Quantum mechanics of open systems: Dissipaton theories

Yao Wang and YiJing Yan[a)]
University of Science and Technology of China, Hefei, Anhui 230026, China

(Dated: 17 November 2022)

This Perspective presents a comprehensive account of the dissipaton theories developed in our group since 2014, including the physical picture of dissipatons and the phase–space dissipaton algebra. The dissipaton–equation–of–motion–space (DEOM–space) formulations cover the Schrödinger picture, the Heisenberg picture, and further the imaginary–time DEOM. Recently developed are also the dissipaton theories for studying equilibrium and nonequilibrium thermodynamic mixing processes. The Jarzynski equality and Crooks relation are accurately reproduced numerically. It is anticipated that dissipaton theories would remain essential towards a maturation of quantum mechanics of open systems.

I. INTRODUCTION

Open quantum systems are ubiquitous in various fields of science,[1–4] covering quantum optics,[5–9] nuclear magnetic resonance,[10–12] condensed matter and material physics,[13–17] quark-gluon plasma,[18–21] nonlinear spectroscopy,[22–29] chemical and biological physics.[30–35] In all these studies, the total system–plus–bath composite Hamiltonian assumes the form of $H_{\rm T} = H_{\rm S}+h_{\rm B}+H_{\rm SB}$, which together with temperature and/or chemical potentials constitute a *thermodynamic* system. Irreversibility takes place, in terms of not only relaxation, dephasing and quantum transport events, but also those fundamental processes subject to the Laws of Thermodynamics.

In literature, quantum dissipation theories (QDTs), such as quantum master equations,[36–40] focus mainly on the reduced system density operator, $\rho_{\rm S}(t) \equiv {\rm tr}_{\rm B}\rho_{\rm T}(t)$. Exact QDTs include the Feynman–Vernon influence functional path integral formalism[41] and its time–derivative equivalence, hierarchical equations of motion (HEOM), with either bosonic[42–49] or fermionic bath environment influence.[50–52] However, as mentioned earlier, the reduced system ($H_{\rm S}$) is just the primarily interested part of the thermodynamic system that is characterized by not only the total composite $H_{\rm T}$, but also temperatures and other thermodynamic parameters. The relevant information encoded in the reduced system dynamics alone would be insufficient to deal with experimental measurements on open systems. The entangled system–and–environment dynamics are also crucially important.[53,54]

In this paper, we present a systematic framework of quantum mechanics of open systems, in terms of dissipaton theories. These are universal theories developed on the basis of both quantum mechanics and statistical thermodynamics principles. In Sec. II, we present the statistical quasi-particle picture of dissipatons, followed by the related algebraic constructions.[55,56] Adopted for the bath Hamiltonian ($h_{\rm B}$) is the Gaussian environments ansatz that is rooted at the well–known central limit theorem. In other words, the bath effectively consists of infinite number of noninteracting (quasi) particles, either bosonic or fermionic. Consider further the system–bath coupling ($H_{\rm SB}$), a superposition of $\{\hat{Q}_u^{\rm S}\hat{F}_u^{\rm B}\}$, in which the dissipative system modes $\{\hat{Q}_u^{\rm S}\}$ are arbitrary and the hybrid bath modes $\{\hat{F}_u^{\rm B}\}$ assume linear. This is the scenario of Gauss–Wick's environments. The bath influences are then completely characterized by the hybridization bath correlation functions. Dissipatons can now be deduced for satisfying the generalized diffusion equation as required by the theory. Dynamical variables are dissipaton density operators (DDOs), whose time–evolutions are governed by the dissipaton equation of motion (DEOM). The reduced system density operator ($\rho_{\rm S}$) is just a member of DDOs. Another fundamental ingredient of dissipaton algebra is the generalized Wick's theorem. This enables dissipaton theories for not only the reduced system but also the hybrid bath modes.

Section III comprises a complete description of DEOM–space quantum mechanics of open systems, constructed in parallel to those traditional Liouville–space formulations. These include the real–time dynamics in Schrödinger versus Heisenberg pictures, the imaginary–time dynamics, and the DEOM evaluations on such as expectation values and correlation functions.

Section IV is concerned with the thermodynamic mixing via the dissipaton implementations. These include the equilibrium λ-DEOM for the Helmholtz free–energy change[57] and the nonequilibrium $\lambda(t)$-DEOM for the work distributions.[58] The Jarzynski equality and Crooks relation are accurately reproduced with numerical DEOM evaluations.[58]

Section V is concerned with the dissipaton thermofield (DTF) theory. This covers the thermofield dissipaton Langevin equation and the nonequilibrium system–bath entanglement theorem. Established are the relations between the local system correlation functions and those involving the nonlocal hybrid bath modes. In Sec. VI, we discuss the future prospect of the dissipaton theories towards the quantum mechanics of open systems. Finally, we conclude this paper.

[a)]Electronic mail: yanyj@ustc.edu.cn

II. ONSETS OF DISSIPATONS

A. Prelude

Let us start with the total system–plus–bath composite Hamiltonian in the generic form of

$$H_{\rm T} = H_{\rm S} + h_{\rm B} + H_{\rm SB} = H_{\rm S} + \sum_\alpha h_\alpha + \sum_{\alpha u} \hat{Q}_u \hat{F}_{\alpha u}. \quad (1)$$

Both the system Hamiltonian $H_{\rm S}$ and the dissipative system modes $\{\hat{Q}_u\}$ are arbitrary, including the time–dependence via the classical external fields, which act on the system and/or the neighboring environment. For brevity, we set throughout this paper $\hbar = 1$ and $\beta_\alpha = 1/(k_B T_\alpha)$, the inverse temperature of the α–reservoir.

The hybrid reservoir bath modes $\{\hat{F}_{\alpha u}\}$ assume to be linear. This together with noninteracting and independent reservoir bath, $h_{\rm B} = \sum_\alpha h_\alpha$, constitute the so–called Gaussian–Wick's coupling environments.[1,2] Their influences are *fully* characterized by the hybridization bath correlation functions, satisfying the fluctuation–dissipation theorem,[1–4,59]

$$\langle \hat{F}^{\rm B}_{\alpha u}(t) \hat{F}^{\rm B}_{\alpha v}(0)\rangle_{\rm B} = \frac{1}{\pi}\int_{-\infty}^{\infty} {\rm d}\omega\, \frac{e^{-i\omega t} J_{\alpha uv}(\omega)}{1 - e^{-\beta_\alpha \omega}}. \quad (2)$$

Here, $\hat{F}^{\rm B}_{\alpha u}(t) \equiv e^{ih_{\rm B}t}\hat{F}_{\alpha u} e^{-ih_{\rm B}t} = e^{ih_\alpha t}\hat{F}_{\alpha u} e^{-ih_\alpha t}$ and $\langle(\,\cdot\,)\rangle_{\rm B} \equiv {\rm tr}_{\rm B}[(\,\cdot\,)\rho^0_{\rm B}]$, with $\rho^0_{\rm B} = \otimes_\alpha [e^{-\beta_\alpha h_\alpha}/{\rm tr}_{\rm B}(e^{-\beta_\alpha h_\alpha})]$. The involving hybridization bath spectral densities are

$$J_{\alpha uv}(\omega) = \frac{1}{2i}\int_{-\infty}^{\infty} {\rm d}t\, e^{i\omega t}\phi_{\alpha uv}(t) \quad (3)$$

with

$$\phi_{\alpha uv}(t) \equiv i\langle [\hat{F}^{\rm B}_{\alpha u}(t), \hat{F}^{\rm B}_{\alpha v}(0)]\rangle_{\rm B}. \quad (4)$$

To proceed, we decompose Eq. (2) into ($t \geq 0$)

$$c_{\alpha uv}(t) \equiv \langle \hat{F}^{\rm B}_{\alpha u}(t)\hat{F}^{\rm B}_{\alpha v}(0)\rangle_{\rm B} \simeq \sum_{k=1}^K \eta_{\alpha uvk} e^{-\gamma_{\alpha k} t}. \quad (5)$$

This can be readily achieved with some sum–over–pole schemes[49,59–62] or the time–domain Prony fitting decomposition scheme.[63] For simplicity of formulations, we assume all $\gamma_{\alpha uvk} = \gamma_{\alpha k}$ (valid at least when the poles of $J_{\alpha uv}(\omega)$ contain no explicit system–mode dependence). Let further $\bar{k} \in \{k = 1, \cdots, K\}$ via $\gamma_{\alpha\bar{k}} \equiv \gamma^*_{\alpha k}$, since the exponents $\{\gamma_{\alpha k}\}$ are either real or complex conjugate paired. We can then report the required time–reversal relation, $\langle \hat{F}^{\rm B}_{\alpha v}(0)\hat{F}^{\rm B}_{\alpha u}(t)\rangle_{\rm B} = \langle \hat{F}^{\rm B}_{\alpha u}(t)\hat{F}^{\rm B}_{\alpha v}(0)\rangle^*_{\rm B}$, in terms of

$$\langle \hat{F}^{\rm B}_{\alpha v}(0)\hat{F}^{\rm B}_{\alpha u}(t)\rangle_{\rm B} = \sum_{k=1}^K \eta^*_{\alpha uv\bar{k}} e^{-\gamma_{\alpha k} t}. \quad (6)$$

Apparently, $\bar{k} = k$ if $\gamma_{\alpha k}$ is real, since $\gamma_{\alpha\bar{k}} \equiv \gamma^*_{\alpha k}$.

B. Dissipaton decomposition

The dissipaton theory provides a statistical quasi-particle (dissipaton) picture to account for the environment, starting with the dissipaton decomposition,

$$\hat{F}_{\alpha u} = \sum_{k=1}^K \hat{f}_{\alpha uk}, \quad (7)$$

where $\{\hat{f}_{\alpha uk}\}$ are known as dissipaton operator. To reproduce the required Eqs. (5) and (6), we set

$$\begin{aligned} \langle \hat{f}^{\rm B}_{\alpha uk}(t)\hat{f}^{\rm B}_{\alpha' vk'}(0)\rangle_{\rm B} &= \delta_{\alpha\alpha'}\delta_{kk'}\eta^{>}_{\alpha uvk} e^{-\gamma_{\alpha k}t}, \\ \langle \hat{f}^{\rm B}_{\alpha' vk'}(0)\hat{f}^{\rm B}_{\alpha uk}(t)\rangle_{\rm B} &= \delta_{\alpha\alpha'}\delta_{kk'}\eta^{<}_{\alpha uvk} e^{-\gamma_{\alpha k}t}, \end{aligned} \quad (8)$$

where

$$\begin{aligned} \eta^{>}_{\alpha uvk} &\equiv \langle \hat{f}_{\alpha uk}\hat{f}_{\alpha vk}\rangle^{>}_{\rm B} \equiv \langle \hat{f}_{\alpha uk}(0+)\hat{f}_{\alpha vk}\rangle_{\rm B} = \eta_{\alpha uvk}, \\ \eta^{<}_{\alpha uvk} &\equiv \langle \hat{f}_{\alpha vk}\hat{f}_{\alpha uk}\rangle^{<}_{\rm B} \equiv \langle \hat{f}_{\alpha vk}\hat{f}_{\alpha uk}(0+)\rangle_{\rm B} = \eta^*_{\alpha uv\bar{k}}. \end{aligned} \quad (9)$$

Note that $\langle \hat{f}^{\rm B}_{\alpha' v\bar{k}}(0)\hat{f}^{\rm B}_{\alpha u\bar{k}}(t)\rangle_{\rm B} = \langle \hat{f}^{\rm B}_{\alpha uk}(t)\hat{f}^{\rm B}_{\alpha' vk}(0)\rangle^*_{\rm B}$.

