Entangled system–and–environment dynamics: Phase–space dissipaton theory

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Dissipaton–equation–of–motion (DEOM) theory [Y. J. Yan, J. Chem. Phys. 140, 054105 (2014)] is an exact and nonperturbative many–particle method for open quantum systems. The existing dissipaton algebra treats also the dynamics of hybrid bath solvation coordinates. The dynamics of conjugate moments remain to be addressed within the DEOM framework. In this work, we establish this missing ingredient, the dissipaton algebra on solvation momentums, with rigorous validations against necessary and sufficient criteria. The resulted phase–space DEOM theory will serve as a solid ground for further developments of various practical methods toward a broad range of applications. We illustrate this novel dissipaton algebra with the phase–space DEOM–evaluation on heat current fluctuation.

Entangled system–and–environment dynamics play crucial roles whenever the non-Markovian and nonperturbative quantum nature of environments cannot be neglected. Traditionally this problem was addressed with the “core–system” approach. This is to divide the overall environment into the “first–shell” and “secondary” parts. The core-system comprises both the primary system and the first–shell hybrid bath solvation modes. Various approximate theories such as quantum master equations had been applied to treat the reduced phase-space dynamics. However, the conjugate momentum dynamics is in general too expensive. On the other hand, the dissipaton–equation–of–motion (DEOM) theory exploits the hierarchical–equations–of–motion (HEOM) formalism, which is exact for arbitrary systems coupling with Gaussian environments. However, HEOM involves a vast number of dynamical variables that are just mathematical auxiliaries without physical meanings. In this sense, HEOM is mainly a reduced primary–system theory. Its exact treatment on the system–plus–solvation core dynamics is in general too expensive. On the other hand, the dissipaton–equation–of–motion (DEOM) theory, which recovers the HEOM formalism, is by far capable of treating the hybrid bath solvation coordinate dynamics. However, the conjugate momentum dynamics is yet to be addressed within the DEOM framework.

The main objective of this work is to complete the DEOM theory as an exact and nonperturbative “core–system” phase–space method. To that end, we construct the dissipaton algebra on the conjugate solvation momentum. The resulted phase–space DEOM theory is rigorously validated with respect to necessary and sufficient criteria. It is worth noting that open quantum systems are beyond the total system–plus–bath composite Hamiltonian description. Additional information, such as temperature $T$ and the interacting bath statistics, would be needed. The underlying irreversibility will eventually lead to the total system–plus–bath composite bulk matter the Boltzmann distribution at a given temperature $T$. In fact, the total composite Hamiltonian constitutes a “closed system” in the thermodynamics nomenclature, such as a solution system in chemistry, which is in thermal contact with surroundings. The solute–and–solvent mixing free–energy change is dictated by the coupling between them. The exact and nonperturbative phase–space DEOM theory to be developed in this work would serve as a solid foundation for development of various practical simulation methods toward realistic molecular systems in condensed phases.

Without loss of generality, we focus explicitly on a single–dissipative–mode case, with the system–bath coupling the form of $H_{ab} = Q_x \hat{x}_b$. While the dissipative system mode $\hat{Q}_x$ is arbitrary, the solvation coordinate $\hat{x}_b$ is linear, which together with harmonic bath $h_b$ constitute a Gaussian–Wick’s environment. The total composite Hamiltonian considered explicitly in this work reads

$$H_T = H_s + h_b + Q_x \hat{x}_b. \tag{1}$$

Throughout the paper we set $\hbar = 1$ and $\beta = 1/(k_B T)$, with $k_B$ the Boltzmann constant and $T$ the temperature. Let $\rho_s^M(T)$ be a steady–state density operator in the total system–plus–bath composite space, which defines the ensemble average, $\langle \cdot \rangle = \text{Tr}[\rho_s^M(T) \cdot]$. Denote $\hat{A}(t) \equiv e^{-i H_T t} A e^{i H_T t}$ for an arbitrary dynamical operator. Set the time variable $t \geq 0$, unless further specified.

Let $\hat{x}_b$ and $\hat{p}_b$ be the dimensionless solvation coordinate and momentum respectively. The solvation bath frequency $\omega_b$ can be specified later in relation to the Gaussian–Wick’s environment description; see Eq. (4). We have

$$\dot{\hat{x}}_b = i [H_T, \hat{x}_b] = i [h_b, \hat{x}_b] = \omega_b \hat{p}_b. \tag{2}$$

This leads to $\langle \hat{A}(t) \hat{x}_b(0) \rangle = -\langle \hat{A}(t) \hat{p}_b(0) \rangle$ the expression

$$\langle \hat{A}(t) \hat{x}_b(0) \rangle = -\omega_b \langle \hat{A}(t) \hat{p}_b(0) \rangle. \tag{3}$$

This together with $[\hat{x}_b, \hat{p}_b] = i$ constitutes the necessary and sufficient requirements for the to–be–developed dissipaton algebra on the conjugate solvation momentum, in addition to the existing DEOM framework.
Let us begin with the common setup for constructing the DEOM/HEOM theory—the exponential series expansion on the interacting bath correlation function via
\[ \langle \hat{X}^n(t)\hat{X}^n(0) \rangle_n = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \frac{e^{-i\omega t}J_n(\omega)}{1 - e^{-\beta\omega}}. \] (4)

