Dissipatons as generalized Brownian particles for open quantum systems: Dissipaton–embedded quantum master equation

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Dissipaton theory had been proposed as an exact and nonperturbative approach to deal with open quantum system dynamics, where the influence of Gaussian environment is characterized by statistical quasi-particles named as dissipatons. In this work, we revisit the dissipaton equation of motion theory and establish an equivalent dissipatons–embedded quantum master equation (DQME), which gives rise to dissipatons as generalized Brownian particles. As explained in this work, the DQME supplies a direct approach to investigate the statistical characteristics of dissipatons and thus the physically supporting hybrid bath modes. Numerical demonstrations are carried out on the electron transfer model, exhibiting the transient statistical properties of the solvation coordinate.

I. INTRODUCTION

Open quantum systems are ubiquitous in various realms of physics.[1–17] The system–environment interactions may lead to exchange of energy, particle and information between the open system and its surrounding environment. In literature, the environment is frequently known as baths or reservoirs. When the influence of surrounding environments (baths/reservoirs) cannot be neglected, quantum dissipation theories can be employed to describe the reduced system dynamics. Many quantum dissipation theories, such as the hierarchical equations of motion (HEOM)[18–24] and the stochastic equation of motion (SEOM)[21,25,26] theories, have been proposed, with focus mainly on the reduced system density operator, $\rho_{\rm S}(t) \equiv {\rm tr}_{\rm B}\rho_{\rm T}(t)$.

However, it is well known that the reduced system dynamics alone, with relevant information encoded in $\rho_{\rm S}(t)$, is insufficient to deal with all experimental measurements. The entangled system–and–environment dynamics are also crucially important in the study of strongly correlated quantum impurity systems.[27,28] For example, the entangled system–environment correlation functions are closely related to such as spectroscopy,[29–31] transport[32–36] and thermodynamics[37–39] in quantum impurity systems. These properties are usually considered to be beyond the scope of traditional treatments by quantum dissipation theories. To address this issue, Yan proposed the dissipaton equation of motion (DEOM) in 2014, which provides a statistical quasi-particle picture for the influence of environment that can be either bosonic or fermionic.[40–42] The DEOM recovers fully the HEOM for the dynamics of the primarily reduced system density operator. Meanwhile, the underlying dissipaton algebra[34,40] also makes the DEOM straightforward to study the hybrid bath dynamics, polarization and nonlinear coupling effects.[29,41–47]

The DEOM[40] is not only an "exact" (cf. comments at the end of Sec. II A) and nonperturbative approach to the real–time evolution of open quantum system plus hybrid bath mode, but also serves as a prototype for the development of other equations of motion within the same framework of dissipaton theory but in different scenarios. For example, to study the Helmholtz free energy change due to the isotherm mixing of the system and environment, we proposed two independent approaches, the equilibrium λ-DEOM and imaginary–time DEOM.[38] Nonequilibrium $\lambda(t)$-DEOM is also recently developed to compute the nonequilibrium work distributions in system–environment mixing processes.[48] To exactly treat the nonlinear environment couplings, we propose to incorporate the stochastic fields, which resolve just the nonlinear environment coupling terms, into the DEOM construction. The resultant stochastic-fields-dressed (SFD) total Hamiltonian contains only linear environment coupling terms. On the basis of that, the SFD-DEOM was constructed.[49] Besides, we also propose the dissipaton thermofield theory and obtain the system–bath entanglement theorem for nonequilibrium correlation functions.[36] All these theoretical ingredients comprise the family of dissipaton theories.

Remarkably, in above mentioned dissipaton theories, quasi-particle descriptions for baths can provide a unified treatment for the reduced system and hybridized environment dynamics. This is right the point of constructing an exact dissipaton theory, which is inspired by HEOM formalism and adopts *dissipatons*, etymologically derived from ther verb "dissipate" and the suffix "-on", as quasi-particles associated with the Gaussian bath.[34,40,41,50] In this work, we revisit the dissipaton equation of motion

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theory and establish an equivalent dissipatons–embedded quantum master equation (DQME). In DQME, instead of a hierarchical structure, all the system–plus–dissipatons degrees of freedom are incorporated into a single dynamic equation. Specifically, we will demonstrate that dissipatons as generalized Brownian quasi-particles, whose distribution obeys a Smoluchowski dynamics. The DQME provides a direct approach to investigate the statistical characteristics of dissipatons and makes it convenient to obtain the hybrid bath modes dynamics. Therefore, the DQME itself thus serves as an important member of the family of dissipaton theories.

The remainder of this paper is organized as follows. In Sec. II, we briefly review the basic onsets of dissipaton theories. DQME is constructed in Sec. III. In Sec. IV, we detailedly discuss the statistical characteristics of dissipatons. The numerical demonstration is given in Sec. V, with the electron transfer model. We summarize this paper in Sec. VI. Throughout the paper we set $\hbar = 1$ and $\beta = 1/(k_B T)$, with k_B the Boltzmann constant and T the temperature.

II. ONSETS OF DISSIPATON THEORY AND DEOM

A. Prelude

Let us start from the basic system–plus–bath settings in the bosonic environment scenarios. For brevity, we only consider the single dissipative–mode cases, where the system–bath coupling assumes a linear form of $H_{\rm SB} = \hat{Q}\hat{F}$. The total composite Hamiltonian tractable within the dissipaton theory has the generic form of

$$H_{\rm T} = H_{\rm S} + H_{\rm SB} + h_{\rm B}. \tag{1}$$

Both the system Hamiltonian $H_{\rm S}$ and the dissipative system mode $\hat{Q}$ is arbitrary, whereas the hybrid reservoir bath mode $\hat{F}$ assumes to be linear. This together with noninteracting reservoir model of $h_{\rm B}$ constitutes the Gauss–Wick's environment ansatz, where the environmental influence is fully characterized by the hybridization bath reservoir correlation functions, $\langle\hat{F}_{\rm B}(t)\hat{F}_{\rm B}(0)\rangle_{\rm B}$. Here, both $\hat{F}_{\rm B}(t) \equiv e^{ih_{\rm B}t}\hat{F}e^{-ih_{\rm B}t}$ and the equilibrium canonical ensemble average, $\langle(\,\cdot\,)\rangle_{\rm B} \equiv {\rm tr}_{\rm B}[(\,\cdot\,)e^{-\beta h_{\rm B}}]/{\rm tr}_{\rm B}(e^{-\beta h_{\rm B}})$ are defined in the bare–bath subspace. It can be related to the hybridize spectral density $J_{\rm B}(\omega)$ via the fluctuation–dissipation theorem[1]

$$\langle\hat{F}_{\rm B}(t)\hat{F}_{\rm B}(0)\rangle_{\rm B} = \frac{1}{\pi}\int_{-\infty}^{\infty}{\rm d}\omega\,\frac{e^{-i\omega t}J_{\rm B}(\omega)}{1-e^{-\beta\omega}}. \tag{2}$$

where

$$J_{\rm B}(\omega) \equiv \frac{1}{2}\int_{-\infty}^{\infty}{\rm d}t\,e^{i\omega t}\langle[\hat{F}_{\rm B}(t),\hat{F}_{\rm B}(0)]\rangle_{\rm B}. \tag{3}$$