The dissipaton decomposition, Eqs. (7)–(9), represented by the first mapping arrow in Fig. 1, is concerned with individual $\hat{F}_{\alpha u}$ that assumes by far to be a linear operator in the bare bath h_α–subspace. The resulting $\{\hat{f}^{\rm B}_{\alpha uk}(t) \equiv e^{ih_{\rm B}t}\hat{f}_{\alpha uk}e^{-ih_{\rm B}t}\}$ are *linear* and *statistically independent* diffusive environmental modes [cf. Eq. (8)], with the diffusion constant $\gamma_{\alpha k}$ that can be complex. In other words, Eq. (7) essentially represents a mapping from the α-reservoir bath to K independent auxiliary baths, which intrinsically conserves the correlation functions in Eqs. (5) and (6).

To proceed, we introduce the *irreducible* dissipaton product notation,

$$\big(\hat{f}_k\hat{f}_j\big)^\circ = \big(\hat{f}_j\hat{f}_k\big)^\circ. \quad (10)$$

This is true for bosonic dissipatons. As Eqs. (7)–(9) reproduce the bosonic fluctuation–dissipation theorem, Eq. (2), the dissipatons $\{\hat{f}_{\alpha uk}\}$ in Eq. (7) are bosonic. In this paper the dissipaton theories are illustrated with the bosonic scenario.

C. Disspaton density operators as dynamical variables

Dynamical variables in dissipaton theories are the so-called dissipaton density operators (DDOs):[55,64,65]

$$\rho^{(n)}_{\mathbf{n}}(t) \equiv {\rm tr}_{\rm B}\Big[\Big(\prod_{\alpha uk}\hat{f}^{n_{\alpha uk}}_{\alpha uk}\Big)^\circ \rho_{\rm T}(t)\Big]. \quad (11)$$

This describes a configuration that is irreducible and labeled by an ordered collection of indexes, $\mathbf{n} \equiv \{n_{\alpha uk}\}$, with $n_{\alpha uk} = 0, 1, 2, \cdots$ being the participation number of individual bosonic $\hat{f}_{\alpha uk}$-dissipaton. The total number of dissipaton excitations in $\rho^{(n)}_{\mathbf{n}}(t)$ is given by

$$n = \sum_{\alpha uk} n_{\alpha uk}. \quad (12)$$

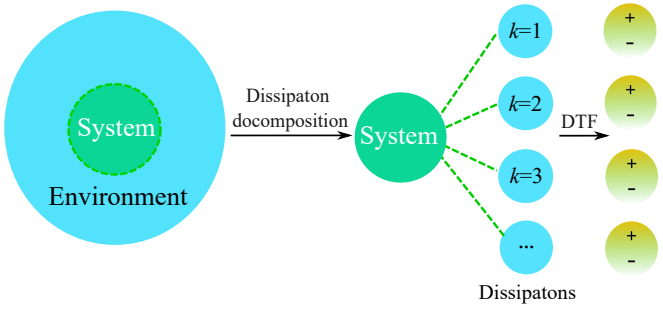

FIG. 1. Dissipaton decomposition [cf. Eq. (7)] followed by the DTF decomposition. The latter will be explained in Sec. V [cf. Eqs. (77a) and (77b)].

The reduced system density operator is $\rho_{\rm S}(t) = \rho^{(0)}_{\mathbf{0}}(t)$, just a special member of DDOs.

Let $\rho^{(n\pm1)}_{\mathbf{n}^{\pm}_{\alpha uk}}$ be the associated $(n\pm1)$-dissipatons configuration, with $\mathbf{n}^{\pm}_{\alpha uk}$ differing from $\mathbf{n}$ only at the specified $\hat{f}_{\alpha uk}$-disspaton participation number, $n_{\alpha uk}$, by ±1. For presenting the related dissipaton algebra, adopt hereafter the following notations:

$$\begin{aligned}
\rho^{(n)}_{\mathbf{n}}(t;\hat{A}^{\times}) &\equiv {\rm tr}_{\rm B}\Big[\Big(\prod_{\alpha uk}\hat{f}^{n_{\alpha uk}}_{\alpha uk}\Big)^{\circ}\hat{A}^{\times}\rho_{\rm T}(t)\Big],\\
\rho^{(n)}_{\mathbf{n}}(t;\hat{A}^{\lessgtr}) &\equiv {\rm tr}_{\rm B}\Big[\Big(\prod_{\alpha uk}\hat{f}^{n_{\alpha uk}}_{\alpha uk}\Big)^{\circ}\hat{A}^{\lessgtr}\rho_{\rm T}(t)\Big],
\end{aligned} \tag{13}$$

where $\hat{A}^{\times}\equiv\hat{A}^{>}-\hat{A}^{<}$,

$$\hat{A}^{>}\rho_{\rm T}(t)\equiv\hat{A}\rho_{\rm T}(t)\ \ \text{and}\ \ \hat{A}^{<}\rho_{\rm T}(t)\equiv\rho_{\rm T}(t)\hat{A}. \tag{14}$$

The above notations will appear in the generalized diffusion equation and the generalized Wick's theorem. These are two fundamental ingredients of dissipaton algebra as follows; see also Sec. III.

D. Generalized diffusion equation

Equation (8) highlights two important features of dissipatons: (i) Dissipatons with different "color-$\gamma_{\alpha k}$" are statistically independent with respective to the (αk)-index; (ii) Each individual dissipaton goes by a *single-exponential* correlation function, with a *same exponent* for both the forward and the backward paths. These features are closely related to the dissipaton algebra used in the DEOM construction. In particular, the feature (ii) above leads to[55]

$${\rm tr}_{\rm B}\Big[\Big(\frac{\partial}{\partial t}\hat{f}_{\alpha uk}\Big)_{\rm B}\rho_{\rm T}(t)\Big] = -\gamma_{\alpha k}\,{\rm tr}_{\rm B}\big[\hat{f}_{\alpha uk}\rho_{\rm T}(t)\big]. \tag{15}$$

This is the *generalized diffusion equation* for dissipatons. It together with $(\frac{\partial}{\partial t}\hat{f}_{\alpha uk})_{\rm B} = i[h_{\rm B},\hat{f}_{\alpha uk}]\equiv ih^{\times}_{\rm B}\hat{f}_{\alpha uk}$ gives rise to the $h^{\times}_{\rm B}$–action on DDOs the result of

$$\rho^{(n)}_{\mathbf{n}}(t;h^{\times}_{\rm B}) = -i\Big(\sum_{\alpha uk}n_{\alpha uk}\gamma_{\alpha k}\Big)\rho^{(n)}_{\mathbf{n}}(t). \tag{16}$$

Denote for bookkeeping later,

$$H_0\equiv H_{\rm S}+h_{\rm B}\ \ \text{and}\ \ \mathcal{L}^{(n)}_{\mathbf{n}}\equiv H^{\times}_{\rm S}-i\sum_{\alpha uk}n_{\alpha uk}\gamma_{\alpha k}\,. \tag{17}$$

Together with Eq. (16), we obtain

$$\rho^{(n)}_{\mathbf{n}}(t;H^{\times}_0) = \mathcal{L}^{(n)}_{\mathbf{n}}\rho^{(n)}_{\mathbf{n}}(t). \tag{18}$$

E. Generalized Wick's theorems

Another important ingredient of dissipaton algebra is the *generalized Wick's theorem* (GWT). Consider first

$$\begin{aligned}
\rho^{(n)}_{\mathbf{n}}(t;\hat{f}^{\gtrless}_{\alpha' vk'}) &\equiv {\rm tr}_{\rm B}\Big[\Big(\prod_{\alpha uk}\hat{f}^{n_{\alpha uk}}_{\alpha uk}\Big)^{\circ}\hat{f}^{>}_{\alpha' vk'}\rho_{\rm T}(t)\Big]\\
&= \sum_{\alpha uk}n_{\alpha uk}\langle\hat{f}_{\alpha uk}\hat{f}_{\alpha' vk'}\rangle^{>}_{\rm B}\rho^{(n-1)}_{\mathbf{n}^{-}_{\alpha uk}}(t)+\rho^{(n+1)}_{\mathbf{n}^{+}_{\alpha' vk'}}(t).
\end{aligned} \tag{19}$$

Here, $\langle\hat{f}_{\alpha uk}\hat{f}_{\alpha' vk'}\rangle^{>}_{\rm B}\equiv\langle\hat{f}_{\alpha uk}(0+)\hat{f}_{\alpha' vk'}\rangle_{\rm B}$ via Eq. (8), with the nonzero value being only $\eta^{>}_{\alpha uvk}\equiv\langle\hat{f}_{\alpha uk}\hat{f}_{\alpha vk}\rangle^{>}_{\rm B}$. The $\hat{f}^{<}_{\alpha' vk'}$–action counterpart to Eq. (19) is similar, but goes with $\langle\hat{f}_{\alpha' vk'}\hat{f}_{\alpha uk}\rangle^{<}_{\rm B}\equiv\langle\hat{f}_{\alpha' vk'}\hat{f}_{\alpha uk}(0+)\rangle_{\rm B}$, whose nonzero value is $\eta^{<}_{\alpha uvk}\equiv\langle\hat{f}_{\alpha vk}\hat{f}_{\alpha uk}\rangle^{<}_{\rm B}$ only. We can then recast Eq. (19) with the unified expression of

$$\rho^{(n)}_{\mathbf{n}}(t;\hat{f}^{\gtrless}_{\alpha uk}) = \rho^{(n+1)}_{\mathbf{n}^{+}_{\alpha uk}}(t)+\sum_{v}n_{\alpha vk}\eta^{\gtrless}_{\alpha vuk}\rho^{(n-1)}_{\mathbf{n}^{-}_{\alpha vk}}(t). \tag{20}$$

This is the GWT for bosonic dissipatons, which as seen later determines $\rho^{(n)}_{\mathbf{n}}(t;H^{\times}_{\rm SB})$, the last two terms in the DEOM (30). Involved are the pre–exponential coefficients in Eq. (5) or Eq. (6), since $\eta^{>}_{\alpha uvk}=\eta_{\alpha uvk}$ and $\eta^{<}_{\alpha uvk}=\eta^{*}_{\alpha uv\bar{k}}$, as specified in Eq. (9).

It is worth re-emphasizing that the GWT, Eq. (20), goes by the irreducibility nature of $\rho^{(n)}_{\mathbf{n}}(t)$: In Eq. (11), the product of dissipaton operators inside $(\cdots)^{\circ}$ is irreducible, satisfying the bosonic permutation relation of Eq. (10). In comparison, we may recall some properties about the "normal order" in textbooks, which arranges creation operators before annihilation operators. Denote this also with $(\,\cdot\,)^{\circ}$, such that $(\hat{a}^{\dagger}\hat{a})^{\circ}=(\hat{a}\hat{a}^{\dagger})^{\circ}=\hat{a}^{\dagger}\hat{a}$. The ground state $|0\rangle$ satisfies $\hat{a}|0\rangle=0$. Set $\hat{f}\equiv\sqrt{\eta}\,(\hat{a}+\hat{a}^{\dagger})$, with η being an arbitrary real parameter. It is easy to obtain $(\hat{f}^{n})^{\circ}\hat{f}=(\hat{f}^{n+1})^{\circ}+n\eta(\hat{f}^{n-1})^{\circ}=\hat{f}(\hat{f}^{n})^{\circ}$. Equation (20) is just the dissipaton generalization of this result.

