Nonequilibrium work distributions in controlled system–bath mixing processes

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(Dated: March 31, 2022)

The fluctuation theorem provides a powerful tool to investigate the thermodynamics out of equilibrium, where the central quantity is the work distribution. In this work, we establish an exact formalism to study the work distributions in isothermal system–bath mixing processes, under certain controllable protocols denoted as $\lambda$. This formalism extends the original framework of $\lambda$-dissipaton–equation–of–motion ($\lambda$–DEOM) from equilibrium to nonequilibrium scenarios. Using this nonequilibrium $\lambda$–DEOM, we accurately verify Jarzynski equality and Crooks relation, two foundational components of the fluctuation theorem.

I. INTRODUCTION

The fluctuation theorem plays pivotal roles in investigating nonequilibrium thermodynamics [1–4]. The celebrated Jarzynski equality [4, 5] and Crooks relation [6, 7] are considered as two foundational components of the fluctuation theorem, which have been experimentally tested in several systems [8–12]. At the center of fluctuation theorem is the work distribution $p(w)$ during a nonequilibrium process [13–16]. Practically, the work distribution is equivalent to the characteristic function of work (CFW),

$$\varphi(\tau) = \int_{-\infty}^{\infty} dw \, e^{i\tau w} p(w),$$  \hspace{1cm} (1)

the Fourier transform of work distribution. Generally, the CFW is ubiquitous in modern physical researches, such as Loschmidt echo [17, 18] and dynamical quantum phase transitions [19, 20].

In this work, we aim at investigating the CFW of system–bath mixing processes, which are under certain controllable protocols. To that end, we extend the original formalism of $\lambda$–dissipaton–equation–of–motion ($\lambda$–DEOM) from equilibrium to nonequilibrium scenarios. The original $\lambda$–DEOM is developed for equilibrium system–bath mixing thermodynamics in our previous works [21, 22], while the nonequilibrium $\lambda$–DEOM (neq–$\lambda$–DEOM) is developed as a theoretical method to study the nonequilibrium mixing processes under controllable protocols. Using neq–$\lambda$–DEOM, we successfully verify the Jarzynski equality and Crooks relation during these mixing processes.

This work is organized as follows. In Sec. II, we simply review the fluctuation theorems, including Jarzynski equality and the Crooks relation, in the system–bath mixing scenarios. In Sec. III, we establish the neq–$\lambda$–DEOM for nonequilibrium system–bath mixing processes. Numerical demonstrations are displayed in Sec. IV, together with further explanations and analysis.

We summarize this paper in Sec. V. Throughout this paper we set $\hbar = 1$ and $\beta = 1/(k_B T)$ with $k_B$ being the Boltzmann constant and $T$ the temperature.

II. FLUCTUATION THEOREM IN SYSTEM–BATH MIXING SCENARIOS

A. Basic settings and work generating operator

In this section, we focus on the work functional, $w[\lambda(t)]$, for system–bath mixing processes. Here, $\lambda(0 \leq t \leq t_f)$ denotes a generic mixing protocol and regulates the strength of system–bath coupling $H_{sb}$, with $\lambda(0) = 0$ and $\lambda(t_f) = 1$. The time-dependent system–bath composite Hamiltonian reads

$$\hat{H}(t) = H_S + H_B + \lambda(t) H_{SB}.$$  \hspace{1cm} (2)

The total system is initially unhybrid, i.e., $H_0 \equiv \hat{H}(0) = H_S + H_B$, at thermal equilibrium $\rho_{eq}^0(T) = e^{-\beta H_0}/Z_0$ with $Z_0 = \text{Tr}(e^{-\beta H_0})$. The fully hybridized system–bath composite amounts to the total Hamiltonian, $H_T \equiv \hat{H}(t_f) = H_S + H_B + H_{SB}$ since $\lambda(t_f) = 1$. Denote $\rho_0^S(n) = \epsilon_n |n\rangle$ and $H_T |N\rangle = E_N |N\rangle$. The distribution of hybridization work is then

$$p(w) = \sum_{N,n} \delta(w - E_N + \epsilon_n) P_{N,n}(t_f, 0) P_n(0).$$  \hspace{1cm} (3)

While $P_n(0) = e^{-\beta \epsilon_n}/Z_0$ is the initial probability distribution, $P_{N,n}(t_f, 0) = |\langle N | U(t_f, 0) | n \rangle|^2$ is the transition probability with the propagator $U(t, 0)$ being governed by the Hamiltonian $\hat{H}(t)$.