The concept of *dissipatons* originates from an exponential series expansion of the hybridized bath correlation function,[41]

$$\langle\hat{F}_{\rm B}(t)\hat{F}_{\rm B}(0)\rangle_{\rm B} = \sum_{k=1}^{K}\eta_k e^{-\gamma_k t}. \tag{4a}$$

$$\langle\hat{F}_{\rm B}(0)\hat{F}_{\rm B}(t)\rangle_{\rm B} = \sum_{k=1}^{K}\eta_k^* e^{-\gamma_k^* t} \equiv \sum_{k=1}^{K}\eta_{\bar{k}}^* e^{-\gamma_k t}. \tag{4b}$$

The exponential series expansion on $\langle\hat{F}_{\rm B}(t)\hat{F}_{\rm B}(0)\rangle_{\rm B}$ can be achieved by adopting a certain sum–over–poles expression for the Fourier integrand on the right–hand–side of Eq.(2), followed by the Cauchy's contour integration,[51–55] or using the time–domain Prony fitting decomposition scheme.[56] Together with the time–reversal relation $\langle\hat{F}_{\rm B}(0)\hat{F}_{\rm B}(t)\rangle_{\rm B} = \langle\hat{F}_{\rm B}(t)\hat{F}_{\rm B}(0)\rangle_{\rm B}^*$ for $t \geq 0$. The second equality of Eq. (4b) is due to the fact that the exponents in Eq. (4a) must be either real or complex conjugate paired, and thus we may determine $\bar{k}$ in the index set $\{k = 1, 2, ..., K\}$ by the pairwise equality $\gamma_{\bar{k}} = \gamma_k^*$.This is a crucial property. The exponential series expansion in Eqs. (4a) and (4b) inspired the idea of relating each exponential mode of correlation function to a statistical quasi-particle, i.e., a *dissipaton*.[40]

It is worth noting that the decomposition in Eqs. (4a) and (4b) can be obtained via alternative methods including the Fano spectrum decomposition,[57,58] the discrete Fourier series,[59] the extended orthogonal polynomials expansions,[60–64] the time–domain Prony fitting scheme,[56] and others. These methods have expanded the scope of application of HEOM/DEOM to the bath correlations in type of $\{t^m e^{-\gamma t}\}$ with m a positive integer. The dissipaton theory can be extended to these scenarios and is numerically exact in these cases. However, the quest of the most general and exact decomposition scheme is still a challenge.

B. Dissipaton equation of motion (DEOM)

The dissipaton theory begins with the *dissipatons decomposition* that reproduces the correlation function in Eqs. (4a) and (4b). It decomposes $\hat{f}$ into a number of dissipaton operators $\{\hat{f}_k\}$, as

$$\hat{F} = \sum_{k=1}^{K}\hat{f}_k. \tag{5}$$

In accordance with the dissipatons decomposition, the dynamical variables in DEOM are the dissipaton density operators (DDOs),[40,41,50]

$$\rho_{\mathbf{n}}^{(n)}(t) \equiv \rho_{n_1\cdots n_K}^{(n)}(t) \equiv {\rm tr}_{\rm B}\big[\big(\hat{f}_K^{n_K}\cdots\hat{f}_1^{n_1}\big)^\circ\rho_{\rm T}(t)\big]. \tag{6}$$

Here, $n = n_1 + \cdots + n_K$, with $n_k \geq 0$ for the bosonic dissipatons. The product of dissipaton operators inside $(\cdots)^\circ$ is considered as *irreducible*, which satisfies

$(\hat{f}_k\hat{f}_j)^\circ = (\hat{f}_j\hat{f}_k)^\circ$ for bosonic dissipatons. Each n–particles DDO, $\rho^{(n)}_{\mathbf{n}}(t)$, is associated with an ordered set of indexes, $\mathbf{n}\equiv\{n_1\cdots n_K\}$. Denote for later use also $\mathbf{n}^\pm_k$ that differs from $\mathbf{n}$ only at the specified $\hat{f}_k$-disspaton occupation number n_k by ±1. The reduced system density operator is a member of DDOs, $\rho^{(0)}_{\mathbf{0}}(t)\equiv\rho^{(0)}_{0\cdots0}(t)\equiv\rho_{\rm S}(t)$.

For presenting the related dissipaton algebra later, we adopt hereafter the following notations,

$$\begin{aligned}\rho^{(n)}_{\mathbf{n}}(t;\hat{A}^\times)&\equiv{\rm tr}_{\rm B}\Big[\big(\hat{f}_K^{n_K}\cdots\hat{f}_1^{n_1}\big)^\circ\hat{A}^\times\rho_{\rm T}(t)\Big],\\ \rho^{(n)}_{\mathbf{n}}(t;\hat{A}^\leqslant)&\equiv{\rm tr}_{\rm B}\Big[\big(\hat{f}_K^{n_K}\cdots\hat{f}_1^{n_1}\big)^\circ\hat{A}^\leqslant\rho_{\rm T}(t)\Big],\end{aligned}\tag{7}$$

where $\hat{A}$ is an arbitrary operator, and $A^\times\equiv\hat{A}^>-\hat{A}^<$ with $\hat{A}^>\rho_{\rm T}(t)\equiv\hat{A}\rho_{\rm T}(t)$ and $\hat{A}^<\rho_{\rm T}(t)\equiv\rho_{\rm T}(t)\hat{A}$. The dissipaton theory comprises the following three basic ingredients.