To complete phase–space dissipaton algebra,[66] consider further

$$\hat{\Phi}_{\alpha u}\equiv\dot{\hat{F}}_{\alpha u}=i[h_{\alpha},\hat{F}_{\alpha u}], \tag{21}$$

which satisfies

$$[\hat{F}_{\alpha u},\hat{\Phi}_{\alpha' v}] = i\delta_{\alpha\alpha'}\Theta_{\alpha uv}, \tag{22}$$

with

$$\Theta_{\alpha uv}\equiv\frac{1}{\pi}\int_{-\infty}^{\infty}{\rm d}\omega\,\omega J_{\alpha uv}(\omega). \tag{23}$$

The dissipaton momentum decomposition is [cf. Eq. (7)]

$$\hat{\Phi}_{\alpha u} = \sum_{k=1}^{K} \hat{\varphi}_{\alpha u k}. \tag{24}$$

The resulting GWT for dissipaton momentums reads[66]

$$\begin{aligned}\rho^{(n)}_{\mathbf{n}}(t;\hat{\varphi}^{\gtrless}_{\alpha u k}) = \gamma_{\alpha k}\sum_{v} n_{\alpha v k}\eta^{\gtrless}_{\alpha v u k}\rho^{(n-1)}_{\mathbf{n}^{-}_{\alpha v k}}(t) \\ - \gamma_{\alpha k}\rho^{(n+1)}_{\mathbf{n}^{+}_{\alpha u k}}(t).\end{aligned} \tag{25}$$

Introduce now

$$\hat{\theta}^{\pm}_{\alpha u k} \equiv \frac{1}{2}\Big(\hat{f}_{\alpha u k} \mp \frac{\hat{\varphi}_{\alpha u k}}{\gamma_{\alpha k}}\Big). \tag{26}$$

We obtain Eqs. (20) and (25) the alternative expressions,

$$\begin{aligned}\rho^{(n)}_{\mathbf{n}}(t;\hat{\theta}^{+;\gtrless}_{\alpha u k}) &= \rho^{(n+1)}_{\mathbf{n}^{+}_{\alpha u k}}(t), \\ \rho^{(n)}_{\mathbf{n}}(t;\hat{\theta}^{-;\gtrless}_{\alpha u k}) &= \sum_{v} n_{\alpha v k}\eta^{\gtrless}_{\alpha v u k}\rho^{(n-1)}_{\mathbf{n}^{-}_{\alpha v k}}(t).\end{aligned} \tag{27}$$

III. DEOM–SPACE QUANTUM MECHANICS

A. Time-evolutions of DDOs

The construction of DEOM starts with

$$\dot{\rho}_{\rm T}(t) = -i[H_0 + H_{\rm SB}, \rho_{\rm T}(t)], \tag{28}$$

where $H_0 \equiv H_{\rm S} + h_{\rm B}$ and [cf. Eq. (7)]

$$H_{\rm SB} = \sum_{\alpha u}\hat{Q}_u\hat{F}_{\alpha u} = \sum_{\alpha u k}\hat{Q}_u\hat{f}_{\alpha u k}. \tag{29}$$

Applying Eq. (28) to Eq. (11) and further Eqs. (18)–(20), we obtain

$$\begin{aligned}\dot{\rho}^{(n)}_{\mathbf{n}} = -i\mathcal{L}^{(n)}_{\mathbf{n}}\rho^{(n)}_{\mathbf{n}} - i\sum_{\alpha u k}\hat{Q}^{\times}_u\rho^{(n+1)}_{\mathbf{n}^{+}_{\alpha u k}} \\ - i\sum_{\alpha u v k} n_{\alpha u k}\big(\eta_{\alpha u v k}\hat{Q}^{>}_v - \eta^{*}_{\alpha u v\bar{k}}\hat{Q}^{<}_v\big)\rho^{(n-1)}_{\mathbf{n}^{-}_{\alpha u k}}.\end{aligned} \tag{30}$$

In parallel to $\dot{\rho}_{\rm T}(t) = -i\mathcal{L}_{\rm T}\rho_{\rm T}(t)$ [cf. Eq. (28)], we can recast the set of linear equations (30) as

$$\dot{\boldsymbol{\rho}}(t) = -i\boldsymbol{\mathcal{L}}\boldsymbol{\rho}(t), \;\; \text{with} \;\; \boldsymbol{\rho}(t) \equiv \{\rho^{(n)}_{\mathbf{n}}(t)\}. \tag{31}$$

The dynamical generator $\boldsymbol{\mathcal{L}}$, defined via Eq. (30), can be time–dependent in general. In line with $\rho_{\rm T} \to \boldsymbol{\rho}$ and $\mathcal{L}_{\rm T} \to \boldsymbol{\mathcal{L}}$, the DEOM–space formulations are those of the Liouville–space mappings, as follows.

Evidently, DEOM (30) is identical to the well–established HEOM formalism.[42–49] All numerical methods developed for HEOM, illustrated in Sec. III D, are applicable in DEOM evaluations. Now the observables cover not only the reduced system but also the hybrid bath properties [cf. Eq. (33)]; see also Sec. IV for the dissipaton theory implementations of equilibrium and nonequilibrium thermodynamics. It is worth emphasizing that the underlying dissipaton algebra can be readily extended to nonlinear coupling environments.[67–69] This scenario is beyond the conventional HEOM approach that is rooted at the Feynman–Vernon influence functional path integral formalism.

B. DEOM–space observables

Consider the expectation values,

$$\begin{aligned}\bar{A}(t) &\equiv {\rm Tr}[\hat{A}\rho_{\rm T}(t)] \equiv \langle\langle\hat{A}|\rho_{\rm T}(t)\rangle\rangle \\ &= \langle\langle\hat{\boldsymbol{A}}|\boldsymbol{\rho}(t)\rangle\rangle \equiv \sum_{\mathbf{n}}{\rm tr}_{\rm S}\big[\hat{A}^{(n)}_{\mathbf{n}}\rho^{(n)}_{\mathbf{n}}(t)\big].\end{aligned} \tag{32}$$

The second line denotes the DEOM–space evaluation, which as inferred from the Eqs. (20) and (25), supports the following types of operators,

$$\hat{A} \in \{\hat{A}_{\rm S}, \hat{B}_{\rm S}\hat{f}_{\alpha u k}, \hat{B}_{\rm S}\hat{\varphi}_{\alpha u k}\}. \tag{33}$$

Here, $\hat{A}_{\rm S}$ and $\hat{B}_{\rm S}$ are arbitrary observables in the system subspace, including $\hat{B}_{\rm S} = \hat{I}_{\rm S}$, whereas $\{\hat{f}_{\alpha u k}\}$ and $\{\hat{\varphi}_{\alpha u k}\}$ are related to hybrid bath modes $\{\hat{F}_{\alpha u}\}$ and $\{\hat{\Phi}_{\alpha u} \equiv \dot{\hat{F}}_{\alpha u}\}$ via Eqs. (7) and (24), respectively. To complete Eq. (32), we map $\hat{A}$ into the DEOM–space operators,

$$\hat{A} \to \hat{\boldsymbol{A}} \equiv \{\hat{A}^{(n)}_{\mathbf{n}}; n = 0, 1, 2, \cdots\}. \tag{34}$$

The dissipaton algebra established earlier results in

$$\hat{A}_{\rm S} \to \hat{\boldsymbol{A}} = \{\hat{A}^{(0)} = \hat{A}_{\rm S}; \;\; \hat{A}^{(n>0)}_{\mathbf{n}} = 0\}, \tag{35a}$$

$$\hat{B}_{\rm S}\hat{f}_{\alpha u k} \to \hat{\boldsymbol{A}} = \{\hat{A}^{(1)}_{\alpha u k} = \hat{B}_{\rm S}; \;\; \text{others} = 0\}, \tag{35b}$$

$$\hat{B}_{\rm S}\hat{\varphi}_{\alpha u k} \to \hat{\boldsymbol{A}} = \{\hat{A}^{(1)}_{\alpha u k} = -\gamma_{\alpha k}\hat{B}_{\rm S}; \;\; \text{others} = 0\}. \tag{35c}$$

We can then evaluate the expectation values for these types of operators via the last identity of Eq. (32).

Turn to the steady–state correlation functions, which in general can be recast as [cf. Eq. (32)]

$$\langle\hat{A}(t)\hat{B}(0)\rangle = \langle\langle\hat{A}|\rho_{\rm T}(t;\hat{B}^{>})\rangle\rangle = \langle\langle\hat{\boldsymbol{A}}|\boldsymbol{\rho}(t;\hat{B}^{>})\rangle\rangle, \tag{36}$$

with $\rho_{\rm T}(t;\hat{B}^{>}) = e^{-i\mathcal{L}_{\rm T}t}\rho_{\rm T}(0;\hat{B}^{>}) \equiv e^{-i\mathcal{L}_{\rm T}t}(\hat{B}\rho^{\rm st}_{\rm T})$ and

$$\rho_{\rm T}(t;\hat{B}^{>}) \to \boldsymbol{\rho}(t;\hat{B}^{>}) \equiv \{\rho^{(n)}_{\mathbf{n}}(t;\hat{B}^{>})\}. \tag{37}$$

Both $\hat{A}$ and $\hat{B}$ belong to the types of Eq. (33). Moreover, in relation to $\rho_{\rm T}(0;\hat{B}^{>}) \equiv \hat{B}\rho^{\rm st}_{\rm T}$, the initial values of DDOs in evaluating Eq. (36) are given by

$$\rho^{(n)}_{\mathbf{n}}(0;\hat{B}^{>}) \equiv {\rm tr}_{\rm B}\Big[\Big(\prod_{\alpha u k}\hat{f}^{n_{\alpha u k}}_{\alpha u k}\Big)^{\circ}\hat{B}^{>}\rho^{\rm st}_{\rm T}\Big]. \tag{38}$$

For the first type operator of Eq. (34), we have

$$\rho^{(n)}_{\mathbf{n}}(0;\hat{B}^{>}_{\rm S}) = \hat{B}_{\rm S}\rho^{(n);{\rm st}}_{\mathbf{n}}. \tag{39a}$$

The other two types are related to [cf. Eq. (27)]

$$\begin{aligned}
\rho^{(n)}_{\mathbf{n}}(0;\hat{B}^{>}_{\rm S}\hat{\theta}^{+;>}_{\alpha uk}) &= \hat{B}_{\rm S}\rho^{(n+1)}_{\mathbf{n}^{+}_{\alpha uk}}(t),\\
\rho^{(n)}_{\mathbf{n}}(0;\hat{B}^{>}_{\rm S}\hat{\theta}^{-;>}_{\alpha uk}) &= \sum_{v} n_{\alpha vk}\eta_{\alpha vuk}\hat{B}_{\rm S}\rho^{(n-1)}_{\mathbf{n}^{-}_{\alpha vk}}(t),
\end{aligned} \tag{39b}$$

since $\hat{f}_{\alpha uk} = \hat{\theta}^{-}_{\alpha uk} + \hat{\theta}^{+}_{\alpha uk}$ and $\hat{\varphi}_{\alpha uk} = \gamma_{\alpha k}(\hat{\theta}^{-}_{\alpha uk} - \hat{\theta}^{+}_{\alpha uk})$; Eq. (26).

