\Omega} &\equiv \lambda_-(t) \eta_{kk'} \hat{\Omega}_{kk'} \hat{\lambda} + \lambda_+(t) \eta_{kk'} \hat{\Omega}_{kk'} \hat{\lambda}, \\
\hat{\Omega}_{kk'} &\equiv \lambda_-(t) \eta_{kk'} \hat{\Omega}_{kk'} \hat{\lambda} + \lambda_+(t) \eta_{kk'} \hat{\Omega}_{kk'} \hat{\lambda}.
\end{align*}
\]

In relation to \( \hat{\Phi}_1(0; \tau) = \rho_0^{eq}(T) = e^{-\beta H_0} / Z_0 \), the initial values to Eq. (61) are

\[
\hat{\Phi}_1^{(0)}(0; \tau) = e^{-\beta H_0} / Z_0 \text{ and } \hat{\Phi}_1^{(n>0)}(0; \tau) = 0.
\]

Finally, by using Eq. (61) with Eqs. (62) and (59), we evaluate

\[
p(w) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\tau e^{-\nu \tau} \text{Tr} \{ \hat{\Phi}_1^{(0)}(t_f; \tau) \}.
\]

C. Numerical demonstrations

In our simulations, we set the forward and backward time-dependent mixing function to be

\[
\lambda(t) = \frac{1 - e^{-at}}{1 - e^{-at_f}},
\]

and

\[
\tilde{\lambda}(t) = \lambda(t_f - t) = e^{at_f - e^{at}} - e^{at_f - 1},
\]
respectively. Figure 4 reports the DEOM results in terms of the Jarzynski equality (52) and the Crooks relation (53). The $e^{-\beta_{b_0}b}$ and the $v$ related functions are evaluated by the methods described in Sec. IV A and Sec. IV B, respectively. Numerical simulations are carried out with the same setup as in Fig. 3. The upper panel shows that the Jarzynski equality is recovered. At the high-temperature regime, the classical equipartition theorem holds as seen from the coincidence between the results of $L$ and $L+Q$ scenarios. The lower panel reproduces the Crooks relation. The resulting work distribution function can be analyzed in using the cumulants of various orders, including the center, the variance, the skewness and so on.\textsuperscript{77} It is worth reemphasizing that Fig. 4 in turn confirms the rigorousness of the extended DEOM theories, covering the real–time, the imaginary–time and the nonequilibrium $\lambda(t)$ dynamics.

V. SUMMARY

To conclude, we present a comprehensive account of extended DEOM with quadratic environments, which could in principle be generalized to arbitrary nonlinear bath coupling scenarios. The developments include also an equivalent core-system phase–space hierarchy construction, BSM-HQME, as verified both theoretically and numerically. The extended DEOM is numerically more efficient, whereas the core–system BSM-HQME is favorable for “visualizing” the correlated solvation dynamics.

While the present theories are elaborated with the single dissipative mode case, the extensions to multiple dissipative modes, including modes mixing (i.e. Duschinsky rotation), are straightforward. Moreover, the existing system–bath entanglement theorem with linear environment coupling\textsuperscript{51,58,78,79} can be further investigated with the inclusion of quadratic environment coupling. The aforementioned theoretical developments would comprise required toolkits for the construction of practical dissipaton–correlated coarse-graining molecular dynamics and thermodynamics methods.

It is also worth noting that the GWTs are validated within the canonical Feynman–Vernon influence functional formalism with the linear environmental couplings.\textsuperscript{65} However, it is rather cumbersome to prove the GWTs and derive the EOM in nonlinear coupling scenarios using the Feynman–Vernon influence functional approach. There is no simple analytical expression of nonlinear influence functionals. On the other hand, the dissipaton algebra enables the GWT-2 in the most direct manner. The resulting Eq. (18), the extended DEOM formalism,\textsuperscript{41,42} is numerically validated by comparing with other two very different approaches, BSM-HQME and SFD-DEOM, in this work. This indicates that the dissipaton theory would be an important building block towards the future development of open quantum systems.