To compute the CFW in Eq. (1) with respect to Eq. (3), we introduce the work generating operator [23, 24]

$$\Phi(t; \tau) = U(t, 0) V_+ (t; \tau) \rho_0^S(T) V_- (t; \tau) U^\dagger (t, 0),$$  \hspace{1cm} (4)

where

$$V_{\pm} (t; \tau) = \exp_{\pm} \left[ \frac{\tau}{2} \int_0^t dt' \frac{\partial \hat{H}(t')}{\partial V'} \right],$$  \hspace{1cm} (5)

with

$$\hat{H}(t) \equiv U^\dagger (t, 0) \hat{H}(t) U(t, 0).$$  \hspace{1cm} (6)
It can be shown that
\[ \varphi(\tau) = \text{Tr}[\Phi(tf; \tau)]. \tag{7} \]
See Appendix for details.

Turn to the equation of motion (EOM) for the work generating operator \( \Phi(t; \tau) \), abbreviated as \( \Phi(t) \) since \( \tau \) is a parameter throughout this paper. As detailed in Appendix, we obtain
\[ \dot{\Phi}(t) = -i[H^\lambda + A_{\text{hyb}} + \Lambda_- (t) H_{\text{sb}} - \Lambda_+ (t) H_{\text{sb}}^*] \Phi(t) \tag{8} \]
with
\[ \Lambda_\pm (t) \equiv \lambda(t) \pm \frac{\tau}{2} \lambda(t), \tag{9} \]
whereas \( \hat{A}^\times \equiv \hat{A}^\gamma - \hat{A}^\delta \), \( \hat{A}^\gamma \hat{O} = \hat{A} \hat{O} \) and \( \hat{A}^\delta \hat{O} = \hat{O} \hat{A} \). The initial value to Eq. (8) is \( \Phi(t = 0) = \rho_{0}^q(T) \).

B. Jarzynski equality

According to Eq. (1), we know that
\[ \varphi(i\beta) = \int_{-\infty}^{\infty} dw \ e^{-\beta w} p(w) \equiv \langle e^{-\beta w} \rangle. \tag{10} \]
Jarzynski equality claims [4]
\[ \varphi(i\beta) = e^{-\beta A_{\text{hyb}}} = Z_T/Z_0. \tag{11} \]
This is the equality between the hybridization work \( w \) and the hybridization free-energy \( A_{\text{hyb}} \), relating further to the ratio between \( Z_T = \text{Tr}(e^{-\beta HT}) \) and \( Z_0 = \text{Tr}(e^{-\beta H_0}) \). These are the partition function of fully hybridized and unhybrid system–bath composite, respectively. On the right–hand–side of Eq. (11), the hybridization free-energy \( A_{\text{hyb}} \), is equilibrium thermodynamic quantities, which can be evaluated various methods, including \( \lambda \)–DEOM, imaginary–time DEOM and free–energy spectrum approaches [21, 22]. The left–hand–side of Eq. (11) is to be handled with the neq–\( \lambda \)–DEOM developed in this work; see Sec. IV.

C. Crooks relation

Crooks relation is about a pair of conjugate processes: the forward process controlled by \( \lambda(t) \) and the backward process controlled by \( \hat{\lambda}(t) = \lambda(t_f - t) \). The backward process represents a system–bath separation, with \( \lambda(0) = 1 \) and \( \hat{\lambda}(t_f) = 0 \). We denote the work distributions in the forward and backward processes as \( p(w) \) and \( \bar{p}(w) \), respectively.