This is the fluctuation–dissipation theorem with both \( \hat{X}^n(t) \equiv e^{ih_{\text{bath}}} \hat{x} e^{-ih_{\text{bath}}} t \) and the equilibrium ensemble average, \( \langle \cdot \rangle_n \equiv \text{tr}_n(\cdot) / \text{tr}_n(e^{-\beta h_{\text{bath}}}) \), are defined in the uncorrelated bare–bath subspace. Note that \( \hat{x}_n(t) \neq \hat{x}_n(t) \) and \( \langle \cdot \rangle_n \neq \langle \cdot \rangle \) used in Eq. (3). The involving hybridization bath spectral density in Eq. (4), which satisfies \( J_n(-\omega) = -J_n(\omega) \), is given by
\[ J_n(\omega) = \frac{1}{2} \int_{-\infty}^{\infty} dt e^{i\omega t} \langle \{ \hat{x}^n(t), \hat{x}^n(0) \} \rangle_n. \] (5)

This also determines the solvation frequency with
\[ \omega_n = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \omega J_n(\omega). \] (6)

The required exponential series expansion on Eq. (4) can be achieved by adopting a certain the sum-over–poles scheme to expand the Fourier integrand there, followed by Cauchy’s contour integration. Together with the identity \( \langle \hat{x}^n(0)\hat{x}^n(0) \rangle_n = \langle \hat{x}^n(t)\hat{x}^n(0) \rangle_n \), we obtain
\[
\langle \hat{x}^n(t)\hat{x}^n(0) \rangle_n = \sum_{k=1}^{K} \eta_k e^{-\gamma_k t}; \quad (t \geq 0), \quad (K) \equiv \gamma_k \equiv \gamma_k.
\] (7)

The second expression follows the fact that \( \{ \gamma_k \} \) must be either real or complex conjugate paired. The associated index \( k \in \{ k = 1, \cdots, K \} \) is defined via \( \gamma_k \equiv \gamma_k \).

Note that \( \hat{x}^n(0) = \hat{x}_n(0) = \hat{x}_n \) and \( \hat{x}^n(t) = \omega_n^* \hat{p}_n(0) = \omega_n^* \hat{p}_n = \hat{x}_n \), as inferred from Eq. (4). Thus, from Eq. (4), we have
\[
\langle \hat{x}_n\hat{x}_n \rangle = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \frac{\omega J_n(\omega)}{1 - e^{-\beta\omega}} = \frac{1}{2\pi i} \int_{-\infty}^{\infty} d\omega \omega J_n(\omega) = \frac{\omega_n}{2\pi i}. \] (8)

While the second expression uses the property of \( J_n(-\omega) = -J_n(\omega) \), the last one is from Eq. (9). Moreover, from the identity, \( \langle \hat{x}_n\hat{x}_n \rangle = -\langle \hat{x}_n\hat{x}_n \rangle \), and Eq. (7), we obtain
\[ \omega_n = -2i \sum_k \gamma_k \eta_k = 2i \sum_k \gamma_k \eta_k. \] (9)

We have also
\[ \langle \hat{x}^2 \rangle_n = \sum_k \eta_k = \sum_k \eta_k. \] (10)

Turn to the existing DEOM framework. First of all, dissipators \( \{ f_k \} \) are statistically independent quasi–particles and characterize Gaussian solvation environments. To reproduce Eq. (7), we set
\[ \hat{x}_n = \sum_{k=1}^{K} f_k, \] (11)

\[ \hat{f}_k(t) = e^{ih_{\text{bath}}} f_k e^{-ih_{\text{bath}}} t, \] and
\[
\langle \hat{f}_k(t)\hat{f}_k(0) \rangle_n = \langle \hat{f}_k \hat{f}_k^\dagger \rangle_n \equiv \delta_{kk} \langle \eta_k e^{-\gamma_k t} \rangle, \quad \langle \hat{f}_k(0)\hat{f}_k(t) \rangle_n = \langle \hat{f}_k \hat{f}_k^\dagger \rangle_n e^{-\gamma_k t} = \delta_{kk} \langle \eta_k e^{-\gamma_k t} \rangle, \] (12)

with \( \langle \hat{A}\hat{B} \rangle = \langle \hat{A}(0)\hat{B}(0) \rangle \) and \( \langle \hat{A}\hat{B} \rangle \equiv \langle \hat{A}(0)\hat{B}(0) \rangle \). Each forward–and–backward pair of dissipation correlation functions are associated with a single–exponent \( \gamma_k \). The resultant generalized diffusion equation reads
\[ \text{tr}_n \left[ \left( \frac{\partial}{\partial t} \hat{f}_k \right) \rho_n(t) \right] = -\gamma_k \text{tr}_n \left[ [\hat{f}_k \rho_n(t)] \right]. \] (13)

Dynamical variables in DEOM are the dissipator–augmented–reduced density operators (DDOs)
\[ \rho_n^{(n)}(t) \equiv \rho_{n_1,\cdots,n_K}(t) \equiv \text{tr}_n \left[ (\hat{f}_K^{n_K} \cdots \hat{f}_1^{n_1})^\circ \rho(t) \right]. \] (14)