(*i*) *Onset of dissipaton correlations.* To reproduce Eq. (4a) and (4b), the dissipatons correlation functions read

$$\langle\hat{f}^{\rm B}_k(t)\hat{f}^{\rm B}_{k'}(0)\rangle_{\rm B}=\delta_{kk'}\eta_k e^{-\gamma_k t},\tag{8a}$$

$$\langle\hat{f}^{\rm B}_{k'}(0)\hat{f}^{\rm B}_k(t)\rangle_{\rm B}=\delta_{kk'}\eta^*_k e^{-\gamma_k t},\tag{8b}$$

with $\hat{f}^{\rm B}_k(t)\equiv e^{ih_{\rm B}t}\hat{f}_k e^{-ih_{\rm B}t}$. Each forward–backward pair of dissipaton correlation functions is specified by a single–exponent γ_k.

(*ii*) *Onset of generalized diffusion equation.* The generalized diffusion equation of a dissipaton operator reads[40,41]

$${\rm tr}_{\rm B}[(\partial_t\hat{f}_k)_{\rm B}\rho_{\rm T}(t)]=-\gamma_k{\rm tr}_{\rm B}\big[\hat{f}_k\rho_{\rm T}(t)\big].\tag{9}$$

Together with $(\partial_t\hat{f}_k)_{\rm B}=-i[\hat{f}_k,h_{\rm B}]$, we obtain[40]

$$\rho^{(n)}_{\mathbf{n}}(t;h^\times_{\rm B})=-i\bigg(\sum_k n_k\gamma_k\bigg)\rho^{(n)}_{\mathbf{n}}(t).\tag{10}$$

Equation (10) is the generalized diffusion equation in terms of DDOs.

(*iii*) *Onset of generalized Wick's theorem.* For the left and right actions of dissipaton operators, there exist

$$\begin{aligned}\rho^{(n)}_{\mathbf{n}}(t;\hat{f}^>_k)&=\rho^{(n+1)}_{\mathbf{n}^+_k}(t)+n_k\eta_k\rho^{(n-1)}_{\mathbf{n}^-_k}(t),\\ \rho^{(n)}_{\mathbf{n}}(t;\hat{f}^<_k)&=\rho^{(n+1)}_{\mathbf{n}^+_k}(t)+n_k\eta^*_k\rho^{(n-1)}_{\mathbf{n}^-_k}(t).\end{aligned}\tag{11}$$

This is known as the generalized Wick's theorem.

Based on the above three onsets, by applying the Liouville-von Neumann equation, $\dot{\rho}_{\rm T}(t)=-i[H_{\rm S}+h_{\rm B}+H_{\rm SB},\rho_{\rm T}(t)]$ in Eq. (6), followed by using Eqs. (9)–(11), we obtain[40]

$$\begin{aligned}\dot{\rho}^{(n)}_{\mathbf{n}}=&-\Big(i\mathcal{L}_{\rm S}+\sum_k n_k\gamma_k\Big)\rho^{(n)}_{\mathbf{n}}-i\sum_k\hat{Q}^\times\rho^{(n+1)}_{\mathbf{n}^+_k}\\&-i\sum_k n_k\big(\eta_k\hat{Q}^>-\eta^*_k\hat{Q}^<\big)\rho^{(n-1)}_{\mathbf{n}^-_k}.\end{aligned}\tag{12}$$

This is the DEOM for DDOs, where $\mathcal{L}_{\rm S}\equiv H^\times_{\rm S}$ and the parameters are given in Eqs. (4a) and (4b). The resulting DEOM fully recovers the HEOM formalism.[18–24] The latter is the time–derivative equivalent to Feynman–Vernon influence functional,[65] with the primary focus on the reduced system density operator.

C. Hybrid mode moments versus DDOs

Based on the generalized Wick's theorem in Eq. (11), it is easy to relate the hybrid mode moments, $\{\langle\hat{F}^n(t)\rangle\}$, to DDOs, since

$$\langle\hat{F}^n\rangle=\sum_{m=0}^{\lfloor n/2\rfloor}\binom{n}{2m}\cdot(2m-1)!!\langle\hat{F}^2_{\rm B}\rangle^m_{\rm B}\cdot\langle(\hat{F}^{n-2m})^\circ\rangle,\tag{13}$$

$\hat{F}=\sum_k\hat{f}_k$ and

$$\begin{aligned}\langle(\hat{F}^n)^\circ\rangle&=\sum_{\{n_k\}}{}'\frac{n!}{n_1!\cdots n_K!}\langle\big(\hat{f}_K^{n_K}\cdots\hat{f}_1^{n_1}\big)^\circ\rangle\\&=\sum_{\{n_k\}}{}'\frac{n!}{n_1!\cdots n_K!}{\rm tr}_{\rm S}\rho^{(n)}_{\mathbf{n}},\end{aligned}\tag{14}$$

with the summation being subject to $n_1+\cdots+n_K=n$. We thus complete Eq. (13) in terms of DDOs; see Eq. (B1) for $\langle\hat{F}^2_{\rm B}\rangle_{\rm B}$. The above results can also be obtained via the path integral influence functional approach.[66] As special cases, we have

$$\langle\hat{F}(t)\rangle=\sum_{k=1}^K{\rm tr}_{\rm S}\rho^{(1)}_{\mathbf{0}^+_k}(t),\tag{15}$$

and

$$\langle\hat{F}^2(t)\rangle=\sum_{k=1}^K\eta_k+\sum_{k,j=1}^K{\rm tr}_{\rm S}\rho^{(2)}_{\mathbf{0}^{++}_{kj}}(t).\tag{16}$$

III. DISSIPATONS–EMBEDDED QUANTUM MASTER EQUATION (DQME)

In this section, we will establish an equivalent dissipatons–embedded quantum master equation (DQME). This is concerned with the core system; i.e., the system–plus–dissipatons composite. First of all, there is a one–to–one correspondence between the dissipaton operators and *real* dimensionless variables:

$$\hat{f}_k/\zeta_k\xleftrightarrow{\text{effective}}x_k\in(-\infty,\infty),\tag{17}$$

where

$$\zeta_k\equiv\sqrt{(\eta_k+\eta^*_k)/2}\ \ \text{and}\ \ \xi_k\equiv\frac{\eta_k-\eta^*_k}{2i\zeta_k}.\tag{18}$$