Assuming the total system–and–bath composite is time–reversal invariant, the Crooks relation claims [6]
\[ p(w) = e^{\beta(w - A_{\text{hyb}})} \bar{p}(-w). \tag{12} \]
Equivalently, we can express Eq. (12) using the CFWs as
\[ \varphi(\tau) = e^{-\beta A_{\text{hyb}}} \bar{\varphi}(i\beta - \tau). \tag{13} \]
Here, \( \bar{\varphi} \) is the backward CFW [3]. Evidently, if we set \( \tau = i\beta \) in Eq. (13), it recovers Jarzynski equality Eq. (11).

III. NONEQUILIBRIUM \( \lambda \)–DEOM

A. Prelude

In this section, we introduce the neq–\( \lambda \)–DEOM formalism to evaluate the CFWs of the system–bath mixing processes. We set the interaction Hamiltonian to be
\[ H_{\text{sb}} = \hat{Q}_B \hat{F}_B. \tag{14} \]
While the dissipative system mode \( \hat{Q}_B \) is an arbitrary dimensionless Hermitian operator, the hybridization mode \( \hat{F}_B \) is linear. It together with harmonic bath \( h_B \) constitute a Gaussian environment. For the Gaussian bath, the correlation function of hybrid mode, \( \langle \hat{F}_B(t) \hat{F}_B(0) \rangle_B \), completely characterizes the environmental influences. Here, \( \hat{F}_B(t) \equiv e^{i\hbar t \hat{F}} e^{-i\hbar t \hat{F}} \) and \( \langle \cdot \rangle_B \equiv \text{tr}_B([\cdot] e^{-\beta h_B})/\text{tr}_B(e^{-\beta h_B}) \). We can do exponential series expansion by adopting a certain the sum–over–poles scheme to expand the Fourier integrand there, followed by Cauchy’s contour integration. Together with the identity \( \langle \hat{F}_B^n(0) \hat{F}_B^n(0) \rangle_B = \langle \hat{F}_B^n(t) \hat{F}_B^n(0) \rangle_B \), we obtain that [25]
\[ \langle \hat{F}_B^n(t) \hat{F}_B^n(0) \rangle_B = \sum_{k=1}^{K} \eta_k e^{-\gamma_k t}, \tag{15} \]
\[ \langle \hat{F}_B^n(t) \hat{F}_B^n(0) \rangle_B = \sum_{k=1}^{K} \eta_k^* e^{-\gamma_k t}. \]
Here, since the exponents \( \{ \gamma_k \} \) in Eq. (15) must be either real or complex conjugate paired [25], we may set \( \gamma_k = \gamma_k^* \).

The DEOM theory adopts dissipatons as quasi–particles associated with the coupling bath influence [25–27]. It is a second–quantization version HEOM, which is also able to deal with the hybrid mode dynamics. To be concrete, DEOM decompose \( \hat{F} \) into many dissipaton operators
\[ \hat{F}_B = \sum_{k=1}^{K} \hat{f}_k, \tag{16} \]
To reproduce Eq. (15), we set
\[ \langle \hat{f}_k(t) \hat{f}_k'(0) \rangle_B = \delta_{kk'} \eta_k e^{-\gamma_k t}, \tag{17} \]
\[ \langle \hat{f}_k'(0) \hat{f}_k(t) \rangle_B = \delta_{kk'} \eta_k^* e^{-\gamma_k t}. \]
Each forward–and–backward pair of dissipaton correlation functions are associated with a single–exponent \( \gamma_k \).