The DEOM evaluations of correlation functions are as follows: (*i*) Compute the steady–state DDOs, $\{\rho^{(n);{\rm st}}_{\mathbf{n}}\}$; (*ii*) Determine the initial values $\{\rho^{(n)}_{\mathbf{n}}(0;\hat{B}^{>})\}$ via applicable Eq. (39) in study; (*iii*) Propagate DDOs with Eq. (30) to obtain the required $\{\rho^{(n)}_{\mathbf{n}}(t;\hat{B}^{>})\}$; (*iv*) Evaluate $\langle\hat{A}(t)\hat{B}(0)\rangle$ as the expectation value problem by using Eqs. (32)–(35). Demonstrated examples of these evaluations include such as Fano interferences,[64,70] Herzberg–Teller vibronic spectroscopy[71,72] and transport current noise spectrum.[66,73,74]

C. DEOM in the Heisenberg picture

The Heisenberg picture of DEOM is concerned with

$$\hat{A}(t) = \hat{A}e^{-i\mathcal{L}_{\rm T}t} \rightarrow \hat{\boldsymbol{A}}(t) = \hat{\boldsymbol{A}}e^{-i\boldsymbol{\mathcal{L}}t} \equiv \{\hat{A}^{(n)}_{\mathbf{n}}(t)\},$$

satisfying

$$\dot{\hat{\boldsymbol{A}}}(t) = -i\hat{\boldsymbol{A}}(t)\boldsymbol{\mathcal{L}} \tag{40}$$

and

$$\langle\hat{A}(t)\rangle = \langle\!\langle\hat{\boldsymbol{A}}(t)\big|\boldsymbol{\rho}(0)\rangle\!\rangle = \langle\!\langle\hat{\boldsymbol{A}}(0)\big|\boldsymbol{\rho}(t)\rangle\!\rangle \tag{41}$$

with $\hat{\boldsymbol{A}}(t=0)\equiv\hat{\boldsymbol{A}}$. From $\langle\!\langle\dot{\hat{\boldsymbol{A}}}|\boldsymbol{\rho}\rangle\!\rangle = \langle\!\langle\hat{\boldsymbol{A}}|\dot{\boldsymbol{\rho}}\rangle\!\rangle$, we obtain

$$\begin{aligned}
\dot{\hat{A}}^{(n)}_{\mathbf{n}} = -i\hat{A}^{(n)}_{\mathbf{n}}\mathcal{L}^{(n)}_{\mathbf{n}} - i\sum_{\alpha uk}\hat{A}^{(n-1)}_{\mathbf{n}^{-}_{\alpha uk}}\hat{Q}^{\times}_{u} - i\sum_{\alpha uvk}(n_{\alpha uk}+1)\\
\times\hat{A}^{(n+1)}_{\mathbf{n}^{+}_{\alpha uk}}(\eta_{\alpha uvk}\hat{Q}^{>}_{v} - \eta^{*}_{\alpha uv\bar{k}}\hat{Q}^{<}_{v}).
\end{aligned} \tag{42}$$

This is the Heisenberg picture counterpart to Eq. (30), where $\hat{O}\hat{B}^{>} = \hat{O}\hat{B}$ and $\hat{O}\hat{B}^{<} = \hat{B}\hat{O}$, in line with Eq. (14).

The main usage of Eq. (42) is concerned with efficient evaluations of nonlinear correlation functions, such that $\langle\hat{A}(t_2)\hat{B}(t_1)\hat{C}(0)\rangle = \langle\!\langle\hat{\boldsymbol{A}}(t_2)|\hat{\boldsymbol{B}}|\boldsymbol{\rho}(t_1;\hat{C}^{>})\rangle\!\rangle$, via the mixed Heisenberg–Schrödinger DEOM dynamics. The formulation here is closely related to the doorway–window picture of pump–probe spectroscopy.[75] As also known, the pump can be an optimal control field, whereas the probe provides a means of feedback.

D. DEOM toolkits and related considerations

As mentioned earlier, the DEOM (30) itself is identical to the well–established HEOM.[46–49] Various methods developed there can be directly applied; see the recent Perspective by Y. Tanimura.[42] New developments include the follows: (*i*) The adiabatic terminator for hierarchy level truncation, which alleviates the numerical long–time instability problems;[76] (*ii*) The time–domain Prony fitting decomposition scheme for accurate and minimum dissipaton basis set, applicable to arbitrary hybridization bath spectral densities;[63] (*iii*) The implementation of matrix product state;[77–83] (*iv*) The transformed Brownian oscillator basis;[84,85] (*v*) The construction of rate kernels via DEOM by utilizing the Nakajima–Zwanzig projection techniques[86,87] and so on.

In the following, we focus on the steady–state solver and related imaginary–time DEOM formalism.

1. *Efficient steady–state solver*

Steady states play crucial roles in many equilibrium and non-equilibrium open system studies, including aforementioned correlation function problems. The standard choices for solving high-dimension linear equations are the Krylov subspace methods.[88] Nevertheless, solving the steady states DDOs, $\dot{\boldsymbol{\rho}}^{\rm st} = 0$ or $\boldsymbol{\rho}(t\rightarrow\infty)$, via HEOM/DEOM (30) is often a challenging task, since the vast number of dynamical quantities are involved. The proposed self–consistent iteration (SCI) approach would be the choice.[89] To be concrete, we set $\dot{\rho}^{(n)}_{\mathbf{n}} = 0$ and obtain

$$\begin{aligned}
0 = -i\mathcal{L}^{(n)}_{\mathbf{n}}\rho^{(n);{\rm st}}_{\mathbf{n}} - i\sum_{\alpha uk}\hat{Q}^{\times}_{u}\rho^{(n+1);{\rm st}}_{\mathbf{n}^{+}_{\alpha uk}}\\
- i\sum_{\alpha uvk} n_{\alpha uk}\big(\eta_{\alpha uvk}\hat{Q}^{>}_{v} - \eta^{*}_{\alpha uv\bar{k}}\hat{Q}^{<}_{v}\big)\rho^{(n-1);{\rm st}}_{\mathbf{n}^{-}_{\alpha uk}}.
\end{aligned}$$

Then recast it into the SCI equation,[89]

$$\begin{aligned}
\rho^{(n);{\rm st}}_{\mathbf{n}} = (i\mathcal{L}^{(n)}_{\mathbf{n}} + \epsilon)^{-1}\Big[\epsilon\rho^{(n);{\rm st}}_{\mathbf{n}} - i\sum_{\alpha uk}\hat{Q}^{\times}_{u}\rho^{(n+1);{\rm st}}_{\mathbf{n}^{+}_{\alpha uk}}\\
- i\sum_{\alpha uvk} n_{\alpha uk}\big(\eta_{\alpha uvk}\hat{Q}^{>}_{v} - \eta^{*}_{\alpha uv\bar{k}}\hat{Q}^{<}_{v}\big)\rho^{(n-1);{\rm st}}_{\mathbf{n}^{-}_{\alpha uk}}\Big]
\end{aligned} \tag{43}$$

where $\epsilon > 0$ is an arbitrary parameter. The SCI evaluation is subject to the constraint ${\rm tr}_{\rm S}\rho^{(0)}_{\mathbf{0}} = 1$. The iteration will converge as long as the diagonal part of $(i\mathcal{L}^{(n)}_{\mathbf{n}} + \epsilon)$ dominates. Increasing ϵ will increase the numerical stability, but decrease the convergence speed. For a good balance between accuracy and efficiency, it is appropriate to have ϵ the value about the spectrum span of the system Hamiltonian.

As known, the SCI equation (43) accommodates the hierarchical structure and the efficient on-the-fly filtering algorithm.[90] The numerical practices also show the

remarkable advantages of SCI scheme over the Krylov subspace methods.[89]

2. Imaginary-time DEOM (*i*-DEOM)

Alternatively, the equilibrium state can be related to the imaginary–time DEOM,[57] which aims at hybridization partition function,

$$Z_{\rm hyb} \equiv Z_{\rm T}/Z_0 \equiv {\rm Tr}\varrho_{\rm T}(\beta), \tag{44}$$

with $Z_{\rm T} \equiv {\rm Tr}\, e^{-\beta H_{\rm T}}$ and $Z_0(T) \equiv {\rm Tr}\, e^{-\beta H_0}$. Only single bath is involved so that the α-index is dropped. Evidently, $Z_{\rm hyb}$ is related to the hybridization free–energy that can also be evaluated via the λ–thermodynamic integral; cf. Sec. IV A. The imaginary–time dynamics is concerned with

$$\varrho_{\rm T}(\tau) = e^{-\tau H_{\rm T}} e^{-(\beta-\tau)H_0}\big/ Z_0, \tag{45}$$

which satisfies [cf. Eq. (14)]

$$\frac{\rm d}{{\rm d}\tau}\varrho_{\rm T}(\tau) = -\big(H_0^{\times} + H_{\rm SB}^{>}\big)\varrho_{\rm T}(\tau). \tag{46}$$

The *i*-DEOM–space mappings then go by

$$\varrho_{\rm T}(\tau) \to \boldsymbol{\varrho}(\tau) \equiv \{\varrho_{\mathbf{n}}^{(n)}(\tau)\}, \tag{47}$$

with the *i*-DDOs satisfying

$$\frac{\rm d}{{\rm d}\tau}\varrho_{\mathbf{n}}^{(n)}(\tau) = -\varrho_{\mathbf{n}}^{(n)}(\tau; H_0^{\times}) - \sum_{uk}\hat{Q}_u\varrho_{\mathbf{n}}^{(n)}(\tau; \hat{f}_{uk}^{>}). \tag{48}$$

In parallel to Eqs. (18) and (20), we obtain[57]

$$\begin{aligned}
&\varrho_{\mathbf{n}}^{(n)}(\tau; H_0^{\times}) = \mathcal{L}_{\mathbf{n}}^{(n)}\varrho_{\mathbf{n}}^{(n)}(\tau),\\
&\varrho_{\mathbf{n}}^{(n)}(\tau; \hat{f}_{uk}^{>}) = \varrho_{\mathbf{n}_{uk}^{+}}^{(n+1)}(\tau) + \sum_v n_{vk}\eta_{vuk}\varrho_{\mathbf{n}_{vk}^{-}}^{(n-1)}(\tau).
\end{aligned} \tag{49}$$

In line with $\varrho_{\rm T}(0) = e^{-\beta H_0}/Z_0$ of Eq. (45), the initial values of *i*-DDOs are

$$\varrho_{\mathbf{0}}^{(0)}(0) = e^{-\beta H_{\rm S}}/Z_{\rm S} \;\;\text{and}\;\; \varrho_{\mathbf{n}}^{(n>0)}(0) = 0, \tag{50}$$

where $Z_{\rm S} = {\rm tr}_{\rm S}e^{-\beta H_{\rm S}}$. We then propagate the *i*–DEOM until $\tau = \beta$ and evaluate

$$Z_{\rm hyb} = {\rm tr}_{\rm S}\varrho_{\mathbf{0}}^{(0)}(\beta). \tag{51}$$

It can be further verified that[57]

$$\frac{\varrho_{\mathbf{n}}^{(n)}(\beta)}{{\rm tr}_{\rm S}[\varrho_{\mathbf{0}}^{(0)}(\beta)]} = \rho_{\mathbf{n}}^{(n);{\rm eq}}. \tag{52}$$

The right–hand–side are the equilibrium DDOs, which can be obtained via steady–state solvers, such as the SCI [cf. Eq. (43)].

IV. DISSIPATON IMPLEMENTATIONS OF THERMODYNAMIC MIXING

The system–bath entanglement plays crucially important roles in not only dynamics but also the thermodynamic properties.[57,91,92] The latter has just been illustrated with the *i*-DEOM formalism. In the following, we will introduce an alternative approach and further extend this method to the nonequilibrium scenarios.

A. Equilibrium λ-DEOM formalism

The equilibrium λ-DEOM focuses on the free–energy change before and after isotherm system–bath mixing,

$$A_{\rm hyb}(T) \equiv A_{\rm T}(T) - A_0(T). \tag{53}$$

Evidently, $A_{\rm hyb}(T) = -\beta^{-1}\ln Z_{\rm hyb}(T)$ [cf. Eq. (44)]. According to the thermodynamic integral formalism, the hybridization free–energy can be expressed as[57,91–95]

$$A_{\rm hyb}(T) = \int_0^1 \frac{{\rm d}\lambda}{\lambda}\langle H_{\rm SB}\rangle_\lambda \tag{54}$$

where λ is the mixing parameter and

$$\langle H_{\rm SB}\rangle_\lambda \equiv {\rm Tr}[(\lambda H_{\rm SB})\rho_{\rm T}^{\rm eq}(T;\lambda)] \tag{55}$$

with $\rho_{\rm T}^{\rm eq}(T;\lambda) = e^{-\beta H_{\rm T}(\lambda)}/Z_\lambda(T)$ and $Z_\lambda(T) \equiv {\rm Tr}\, e^{-\beta H_{\rm T}(\lambda)}$ [cf. Eq. (56)]. The involving total composite Hamiltonian reads

$$H_{\rm T}(\lambda) = H_0 + \lambda H_{\rm SB}, \tag{56}$$

with $H_0 \equiv H_{\rm S} + h_{\rm B}$ [cf. Eq. (17)].