Here, \( n = n_1 + \cdots + n_K \), with \( n_k \geq 0 \) for bosonic dissipators. The product of dissipator operators inside \( \{ \cdots \} \) is irreducible, satisfying \( \langle \hat{f}_k \hat{f}_k^\dagger \rangle \equiv \langle \hat{f}_k \hat{f}_k^\dagger \rangle \) for bosonic dissipators. Each \( n \)–particles DDO, \( \rho_n^{(n)}(t) \), is specified with an ordered set of indexes, \( n \equiv \{ n_1 \cdots n_K \} \). Denote for later use also \( \eta_k^\pm \) that differs from \( \eta_k^* \) only at the specified \( \hat{f}_k \)–disapssator participation number \( n_k \) by \( \pm 1 \). The reduced system density operator is just \( \rho_0^{(0)} \equiv \rho_0^{(0)} \).

In Eq. (14), \( \rho_n(t) \) denotes the total composite density operator that satisfies
\[ \hat{\rho}_n(t) = -i[H_n, \rho_n(t)] = -i[H_n \rho_n(t) + \hat{Q}_n \hat{x}_n \rho_n(t)]. \] (15)

For presenting the related dissipator algebra, we adopt hereafter the following notations:
\[
\rho_n^{(n)}(t; \hat{A}^\times) \equiv \text{tr}_n \left[ (\hat{f}_K^{n_K} \cdots \hat{f}_1^{n_1})^\circ \hat{A}^\times \rho_n(t) \right], \quad \rho_n^{(n)}(t; \hat{A}^c) \equiv \text{tr}_n \left[ (\hat{f}_K^{n_K} \cdots \hat{f}_1^{n_1})^\circ \hat{A}^c \rho_n(t) \right]. \] (16)

where \( \hat{A}^\times \equiv \hat{A}^+ - \hat{A}^< \), with
\[ \hat{A}^+ \rho_n(t) = \hat{A} \rho_n(t), \quad \hat{A}^c \rho_n(t) = \rho_n(t) \hat{A}. \] (17)

The generalized diffusion equation (13) is now used together with \( \langle \frac{\partial}{\partial t} \hat{f}_k \rangle_n = -i[H_n, h_n] \) and results in
\[ \rho_n^{(n)}(t; h_n^2) = -i \left( \sum_k n_k \gamma_k \right) \rho_n^{(n)}(t). \] (18)

This is the dissipator algebra on the bath \( h_n \)–action.
The action of system–bath coupling is treated with the generalized Wick's theorem: \[ \rho^{(n)} (t; \hat{\varphi}^\gamma) = \rho^{(n+1)} (t; \varphi^\gamma) + \sum_{k} n_{k} \rho^{(n+1)} (t; \hat{\varphi}^\gamma). \]

Here, \( \langle \hat{f} \hat{k} \rangle^\gamma = \delta_{kk} \eta_k \) and \( \langle \hat{f} \hat{k} \rangle^\gamma = \delta_{kk} \eta^\gamma_k \) via Eq. (12). Together with Eq. (11), we have

\[ \rho^{(n)} (t; \hat{x}^\gamma) = \sum_{k} \rho^{(n)} (t; \hat{x}^\gamma), \]

with

\[ \rho^{(n)} (t; \hat{x}^\gamma) = \rho^{(n+1)} (t; \eta_k \hat{\psi}^\gamma_n), \]

\[ \rho^{(n)} (t; \hat{f}^\gamma) = \rho^{(n+1)} (t; \eta_k \hat{\psi}^\gamma_n). \]

By applying Eq. (13) for the total composite density operator \( \rho (t) \) in Eq. (14), followed by using Eqs. (18)–(20), we obtain \[ \rho^{(n)} = - \left( iH^\omega + \sum_{k} n_{k} \gamma_{k} \right) \rho^{(n)} - i \sum_{k} \hat{Q}^\gamma_{n} \rho^{(n+1)} - i \sum_{k} n_{k} \eta \hat{Q}^\gamma_{n} \rho^{(n)} \]

\[ (21) \]

As this recovers the HEOM formalism, \[ \text{we would have also de facto validated the existing dissipaton algebra on the solvation coordinate} \hat{x}^\gamma, \text{Eqs. (14)–(20)}. \]

We are now in the position to develop the dissipaton algebra on the solvation momentum \( \rho_{\hat{n}} \), in addition to the existing DEOM framework. To proceed, we set in analogy to Eq. (14) the decomposition,

\[ \rho_{\hat{n}} = \sum_{k=1}^{K} \hat{\phi}_k, \]

thus

\[ \rho^{(n)} (t; \hat{x}^\gamma) = \sum_{k} \rho^{(n)} (t; \hat{x}^\gamma). \]

The proposed new ingredients read

\[ \rho^{(n)} (t; \hat{\varphi}^\gamma) = - \frac{\gamma}{\omega} \rho^{(n+1)} (t; \eta_k \hat{\psi}^\gamma_n), \]

\[ \rho^{(n)} (t; \hat{\varphi}^\gamma) = - \frac{\gamma}{\omega} \rho^{(n+1)} (t; \eta_k \hat{\psi}^\gamma_n). \]

The proof below goes with their satisfying two basic requirements.