The conventional DEOM defines also the dynamical variables, the dissipatons–augmented–reduced density operators (DDOs), as [25–27]
\[ \rho^{(n)}(t) \equiv \rho_{n_1 \cdots n_K}(t) = \text{tr}_B \left[ (\hat{f}_K^{\dagger} \cdots \hat{f}_1^{\dagger})^n \rho_B(t) \right]. \tag{18} \]
Here, \( n = n_1 + \cdots + n_K \), with \( n_k \geq 0 \) for bosonic dissipatons. The product of dissipaton operators inside \( (\cdot \cdot \cdot)^p \) is
irreducible, satisfying \((\hat{f}_k \hat{f}_k)^\circ = (\hat{f}_k \hat{f}_k)^\circ\) for bosonic dissipatons. Each \(n\)-particles DDO, \(\rho^{(n)}_{\text{n}}(t)\), is specified with an ordered set of indexes, \(n = \{n_1 \cdots n_K\}\). Denote for later use also \(n_k^\pm\) that differs from \(n\) only at the specified \(\hat{f}_k\)-dissipaton participation number \(n_k\) by \(\pm 1\). The reduced system density operator is just \(\rho_{\text{n}}^{(0)} = \rho_{\text{0}}^{(0)}\). We will extend the definition (18) from the density operator \(\rho(t)\) to the work generating operator \(\Phi(t)\) in the following.

B. Dissipatons–augmented work generating operator and its EOM

Similar to DDo’s, we introduce the dissipatons–augmented work generating operators (DWOs),

\[
\Phi^{(n)}_{\text{n}}(t) = \text{tr}_n[(\hat{f}_k^{n_K} \cdots \hat{f}_1^{n_1})^\circ \Phi(t)],
\]

where \(\Phi^{(n)}_{\text{n}}(t) = \Phi^{(n)}_{\text{n}_1, \cdots, n_k}(t)\) specifies certain configuration of given \(n\)-dissipatons excitation. Initially, \(\Phi \equiv (\Phi_{\text{n}}^{(0)}) = \delta_{\text{n0}} \exp(-\beta H) / \text{tr}_n(\exp(-\beta H))\). Evidently, \(\varphi(t) = \text{tr}_n[\Phi^{(0)}(t)]\) [cf. Eq. (7)].

To obtain the EOM that governs the time evolution of DWOs, we apply for \(\Phi^{(n)}_{\text{n}}(t)\) of Eq. (19) the equation Eq. (8). We evaluate, one-by-one, the specified four components in total composite Hamiltonian, for their contributions.

(i) The \(H_{\Sigma}^x\)-contribution: Apparently,

\[
\text{tr}_n[(\hat{f}_k^{n_K} \cdots \hat{f}_1^{n_1})^\circ H_{\Sigma}^x \Phi(t)] = H_{\Sigma}^x \Phi^{(n)}_{\text{n}}(t).
\]

This is the coherent dynamics contribution.

(ii) The \(h^n_x\)-contribution: Each dissipaton is subject a sort of “diffusive” motion in bare–bath, satisfying

\[
\text{tr}_n[(\delta f_k / \partial t)_{\text{n}} \Phi(t)] = -\gamma_k \text{tr}_n[\hat{f}_k \Phi(t)].
\]

Together with \(i(\hat{f}_k / \partial t) \equiv [\hat{f}_k, h_{\text{n}}]\), we obtain

\[
\text{tr}_n[(\hat{f}_k^{n_K} \cdots \hat{f}_1^{n_1})^\circ h_{\text{n}}^x \Phi(t)] = -i\gamma_k \Phi^{(n)}_{\text{n}}(t),
\]

with \(\gamma_k = \sum_k n_k \gamma_k \). This is the “diffusive” dynamics contribution.

(iii) The \(H_{\Sigma}^a\)-contribution: By applying Eq. (14), we obtain readily the following expressions,

\[
\text{tr}_n[(\hat{f}_k^{n_K} \cdots \hat{f}_1^{n_1})^\circ H_{\Sigma}^a \Phi(t)]
\]

\[
= \text{tr}_n[(\hat{f}_k^{n_K} \cdots \hat{f}_1^{n_1})^\circ \hat{Q}_{\Sigma}^a \hat{F}_{\text{n}}^a \Phi(t)]
\]

\[
= \hat{Q}_{\Sigma}^a \sum_k \text{tr}_n[(\hat{f}_k^{n_K} \cdots \hat{f}_1^{n_1})^\circ \hat{f}_k^{n_k} \Phi(t)]
\]

\[
= \hat{Q}_{\Sigma}^a \sum_k \Phi^{(n+1)}_{\text{n}_k}(t) + n_k \eta_k \Phi^{(n-1)}_{\text{n}_k}(t).
\]