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Appendix: Onset of algebra for Brownian solvation mode

1. The Fokker–Planck operator and basis set construction

The following part is the procedure to generate the FP basis set for describing the solvation mode inside the core system. Let us start from Eq. (5) with Eq. (21). In the Markovian limit, $\zeta_a(\omega) = \zeta_a$, by further adopting the high–temperature approximation,\textsuperscript{57} we have

$$\langle \hat{x}_a(t) \hat{x}_a(0) \rangle_a \approx \eta_+ e^{-\gamma_+ t} + \eta_- e^{-\gamma_- t}, \quad (A.1)$$

with

$$\gamma_\pm = \frac{1}{2} \left[ \zeta_a \pm (\zeta_a^2 - 4 \omega_a^2)^{1/2} \right], \quad (A.2)$$

and

$$\eta_\pm = \mp \frac{\omega_a}{\gamma_+ \gamma_-} \left( \frac{1}{\beta \gamma_\pm} - \frac{i}{2} \right). \quad (A.3)$$

It should be noticed that the Markovian and high–temperature limits are needed only for the construction of FP operator and FP algebra, which are not necessary for the BSM-HQME, which is exact at any temperature.

Then one may construct the FP operator $\mathcal{L}_w$ that would generate the FP basis set.\textsuperscript{55-57}

$$\mathcal{L}_w(\cdot) = \frac{\omega_a}{2} \left[ \hat{x}_a^2 + \hat{p}_a^2, \cdot \right] + \frac{\zeta_a}{\beta \omega_a} [\hat{x}_a, \{\hat{x}_a, \cdot \}]$$

$$+ i \frac{\zeta_a}{2} [\hat{x}_a, \{\hat{p}_a, \cdot \}] + \cdots. \quad (A.4)$$

In Wigner representation, the FP operator, Eq. (A.4), can be converted to a solvation phase–space operator as

$$L_{wp} \equiv \omega_a \left( \frac{\partial}{\partial x_a} p_a - \frac{\partial}{\partial p_a} x_a \right) - \frac{\zeta_a}{\beta \omega_a} \frac{\partial^2}{\partial p_a^2} - \frac{\zeta_a}{\beta} \frac{\partial}{\partial p_a} p_a, \quad (A.5)$$

where $x_a$ and $p_a$ are c–number valued solvation coordinate and momentum, respectively. Under the similarity transformation

$$L_{wp} = e^S L_{wp} e^{-S}, \quad (A.6)$$

with $S \equiv \frac{\beta \omega_a}{2} (x_a^2 + p_a^2)$, we can recast $L_{wp}$ as

$$L_{wp} = \omega_a (\hat{c}_1^\dagger a_2^\dagger - a_1^\dagger a_2) + \zeta_a a_1^\dagger a_2,$$

$$\gamma_+ c_1^\dagger c_1^\dagger + \gamma_- c_2^\dagger c_2^\dagger. \quad (A.7)$$
The first line involves solvation phase–space operators,

\[ a_1 = \frac{\sqrt{\beta \omega_b}}{2} x_b + \frac{1}{\sqrt{\beta \omega_b}} \frac{\partial}{\partial x_b}, \]
\[ a_2 = \frac{\sqrt{\beta \omega_b}}{2} p_b + \frac{1}{\sqrt{\beta \omega_b}} \frac{\partial}{\partial p_b}, \] (A.8a)

and the corresponding

\[ a_1^\dagger = \frac{\sqrt{\beta \omega_b}}{2} x_b - \frac{1}{\sqrt{\beta \omega_b}} \frac{\partial}{\partial x_b}, \]
\[ a_2^\dagger = \frac{\sqrt{\beta \omega_b}}{2} p_b - \frac{1}{\sqrt{\beta \omega_b}} \frac{\partial}{\partial p_b}. \] (A.8b)