Consider the result on \( [\hat{x}^\gamma, \hat{\psi}_n] = i \). In the DEOM–space algebra, this necessary requirement amounts to

\[ \rho^{(n)} (t; [\hat{x}^\gamma, \hat{\psi}_n]) = i \rho^{(n)} (t). \]

**Proof** – Equation (24), together with Eq. (20), lead to

\[ \rho^{(n)} (t; \hat{f} \hat{\varphi}^\gamma) = \rho^{(n+1)} (t; \varphi^\gamma) + n_{kk} \eta_k \rho^{(n-1)} (t; \varphi^\gamma) \]

\[ = - \frac{\gamma_k}{\omega} \left[ \rho^{(n+2)} (t) - \frac{2 n_k}{2} \eta_k \rho^{(n-2)} (t) \right] \]

\[ + \frac{\gamma_k}{\omega} \rho^{(n)} (t), \]

\[ \text{(26a)} \]

and

\[ \rho^{(n)} (t; (\hat{\varphi} \hat{\varphi}^\gamma) = - \frac{\gamma_k}{\omega} \rho^{(n+1)} (t; \hat{\varphi}^\gamma) - n_{kk} \eta_k \rho^{(n-1)} (t; \hat{\varphi}^\gamma) \]

\[ = - \frac{\gamma_k}{\omega} \left[ \rho^{(n+2)} (t) - \frac{2 n_k}{2} \eta_k \rho^{(n-2)} (t) \right] \]

\[ - \frac{\gamma_k}{\omega} \rho^{(n)} (t), \]

\[ \text{(26b)} \]

The \( \rho^{(n)} (t; \hat{f} \hat{\varphi}^\gamma) \) and \( \rho^{(n)} (t; (\hat{\varphi} \hat{\varphi}^\gamma) \) counterparts are similar to \( \rho^{(n)} (\hat{f} \hat{\varphi}^\gamma) \) and \( \rho^{(n)} (t; (\hat{\varphi} \hat{\varphi}^\gamma) \), respectively, but with \( \eta_k \) being replaced by \( \eta_k^\gamma \). Together with

\[ \rho^{(n)} (t; \hat{f} \hat{\varphi}^\gamma) \equiv \rho^{(n)} (t; \hat{f} \hat{\varphi}^\gamma) - \rho^{(n)} (t; (\hat{\varphi} \hat{\varphi}^\gamma)), \]

we obtain

\[ \rho^{(n)} (t; \hat{f} \hat{\varphi}^\gamma) = 2 \delta_{kk} \frac{\gamma_k \eta_k}{\omega} \rho^{(n)} (t), \]

\[ \rho^{(n)} (t; \hat{f} \hat{\varphi}^\gamma) = - 2 \delta_{kk} \frac{\gamma_k \eta_k}{\omega} \rho^{(n)} (t). \]

Consequently,

\[ \rho^{(n)} (t; \hat{f} \hat{\varphi}^\gamma) = \frac{2 \omega}{\sum_k \gamma_k \eta_k} \rho^{(n)} (t), \]

\[ \rho^{(n)} (t; \hat{f} \hat{\varphi}^\gamma) = - \frac{2 \omega}{\sum_k \gamma_k \eta_k} \rho^{(n)} (t). \]
It is noticed there are other conventions of heat current adopted in various contexts. Nevertheless, for the main purpose of the present work, we adopt Eq. (29) to “visualize” the dissipaton momentum and the resulted phase–space DEOM–based evaluations. Figure 2 depicts the heat current correlation,

$$C(t) \equiv \langle \delta \hat{J}(t) \delta \hat{J}(0) \rangle,$$

with $\delta \hat{J} \equiv \hat{J} - \langle \hat{J} \rangle$, where the average current $\langle \hat{J} \rangle = 0$ at the equilibrium scenario considered here. The inset reports the zero–current fluctuation spectrum. The phase–space DEOM–based quantum mechanics evaluation is detailed in SM.

In summary, we complete the phase–space DEOM theory with adding the dissipaton algebra for the hybrid bath solvation momentum. The new ingredients, Eqs. (22)-(23), are shown to satisfy the requirements of both necessary and sufficient criteria. The exemplified quantum heat current fluctuation, Eq. (30) with Eq. (29), is a new class of properties which would not be accessible without the present development. The resulted phase–space DEOM is a universal and versatile tool for accurate evaluations on system–plus–hybrid bath dynamics. The extension to non-equilibrium scenario involving multiple bath reservoirs and multiple dissipative modes would be straightforward. It would also be anticipated that the phase–space DEOM theory will serve as a solid ground for development of various practical simulation methods toward realistic molecular systems in condensed phases.

See supplementary materials including the DEOM–space DEOM–based evaluations. Figure 2 depicts the heat current correlation, $C(t) \equiv \langle \delta \hat{J}(t) \delta \hat{J}(0) \rangle$, with $\delta \hat{J} \equiv \hat{J} - \langle \hat{J} \rangle$, where the average current $\langle \hat{J} \rangle = 0$ at the equilibrium scenario considered here. The inset reports the zero–current fluctuation spectrum. The phase–space DEOM–based quantum mechanics evaluation is detailed in SM.