In the last step, we have used the forward generalized Wick’s theorem:

\[
\text{tr}_n[(\hat{f}_k^{n_K} \cdots \hat{f}_1^{n_1})^\circ \hat{f}_k \Phi] = \Phi^{(n+1)}_{\text{n}_k} + n_k \eta_k \Phi^{(n-1)}_{\text{n}_k}.
\]

(iv) The \(H_{\Sigma}^0\)-contribution: Similarly, we obtain

\[
\text{tr}_n[(\hat{f}_k^{n_K} \cdots \hat{f}_1^{n_1})^\circ H_{\Sigma}^0 \Phi(t)]
\]

\[
= \hat{Q}_{\Sigma}^0 \sum_k \Phi^{(n+1)}_{\text{n}_k}(t) + n_k \eta_k \Phi^{(n-1)}_{\text{n}_k}(t)
\]

by using the backward generalized Wick’s theorem

\[
\text{tr}_n[(\hat{f}_k^{n_K} \cdots \hat{f}_1^{n_1})^\circ \hat{f}_k \Phi] = \Phi^{(n+1)}_{\text{n}_k} + n_k \eta_k \Phi^{(n-1)}_{\text{n}_k}.
\]

The above (i)–(iv) lead to the EOM of DWOs in the neq–\(\lambda\)-DEOM formalism the expression

\[
\Phi^{(n)}_{\text{n}}(t) = -i(H_{\Sigma}^x - i\gamma) \Phi^{(n)}_{\text{n}}(t) - i \sum_k A(t) \Phi^{(n+1)}_{\text{n}_k}(t)
\]

\[
- i \sum_k C_k(t) n_k \Phi^{(n-1)}_{\text{n}_k}(t)
\]

where

\[
A(t) \equiv \Lambda_\gamma(t) \hat{Q}_{\Sigma}^\gamma - \Lambda_\gamma(t) \hat{Q}_{\Sigma}^\gamma,
\]

\[
C_k(t) \equiv \eta_k \Lambda_\gamma(t) \hat{Q}_{\Sigma}^\gamma - \eta_k^* \Lambda_\gamma(t) \hat{Q}_{\Sigma}^\gamma,
\]

with \(\Lambda_\gamma(t)\) being given in Eq. (9) that depends also on the parameter \(\tau\).

IV. NUMERICAL DEMONSTRATIONS

For numerical demonstrations, we consider a spin–boson model, in which system Hamiltonian and dissipative mode are

\[
\hat{H}_s = \varepsilon \hat{\sigma}_z + \Delta \hat{\sigma}_x \quad \text{and} \quad \hat{Q}_s = \hat{\sigma}_z,
\]

respectively. Here, \(\{\hat{\sigma}_i\}\) are the Pauli matrices, \(\varepsilon\) is the energy bias parameter and \(\Delta\) the interstate coupling. Adopt for the bath spectral density the Drude model,

\[
J(\omega) = \eta \gamma \omega / \omega^2 + \gamma^2,
\]

where \(\eta\) and \(\gamma\) are the system-bath coupling strength and bath cut–off frequency, respectively. In all the simulations below, we set \(\varepsilon = 0.5\Delta\), \(\gamma = 4\Delta\) and \(\eta = 0.5\Delta\). We set the protocol to be

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

as the forward protocol, with \(\alpha \geq 0\). Correspondingly, the backward protocol

\[
\tilde{\lambda}(t) = \lambda(t + t) = \frac{e^{\alpha t} - e^{\alpha t}}{e^{\alpha t} - 1}.
\]

In Fig. 1, we evaluate the left–hand–side and right–hand–side of Eq. (11), the Jarzynski equality, respectively. On the right–hand–side of Eq. (11), the hybridization free–energy, \(A_{\text{hyb}}\), is computed via the equilibrium
FIG. 1. Validation of Jarzynski equality: $\langle e^{-\beta w} \rangle$ versus $e^{-\beta A_{\text{hyb}}}$ with different temperatures. We set $\varepsilon = 0.5\Delta$, $\gamma = 4\Delta$ and $\eta = 0.5\Delta$ in the spectral density (30) and $\alpha = 0.01$ and $t_f = 50$ in the forward and backward protocols Eqs. (31) and (32).