Equation (55) implies that $\langle H_{\rm SB}\rangle_\lambda$ is just the λ–augmented equivalence to the original $\langle H_{\rm SB}\rangle$ where $\lambda = 1$. As seen from Sec. III, DEOM supports accurate evaluations of $\langle H_{\rm SB}\rangle_\lambda$ for the Gauss–Wick's bath. In particular, for $H_{\rm SB} = \sum_u \hat{Q}_u\hat{F}_u$, by using Eqs. (32) with (35b), we obtain

$$\langle H_{\rm SB}\rangle_\lambda = \lambda\sum_{uk}{\rm tr}_{\rm S}\big[\hat{Q}_u\rho_{uk}^{\rm eq}(T;\lambda)\big]. \tag{57}$$

Here, $\rho_{uk}^{\rm eq}(T;\lambda) \equiv \rho_{\mathbf{0}_{uk}^{+}}^{(1);{\rm eq}}(T;\lambda)$ is a λ–augmented DDO at thermal equilibrium, with the generic form of Eq. (11) but

$$\rho_{\mathbf{n}}^{(n);{\rm eq}}(T;\lambda) \equiv {\rm tr}_{\rm B}\Big[\Big(\prod_{uk}\hat{f}_{uk}^{n_{uk}}\Big)^{\circ}\rho_{\rm T}^{\rm eq}(T;\lambda)\Big]. \tag{58}$$

The hybridization free–energy in Eq. (53) can be then obtained via the integration of λ by using Eq. (54). This is the equilibrium λ-DEOM formalism. Practically, we evaluate $\boldsymbol{\rho}^{\rm eq}(T;\lambda) \equiv \big\{\rho_{\mathbf{n}}^{(n);{\rm eq}}(T;\lambda)\big\}$ progressively, by noting that $\rho_{\mathbf{0}}^{(0);{\rm eq}}(T;0) = e^{-\beta H_{\rm S}}/Z_{\rm S}$ and $\rho_{\mathbf{n}}^{(n>0);{\rm eq}}(T;0) = 0$. Then use the known $\boldsymbol{\rho}^{\rm eq}(T;\lambda)$ as

the initial values for calculating $\boldsymbol{\rho}^{\rm eq}(T;\lambda+\delta\lambda)$ via either the real–time ($t\to\infty$) propagation or the steady–state solver. We have also developed the free–energy spectrum theory for thermodynamics of open quantum impurity systems, which relates the thermodynamic spectral functions to the local impurity properties.[92]

B. Nonequilibrium $\lambda(t)$-DEOM formalism

Turn to the isotherm mixing processes that are irreversible. A time–dependent mixing function $\lambda(t)$, subject to $\lambda(t=0)=0$ and $\lambda(t=t_f)=1$, would be used instead. This represents nonequilibrium scenarios in general, where the work distribution $p(w)$ is the key quantity in related studies. There are the Jarzynski equality,[96]

$$\big\langle e^{-\beta w}\big\rangle \equiv \int_{-\infty}^{\infty}\mathrm{d}w\, e^{-\beta w}p(w) = e^{-\beta A_{\rm hyb}} \tag{59}$$

and the Crooks relation,[97]

$$p(w) = e^{\beta(w-A_{\rm hyb})}\bar{p}(-w). \tag{60}$$

The latter is about a pair of conjugate processes, with the forward and backward processes being controlled by $\lambda(t)$ and $\bar{\lambda}(t)\equiv\lambda(t_f-t)$, respectively.[98] Evidently, the forward work distribution $p(w)$ and the backward $\bar{p}(-w)$ cross at the point of reversible work, $w=A_{\rm hyb}$ that can be obtained via the equilibrium λ-DEOM formalism.

The nonequilibrium $\lambda(t)$–DEOM is a viable means to the accurate evaluation of $p(w)$. The formulations start with $H_0|n\rangle = H_{\rm T}(\lambda=0)|n\rangle = \varepsilon_n|n\rangle$ and $H_{\rm T}(\lambda=1)|N\rangle = E_N|N\rangle$ before and after mixing. The distribution of mixing work is given by[99]

$$p(w) = \sum_{N,n}\delta(w-E_N+\varepsilon_n)P_{N,n}(t_f,0)P_n(0). \tag{61}$$

Here, $P_n(0)=e^{-\beta\varepsilon_n}/Z_0$ is the initial probability distribution, and $P_{N,n}(t,0)=\big|\langle N|\hat{U}_{\rm T}(t)|n\rangle\big|^2$ is the transition probability with the propagator $U_{\rm T}(t)$ being governed by the Hamiltonian $H_{\rm T}(t)=H_0+\lambda(t)H_{\rm SB}$. The non-zero $\dot{\lambda}(t)$ that describes the irreversibility engages in

$$\hat{V}_{\pm}(t;\tau) = \exp_{\pm}\left[\frac{i\tau}{2}\int_0^t \mathrm{d}t'\,\dot{\lambda}(t')H_{\rm SB}\right], \tag{62}$$

which participates in the work generating operator,[99,100]

$$\hat{W}_{\rm T}(t;\tau) = \hat{U}_{\rm T}(t)\hat{V}_+(t;\tau)\rho_0^{\rm eq}(T)\hat{V}_-(t;\tau)\hat{U}_{\rm T}^{\dagger}(t). \tag{63}$$

It can be shown that[99,100]

$$p(w) = \frac{1}{2\pi}\int_{-\infty}^{\infty}\mathrm{d}\tau\, e^{-iw\tau}\big\{\mathrm{Tr}[\hat{W}_{\rm T}(t_f;\tau)]\big\}. \tag{64}$$

Turn to the equation of motion for the work generating operator $\hat{W}(t;\tau)$. Its dynamics can be obtained as

$$\frac{\partial\hat{W}_{\rm T}}{\partial t} = -i[H_0^{\times}+\lambda_-(t)H_{\rm SB}^{>}-\lambda_+(t)H_{\rm SB}^{<}]\hat{W}_{\rm T}, \tag{65}$$

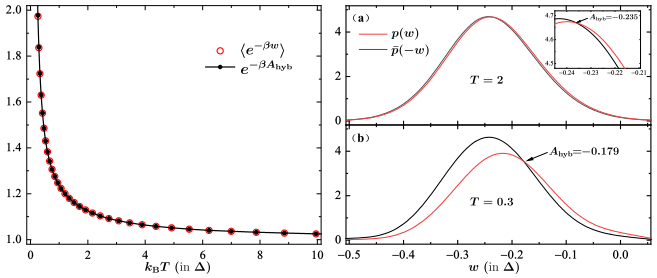

FIG. 2. Jarzynski equality (left panel) and Crooks relation (right panel), cited from Ref. 58. Numerical demonstrations are carried out with a spin-boson model, in which the system Hamiltonian and dissipative mode are $H_{\rm S}=\varepsilon\hat{\sigma}_z+\Delta\hat{\sigma}_x$ and $\hat{Q}=\hat{\sigma}_z$, respectively. Adopt for the bath spectral density the Drude model, $J(\omega)=\eta\gamma\omega/(\omega^2+\gamma^2)$. In all the simulations, we set $\varepsilon=0.5\Delta$, $\gamma=4\Delta$ and $\eta=0.5\Delta$. The forward time–dependent mixing function adopts $\lambda(t)=(1-e^{-\alpha t})/(1-e^{-\alpha t_f})$, with $\alpha=0.01\Delta$ and $t_f=50\Delta^{-1}$. Simulations are carried out at different temperatures. In the left panel T ranges from near 0 to 10Δ, while it adopts (a) $T=2\Delta$ and (b) $T=0.3\Delta$ in the right panel.

with $\lambda_\pm(t)\equiv\lambda(t)\pm(\tau/2)\dot{\lambda}(t)$. Initially, $\hat{W}_{\rm T}(0;\tau)=\rho_0^{\rm eq}(T)=e^{-\beta H_0}/Z_0$, as inferred from Eq. (63). Similar to DDOs in Eq. (11), we introduce the dissipatons–augmented work generating operators (D-WGOs),

$$\hat{W}_{\rm T}(t;\tau)\to\hat{\boldsymbol{W}}(t;\tau)\equiv\{\hat{W}_{\mathbf{n}}^{(n)}(t;\tau)\}. \tag{66}$$

The same procedure from Eq. (28) to Eq. (30) now gives rise to Eq. (65) the D-WGO correspondence,[58]

$$\begin{aligned}\frac{\partial\hat{W}_{\mathbf{n}}^{(n)}}{\partial t} =& -i\mathcal{L}_{\mathbf{n}}^{(n)}\hat{W}_{\mathbf{n}}^{(n)} - i\sum_{uk}\mathcal{A}_u(t)\hat{W}_{\mathbf{n}_{uk}^{+}}^{(n+1)}\\ &- i\sum_{uk}n_{uk}\mathcal{C}_{uk}(t)\hat{W}_{\mathbf{n}_{uk}^{-}}^{(n-1)},\end{aligned} \tag{67}$$

where

$$\begin{aligned}\mathcal{A}_u(t) &\equiv \lambda_-(t)\hat{Q}_u^{>}-\lambda_+(t)\hat{Q}_u^{<},\\ \mathcal{C}_{uk}(t) &\equiv \sum_v\big[\lambda_-(t)\eta_{uvk}\hat{Q}_v^{>}-\lambda_+(t)\eta_{uv\bar{k}}^{*}\hat{Q}_v^{<}\big].\end{aligned} \tag{68}$$

In relation to $\hat{W}_{\rm T}(0;\tau)=\rho_0^{\rm eq}(T)=e^{-\beta H_0}/Z_0$, the initial values to Eq. (67) are

$$\hat{W}_{\mathbf{0}}^{(0)}(0;\tau)=e^{-\beta H_{\rm S}}/Z_{\rm S}\ \text{ and }\ \hat{W}_{\mathbf{n}}^{(n>0)}(0;\tau)=0. \tag{69}$$

Finally, in line with Eq. (64), we evaluate

$$p(w)=\frac{1}{2\pi}\int_{-\infty}^{\infty}\mathrm{d}w\, e^{-iw\tau}\mathrm{tr}_{\rm S}[\hat{W}_{\mathbf{0}}^{(0)}(t_f;\tau)]. \tag{70}$$

Figure 2 reports the results in terms of the Jarzynski equality (59) and the Crooks relation (60); see the figure caption for the details of model system.

V. DISSIPATON THERMOFIELD THEORY

A. Prelude

Generally speaking, thermofield theory[101] is an important ingredient for quantum mechanics of open systems and closely related to nonequilibrium Green's function formalisms.[102–104] The dissipaton thermofield theory (DTF)[105] to be presented in this section comprises in particular the nonequilibrium system–bath entanglement theorem. This gives rise to relations between the local system correlation functions and those involving the nonlocal hybrid bath modes. The development exploits further decomposition of each dissipaton into the absorptive ($+$) and emissive ($-$) components, as schematically represented in the last column of Fig. 1.