In summary, we complete the phase–space DEOM theory with adding the dissipaton algebra for the hybrid bath solvation momentum. The new ingredients, Eqs. (22)-(23), are shown to satisfy the requirements of both necessary and sufficient criteria. The exemplified quantum heat current fluctuation, Eq. (30) with Eq. (29), is a new class of properties which would not be accessible without the present development. The resulted phase–space DEOM is a universal and versatile tool for accurate evaluations on system–plus–hybrid bath dynamics. The extension to non-equilibrium scenario involving multiple bath reservoirs and multiple dissipative modes would be straightforward. It would also be anticipated that the phase–space DEOM theory will serve as a solid ground for development of various practical simulation methods toward realistic molecular systems in condensed phases.

See supplementary materials including the DEOM–space DEOM–based quantum mechanics and an analytical proof of dissipaton momentum algebra satisfying Eq. (3).

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1 A. A. Golosov, R. A. Friesner, and P. Pechukas, “Reduced dynamics in spin-Boson models: A method for both slow and fast bath,” J. Chem. Phys. 112, 2055 (2000).
2 M. Thoss, H. B. Wang, and W. H. Miller, “Self-consistent hybrid approach for complex systems: Application to the spin-boson model with Debye spectral density,” J. Chem. Phys. 115, 2991 (2001).
3 A. Garg, J. N. Onuchic, and V. Ambegaokar, “Effect of friction on electron transfer in biomolecules,” J. Chem. Phys. 83, 4491 (1985).
4 L. D. Zusman, “Outer-sphere electron transfer in polar solvents,” Chem. Phys. 49, 295 (1980).
5 L. D. Zusman, “The theory of transitions between electronic states. Application to radiationless transitions in polar solvents,” Chem. Phys. 80, 29 (1983).
6 A. O. Caldeira and A. J. Leggett, “Path integral approach to quantum Brownian motion,” Physica A 121, 587 (1983).
7 Y. Tanimura and R. Kubo, “Time evolution of a quantum system in contact with a nearly Gaussian-Markovian noise bath,” J. Phys. Soc. Jpn. 58, 101 (1989).
8 Y. Tanimura, “Nonperturbative expansion method for a quantum system coupled to a harmonic-oscillator bath,” Phys. Rev. A 41, 6676 (1990).
9 Y. Tanimura, “Stochastic Liouville, Langevin, Fokker-Planck, and master equation approaches to quantum dissipative systems,” J. Phys. Soc. Jpn. 75, 082001 (2006).
10 Y. A. Yan, F. Yang, Y. Liu, and J. S. Shao, “Hierarchical approach based on stochastic decoupling to dissipative
systems,” Chem. Phys. Lett. 395, 216 (2004).
11 R. X. Xu, P. Cui, X. Q. Li, Y. Mo, and Y. J. Yan, “Exact quantum master equation via the calculus on path integrals,” J. Chem. Phys. 122, 041103 (2005).
12 R. X. Xu and Y. J. Yan, “Dynamics of quantum dissipation systems interacting with bosonic canonical bath: Hierarchical equations of motion approach,” Phys. Rev. E 75, 031107 (2007).
13 R. P. Feynman and F. L. Vernon, Jr., “The theory of a general quantum system interacting with a linear dissipative system,” Ann. Phys. 24, 118 (1963).
14 Y. J. Yan, “Theory of open quantum systems with bath of electrons and phonons and spins: Many-dissipaton density matrices approach,” J. Chem. Phys. 140, 054105 (2014).
15 Y. J. Yan, J. S. Jin, R. X. Xu, and X. Zheng, “Dissipaton equation of motion approach to open quantum systems,” Frontiers Phys. 11, 110306 (2016).
16 H. D. Zhang, R. X. Xu, X. Zheng, and Y. J. Yan, “Statistical quasi-particle theory for open quantum systems,” Mol. Phys. 116, 780 (2018), Special Issue, “Molecular Physics in China”.
17 U. Weiss, Quantum Dissipative Systems, World Scientific, Singapore, 2008, 3rd ed. Series in Modern Condensed Matter Physics, Vol. 13.
18 H. Kleinert, Path Integrals in Quantum Mechanics, Statistics, Polymer Physics, and Financial Markets, World Scientific, Singapore, 5th edition, 2009.
19 Y. J. Yan and R. X. Xu, “Quantum mechanics of dissipative systems,” Annu. Rev. Phys. Chem. 56, 187 (2005).
20 J. G. Kirkwood, “Statistical Mechanics of Fluid Mixtures,” J. Chem. Phys. 3, 300 (1935).
21 Y. Wang, R. X. Xu, and Y. J. Yan, “Supplementary materials on Entangled system and environment dynamics: Phasespace dissipaton theory,” See the Supplemental Material at xxx.
22 D. H. He, J. Thingna, and J. S. Cao, “Interfacial thermal transport with strong system-bath coupling: A phonon delocalization effect,” Phys. Rev. B 97, 195437 (2018).
23 L. Song and Q. Shi, “Hierarchical equations of motion method applied to nonequilibrium heat transport in model molecular junctions: Transient heat current and high-order moments of the current operator,” Phys. Rev. B 95, 064308 (2017).
24 M. Esposito, M. A. Ochoa, and M. Galperin, “Nature of heat in strongly coupled open quantum systems,” Phys. Rev. B 92, 235440 (2015).
25 R. Schmidt, M. F. Carusela, J. P. Pekola, S. Suomela, and J. Ankerhold, “Work and heat for two-level systems in dissipative environments: Strong driving and non-Markovian dynamics,” Phys. Rev. B 91, 224303 (2015).
26 T. Motz, J. Ankerhold, and J. T. Stockburger, “Currents and fluctuations of quantum heat transport in harmonic chains,” New J. Phys. 19, 053013 (2017).
27 T. Motz, M. Wiedmann, J. T. Stockburger, and J. Ankerhold, “Rectification of heat currents across nonlinear quantum chains: A versatile approach beyond weak thermal contact,” New J. Phys. 20, 113020 (2018).
28 M. Wiedmann, J. T. Stockburger, and J. Ankerhold, “Out-of-equilibrium operation of a quantum heat engine: The cost of thermal coupling control,” [arXiv:1903.11368] (2019).
Supplementary materials on “Entangled system–and–environment dynamics: Phase–space dissipaton theory”