FIG. 2. $\varphi(\tau)$ versus $\tilde{\varphi}(i\beta - \tau)$. We choose $\beta = 0.5\Delta^{-1}$. Other parameters are the same with that in Fig. 1.

$\lambda$–DEOM approach developed in our previous work (in red) [21]. On the left–hand–side, $\varphi(i\beta)$ can be obtained by propagating Eq. (27), with the parameter $\tau = i\beta$ (in blue). As shown in the figure, the results match perfectly in at different temperatures.

We may also interested in the numerical validation of Crook relation. In Fig. 2, the CFWs of both mixing process with $\lambda(t)$ [cf. Eq. (31)] and separation process with $\tilde{\lambda}(t)$ [cf. Eq. (32)] are exhibited. Intentionally, we compare the two sides of Eq. (13), with both the real and imaginary parts. We also plot the hybridization and separation work distributions in Fig. 3, where $p(w)$ and $\bar{p}(-w)$ coincide at $w = A_{\text{hyb}}$ [cf. Eq. (12)]. Besides, according to Jensen’s inequality, Eq. (11) implies

$$\langle w \rangle \geq A_{\text{hyb}}.$$  \hspace{1cm} (33)

This is the second law of thermodynamics applied to the system–bath mixing. One may define the irreversible work as

$$w_{\text{irr}} = \langle w \rangle - A_{\text{hyb}} = \langle w \rangle - \beta^{-1} \ln(e^{-\beta w}).$$  \hspace{1cm} (34)

It sometimes is approximated as [28]

$$w_{\text{irr}} = \langle w \rangle - \beta^{-1} \sum_{n=1}^{\infty} \kappa_n \frac{(-\beta)^n}{n!} \approx \frac{\beta}{2} k_2.$$  \hspace{1cm} (35)
where $\kappa_n$ is the $n$th–order cumulant of the work distribution. Specifically, $\kappa_1 = \langle w \rangle$ and $\kappa_2 = \langle w^2 \rangle - \langle w \rangle^2$. The error of Eq. (35) originates from the non-Gaussianity of $p(w)$. In Fig. 4, we compare the approximate result with the exact one, which is obtained directly from the definition (34). As shown in the figure, the non-Gaussianity remains over the full temperature range and becomes larger as the temperature increases.

V. CONCLUDING REMARKS

To conclude, we establish the neq–$\lambda$–DEOM formalism to study the work distributions in isothermal systems-bath mixing processes under certain controllable protocols. This formalism extends the original framework of $\lambda$–DEOM nonequilibrium scenarios. Using neq–$\lambda$–DEOM, we accurately verify Jarzynski equality and Crooks relation, two foundational components of the fluctuation theorem. We also study the irreversible work during the mixing processes. On the other hand, according to Eq. (11) or Eq. (12), the hybridization free–energy in the mixing process can be related to the hybridization work distributions. It thus provides us with a new tool to calculate the hybridization free energy.

The current state-of-the-art devices for quantum simulation include quantum dots, cold atoms, trapped ions, and superconducting circuits [29–34]. These established technologies on manipulations could be exploited for the required protocols. Therefore, it is anticipated that the theoretical framework developed in this work would constitute a crucial component for nonequilibrium thermodynamics in the quantum regime, which is measurable in experiments.

ACKNOWLEDGMENTS

Support from the Ministry of Science and Technology of China (Nos. 2017YFA0204904 and 2021YFA1200103) and the National Natural Science Foundation of China (Nos. 22103073 and 22173088) is gratefully acknowledged. We would like to thank Yu Su and Zi-Hao Chen for valuable discussions. Y. Wang acknowledges also the partial support from GHfund B (No. 20210702).