In Eq. (A.7), the \( \omega_b \)-term describes the coherent dynamics and the \( \zeta_b \)-term is responsible for dissipation. The second line describes the quasi-particle diagonalization, with

\[ c_1^\dagger = r_2 a_1 + r_1 a_2, \quad c_2^\dagger = r_2 a_1 - r_1 a_2, \]
\[ c_1^\dagger = -r_2 a_1^\dagger + r_1 a_2^\dagger, \quad c_2^\dagger = r_1 a_1^\dagger - r_2 a_2^\dagger, \] (A.9)

and

\[ r_1 = \sqrt{\gamma_+/\gamma_+ - \gamma_-,} \quad r_2 = \sqrt{\gamma_-/\gamma_+ - \gamma_-}. \] (A.10)

Note that \( c_{1,2}^\dagger \neq (c_{1,2})^\dagger \). It is easy to verify that they satisfy the bosonic commutation relations as

\[ [c_j^\dagger, c_j] = [a_j, a_j^\dagger] = \delta_{jj}, \]
\[ [c_j^\dagger, c_j^\dagger] = [a_j, a_j] = [a_j^\dagger, a_j^\dagger] = 0. \] (A.11)

The eigenfunctions of \( L_{qs} \) can now be obtained as

\[ \Psi_{n_1, n_2}(x_b, p_b) = \frac{1}{\sqrt{n_1 n_2!}} (c_1^\dagger)^{n_1} (c_2^\dagger)^{n_2} \Psi_{00}(x_b, p_b), \] (A.12)

with

\[ \Psi_{00}(x_b, p_b) \equiv \left( \frac{\beta \omega_b}{2\pi} \right)^{\frac{1}{2}} e^{-\frac{\beta \omega_b}{2\pi} (x_b^2 + p_b^2)}. \] (A.13)

It can be verified that

\[ L_{qs} \Psi_{n_1, n_2} = (n_1 \gamma_+ + n_2 \gamma_-) \Psi_{n_1, n_2}. \] (A.14)

Furthermore, by denoting \( \tilde{c}_j^\dagger \equiv (c_j^\dagger)^\dagger \), we can also construct the eigenfunctions \( \{ \tilde{\Psi}_{n_1, n_2} \} \) of \( L_{qs} \) in a similar way, reading

\[ \tilde{\Psi}_{n_1, n_2}(x_b, p_b) = \frac{1}{\sqrt{n_1 n_2!}} (\tilde{c}_1^\dagger)^{n_1} (\tilde{c}_2^\dagger)^{n_2} \Psi_{00}(x_b, p_b), \] (A.15)

satisfying

\[ \tilde{L}_{qs} \tilde{\Psi}_{n_1, n_2} = (n_1 \gamma_+ + n_2 \gamma_-) \tilde{\Psi}_{n_1, n_2}. \] (A.16)

The functions \( \{ \tilde{\Psi}_{n_1, n_2} \} \) are orthonormal with respect to \( \{ \Psi_{n_1, n_2} \} \) as

\[ \int \int dx_b dp_b \tilde{\Psi}_{n_1, n_2}(x_b, p_b) \Psi_{n_1', n_2'}(x_b, p_b) = \delta_{n_1 n_1'} \delta_{n_2 n_2'}. \] (A.17)

Any function \( W(x_b, p_b) \), including that of Eq. (30), can be expanded under this set of eigenfunctions \( \{ \Psi_{n_1, n_2} \} \) as

\[ W(x_b, p_b) = \left( \frac{\beta \omega_b}{2\pi} \right)^{\frac{1}{2}} \sum_{n_1, n_2} \frac{s_{n_1, n_2}}{\sqrt{n_1! n_2!}} \rho_{n_1, n_2} \]
\[ \times e^{-\frac{\beta \omega_b}{2 \pi} (x_b^2 + p_b^2)} \Psi_{n_1, n_2}(x_b, p_b). \] (A.18)

Here, the parameters

\[ s_{n_1, n_2} = (-1)^{n_1} \left( \frac{\beta \omega_b}{2\pi} \right)^{\frac{1}{2}} \int \int dx_b dp_b \Psi_{n_1, n_2}(x_b, p_b) \]
\[ \times e^{-\frac{\beta \omega_b}{2 \pi} (x_b^2 + p_b^2)} W(x_b, p_b). \] (A.19)