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These supplementary materials on “Entangled system–and–environment dynamics: Phase–space dissipaton theory” contain (1) A comprehensive description of DEOM–space quantum mechanics, which had been well–established; (2) An analytical proof of the fact that the dissipaton momentum as Eq. (24) algebra satisfies Eq. (3).

I. DEOM–SPACE QUANTUM MECHANICS

The DEOM theory describes both the reduced system and hybrid bath dynamics. For later convenience, we repeat the Eq. (21):
\[
\rho_n^{(n)} = -\left(i\mathcal{H}_n^x + \sum_k n_k \gamma_k\right)\rho_n^{(n)} - i \sum_k \hat{Q}_k^x \rho_n^{(n+1)} - i \sum_k n_k (\eta_k \hat{Q}_k^+ - \eta_k^* \hat{Q}_k^-) \rho_n^{(n-1)}. \tag{S1}
\]

It is worth re-emphasizing that the DEOM theory contains not only the above hierarchical dynamics, but also the dissipaton algebra. In particular, this includes Eq. (19) with Eq. (20), and also Eq. (23) with Eq. (24) that is the new ingredient developed in the present work. As results, the DEOM theory now supports the accurate evaluations on the expectation values and correlation functions engaging operators of the following types,
\[
\hat{A} \in \{\hat{A}_A, \hat{A}_B, \hat{A}_S, \hat{A}_B \hat{p}_B\}, \tag{S2}
\]
with individual \(\hat{A}_A\) being an arbitrary system dynamical operator.

A. Expectation values via the DEOM–space mapping

The DEOM–space quantum mechanics is a natural extension of Liouville–space formalism. To this end, we express the Eq. (S1) in the form of
\[
\dot{\rho}(t) = -i\mathcal{L}\rho(t). \tag{S3}
\]
This resembles \(\dot{\rho}_T = -i\mathcal{L}_T\rho_T\) with mapping the total system–plus–bath composite Liouvillian to the DEOM–space dynamics generator as defined in Eq. (S1), \(\mathcal{L}_T \rightarrow \mathcal{L}\), and
\[
\rho_T(t) \rightarrow \rho(t) = \{\rho_n^{(n)}(t); n = 0, 1, 2, \cdots\}. \tag{S4}
\]
In parallel, we should map dynamical operators into the DEOM–space,
\[
\hat{A} \rightarrow \hat{\mathcal{A}} \equiv \{\hat{A}_n^{(n)}; n = 0, 1, 2, \cdots\}, \tag{S5}
\]
such that the expectation value can be evaluated via
\[
\bar{A}(t) \equiv \text{Tr}[\hat{A}\rho_T(t)] \equiv \langle \langle \hat{A}|\rho_T(t)\rangle \rangle = \langle \langle \hat{A}|\rho(t)\rangle \rangle \equiv \sum_n \text{tr}_n[\hat{A}_n^{(n)}\rho_n^{(n)}(t)]. \tag{S6}
\]

The DEOM–space correspondences to the three types of dynamical operators in Eq. (S2) are
\[
\begin{align*}
\hat{A}_A \rightarrow \hat{\mathcal{A}} &= \{\hat{A}_A^{(0)} = \hat{A}_A; \hat{A}_A^{(n>0)} = 0\}; \tag{S7}
\hat{A}_A \hat{x}_B \rightarrow \hat{\mathcal{A}} &= \{\hat{A}_k^{(1)} = \hat{A}_A; \hat{A}_n^{(n \neq 1)} = 0\}; \tag{S8}
\hat{A}_B \hat{p}_B \rightarrow \hat{\mathcal{A}} &= \{\hat{A}_k^{(1)} = -\frac{\gamma_k}{\omega_n}\hat{A}_S; \hat{A}_n^{(n \neq 1)} = 0\}. \tag{S9}
\end{align*}
\]
The first two relations had been established in our previous works. Demonstrated properties of study include such as Fano interference, Herzberg–Teller vibronic coupling spectroscopy, and transport current shot noise spectrum. The relation (S9) can be obtain as follows. According to Eq. (S6),
\[
\text{Tr}[\hat{A}_S\hat{p}_n(t)] = \text{tr}_S\{\hat{A}_S\text{tr}_n[\hat{p}_n\rho_T(t)]\} = \text{tr}_S\{\hat{A}_S\rho_T^0(t; \hat{p}_n^0)\} = -\sum_k (\gamma_k/\omega_n)\text{tr}_S\{\hat{A}_S\rho_T^{(1)}(t)\}.
\]

The last identity that leads to Eq. (S9) is obtained by using Eqs. (23) and (24).