Appendix A: Derivation of Eqs. (7) and (8)

To derive the relation given in Eq. (7), we first rewrite Eq. (3) as

$$p(w) = \frac{1}{2\pi} \sum_{N,n} \int_{-\infty}^{\infty} d\tau \ e^{-i(w-E_{N}+\varepsilon_n)\tau} P_{N,n}(t_f,0)P_n(0).$$

(A1)

By further noting

$$P_{N,n}(t_f,0) = \langle N|U(t_f,0)|n\rangle\langle n|U\dagger(t_f,0)|N\rangle,$$  

(A2)

we obtain

$$p(w) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\tau \ e^{-i\omega\tau} \varphi(\tau),$$

(A3)

with $\varphi(\tau) = \text{Tr}[\Phi(\tau; t_f)]$ where $\Phi(\tau; t_f) = e^{i\hat{H}_{\tau}/2}U(t_f,0)e^{-i\hat{H}_{\tau}/2}\rho^\text{eq}_0(T)e^{-i\hat{H}_{\tau}/2}U\dagger(t_f,0)e^{i\hat{H}_{\tau}/2}$ is the work generating operator. Equation (A3) is seen as the inverse Fourier transform with respect to Eq. (1). According to Eq. (6), we can then rewrite the work generating operator as

$$\Phi(\tau; t_f) = U(t_f,0)e^{i\hat{H}(\tau)/2}e^{-i\hat{H}(0)\tau/2}\rho^\text{eq}_0(T)e^{-i\hat{H}(0)\tau/2} \times e^{i\hat{H}(t_f)/2}U\dagger(t_f,0)$$

$$=U(t_f,0)V_{+}(\tau; t_f)\rho^\text{eq}_0(T)V_{-}(\tau; t_f)U\dagger(t_f,0).$$

(A4)

Here, $V_{\pm}(t; \tau) \equiv \exp_{\pm}[i[H(t) - \hat{H}(0)]\tau/2]$ and it is equivalent to that in Eq. (5) due to the existence of time–ordering operators together with the fact that $d\hat{H}(t)/dt = \partial\hat{H}(t)/\partial t$ as inferred from Eq. (6). This concludes the derivation of Eq. (7).

Now turn to the derivation of Eq. (8). According to the definition in Eq. (4), we can obtain

$$\dot{\Phi}(t) = -i \left[ \hat{H}^\times(t) - \frac{\tau}{2} \hat{H}^\circ(t) \right] \Phi(t).$$

(A5)

Here, $\hat{A}^\circ \equiv \hat{A}^+ + \hat{A}^–$ and $\dot{\hat{H}}^\circ(t) = \partial\hat{H}^\circ(t)/\partial t$. While the derivation of $-i\hat{H}^\times(t)$ term is rather direct, the derivation of $i(\tau/2)\hat{H}^\circ(t)$ is as follows:

$$U(t,0)V_{+}(t)\rho^\text{eq}_0(T)V_{-}(t)U\dagger(t,0)$$

$$=U(t,0)\left[ \frac{\tau}{2} \frac{\partial\hat{H}(t)}{\partial t} \right] V_{+}(t)\rho^\text{eq}_0(T)V_{-}(t)U\dagger(t,0)$$

$$\frac{\tau}{2} \frac{\partial\hat{H}(t)}{\partial t} U(t,0)V_{+}(t)\rho^\text{eq}_0(T)V_{-}(t)U\dagger(t,0)$$

$$= \frac{\tau}{2} \frac{\partial\hat{H}(t)}{\partial t} \Phi(t).$$

(A6)

In the first step, we use the property of time–ordering operator and the definition (5), while in the second step we used the relation $\partial\hat{H}(t)/\partial t = U\dagger(t,0)[\partial\hat{H}(t)/\partial t]U(t,0)$. The $U(t,0)V_{+}(t)\rho^\text{eq}_0(T)V_{-}(t)U\dagger(t,0)$ contribution is similar. Substitute the Hamiltonian (2) into Eq. (A5), and we readily obtain Eq. (8).
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