Moreover, the \( \Psi_{n_1, n_2}(x_b, p_b) \) can be explicitly expressed via Eq. (A.12) with Eqs. (A.8b) and (A.9), as

\[ \Psi_{n_1, n_2}(x_b, p_b) = \sum_{j_1 j_2} \frac{n_1}{j_1} \frac{n_2}{j_2} \frac{1}{\sqrt{n_1! n_2!}} \Psi_{11} \times \sqrt{(n_1 + n_2 - j_1 - j_2)!(j_1 + j_2)!} \]
\[ \times \Psi_{n_1+n_2-j_1-j_2}(x_b) \Psi_{j_1+j_2}(p_b). \] (A.21)

Here, the harmonic eigenfunctions, \( \psi_n(z) \), read

\[ \psi_n(z) \equiv \left( \frac{\beta \omega_b}{2\pi} \right)^{\frac{1}{2}} e^{-\frac{\beta \omega_b}{2 \pi} z^2} H_n \left( \sqrt{\beta \omega_b} z \right) \] (A.22)

where \( H_n(z) \) is the \( n \)-order Hermitian polynomials. Thus we finish the procedure to generate the FP basis set, \( \{ \Psi_{n_1, n_2} \} \) [cf. Eq. (A.21)].

2. Actions of coordinate and momentum operators

In this subsection, we derive the actions of coordinate and momentum operators on \( W(x_b, p_b) \) expressed in Eq. (A.18). Firstly we map the left/right actions of coordinate and momentum operators \( \hat{x}_b^\pm \) and \( \hat{p}_b^\pm \) into the Wigner representation as

\[ \hat{x}_b^\pm \rightarrow x_b \pm \frac{i}{2} \frac{\partial}{\partial p_b} \text{ and } \hat{p}_b^\pm \rightarrow p_b \pm \frac{i}{2} \frac{\partial}{\partial x_b}. \] (A.23)
Then by using Eq. (A.18), we obtain the solvation mode actions on $\rho_{n_1,n_2}$ as

$$
\dot{\bar{x}}_{\beta} \rho_{n_1,n_2} = \rho_{n_1+1,n_2} + \rho_{n_1,n_2+1} + n_1 \eta_{+} \rho_{n_1-1,n_2} + n_2 \eta_{-} \rho_{n_1,n_2-1}, \tag{A.24a}
$$

$$
\dot{x}_{\beta} \rho_{n_1,n_2} = \rho_{n_1+1,n_2} + \rho_{n_1,n_2+1} + n_1 \eta_{+} \rho_{n_1-1,n_2} + n_2 \eta_{-} \rho_{n_1,n_2-1}, \tag{A.24b}
$$

$$
\omega_{\rho} \bar{p}_{\rho} \rho_{n_1,n_2} = -\gamma \rho_{n_1+1,n_2} - \gamma \rho_{n_1,n_2+1} - n_1 \bar{\eta}_{+} \gamma \rho_{n_1-1,n_2} - n_2 \eta_{-} \gamma \rho_{n_1,n_2-1}, \tag{A.24c}
$$

$$
\omega_{\rho} \bar{p}_{\rho} \rho_{n_1,n_2} = -\gamma \rho_{n_1+1,n_2} - \gamma \rho_{n_1,n_2+1} - n_1 \bar{\eta}_{+} \gamma \rho_{n_1-1,n_2} - n_2 \eta_{-} \gamma \rho_{n_1,n_2-1}. \tag{A.24d}
$$

Here, we denote

$$
\bar{\eta}_{+} = \mp \frac{\omega_{\rho}}{\gamma_{+} - \gamma} \left( \frac{1}{\beta \gamma_{+}} + i \frac{\lambda}{2} \right). \tag{A.25}
$$