**B. Correlation functions via the DEOM–space mapping**

Mathematically, one can recast correlation functions in form of expectation values as [cf. Eq. (S6)]
\[
\langle \hat{A}(t)\hat{B}(0) \rangle = \langle \langle \hat{A}|e^{-i\mathcal{L}_T t}\hat{B}^\dagger|\rho_T^\text{st} \rangle \rangle \equiv \langle \langle \hat{A}|\rho_T(t; \hat{B}^\dagger) \rangle \rangle
\]
where
\[
\rho_T(t; \hat{B}^\dagger) \equiv e^{-i\mathcal{L}_T t}(\hat{B}^\dagger\rho_T^\text{st} \hat{B}) \equiv e^{-i\mathcal{L}_T t}(\hat{B}\rho_T^\text{st}).
\]

In line with Eq. (S6), we obtain
\[
\langle \hat{A}(t)\hat{B}(0) \rangle = \langle \langle \hat{A}|\rho_T(t; \hat{B}^\dagger) \rangle \rangle = \sum_n \text{tr}_S[\hat{A}_n^{(n)}\rho_n^{(n)}(t; \hat{B}^\dagger)].
\]

Here, \(\rho(t; \hat{B}^\dagger) \equiv \{\rho_n^{(n)}(t; \hat{B}^\dagger)\} \) satisfies the Eq. (S1). The initial values that correspond to \(\rho_T(t = 0; \hat{B}^\dagger) = \hat{B}^\dagger\rho_T^\text{st}\) following Eq. (16), is to be identified via
\[
\rho_n^{(n)}(0; \hat{B}^\dagger) \equiv \text{tr}_n[(\hat{B}^\dagger)^0 \hat{B}^\dagger\rho_T^\text{st}].
\]

We obtained immediately
\[
\rho_n^{(n)}(0; \hat{B}^\dagger) = \hat{B}_n\rho_n^{(n)}; \quad \rho_n^{(n)}(0; \hat{B}_n\hat{B}^\dagger) = \hat{B}_n\rho_n^{(n)}(0; \hat{B}^\dagger); \quad \rho_n^{(n)}(0; \hat{B}_n\hat{B}_n^\dagger) = \hat{B}_n\rho_n^{(n)}(0; \hat{B}_n^\dagger),
\]
for the three types of dynamical operators in Eq. (S2), respectively. From Eq. (19) with Eq. (20), we obtain
\[
\rho_n^{(n)}(0; \hat{B}^\dagger) = \sum_k \left[\rho_n^{(n+1)} + n_k\eta_k\rho_n^{(n-1)}\right].
\]

Moreover, from Eq. (23) with Eq. (24) we have
\[
\rho_n^{(n)}(0; \hat{p}_n^\dagger) = -\frac{1}{\omega_n} \sum_k \gamma_k \left[\rho_n^{(n+1)} - n_k\eta_k\rho_n^{(n-1)}\right].
\]
The involved \(\{\rho_n^{(n)}\} \) are the steady-state solutions of Eq. (S1).

We summarize the DEOM–evaluation on correlation functions as follows. (i) Compute the steady–state DDOs \(\{\rho_n^{(n)}\} \) via such as the self-consistent iteration method; (ii) Determine the initial values \(\rho_n^{(n)}(0; \hat{B}^\dagger) \) via Eqs. (S15)–(S17); (iii) Propagate DDOs with Eq. (S1) to obtain the required \(\{\rho_n^{(n)}(t; \hat{B}^\dagger)\} \) for Eq. (S13); (iv) Evaluate \(\langle \hat{A}(t)\hat{B}(0) \rangle \) as the expectation value problem by using Eqs. (S6)–(S9). Individual \(\hat{A}\) or \(\hat{B}\) can be any dynamical operator in Eq. (S2).

**II. DISSIPATION MOMENTUM ALGEBRA SATISFYING EQ.(3): ANALYTICAL PROOF**

For convenience, we repeat Eq.(3) here,
\[
\langle \hat{A}(t)\hat{x}_n(0) \rangle = -\omega_n\langle \hat{A}(t)\hat{p}_n(0) \rangle.
\]
In the DEOM space [cf. Eqs. (S11) and (S13)], it reads

$$\langle A | \dot{\rho}(t; \hat{x}_n^\pm) \rangle = -\omega_n \langle A | \rho(t; \hat{\rho}_n^\pm) \rangle.$$  \hspace{1cm} (S19)

As $\hat{A}$ is arbitrary, the above expression amounts to

$$\dot{\rho}(t; \hat{x}_n^\pm) = -\omega_n \rho(t; \hat{\rho}_n^\pm).$$  \hspace{1cm} (S20)