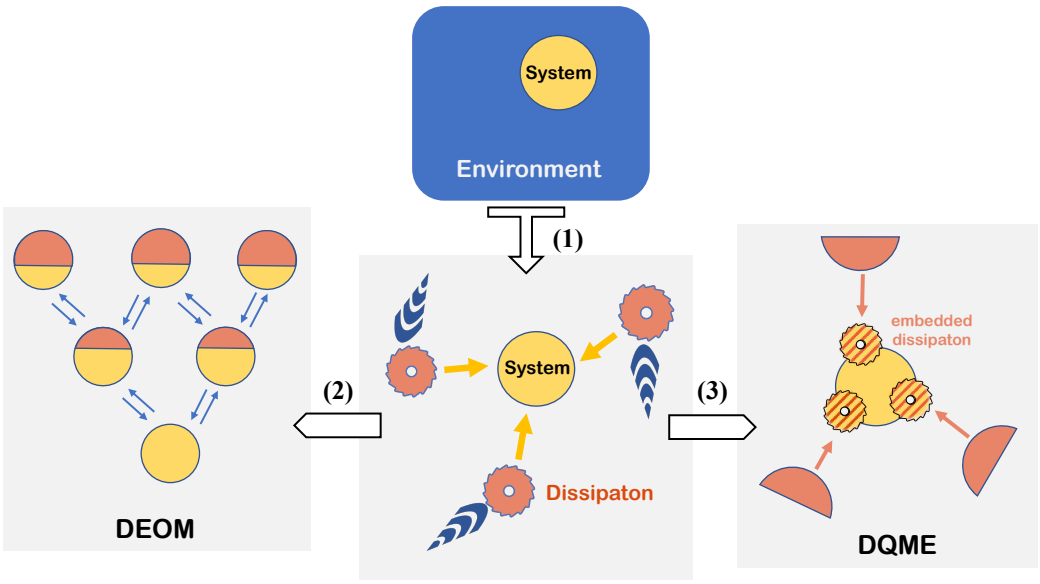

FIG. 1. A schematic illustration of dissipaton equation of motion (DEOM) versus dissipatons–embedded quantum master equation (DQME). Block arrow (1) is a mapping that decomposes the original environment (blue square) into multiple dissipatons (red gears), conserving the hybridized correlation function. Dissipatons behave as quantum Brownian particles. Block arrow (2) represents the establishment of the DEOM of hierarchical structure. Each DDO (mixed red–yellow circle) incorporates a configuration of dissipatons. Block arrow (3) represents the establishment of the DQME, where the disspaton degrees of freedom are embedded into the system (dashed red vortex). Instead of a hierarchical structure, all the system–plus–dissipatons degrees of freedom are incorporated into a single dynamic equation, influenced by dissipaton Smoluchowski operators (red arches).

The "effective" correspondence means that the statistical characteristics of hybrid modes [cf. Eq. (13)] can be completely recovered by the moments of $\boldsymbol{x} \equiv \{x_k\}$; see Eq. (36) and the discussions therein.

To proceed, we write the core–system distribution as

$$\hat{\rho}(\boldsymbol{x},t) = \sum_{\mathbf{n}} \Big[\rho^{(n)}_{\mathbf{n}}(t) \prod_k \phi_{n_k}(x_k) \Big], \tag{19}$$

with the dissipaton subspace basis functions,

$$\phi_{n_k}(x_k) = (2\pi)^{-\frac{1}{4}} \frac{e^{-x_k^2/4}}{\zeta_k^{n_k}\sqrt{n_k!}} \phi^{\rm har}_{n_k}(x_k). \tag{20}$$

Involved are the standard harmonic oscillator wave functions,

$$\phi^{\rm har}_n(x) = (2\pi)^{-\frac{1}{4}} (2^n n!)^{-\frac{1}{2}} e^{-\frac{x^2}{4}} H_n\Big(\frac{x}{\sqrt{2}}\Big), \tag{21}$$

with $H_n(x)$ is the nth Hermite polynomial. The reason for choosing $\{\phi_n(x)\}$ as the basis will be discussed in the next section; see Eq. (36) and the discussions therein. Due to the orthogonal relation:

$$\int e^{-x^2/2} H_n\Big(\frac{x}{\sqrt{2}}\Big) H_{n'}\Big(\frac{x}{\sqrt{2}}\Big) {\rm d}x = (2\pi)^{\frac{1}{2}} 2^n n! \delta_{nn'}, \tag{22}$$

we can then recast Eq. (19) as

$$\rho^{(n)}_{\mathbf{n}}(t) = \int \hat{\rho}(\boldsymbol{x},t) \prod_k \Big[\Big(\frac{\zeta_k}{\sqrt{2}}\Big)^{n_k} H_{n_k}\Big(\frac{x_k}{\sqrt{2}}\Big) \Big] {\rm d}\boldsymbol{x}. \tag{23}$$

This is an alternative expression of DDOs, where ${\rm d}\boldsymbol{x} \equiv {\rm d}x_1 \cdots {\rm d}x_K$.

By using Eq. (19) with DEOM (12), followed by some detailed algebra in Appendix A, we obtain the DQME,

$$\begin{aligned} \frac{\partial}{\partial t}\hat{\rho}(\boldsymbol{x},t) =& -i[H_{\rm S},\hat{\rho}] + \sum_k \hat{\Gamma}_k \hat{\rho} - i\sum_k \zeta_k [\hat{Q}, x_k\hat{\rho}] \\ & - \sum_k \xi_k \Big\{ \hat{Q}, \frac{\partial \hat{\rho}}{\partial x_k} \Big\}, \end{aligned} \tag{24}$$

where

$$\hat{\Gamma}_k \equiv \gamma_k \frac{\partial}{\partial x_k}\Big(\frac{\partial}{\partial x_k} + x_k\Big). \tag{25}$$

This is the generalized Smoluchowski operator and corresponds to the generalized diffusion equation (9); see also Eq. (A7). The last two terms in Eq. (24) correspond to the generalized Wick's theorem (11), describing the effect of system–bath coupling $H_{\rm SB}$; see also Eqs. (A8) and (A9). It is worth reemphasizing that the parameters γ_k, ζ_k and ξ_k can all be complex, whereas the variable x_k is real. As also known, $\gamma_{\bar{k}} = \gamma_k^*$, $\zeta_{\bar{k}} = \zeta_k^*$ and $\xi_{\bar{k}} = \xi_k^*$; see Eq. (18), with $\bar{k} \in \{k = 1, \cdots, K\}$.