The derivations of Eqs. (A.24a)–(A.24d) are as follows. Let us start with the actions of coordinate operator, $\bar{x}_{\beta}$, in the Wigner representation [cf. Eq. (A.18) with Eq. (A.8b)],

$$
\dot{\bar{x}}_{\beta} W(x_{\beta}, p_{\beta}) = \left( x_{\beta} \pm i \frac{\partial}{2 \partial p_{\beta}} \right) W(x_{\beta}, p_{\beta}),
$$

$$
\dot{\bar{x}}_{\beta} W(x_{\beta}, p_{\beta}) = \left( \frac{\beta \omega_{\beta}}{2 \pi} \right)^{\frac{1}{2}} \sum_{n_1,n_2} \frac{S_{n_1,n_2}}{\sqrt{n_1! n_2!}} \rho_{n_1,n_2} \left( x_{\beta} \pm i \frac{\partial}{2 \partial p_{\beta}} \right) \times e^{-\frac{\beta \omega_{\beta}}{2} \left( \bar{x}_{\beta}^2 + \bar{p}_{\beta}^2 \right)} \Psi_{n_1,n_2},
$$

$$
\dot{\bar{x}}_{\beta} W(x_{\beta}, p_{\beta}) = \left( \frac{\beta \omega_{\beta}}{2 \pi} \right)^{\frac{1}{2}} \sum_{n_1,n_2} \frac{S_{n_1,n_2}}{\sqrt{n_1! n_2!}} \rho_{n_1,n_2} e^{-\frac{\beta \omega_{\beta}}{2} \left( \bar{x}_{\beta}^2 + \bar{p}_{\beta}^2 \right)} \times \left( \frac{a_1 + a_1^\dagger}{\sqrt{\beta \omega_{\beta}}} + \frac{i \beta \omega_{\beta}^2}{2} \right) \Psi_{n_1,n_2}.
$$

Apply then Eq. (A.9) and the FP algebra, resulting in

$$
\dot{\bar{x}}_{\beta} W = \left( \frac{\beta \omega_{\beta}}{2 \pi} \right)^{\frac{1}{2}} \sum_{n_1,n_2} \frac{S_{n_1,n_2}}{\sqrt{n_1! n_2!}} \rho_{n_1,n_2} e^{-\frac{\beta \omega_{\beta}}{2} \left( \bar{x}_{\beta}^2 + \bar{p}_{\beta}^2 \right)} \times \frac{1}{\sqrt{\beta \omega_{\beta}}} \left[ -r_2 c_{1-} + r_1 c_{2+} + (r_2 + ir_2 \sqrt{\beta \omega_{\beta}}/2) c_{1+}^+ \right. \\
+ (r_1 + ir_2 \sqrt{\beta \omega_{\beta}}/2) c_{2+}^+ \left] \Psi_{n_1,n_2},
$$

$$
\dot{\bar{x}}_{\beta} W = \left( \frac{\beta \omega_{\beta}}{2 \pi} \right)^{\frac{1}{2}} \sum_{n_1,n_2} \frac{S_{n_1,n_2}}{\sqrt{n_1! n_2!}} \rho_{n_1,n_2} e^{-\frac{\beta \omega_{\beta}}{2} \left( \bar{x}_{\beta}^2 + \bar{p}_{\beta}^2 \right)} \times \frac{1}{\sqrt{\beta \omega_{\beta}}} \left[ -r_2 \sqrt{n_1 \Psi_{n_1-1,n_2} + r_1 \sqrt{n_2 \Psi_{n_1,n_2-1}} \right. \\
+ (r_2 + ir_2 \sqrt{\beta \omega_{\beta}}/2) \sqrt{n_1} + 1 \Psi_{n_1+1,n_2} \\
+ (r_1 + ir_2 \sqrt{\beta \omega_{\beta}}/2) \sqrt{n_2} + 1 \Psi_{n_1,n_2+1} \right] \\
= \left( \frac{\beta \omega_{\beta}}{2 \pi} \right)^{\frac{1}{2}} e^{-\frac{\beta \omega_{\beta}}{2} \left( \bar{x}_{\beta}^2 + \bar{p}_{\beta}^2 \right)} \left[ (1) + (2) + (3) + (4) \right].
$$

where

$$
(1) = \sum_{n_1,n_2} \frac{S_{n_1+1,n_2}}{(n_1+1)! n_2!} \rho_{n_1+1,n_2} \frac{-r_2}{\sqrt{\beta \omega_{\beta}}} \sqrt{n_1} + 1 \Psi_{n_1,n_2}
$$