To proceed, we consider the $H_{\rm T}$–based Heisenberg picture of the hybrid bath modes. It is easy to obtain[106,107]

$$\hat{F}_{\alpha u}(t) = \hat{F}^{\rm B}_{\alpha u}(t) - \sum_v \int_0^t {\rm d}\tau\, \phi_{\alpha uv}(t-\tau)\hat{Q}_v(\tau). \quad (71)$$

This is the precursor to conventional quantum Langevin equation, with $\hat{F}^{\rm B}_{\alpha u}(t)$ being the random force and the related $\phi_{\alpha uv}(t)$ of Eq. (4). Together with $[\hat{F}^{\rm B}_{\alpha u}(t), \hat{Q}_v(0)] = 0$, we obtain the system–bath entanglement theorem for response functions, which is a type of input–output relations in the total composite space.[106,107]

On the other hand, $\langle \hat{F}^{\rm B}_{\alpha u}(t)\hat{Q}_v(0)\rangle \neq 0$. Equation (71) is insufficient to obtain the input–output relations between nonequilibrium correlation functions, such as

$$\boldsymbol{C}_{\rm SS}(t) = \{C^{\rm SS}_{uv}(t) \equiv \langle \hat{Q}_u(t)\hat{Q}_v(0)\rangle\}, \quad (72a)$$

$$\boldsymbol{C}_{\alpha{\rm S}}(t) = \{C^{\alpha{\rm S}}_{uv}(t) \equiv \langle \hat{F}_{\alpha u}(t)\hat{Q}_v(0)\rangle\}. \quad (72b)$$

More specifically, from Eq. (71) we have

$$\boldsymbol{C}_{\alpha{\rm S}}(t) = \boldsymbol{X}_{\alpha{\rm S}}(t) - \int_0^t {\rm d}\tau\, \boldsymbol{\phi}_\alpha(t-\tau)\boldsymbol{C}_{\rm SS}(\tau), \quad (73)$$

with

$$\boldsymbol{X}_{\alpha{\rm S}}(t) = \{X^{\alpha{\rm S}}_{uv}(t) \equiv \langle \hat{F}^{\rm B}_{\alpha u}(t)\hat{Q}_v(0)\rangle\}, \quad (74)$$

to be further resolved. To that end, we exploit the statistical quasi-particles picture, which is used in the DEOM theory[55], and obtain

$$\boldsymbol{X}_{\alpha{\rm S}}(t) = \sum_k \boldsymbol{X}_{\alpha{\rm S}k}(t), \quad (75)$$

with

$$X^{\alpha{\rm S}}_{uvk}(t) \equiv \langle \hat{f}^{\rm B}_{\alpha uk}(t)\hat{Q}_v(0)\rangle = \langle \hat{f}_{\alpha uk}(0)\hat{Q}_v(0)\rangle e^{-\gamma_{\alpha k}t}. \quad (76)$$

Here, $\{\gamma_{\alpha k}\}$ originates from the exponential decomposition of the interacting bath correlations as in Eq. (5). Evidently, to establish the aforementioned correlation function type input–output relations, the key step is to formulate $X^{\alpha{\rm S}}_{uvk}(0)$ in terms of $\boldsymbol{C}_{\rm SS}(t)$ [cf. Eq. (72a)] and $\boldsymbol{c}_\alpha(t)$ [cf. Eqs. (2) and (5)]. We address this issue within the scope of DTF theory to be elaborated as follows.

B. Ansatzes

The proposed DTF theory is based on the dissipaton decomposition of the hybrid reservoir modes, as schematically represented in Fig. 1. There are three basic ingredients:

(i) *Dissipaton decomposition ansatz:* The hybrid reservoir modes can be decomposed into dissipatons, as in Eq. (7) with Eq. (8).

(ii) *Thermofield dissipatons ansatz*: Each $\hat{f}_{\alpha uk}$ consists of an absorptive ($+$) and an emissive ($-$) parts (cf. Fig. 1),

$$\hat{f}_{\alpha uk} = \hat{f}^+_{\alpha uk} + \hat{f}^-_{\alpha uk}, \quad (77a)$$

defined via

$$\hat{f}^-_{\alpha uk}\rho^0_{\rm B} = \rho^0_{\rm B}\hat{f}^+_{\alpha uk} = 0. \quad (77b)$$

This results in

$$\begin{aligned} c^-_{\alpha uvk}(t) &\equiv \langle \hat{f}^{-;{\rm B}}_{\alpha uk}(t)\hat{f}^{+;{\rm B}}_{\alpha vk}(0)\rangle_{\rm B} = \eta^>_{\alpha uvk}e^{-\gamma_{\alpha k}t}, \\ c^+_{\alpha uvk}(t) &\equiv \langle \hat{f}^{-;{\rm B}}_{\alpha vk}(0)\hat{f}^{+;{\rm B}}_{\alpha uk}(t)\rangle_{\rm B} = \eta^<_{\alpha uv\bar{k}}e^{-\gamma_{\alpha k}t}. \end{aligned} \quad (78)$$

As the thermofield excitation is concerned, $\hat{f}^\pm_{\alpha uk}$ resembles the creation/annihilation operator onto the reference $\rho^0_{\rm B} = \otimes_\alpha[e^{-\beta_\alpha h_\alpha}/{\rm tr}_{\rm B}(e^{-\beta_\alpha h_\alpha})]$.[101]

(iii) *Thermofield Langevin ansatz*: Each thermofield dissipaton satisfies

$$\hat{f}^\pm_{\alpha uk}(t) = \hat{f}^{\pm;{\rm B}}_{\alpha uk}(t) \pm i\sum_v \int_0^t {\rm d}\tau c^\pm_{\alpha uvk}(t-\tau)\hat{Q}_v(\tau). \quad (79)$$

In compared with Eq. (71), the resolved are not only the absorptive versus emissive contributions, but also the Langevin force that reads $\hat{f}^{\pm;{\rm B}}_{\alpha uk}(t) = \hat{f}^{\pm;{\rm B}}_{\alpha uk}(0)e^{-\gamma_{\alpha k}t}$. This recovers the generalized diffusion equation of the DEOM theory.[55]

C. System–bath entanglement theorem for correlation functions

In the following, we elaborate above basic ingredients of the DTF theory, with a class of input–output relations between local and nonlocal nonequilibrium steady–state correlation functions. Denote $\boldsymbol{C}_{\alpha{\rm S}k}(t) = \{C_{\alpha{\rm S}k}(t) \equiv \langle \hat{f}_{\alpha uk}(t)\hat{Q}_v(0)\rangle\}$ and $\boldsymbol{\phi}_{\alpha k}(t) = i[\boldsymbol{c}^-_{\alpha k}(t) - \boldsymbol{c}^+_{\alpha k}(t)] = \{\phi_{\alpha uvk}(t) = i[c^-_{\alpha uvk}(t) - c^+_{\alpha uvk}(t)]\}$. Equations (77) and (79) give rise to

$$\boldsymbol{C}_{\alpha{\rm S}k}(t) = \boldsymbol{X}_{\alpha{\rm S}k}(t) - \int_0^t {\rm d}\tau\, \boldsymbol{\phi}_{\alpha k}(t-\tau)\boldsymbol{C}_{\rm SS}(\tau) \quad (80)$$

where $X^{\alpha{\rm S}}_{uvk}(t) = X^{\alpha{\rm S}}_{uvk}(0)e^{-\gamma_{\alpha k}t}$ [cf. Eq. (76)] and

$$\boldsymbol{X}_{\alpha{\rm S}k}(0) = i\int_0^\infty {\rm d}\tau\big[\boldsymbol{c}^+_{\alpha k}(\tau)\boldsymbol{C}^\dagger_{\rm SS}(\tau) - \boldsymbol{c}^-_{\alpha k}(\tau)\boldsymbol{C}^T_{\rm SS}(\tau)\big]. \quad (81)$$

Derivation details of Eq. (81) are shown in the next paragraph. Here, $\boldsymbol{M}^T$ denotes the matrix transpose of $\boldsymbol{M}$. Together with Eq. (80), we obtain further

$$\boldsymbol{X}_{\alpha\mathrm{S}}(t) = 2\,\mathrm{Im}\int_0^\infty \mathrm{d}\tau\, \boldsymbol{c}_\alpha^T(t+\tau)\boldsymbol{C}_{\mathrm{SS}}^T(\tau). \tag{82}$$

This completes Eq. (73), the system–bath entanglement theorem for nonequilibrium steady–state correlation functions.

The derivations of the key expression (81) are as follows. (*i*) Start with $\langle\hat{A}(0)\rangle = \lim_{t\to\infty}\mathrm{Tr}\big[\hat{A}(t)\rho_{\mathrm{T}}^{\mathrm{init}}\big]$ for any operator $\hat{A}$. This asymptotic identity holds for any physically supported initial total composite density operator $\rho_{\mathrm{T}}^{\mathrm{init}}$. In particular, we choose $\rho_{\mathrm{T}}^{\mathrm{init}} = \rho_{\mathrm{S}}^{\mathrm{init}}\otimes\rho_{\mathrm{B}}^0$, with ρ_{B}^0 being the pure bath canonical ensemble density operator; (*ii*) Split $X_{uvk}^{\alpha\mathrm{S}}(0) \equiv \langle\hat{f}_{\alpha uk}(0)\hat{Q}_v(0)\rangle = \langle\hat{f}^+_{\alpha uk}(0)\hat{Q}_v(0)\rangle + \langle\hat{Q}_v(0)\hat{f}^-_{\alpha uk}(0)\rangle$. This is true since the system and reservoir operators are commutable at any given local time; (*iii*) Obtain $\mathrm{Tr}[\hat{f}^+_{\alpha uk}(t)\hat{Q}_v(t)\rho_{\mathrm{T}}^{\mathrm{init}}]$ and $\mathrm{Tr}[\hat{Q}_v(t)\hat{f}^-_{\alpha uk}(t)\rho_{\mathrm{T}}^{\mathrm{init}}]$ from Eq. (79), with focus on their $t\to\infty$ expressions, where $\hat{f}^{\mathrm{B};\pm}_{\alpha uk}(t)$ makes no contribution according to Eq. (77b). The resulting $X_{uvk}^{\alpha\mathrm{S}}(0)$ according to Step (*ii*) is just Eq. (81).

D. Comments

It is worth emphasizing that the DTF formalism, is rather general in relation to the absorptive and emissive processes. Its application to obtain Eqs. (80)–(82) is an example that can be numerically verified by DEOM evaluations. However, Eqs. (80)–(82) can not be obtained within the original DEOM framework. That is to say, although both the DTF theory and DEOM method are numerically exact for Gaussian environments, DTF theory helps reveal more explicit relations. Furthermore, the $t = 0$ behaviour of Eq. (73) with Eq. (82) is closely related to the nonequilibrium Green's function formalism of transport current.[54,102,103,108,109] For example, consider the heat transport from the α–reservoir to the local impurity system. The heat current operator reads

$$\hat{J}_\alpha \equiv -\frac{\mathrm{d}h_\alpha}{\mathrm{d}t} = -i[H_{\mathrm{T}}, h_\alpha] = \sum_u \dot{\hat{F}}_{\alpha u}\hat{Q}_u. \tag{83}$$

This is the electron transport analogue.[110,111] The heat current is then [cf. Eq. (72b)]

$$J_\alpha = \sum_u \langle\dot{\hat{F}}_{\alpha u}\hat{Q}_u\rangle = \sum_u \dot{C}_{uu}^{\alpha\mathrm{S}}(t=0). \tag{84}$$

Now apply Eq. (73), with noticing that its second term does not contribute to $\dot{C}_{uu}^{\alpha\mathrm{S}}(0)$. We obtain[107]

$$J_\alpha = 2\,\mathrm{Im}\int_0^\infty \mathrm{d}\tau\,\mathrm{tr}\big[\dot{\boldsymbol{c}}_\alpha(\tau)\boldsymbol{C}_{\mathrm{SS}}(\tau)\big]. \tag{85}$$

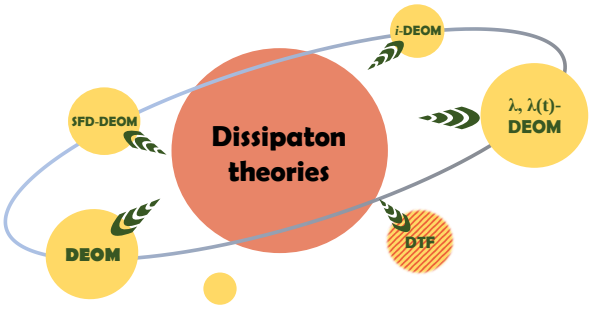

FIG. 3. The family of dissipaton theories, including now real–time DEOM, imaginary–time DEOM (*i*-DEOM), equilibrium λ-DEOM, nonequilibrium $\lambda(t)$-DEOM, stochastic–field–dressed DEOM (SFD-DEOM) and the dissipaton thermofield (DTF) theory. Future family members are anticipated.