Instead of a hierarchical structure, all the system–plus–dissipatons degrees of freedom are incorporated into a single dynamic equation; see Eq. (24), Fig. 1 and the remarks therein. It is worth noting that the methodology here is closely related to that in the Fokker–Planck theory, Zusman theory and the pseudomode

method.[20,64,67–71] The new DQME recovers the reduced system dynamics as specified by $\rho_{\rm S}(t)$ without any approximation.

IV. STATISTICAL CHARACTERISTICS OF DISSIPATONS

A. Dissipatons as generalized Brownian particles

In open quantum dynamics, the wave-particle duality of both system and hybrid bath plays important roles. In contrast to DEOM, DQME describes the influence of hybrid bath in the aspect of waves, with the picture of generalized Brownian particles for dissipatons. To this end, we consider

$$P(\boldsymbol{x},t) \equiv {\rm tr}_{\rm S}\hat{\rho}(\boldsymbol{x},t), \tag{26}$$

and obtain

$$\frac{\partial}{\partial t}P(\boldsymbol{x},t) = \sum_k \hat{\Gamma}_k P(\boldsymbol{x},t) - \sum_k \frac{\partial}{\partial x_k} J_k(\boldsymbol{x},t), \tag{27}$$

with the last term the form of $\boldsymbol{\nabla}\cdot\boldsymbol{J}$, arising from the system–bath coupling. The dissipaton probability current density vector is given by

$$J_k(\boldsymbol{x},t) = 2\xi_k {\rm tr}_{\rm S}\big[\hat{Q}\hat{\rho}(\boldsymbol{x},t)\big]. \tag{28}$$

Equation (27) provides a means to the statistics of hybrid bath. In particular, its equilibrium–state solution reads

$$P^{\rm st} = \hat{\Gamma}^{-1}\boldsymbol{\nabla}\cdot\boldsymbol{J}^{\rm st}. \tag{29}$$

with $\hat{\Gamma} = \sum_k \hat{\Gamma}_k$. However, to evaluate the current density, Eq. (28), $\hat{\rho}(\boldsymbol{x},t)$ via DQME (24) is needed. From Eq. (29), we can derive the input–output relations involving dissipaton moments and dissipative system mode; see Appendix B 2 and comments therein. In the following, we will exploit the equivalent DEOM formalism to evaluate the hybrid bath statistics.

B. Transient dissipaton moments

We will be interested in the expectation values of

$$\boldsymbol{x}_{\mathbf{n}}^{(n)} \equiv x_K^{n_K}\cdots\, x_1^{n_1}. \tag{30}$$

To proceed, denote

$$\hat{X}_{\mathbf{n}}^{(n)}(t) \equiv \int \boldsymbol{x}_{\mathbf{n}}^{(n)}\,\hat{\rho}(\boldsymbol{x},t)\,{\rm d}\boldsymbol{x}, \tag{31}$$

and the transient dissipaton moments

$$\langle \boldsymbol{x}_{\mathbf{n}}^{(n)}(t)\rangle = {\rm tr}_{\rm S}\hat{X}_{\mathbf{n}}^{(n)}(t) = \int \boldsymbol{x}_{\mathbf{n}}^{(n)}\,P(\boldsymbol{x},t)\,{\rm d}\boldsymbol{x}. \tag{32}$$

On the other hand, we have (see Appendix B)

$$\hat{X}_{\mathbf{n}}^{(n)}(t) = \sum_{\{m_k=0\}}^{\{\lfloor n_k/2\rfloor\}} c_{\mathbf{nm}}\rho_{\mathbf{n}-2\mathbf{m}}^{(n-2m)}(t), \tag{33}$$

where

$$\rho_{\mathbf{n}-2\mathbf{m}}^{(n-2m)}(t) \equiv {\rm tr}_{\rm B}\big[\big(\hat{f}_K^{n_K-2m_K}\cdots\hat{f}_1^{n_1-2m_1}\big)^\circ\rho_{\rm T}(t)\big], \tag{34}$$

and

$$c_{\mathbf{nm}} = \prod_{k=1}^K \frac{1}{\zeta_k^{n_k-2m_k}2^{m_k}}\frac{n_k!}{m_k!(n_k-2m_k)!}. \tag{35}$$

We can recast Eq. (13) as [cf. Eq. (B8) and discussion therein]

$$\begin{aligned}\langle \hat{F}^n(t)\rangle &= \int\Big(\sum_k \zeta_k x_k\Big)^n P(\boldsymbol{x},t)\,{\rm d}\boldsymbol{x}\\ &= n!\sum_{\mathbf{n}}\Big(\prod_k \frac{\zeta_k^{n_k}}{n_k!}\Big)\langle \boldsymbol{x}_{\mathbf{n}}^{(n)}(t)\rangle.\end{aligned} \tag{36}$$

This also implies the one–to–one correspondence between the dissipaton operators and *real* dimensionless variables, as specified in Eq. (17).

V. NUMERICAL DEMONSTRATIONS

For demonstration, we consider the electron transfer model,[72,73]

$$H_{\rm S} = (\epsilon+\lambda)|1\rangle\langle 1| + V(|1\rangle\langle 0| + |0\rangle\langle 1|), \tag{37}$$

with the dissipative system mode $\hat{Q} = -|1\rangle\langle 1|$. Here, $|0\rangle$ is the donor state and $|1\rangle$ is the acceptor state, with the energy bias ϵ, the interstate coupling V and the solvent reorganization energy λ. The latter arises from the bath spectral density, which takes the Brownian oscillator model,[3]

$$J_{\rm B}(\omega) = \frac{2\lambda\omega_0^2\zeta\omega}{(\omega^2-\omega_0^2)^2+\omega^2\zeta^2}. \tag{38}$$

Here in the scene of electron transfer, the hybrid mode $\hat{F}(t)$ is interpreted as "solvation coordinate" along the elecron transfer. Its expectation $\langle\hat{F}(t)\rangle$ and standard deviation $\sigma_F = \langle\hat{F}^2(t)\rangle^{1/2}$ measure the reaction progress and the width of solvent wavepackage, respectively.

The influence of anharmonic system induces the non-Gaussian dynamics of the environments. To measure the non-Gaussianity of a distribution, there are two basic dimensionless quantities:[74] the skewness K_3/σ_F^3 and the kurtosis K_4/σ_F^4. They characterize the asymmetry and the tailedness, respectively, in terms of the nth cumulant,

$$K_n(t) = \langle\hat{F}^n(t)\rangle - \sum_{m=1}^{n-1}\binom{n-1}{m}K_{n-m}(t)\langle\hat{F}^m(t)\rangle, \tag{39}$$

with $K_1(t) = \langle \hat{F}(t) \rangle$.