$$
(2) = \sum_{n_1,n_2} \frac{S_{n_1,n_2+1}}{n_1! (n_2+1)!} \rho_{n_1,n_2+1} \frac{r_1}{\sqrt{\beta \omega_{\beta}}} \sqrt{n_2} + 1 \Psi_{n_1,n_2}
$$

$$
(3) = \sum_{n_1,n_2} \frac{S_{n_1,n_2}}{n_1! n_2!} \rho_{n_1,n_2} \psi_{n_1,n_2}
$$

$$
(4) = \sum_{n_1,n_2} \frac{S_{n_1+1,n_2}}{(n_1+1)! n_2!} \rho_{n_1+1,n_2} \psi_{n_1,n_2}
$$

In the last steps of above derivations, Eqs. (A.3) and (A.10) are used. We then finish deriving Eqs. (A.24a) and (A.24b) by adding the four terms together. Similarly, for actions of $p_{\beta}$ on the coefficient function $\rho_{n_1,n_2}$, we obtain Eqs. (A.24c) and (A.24d).

Turn to core–system EOM in Eq. (31) with Eq. (32). By using Eqs. (A.24a)-(A.24d), we obtain

$$
\nu_{n,\bar{n}} = - \left[ i \mathcal{L} - 2(n_1 - n_2) \omega_{\beta} r_1 r_2 + \gamma_{\beta} \right.
\left. + i \sum_{j=1}^{2} \left( 2n_j + 1 \right) \left( \lambda C_j + \omega \mathcal{E}_j \right) + i \omega_{\beta} \mathcal{F} \right] \rho_{n,\bar{n}}
$$

$$
- \sum_{j=1}^{2} \left[ \left( -1 \right)^j n_j \omega_{\beta} r_j r_{1} \left( 1 + \gamma_{\beta} \gamma_{\beta} \right) \right. \\
+ 2i \lambda \left( \lambda C_j + \omega \mathcal{E}_j \right) \left. \rho_{n_j,\bar{n}} \right]
$$

$$
- i \omega_{\beta} \sum_{j=1}^{2} \left( n_j \mathcal{C}_j + n_j \mathcal{E}_j \mathcal{C}_j \right) \left( \lambda B_{j} + \omega \mathcal{E}_j \lambda_{j} \right) \left( \lambda B_{j} + \omega \mathcal{E}_j \lambda_{j} \right) \left( \lambda B_{j} + \omega \mathcal{E}_j \lambda_{j} \right) \rho_{n_j,\bar{n}}
$$

$$
- i \omega_{\beta} \sum_{j=1}^{2} \left( n_j \mathcal{E}_j + n_j \mathcal{E}_j \mathcal{C}_j \right) \left( \lambda B_{j} + \omega \mathcal{E}_j \lambda_{j} \right) \left( \lambda B_{j} + \omega \mathcal{E}_j \lambda_{j} \right) \left( \lambda B_{j} + \omega \mathcal{E}_j \lambda_{j} \right) \rho_{n_j,\bar{n}}
$$

with $\gamma_{1/2} = \gamma_{c}$ and $\lambda$ being given in Eq. (27),

$$
B_{j} = \eta_{j} \eta_{j} - \bar{\eta}_{j} \bar{\eta}_{j}, \quad C_{j} = \eta_{j} - \bar{\eta}_{j}, \quad \bar{\lambda}_{j} = \eta_{j} - \bar{\eta}_{j}. \tag{A.27}
$$

The involved superoperators are similar to those of Eq. (19),
but with

\[
\mathcal{S}_j \hat{\dot{O}} = \hat{\dot{Q}}_j \hat{\dot{O}} - \hat{\dot{O}} \hat{\dot{Q}}_j, \quad \mathcal{R}_{jj} \hat{\dot{O}} = \eta_j \hat{\dot{Q}}_j \hat{\dot{O}} - \eta_j^* \hat{\dot{Q}}_j \hat{\dot{O}},
\]

(A.28)

Note also that \( j = 2 \) when \( j = 1 \), and vice versa.

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