This is the time–domain Meir–Wingreen's formula.[108]

The DTF theory would be better physically supported than the conventional thermofield approach. The latter involves the purification of bare bath canonical thermal states onto effective zero–temperature environments.[101] On the other hand, the DTF approach exploits the of discrete Brownian quasi-particle picture as implied in the dissipaton Langevin equation (79). This not only avoids introducing the auxiliary degrees of freedom, but also goes with the effectively resolved random force, in line with the generalized diffusion equation (15) of the DEOM theory. Moreover, the system–bath entanglement theorem for the properties of Eq. (72) can be readily extended to those such as $\langle\hat{F}_{\alpha u}(t)\hat{F}_{\alpha' v}(0)\rangle$ and also $\langle\hat{F}_{\alpha u}(t)\hat{A}_{\mathrm{S}}(0)\rangle$ via $\langle\hat{Q}_u(t)\hat{A}_{\mathrm{S}}(0)\rangle$ for an arbitrary system operator $\hat{A}_{\mathrm{S}}$.

Additionally, it is also worth noting that Eq. (71) immediately results in[92]

$$\langle\hat{F}_{\alpha u}\rangle = -\sum_v \theta_{\alpha uv}\langle\hat{Q}_v\rangle, \tag{86}$$

with $\theta_{\alpha uv} \equiv \int_0^\infty \mathrm{d}t\,\phi_{\alpha uv}(t)$ [cf. Eq. (4)]. This result can also be obtained via the DEOM formulations.

VI. CONCLUDING AND PROSPECTIVE REMARKS

To conclude, dissipaton theories are essential building blocks of quantum mechanics of open systems, comprising rich ingredients. These include the Brownian quasi-particles picture and the phase–space dissipaton algebra, together with the dynamical variables (Sec. II). The resulting real–time DEOM (30) unambiguously support various formulations such as expectation values, correlation functions, the Heisenberg picture, the imaginary–time DEOM and so on (Sec. III). The λ- and $\lambda(t)$-DEOM formalisms are also readily established for various studies of thermodynamics (Sec. IV). Dissipaton thermofield (DTF) theory is also established along the similar line (Sec. V).

As noticed, the fermionic dissipaton theories can also been readily established in a similar manner, with $\big(\hat{f}_k\hat{f}_j\big)^\circ = -\big(\hat{f}_j\hat{f}_k\big)^\circ$ for fermionic dissipaton operators [cf. Eq. (10)]. Moreover, the fermionic DEOM has been integrated with electronic structure theory for the first–principle simulations on realistic spintronic systems in experimental measurements.[52] These studies include Kondo transport, magnetic anisotropy manipulation, spin–polarized scanning tunneling spectroscopy and so on.[112–115] Furthermore, there would be a so–called dissipaton embedded quantum master equation formalism, with system–plus–dissipatons being all incorporated into a single master equation. This provides an alternative formalism for quantum simulations in both bosonic and fermionic scenarios.

It is worth emphasizing that dissipatons are linear bath hybrid modes. Nevertheless, the unavoidable backaction of system to environment will result in simultaneous actions of two or more dissipatons. The further development of dissipaton theories should take nonlinear environments into account. For the quadratic bath coupling, we proposed the stochastic–field–dressed DEOM (SFD-DEOM).[116] We had also developed the extended Wick's theorem approach to deal with a model quadratic environment.[67–69] Last but not least, it is also anticipated that dissipaton theories discussed in this Perspective would remain essential to relativistic quantum mechanics of open systems.

ACKNOWLEDGMENTS

Support from the Ministry of Science and Technology of China (Grant No. 2021YFA1200103) and the National Natural Science Foundation of China (Grant Nos. 22103073 and 22173088) is gratefully acknowledged.

[1] U. Weiss, *Quantum Dissipative Systems*, World Scientific, Singapore, 2021, 5th ed.
[2] H. Kleinert, *Path Integrals in Quantum Mechanics, Statistics, Polymer Physics, and Financial Markets*, World Scientific, Singapore, 5th edition, 2009.
[3] H. P. Breuer and F. Petruccione, *The Theory of Open Quantum Systems*, Oxford University Press, New York, 2002.
[4] Y. J. Yan and R. X. Xu, "Quantum mechanics of dissipative systems," Annu. Rev. Phys. Chem. **56**, 187 (2005).
[5] M. O. Scully and M. S. Zubairy, *Quantum Optics*, Cambridge University Press, Cambridge, 1997.
[6] W. H. Louisell, *Quantum Statistical Properties of Radiation*, Wiley, New York, 1973.
[7] F. Haake, "Statistical treatment of open systems by generalized master equations," in *Quantum Statistics in Optics and Solid State Physics: Springer Tracts in Modern Physics, Vol. 66*, edited by G. Höhler, pages 98–168, Springer, Berlin, 1973.
[8] H. Haken, *Laser Theory*, Springer, Berlin, 1970.
[9] M. Sargent III, M. O. Scully, and J. W. E. Lamb, *Laser Physics*, Addison-Wesley, Reading, MA, 1974.
[10] P. Reineker, *Exciton Dynamics in Molecular Crystals and Aggregates: Stochastic Liouville Equation Approach: Coupled Coherent and Incoherent Motion, Optical Line Shapes, Magnetic Resonance Phenomena*, Springer, Berlin, 1982.
[11] C. P. Slichter, *Principles of Magnetic Resonance*, Springer Verlag, New York, 1990.
[12] L. M. K. Vandersypen and I. L. Chuang, "NMR techniques for quantum control and computation," Rev. Mod. Phys. **76**, 1037 (2005).
[13] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices*, Oxford University Press, New York, 1985.
[14] T. Holstein, "Studies of polaron motion Part I. The molecular-crystal model," Ann. Phys. **8**, 325 (1959).
[15] T. Holstein, "Studies of polaron motion Part II. The "small" polaron," Ann. Phys. **8**, 343 (1959).
[16] C. F. Klingshirn, *Semiconductor Optics*, Springer-Verlag, Heidelberg, 1997.
[17] J. Rammer, *Quantum Transport Theory*, Perseus Books, Reading, Mass., 1998.
[18] Y. Akamatsu, "Heavy quark master equations in the Lindblad form at high temperatures," Phys. Rev. D **91**, 056002 (2015).
[19] J.-P. Blaizot and M. A. Escobedo, "Quantum and classical dynamics of heavy quarks in a quark-gluon plasma," J. High Energy Phys. **2018**, 1 (2018).
[20] T. Miura, Y. Akamatsu, M. Asakawa, and A. Rothkopf, "Quantum Brownian motion of a heavy quark pair in the quark-gluon plasma," Phys. Rev. D **101**, 034011 (2020).
[21] X. Yao, "Open quantum systems for quarkonia," Int. J. Mod. Phys. A **36**, 2130010 (2021).
[22] S. Mukamel, *The Principles of Nonlinear Optical Spectroscopy*, Oxford University Press, New York, 1995.
[23] Y. R. Shen, *The Principles of Nonlinear Optics*, Wiley, New York, 1984.
[24] S. Mukamel, "Reduced equations of motion for collisionless molecular multiphoton processes," Adv. Chem. Phys. **47**, 509 (1981).
[25] Y. J. Yan and S. Mukamel, "Electronic dephasing, vibrational relaxation, and solvent friction in molecular nonlinear optical lineshapes," J. Chem. Phys. **89**, 5160 (1988).
[26] Y. J. Yan and S. Mukamel, "Photon echoes of polyatomic molecules in condensed phases," J. Chem. Phys. **94**, 179 (1991).
[27] V. Chernyak and S. Mukamel, "Collective coordinates for nuclear spectral densities in energy transfer and femtosecond spectroscopy of molecular aggregates," J. Chem. Phys. **105**, 4565 (1996).
[28] Y. Tanimura and S. Mukamel, "Two-dimensional femtosecond vibrational spectroscopy of liquids," J. Chem. Phys. **99**, 9496 (1993).
[29] Y. Tanimura and S. Mukamel, "Multistate quantum Fokker-Planck approach to nonadiabatic wave packet dynamics in pump-probe spectroscopy," J. Chem. Phys. **101**, 3049 (1994).
[30] A. Nitzan, *Chemical Dynamics in Condensed Phases: Relaxation, Transfer and Reactions in Condensed Molecular Systems*, Oxford University Press, New York, 2006.
[31] H. Lee, Y.-C. Cheng, and G. R. Fleming, "Coherence dynamics in photosynthesis: Protein protection of excitonic coherence," Science **316**, 1462 (2007).
[32] G. S. Engel, T. R. Calhoun, E. L. Read, T. K. Ahn, T. Mančal, Y. C. Cheng, R. E. Blankenship, and G. R. Fleming, "Evidence for wavelike energy transfer through quantum coherence in photosynthetic systems," Nature **446**, 782 (2007).
[33] K. E. Dorfman, D. V. Voronine, S. Mukamel, and M. O. Scully, "Photosynthetic reaction center as a quantum heat engine," Proc. Natl. Acad. Sci. **110**, 2746 (2013).
[34] C. Creatore, M. A. Parker, S. Emmott, and A. W. Chin, "Efficient biologically inspired photocell enhanced by delocalized quantum states," Phys. Rev. Lett. **111**, 253601 (2013).
[35] S. Kundu, R. Dani, and N. Makri, "B800-to-B850 relaxation of excitation energy in bacterial light harvesting: All-state, all-mode path integral simulations," J. Chem. Phys. **157**, 015101 (2022).
[36] A. G. Redfield, "The theory of relaxation processes," Adv. Magn. Reson. **1**, 1 (1965).
[37] G. Lindblad, "Brownian motion of a quantum harmonic oscillator," Rep. Math. Phys. **10**, 393 (1976).
[38] A. O. Caldeira and A. J. Leggett, "Path integral approach to