Figure 2 depicts the results of calculating the statistical characteristics of transient hybrid mode $\hat{F}(t)$ at different coupling strength, i.e. the reorganization energy λ. We can see that all the characteristics of $\hat{F}(t)$ oscillate at the frequency about $\Omega_{\rm S} = \sqrt{\epsilon^2 + 4V^2}$, the characteristic frequency of system, in short time evolution and converge to steady values in the long time asymptotic regime. As the coupling strengthens, the mean value and

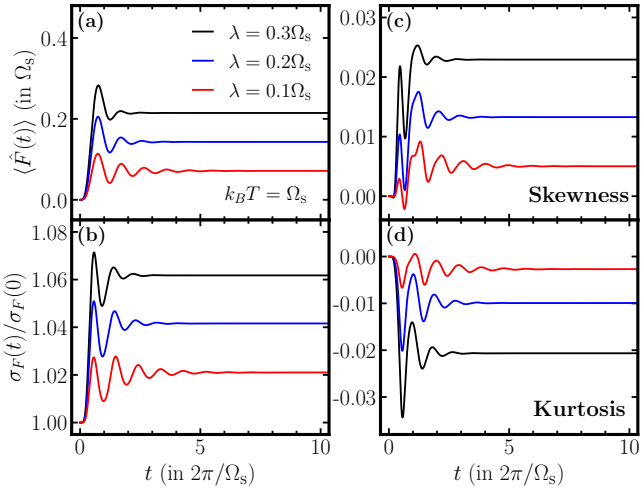

FIG. 2. Statistical characteristics of hybrid mode $\hat{F}(t)$ at three specified λ and the given temperature, where $\Omega_{\rm S} = \sqrt{\epsilon^2 + 4V^2}$: (a) The mean value; (b) The standard deviation $\sigma_F(t)/\sigma_F(0)$; (c) The skewness K_3/σ_F^3; (d) The kurtosis K_4/σ_F^4. Other parameters are $V = 0.4$, $\omega_0 = \zeta = 1$ in unit of $\Omega_{\rm S}$.

the standard deviation increase, measuring the drifting and widening of distribution of reaction coordinate, respectively. The skewness and kurtosis of hybrid mode deviate further from 0 as coupling strengthens, that indicates the influence of the anharmonic system violates the Gaussianity of the environment.

Figure 3 shows the transient evolutions of statistical characteristics of the hybrid mode at different temperatures. Similar dynamical oscillation behaviors as that in Fig. 2 are displayed. On the other hand, when temperature increases, $\langle \hat{F} \rangle$ at the steady state increases (cf. Fig. 3a), while $\sigma_F(t)/\sigma_F(0)$ and the skewness reduce (cf. Fig. 3b and 3c). However, the kurtosis does not varies monotunously in this regime, which suggests the complicated behaviors of the tailedness of relevant distributions.

VI. CONCLUDING REMARKS

To summarize, in this work we construct the dissipaton–embedded quantum master equation (DQME) from the DEOM theory via introducing the one–to–one correspondence between the dissipaton operators and *real* dimensionless variables. Instead of a

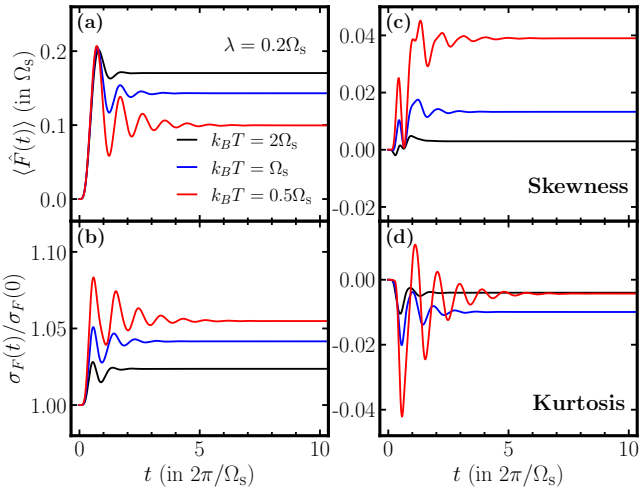

FIG. 3. Statistical characteristics of hybrid mode $\hat{F}(t)$ at three specified temperatures and the given λ, where $\Omega_{\rm S} = \sqrt{\epsilon^2 + 4V^2}$: (a) The mean value; (b) The standard deviation $\sigma_F(t)/\sigma_F(0)$; (c) The skewness K_3/σ_F^3; (d) The kurtosis K_4/σ_F^4. Other parameters are $V = 0.4$, $\omega_0 = \zeta = 1$ in unit of $\Omega_{\rm S}$.

hierarchical structure, all the system–plus–dissipatons degrees of freedom are incorporated into a single dynamic equation in DQME. The new DQME recovers the reduced system dynamics as specified by $\rho_{\rm S}(t)$ without any approximation. Moreover, the statistical characteristics of hybrid modes can be completely recovered.

The formalism of DQME reveals the picture of dissipatons as the Brownian quasi-particles interacting with the system. Based on the DQME, we can discuss the evolution of dissipaton distribution under the influence of system and correlate the transient moments of dissipatons with DDOs.

The fermionic DQME can also been readily established in a similar manner, which would benefit for the simulations on such as spintronic and superconductive systems. The DQME formalism brings the possibility of achieving the quantum simulation of non-Markovian open quantum dynamics. Since all the dissipaton degrees of freedom are represented by continuous real variables in DQME, this makes it a versatile formalism for incorporating matrix product states, real–space renormalization group, and other numerical methods. It is anticipated that DQME developed in this work would become an important tool for quantum mechanics of open systems.

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edged.