The proof is as follows. Let us start with

$$\rho(t; \hat{x}_n^\pm) = e^{-iL_t^1} \rho(0; \hat{x}_n^\pm),$$

which leads to

$$\dot{\rho}(t; \hat{x}_n^\pm) = -e^{-iL_t^1} [iL \rho(0; \hat{x}_n^\pm)] = e^{-iL_t^1} \dot{\rho}(0; \hat{x}_n^\pm).$$  \hspace{1cm} (S21)

On the other hand, $\rho(t; \hat{\rho}_n^\pm) = e^{-iL_t^1} \rho(0; \hat{\rho}_n^\pm)$. Therefore, Eq. (S20) is equivalent to $\dot{\rho}(0; \hat{x}_n^\pm) = -\omega_n \rho(0; \hat{\rho}_n^\pm)$. In other words, it is sufficient to prove

$$\dot{\rho}_n^{(n)}(0; \hat{x}_n^\pm) = -\omega_n \rho_n^{(n)}(0; \hat{\rho}_n^\pm).$$  \hspace{1cm} (S22)

Equations (S11) and (S10) lead to the lhs the expressions,

$$\dot{\rho}_n^{(n)}(0; \hat{x}_n^\pm) = -\left[ i H_0^\pm + \sum_k n_k \gamma_k \right] \rho_n^{(n)}(0; \hat{x}_n^\pm) - i \sum_k \hat{Q}_k^\pm \rho_n^{(n+1)}(0; \hat{x}_n^\pm) - i \sum_k n_k \left( \eta_k \hat{Q}_k^\pm - \eta_k^* \hat{Q}_k^\pm \right) \rho_n^{(n-1)}(0; \hat{x}_n^\pm)$$

$$= -\left[ i H_0^\pm + \sum_k n_k \gamma_k \right] \sum_j \left[ \rho_j^{(n+1)\text{st}} + n_j \eta_j \rho_j^{(n+1)\text{st}} \right] - i \sum_{k,j} \hat{Q}_j^\pm \left[ \rho_j^{(n+2)\text{st}} + (n_j + \delta_k \eta_j) \rho_j^{(n+1)\text{st}} \right]$$

$$- i \sum_{k,j} n_k \left( \eta_k \hat{Q}_j^\pm - \eta_j^* \hat{Q}_j^\pm \right) \left[ \rho_j^{(n\text{st})} + (n_j - \delta_k) \eta_j \rho_j^{(n-2)\text{st}} \right].$$  \hspace{1cm} (S23)

On the other hand, the steady–state solutions to Eq. (S1) satisfy (noting that $n_j^{\pm \pm} = n_{jk}^{\pm \pm}$)

$$0 = -\left[ i H_0^\pm + \sum_k (n_k + \delta_k \eta_k) \gamma_k \right] \rho_j^{(n+1)\text{st}} - i \sum_k \hat{Q}_j^\pm \rho_j^{(n+2)\text{st}} - i \sum_k (n_k + \delta_k \eta_k) \left( \eta_k \hat{Q}_j^\pm - \eta_k^* \hat{Q}_j^\pm \right) \rho_j^{(n)\text{st}},$$

$$0 = -\left[ i H_0^\pm + \sum_k (n_k - \delta_k \eta_k) \gamma_k \right] \rho_j^{(n-1)\text{st}} - i \sum_k \hat{Q}_j^\pm \rho_j^{(n)\text{st}} - i \sum_k (n_k - \delta_k \eta_k) \left( \eta_k \hat{Q}_j^\pm - \eta_k^* \hat{Q}_j^\pm \right) \rho_j^{(n-2)\text{st}}.$$  \hspace{1cm} (S24)

Substituting Eq. (S21) into Eq. (S23), followed by using the identity $\sum_k (\eta_k - \eta_k^* \gamma_k) = 0$ [cf. Eq. (9)] and some elementary algebra, we obtain

$$\dot{\rho}_n^{(n)}(0; \hat{x}_n^\pm) = \sum_k \gamma_n \left[ \hat{\rho}_n^{(n+1)\text{st}} - n_k \eta_k \rho_n^{(n-1)\text{st}} \right] = -\omega_n \rho_n^{(n)}(0; \hat{\rho}_n^\pm),$$  \hspace{1cm} (S25)

with the last identity being just Eq. (S17). We have thus proved that the proposed dissipaton momentum algebra as Eq. (24) does satisfy the sufficient criterion, for the resulted phase–space DEOM evaluation on Eq. (3).

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1. H. D. Zhang, R. X. Xu, X. Zheng, and Y. J. Yan, “Nonperturbative spin-boson and spin-spin dynamics and nonlinear Fano interferences: A unified dissipaton theory based study,” J. Chem. Phys. 142, 024112 (2015).
2. H. D. Zhang, Q. Qiao, R. X. Xu, and Y. J. Yan, “Effects of Herzberg-Teller vibronic coupling on coherent excitation energy transfer,” J. Chem. Phys. 145, 204109 (2016).
3. J. S. Jin, S. K. Wang, X. Zheng, and Y. J. Yan, “Current noise spectra and mechanisms with dissipaton equation of motion theory,” J. Chem. Phys. 142, 234108 (2015).
4. H. D. Zhang, Q. Qiao, R. X. Xu, X. Zheng, and Y. J. Yan, “Efficient steady-state solver for hierarchical quantum master equations,” J. Chem. Phys. 147, 044105 (2017).

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