quantum Brownian motion," Physica A **121**, 587 (1983).
[39]N. G. van Kampen, *Stochastic Processes in Physics and Chemistry*, North-Holland, Amsterdam, 1992.
[40]R. X. Xu and Y. J. Yan, "Theory of open quantum systems," J. Chem. Phys. **116**, 9196 (2002).
[41]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).
[42]Y. Tanimura, "Numerically "exact" approach to open quantum dynamics: The hierarchical equations of motion (HEOM)," J. Chem. Phys **153**, 020901 (2020).
[43]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).
[44]Y. Tanimura, "Nonperturbative expansion method for a quantum system coupled to a harmonic-oscillator bath," Phys. Rev. A **41**, 6676 (1990).
[45]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).
[46]Y. Tanimura, "Stochastic Liouville, Langevin, Fokker-Planck, and master equation approaches to quantum dissipative systems," J. Phys. Soc. Jpn. **75**, 082001 (2006).
[47]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).
[48]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).
[49]J. J. Ding, R. X. Xu, and Y. J. Yan, "Optimizing hierarchical equations of motion for quantum dissipation and quantifying quantum bath effects on quantum transfer mechanisms," J. Chem. Phys. **136**, 224103 (2012).
[50]J. S. Jin, X. Zheng, and Y. J. Yan, "Exact dynamics of dissipative electronic systems and quantum transport: Hierarchical equations of motion approach," J. Chem. Phys. **128**, 234703 (2008).
[51]Z. H. Li, N. H. Tong, X. Zheng, D. Hou, J. H. Wei, J. Hu, and Y. J. Yan, "Hierarchical Liouville-space approach for accurate and universal characterization of quantum impurity systems," Phys. Rev. Lett. **109**, 266403 (2012).
[52]L. Z. Ye, X. L. Wang, D. Hou, R. X. Xu, X. Zheng, and Y. J. Yan, "HEOM-QUICK: A program for accurate, efficient and universal characterization of strongly correlated quantum impurity systems," WIREs Comp. Mol. Sci. **6**, 608 (2016).
[53]I. Imry, *Introduction to Mesoscopic Physics*, Oxford university press, 2002.
[54]H. Haug and A.-P. Jauho, *Quantum Kinetics in Transport and Optics of Semiconductors*, Springer-Verlag, Berlin, 2nd, substantially revised edition, 2008, Springer Series in Solid-State Sciences 123.
[55]Y. J. Yan, "Theory of open quantum systems with bath of electrons and phonons and spins: Many-dissipaton density matrixes approach," J. Chem. Phys. **140**, 054105 (2014).
[56]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).
[57]H. Gong, Y. Wang, H. D. Zhang, Q. Qiao, R. X. Xu, X. Zheng, and Y. J. Yan, "Equilibrium and transient thermodynamics: A unified dissipaton–space approach," J. Chem. Phys. **153**, 154111 (2020).
[58]H. Gong, Y. Wang, X. Zheng, R. X. Xu, and Y. J. Yan, "Nonequilibrium work distributions in quantum impurity system–bath mixing processes," J. Chem. Phys. **157**, 054109 (2022).
[59]X. Zheng, R. X. Xu, J. Xu, J. S. Jin, J. Hu, and Y. J. Yan, "Hierarchical equations of motion for quantum dissipation and quantum transport," Prog. Chem. **24**, 1129 (2012).
[60]J. Hu, R. X. Xu, and Y. J. Yan, "Padé spectrum decomposition of Fermi function and Bose function," J. Chem. Phys. **133**, 101106 (2010).
[61]J. Hu, M. Luo, F. Jiang, R. X. Xu, and Y. J. Yan, "Padé spectrum decompositions of quantum distribution functions and optimal hierarchial equations of motion construction for quantum open systems," J. Chem. Phys. **134**, 244106 (2011).
[62]J. J. Ding, J. Xu, J. Hu, R. X. Xu, and Y. J. Yan, "Optimized hierarchical equations of motion for Drude dissipation with applications to linear and nonlinear optical responses," J. Chem. Phys. **135**, 164107 (2011).
[63]Z. H. Chen, Y. Wang, X. Zheng, R. X. Xu, and Y. J. Yan, "Universal time-domain Prony fitting decomposition for optimized hierarchical quantum master equations," J. Chem. Phys. **156**, 221102 (2022).
[64]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).
[65]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).
[66]Y. Wang, R. X. Xu, and Y. J. Yan, "Entangled system-and-environment dynamics: Phase-space dissipaton theory," J. Chem. Phys. **152**, 041102 (2020).
[67]R. X. Xu, Y. Liu, H. D. Zhang, and Y. J. Yan, "Theory of quantum dissipation in a class of non-Gaussian environments," Chin. J. Chem. Phys. **30**, 395 (2017).
[68]R. X. Xu, Y. Liu, H. D. Zhang, and Y. J. Yan, "Theories of quantum dissipation and nonlinear coupling bath descriptors," J. Chem. Phys. **148**, 114103 (2018).
[69]Z. H. Chen, Y. Wang, R. X. Xu, and Y. J. Yan, "Quantum dissipation with nonlinear environment couplings: A core-system hierarchy construction versus the extended dissipaton equation of motion," arXiv:2206.14375 .
[70]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".
[71]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).
[72]Z. H. Chen, Y. Wang, R. X. Xu, and Y. J. Yan, "Correlated vibration-solvent effects on the non-Condon exciton spectroscopy," J. Chem. Phys. **154**, 244105 (2021).
[73]J. S. Jin, "Nonequilibirum noise spectrum and Coulomb blockade assisted Rabi interference in a double-dot Aharonov–Bohm interferometer," Phys. Rev. B **101**, 235144 (2020).
[74]H. Mao, J. S. Jin, S. K. Wang, and Y. J. Yan, "Nonequilibrium Kondo regime current noise spectrum of quantum dot systems with the single impurity Anderson model," J. Chem. Phys. **155**, 014104 (2021).
[75]Y. J. Yan and S. Mukamel, "Femtosecond pump-probe spectroscopy of polyatomic molecules in condensed phases," Phys. Rev. A **41**, 6485 (1990).
[76]D. C. Zhang, X. Ding, H. D. Zhang, X. Zheng, and Y. J. Yan, "Adiabatic terminator for fermionic hierarchical equations of motion," Chin. J. Chem. Phys. **34**, 905 (2021), Special Issue: John Z. H. Zhang Festschrift.
[77]Q. Shi, Y. Xu, Y.-M. Yan, and M. Xu, "Efficient propagation of the hierarchical equations of motion using the matrix product state method," J. Chem. Phys. **148**, 174102 (2018).
[78]Y.-M. Yan, M. Xu, T.-C. Li, and Q. Shi, "Efficient propagation of the hierarchical equations of motion using the Tucker and hierarchical Tucker tensors," J. Chem. Phys. **154**, 194104 (2021).
[79]Y. Ke, R. Borrelli, and M. Thoss, "Hierarchical equations of motion approach to hybrid fermionic and bosonic environments: Matrix product state formulation in twin space," The Journal of Chemical Physics **156**.
[80]L. Tucker, "Some mathematical notes on three-mode factor analysis," Psychometrika **31**, 279 (1966).
[81]T. G. Kolda and B. W. Bader, "Tensor decompositions and

applications," SIAM Review **51**, 455 (2009).
[82]W. Hackbusch and S. Kühn, "A new scheme for the tensor representation," J. Fourier. Anal. Appl. **15**, 706 (2009).
[83]L. Grasedyck, D. Kressner, and C. Tobler, "A literature survey of low-rank tensor approximation techniques," GAMM-Mitteilungen **36**, 53 (2013).
[84]Y.-M. Yan, T. Xing, and Q. Shi, "A new method to improve the numerical stability of the hierarchical equations of motion for discrete harmonic oscillator modes," J. Chem. Phys. **153**, 204109 (2020).
[85]T.-C. Li, Y.-M. Yan, and Q. Shi, "A low-temperature quantum Fokker-Planck equation that improves the numerical stability of the hierarchical equations of motion for the Brownian oscillator spectral density," J. Chem. Phys. **156**, 064107 (2022).
[86]H. D. Zhang and Y. J. Yan, "Kinetic rate kernels via hierarchical Liouville–space projection operator approach," J. Phys. Chem. A **120**, 3241 (2016), Special Issue: Ronnie Kosloff Festschrift.
[87]Y. Su, Z. H. Chen, H.-J. Zhu, Y. Wang, L. Han, R. X. Xu, and Y. J. Yan, "Electron transfer under the Floquet modulation in donor–bridge–acceptor systems," J. Phys. Chem. A **126**, 4554 (2022).
[88]Y. Saad, *Iterative Methods for Sparse Linear Systems*, Society for Industrial and Applied Mathematics, xx, 2nd edition, 2003.
[89]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).
[90]Q. Shi, L. P. Chen, G. J. Nan, R. X. Xu, and Y. J. Yan, "Efficient hierarchical Liouville space propagator to quantum dissipative dynamics," J. Chem. Phys. **130**, 084105 (2009).
[91]J. G. Kirkwood, "Statistical mechanics of fluid mixtures," J. Chem. Phys. **3**, 300 (1935).
[92]H. Gong, Y. Wang, H. D. Zhang, R. X. Xu, X. Zheng, and Y. J. Yan, "Thermodynamic free–energy spectrum theory for open quantum systems," J. Chem. Phys. **153**, 214115 (2020).
[93]R. C. Shukla and E. R. Muller, "Helmholtz free energy of an anharmonic crystal: A Green function approach," Phys. Stat. Sol. B - Basic Res. **43**, 413 (1971).
[94]R. van Zon, L. Hernández de la Peña, G. H. Peslherbe, and J. Schofield, "Quantum free-energy differences from nonequilibrium path integrals. I. Methods and numerical application," Phys. Rev. E **78**, 041103 (2008).
[95]R. van Zon, L. Hernández de la Peña, G. H. Peslherbe, and J. Schofield, "Quantum free-energy differences from nonequilibrium path integrals. II. Convergence properties for the harmonic oscillator," Phys. Rev. E **78**, 041104 (2008).
[96]C. Jarzynski, "Equalities and inequalities: Irreversibility and the Second Law of Thermodynamics at the nanoscale," Ann. Rev. Cond. Matter Phys. **2**, 329 (2011).
[97]G. E. Crooks, "Entropy production fluctuation theorem and the nonequilibrium work relation for free energy differences," Phys. Rev. E **60**, 2721 (1999).
[98]P. Talkner and P. Hänggi, "The Tasaki–Crooks quantum fluctuation theorem," J. Phys. A: Math. Theor. **40**, F569 (2007).
[99]P. Talkner, E. Lutz, and P. Hänggi, "Fluctuation theorems: Work is not an observable," Phys. Rev. E **75**, 050102 (2007).
[100]S. Sakamoto and Y. Tanimura, "Open quantum dynamics theory for non-equilibrium work: Hierarchical equations of motion approach," J. Phys. Soc. Jpn. **90**, 033001 (2021).
[101]H. Umezawa, *Advanced Field Theory: Micro, Macro, and Thermal Physics*, Springer, New York, 1995.
[102]J. Schwinger, "Brownian motion of a quantum oscillator," J. Math. Phys. **2**, 407 (1961).
[103]L. V. Keldysh, "Diagram technique for nonequilibrium processes," Sov. Phys. JETP **20**, 1018 (1965), [Zh. Eksp. Theor. Fiz. **47**, 1515 (1964)].
[104]J. S. Wang, B. K. Agarwalla, H. Li, and J. Thingna, "Nonequilibrium Green's function method for quantum thermal transport," Front. Phys. **9**, 673 (2014).
[105]Y. Wang, Z. H. Chen, R. X. Xu, X. Zheng, and Y. J. Yan, "A statistical quasi–particles thermofield theory with Gaussian environments: System–bath entanglement theorem for nonequilibrium correlation functions," J. Chem. Phys. **157**, 044012 (2022).
[106]P. L. Du, Y. Wang, R. X. Xu, H. D. Zhang, and Y. J. Yan, "System-bath entanglement theorem with Gaussian environments," J. Chem. Phys. **152**, 034102 (2020).
[107]P. L. Du, Z. H. Chen, Y. Su, Y. Wang, R. X. Xu, and Y. J. Yan, "Nonequilibrium system–bath entanglement theorem versus heat transport," Chem. J. Chin. Univ. **42**, 2155 (2021).
[108]Y. Meir and N. S. Wingreen, "Landauer formula for the current through an interacting electron region," Phys. Rev. Lett. **68**, 2512 (1992).
[109]D. Gruss, K. A. Velizhanin, and M. Zwolak, "Landauer's formula with finite-time relaxation: Kramers' crossover in electronic transport," Phys. Rep. **6**, 24514 (2016).
[110]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).
[111]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).
[112]Y. Wang, X. Zheng, and J. L. Yang, "Environment-modulated Kondo phenomena in FePc/Au (111) adsorption systems," Phys. Rev. B **93**, 125114 (2016).
[113]Y. Wang, X. Zheng, and J. L. Yang, "Kondo screening and spin excitation in few-layer CoPc molecular assembly stacking on Pb (111) surface: A DFT + HEOM study," J. Chem. Phys. **145**, 154301 (2016).
[114]X. L. Wang, L. Q. Yang, L. Z. Ye, X. Zheng, and Y. J. Yan, "Precise control of local spin states in an Adsorbed magnetic molecule with an STM tip: Theoretical insights from first-principles based simulation," J. Phys. Chem. Lett. **9**, 2418 (2018).
[115]Q. F. Zhuang, X. L. Wang, L. Z. Ye, Y. Yan, and X. Zheng, "Origin of asymmetric splitting of Kondo peak in spin-polarized scanning tunneling spectroscopy: Insights from first–principles–based simulations," J. Phys. Chem. Lett. **13**, 2094 (2022).
[116]Z. H. Chen, Y. Wang, R. X. Xu, and Y. J. Yan, "Quantum dissipation with nonlinear environment couplings: Stochastic fields dressed dissipaton equation of motion approach," J. Chem. Phys. **155**, 174111 (2021).