Appendix A: Derivation of DQME (24)

For later use, we first rewrite Eq. (19) as

$$\hat{\rho}(\boldsymbol{x},t)=\sum_{\mathbf{n}}\Big[\tilde{\rho}^{(n)}_{\mathbf{n}}(t)\prod_k\tilde{\phi}_{n_k}(x_k)\Big], \tag{A1}$$

with

$$\tilde{\rho}^{(n)}_{\mathbf{n}}(t)=\rho^{(n)}_{\mathbf{n}}(t)\Big/\prod_k\zeta_k^{n_k}, \tag{A2}$$

and

$$\tilde{\phi}_{n_k}(x_k)=(2\pi)^{-\frac{1}{4}}\frac{e^{-x_k^2/4}}{\sqrt{n_k!}}\phi^{\rm har}_{n_k}(x_k). \tag{A3}$$

Note for $\tilde{\phi}_n(x)$, we have[75]

$$x\tilde{\phi}_n(x)=\tilde{\phi}_{n-1}(x)+(n+1)\tilde{\phi}_{n+1}(x), \tag{A4}$$

and

$$\frac{\partial\tilde{\phi}_n(x)}{\partial x}=-(n+1)\tilde{\phi}_{n+1}(x). \tag{A5}$$

According to DEOM (12), the EOM for $\tilde{\rho}^{(n)}_{\mathbf{n}}(t)$ reads

$$\begin{aligned}\dot{\tilde{\rho}}^{(n)}_{\mathbf{n}}(t)=&-\Big(i\mathcal{L}_{\rm S}+\sum_k n_k\gamma_k\Big)\tilde{\rho}^{(n)}_{\mathbf{n}}(t)\\&-i\sum_k\zeta_k\hat{Q}^{\times}\Big[\tilde{\rho}^{(n+1)}_{\mathbf{n}_k^+}(t)+n_k\tilde{\rho}^{(n-1)}_{\mathbf{n}_k^-}(t)\Big]\\&+\sum_k n_k\xi_k\hat{Q}^{\diamond}\tilde{\rho}^{(n-1)}_{\mathbf{n}_k^-}(t),\end{aligned} \tag{A6}$$

where Eq. (18) is used and $\hat{A}^{\diamond}\rho\equiv\hat{A}\rho+\rho\hat{A}$. With

$$\begin{aligned}&\sum_{\mathbf{n}}\sum_k n_k\gamma_k\tilde{\rho}^{(n)}_{\mathbf{n}}\prod_j\tilde{\phi}_{n_j}(x_j)\\=&-\sum_k\gamma_k\frac{\partial}{\partial x_k}(x_k+\frac{\partial}{\partial x_k})\sum_{\mathbf{n}}\tilde{\rho}^{(n)}_{\mathbf{n}}\prod_j\tilde{\phi}_{n_j}(x_j)\\=&-\sum_k\gamma_k\frac{\partial}{\partial x_k}(x_k+\frac{\partial}{\partial x_k})\hat{\rho}(\boldsymbol{x}),\end{aligned} \tag{A7}$$

$$\begin{aligned}&\sum_{\mathbf{n}}\Big[\Big(\tilde{\rho}^{(n+1)}_{\mathbf{n}_k^+}+n_k\tilde{\rho}^{(n-1)}_{\mathbf{n}_k^-}\Big)\prod_j\tilde{\phi}_{n_j}(x_j)\Big]\\=&\sum_{\mathbf{n}}\Big[\tilde{\rho}^{(n)}_{\mathbf{n}}\prod_j[\tilde{\phi}_{n_j-\delta_{kj}}(x_j)+(n_k+1)\phi_{n_j+\delta_{kj}}(x_j)]\Big]\\=&x_k\hat{\rho}(\boldsymbol{x}),\end{aligned} \tag{A8}$$

and

$$\begin{aligned}&\sum_{\mathbf{n}}n_k\tilde{\rho}^{(n-1)}_{\mathbf{n}_k^-}\prod_j\tilde{\phi}_{n_j}(x_j)\\=&-\sum_{\mathbf{n}}\tilde{\rho}^{(n-1)}_{\mathbf{n}_k^-}\frac{\partial}{\partial x_k}\prod_j\tilde{\phi}_{n_j-\delta_{kj}}(x_j)\\=&-\frac{\partial}{\partial x_k}\hat{\rho}(\boldsymbol{x}),\end{aligned} \tag{A9}$$

we then obtain the DQME (24) from Eq. (A6) together with Eqs. (A7)–(A9).

Appendix B: Moments of dissipatons

1. Basic relations and transient dissipaton moments

Let us start with some basic relations:

$$\langle\hat{F}^2_{\rm B}\rangle_{\rm B}=\sum_k\eta_k=\sum_k\eta_k^*=\sum_k\zeta_k^2. \tag{B1}$$

Applied here are Eqs. (4a), (4b) and (18). Moreover,

$$\boldsymbol{x}^{(n)}_{\mathbf{n}}\frac{\partial}{\partial x_k}=\frac{\partial}{\partial x_k}\boldsymbol{x}^{(n)}_{\mathbf{n}}-n_k\boldsymbol{x}^{(n-1)}_{\mathbf{n}_k^-}, \tag{B2}$$

and [cf. Eq. (25)]

$$\begin{aligned}\boldsymbol{x}^{(n)}_{\mathbf{n}}\hat{\Gamma}_k=\gamma_k\Big[&\Big(\frac{\partial^2}{\partial x_k^2}-n_k\Big)\boldsymbol{x}^{(n)}_{\mathbf{n}}+n_k(n_k-1)\boldsymbol{x}^{(n-2)}_{\mathbf{n}_{kk}^{--}}\\&-n_k\frac{\partial}{\partial x_k}\boldsymbol{x}^{(n-1)}_{\mathbf{n}_k^-}+\frac{\partial}{\partial x_k}\boldsymbol{x}^{(n+1)}_{\mathbf{n}_k^+}\Big].\end{aligned} \tag{B3}$$

With the relation

$$\Big(\frac{x}{\sqrt{2}}\Big)^n=\frac{n!}{2^n}\sum_m^{\lfloor n/2\rfloor}\frac{1}{m!(n-2m)!}H_{n-2m}\Big(\frac{x}{\sqrt{2}}\Big), \tag{B4}$$

we can obtain $\hat{X}^{(n)}_{\mathbf{n}}$ in Eq. (31)

$$\hat{X}^{(n)}_{\mathbf{n}}=\int\boldsymbol{x}^{(n)}_{\mathbf{n}}\rho(t;\{x_k\})\mathrm{d}\boldsymbol{x}=\sum_{\{m_k\}}^{\{[n_k/2]\}}c_{\mathbf{nm}}\rho^{(n-2m)}_{\mathbf{n-2m}}, \tag{B5}$$

expressed by DDOs, where $c_{\mathbf{nm}}$ is given in Eq. (35). Inversely, we have

$$\rho^{(n)}_{\mathbf{n}}(t)=\sum_{\{m_k=0\}}^{\{\lfloor n_k/2\rfloor\}}\bar{c}_{\mathbf{nm}}\hat{X}^{(n-2m)}_{\mathbf{n-2m}}(t), \tag{B6}$$

with

$$\bar{c}_{\mathbf{nm}}=\prod_k\zeta_k^{n_k}2^{-m_k}\frac{(-1)^{m_k}n_k!}{m_k!(n_k-2m_k)!}. \tag{B7}$$

To show that Eq. (36) is equivalent Eq. (13), we first rewrite Eq. (13) as

$$\langle \hat{F}^n \rangle = \sum_{m=0}^{\lfloor n/2 \rfloor} \frac{n!}{2^m m!} \langle \hat{F}_{\rm B}^2 \rangle_{\rm B}^m \sum_{\{n_k - 2m_k\}}{}' \frac{1}{n_1! \cdots n_K!} {\rm tr}_{\rm S} \rho_{\mathbf{n}-\mathbf{2m}}^{(n-2m)}. \tag{B8}$$

By further using the last identity in Eq. (B1), we then reproduce Eq. (13). This validates the effective mapping (17), which conserve the statistics of the hybrid bath.

2. Equilibrium dissipaton statistics

To obtain $\langle \boldsymbol{x}_{\mathbf{n}}^{(n)} \rangle$, the moments of $\{x_k\}$ at thermal equilibrium, we first recast Eq. (29) as

$$\int \boldsymbol{x}_{\mathbf{n}}^{(n)} \hat{\Gamma} P^{\rm st} \, {\rm d}\boldsymbol{x} = \int \boldsymbol{x}_{\mathbf{n}}^{(n)} \boldsymbol{\nabla} \cdot \boldsymbol{J}^{\rm st} \, {\rm d}\boldsymbol{x}. \tag{B9}$$

For Eq. (30), Eqs. (B2) and (B3) gives the input–output relation reading

$$\langle \boldsymbol{x}_{\mathbf{n}}^{(n)} \rangle = \frac{2}{\gamma_{\mathbf{n}}^{(n)}} \sum_k \left[\xi_k n_k \langle \hat{Q} \boldsymbol{x}_{\mathbf{n}_k^-}^{(n-1)} \rangle + \gamma_k \binom{n_k}{2} \langle \boldsymbol{x}_{\mathbf{n}_{kk}^{--}}^{(n-2)} \rangle \right], \tag{B10}$$

where $\gamma_{\mathbf{n}}^{(n)} \equiv \sum_k n_k \gamma_k$.

To close the input–output relation, one may further consider for any operator $\hat{A}$, there exists the relation

$$\begin{aligned} & -i\langle [H_{\rm S}, \hat{A}] \boldsymbol{x}_{\mathbf{n}}^{(n)} \rangle + \sum_k \xi_k n_k \langle \{\hat{A}, \hat{Q}\} \boldsymbol{x}_{\mathbf{n}_k^-}^{(n-1)} \rangle \\ & = \sum_k \gamma_k \Big[n_k \langle \hat{A} \boldsymbol{x}_{\mathbf{n}}^{(n)} \rangle - n_k(n_k-1) \langle \hat{A} \boldsymbol{x}_{\mathbf{n}_{kk}^{--}}^{(n-2)} \rangle \Big]. \end{aligned} \tag{B11}$$

It is evident that the recurrence relation is closed when $\hat{A}$ belongs to a linear space $\mathbb{L}$ of operators. Here, the linearly independent basis set of $\mathbb{L}$ has two parts: (i) basis vectors $\hat{V}$ satisfying $[H_{\rm S}, \hat{V}] = 0$ and $\{\hat{Q}, \hat{V}\} = 0$; (ii) finite basis vectors generated from the identical operator $\hat{I}$ via the operation $\{\hat{Q}, \cdot\}$ and $[H_{\rm S}, \cdot]$. As a result, the basis set is $\{\hat{I}, \hat{Q}, [H_{\rm S}, \hat{Q}], \hat{Q}^2, [H_{\rm S}, [H_{\rm S}, \hat{Q}]], \{\hat{Q}, [H_{\rm S}, \hat{Q}]\}, \cdots\}$.[76]

For example, for the spin–boson system where $H_{\rm S} = \hat{\sigma}_x$, $\hat{Q} = \hat{\sigma}_z$, the linearly dependent basis of $\mathbb{L}$ is $\{\hat{I}, \hat{\sigma}_z, \hat{\sigma}_y, \hat{\sigma}_x\}$, since $[\hat{\sigma}_i, \hat{\sigma}_j] = 2i\varepsilon_{ijk}\hat{\sigma}_k$ and $\{\hat{\sigma}_i, \hat{\sigma}_j\} = 2\delta_{ij}\hat{I}$. Then, when $\hat{A} = \hat{\sigma}_x$, $\hat{\sigma}_y$ and $\hat{\sigma}_z$, we have

$$0 = \sum_k \gamma_k \Big[n_k \langle \hat{\sigma}_x \boldsymbol{x}_{\mathbf{n}}^{(n)} \rangle - n_k(n_k-1) \langle \hat{\sigma}_x \boldsymbol{x}_{\mathbf{n}_{kk}^{--}}^{(n-2)} \rangle \Big], \tag{B12}$$

$$2\langle \hat{\sigma}_z \boldsymbol{x}_{\mathbf{n}}^{(n)} \rangle = \sum_k \gamma_k \Big[n_k \langle \hat{\sigma}_y \boldsymbol{x}_{\mathbf{n}}^{(n)} \rangle - n_k(n_k-1) \langle \hat{\sigma}_y \boldsymbol{x}_{\mathbf{n}_{kk}^{--}}^{(n-2)} \rangle \Big], \tag{B13}$$

and

$$\begin{aligned} & 2\langle \hat{\sigma}_y \boldsymbol{x}_{\mathbf{n}}^{(n)} \rangle - 2 \sum_k \xi_k n_k \langle \hat{\sigma}_z \boldsymbol{x}_{\mathbf{n}_k^-}^{(n-1)} \rangle \\ & = -\sum_k \gamma_k \Big[n_k \langle \hat{\sigma}_z \boldsymbol{x}_{\mathbf{n}}^{(n)} \rangle - n_k(n_k-1) \langle \hat{\sigma}_z \boldsymbol{x}_{\mathbf{n}_{kk}^{--}}^{(n-2)} \rangle \Big], \end{aligned} \tag{B14}$$

separately.

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