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The laws of thermodynamics for quantum dissipative systems: A quasi-equilibrium Helmholtz energy approach

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Shoki Koyanagi (iD) and Yoshitaka Tanimura[a) (iD)

AFFILIATIONS

Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan

[a)]Author to whom correspondence should be addressed: tanimura.yoshitaka.5w@kyoto-u.jp

ABSTRACT

By using the quasi-equilibrium Helmholtz energy, which is defined as the thermodynamic work in a quasi-static process, we investigate the thermal properties of both an isothermal process and a transition process between the adiabatic and isothermal states (adiabatic transition). Here, the work is defined by the change in energy from a steady state to another state under a time-dependent perturbation. In particular, the work for a quasi-static change is regarded as thermodynamic work. We employ a system–bath model that involves time-dependent perturbations in both the system and the system–bath interaction. We conduct numerical experiments for a three-stroke heat machine (a Kelvin–Planck cycle). For this purpose, we employ the hierarchical equations of motion (HEOM) approach. These experiments involve an adiabatic transition field that describes the operation of an adiabatic wall between the system and the bath. Thermodynamic–work diagrams for external fields and their conjugate variables, similar to the P–V diagram, are introduced to analyze the work done for the system in the cycle. We find that the thermodynamic efficiency of this machine is zero because the field for the isothermal processes acts as a refrigerator, whereas that for the adiabatic wall acts as a heat engine. This is a numerical manifestation of the Kelvin–Planck statement, which states that it is impossible to derive the mechanical effects from a single heat source. These HEOM simulations serve as a rigorous test of thermodynamic formulations because the second law of thermodynamics is only valid when the work involved in the operation of the adiabatic wall is treated accurately.

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I. INTRODUCTION

In a process at constant temperature, free energy is an extensive property that describes a mathematically concise relationship between thermodynamic variables under the work done on a system.[1–3] Among free energy functions, the Helmholtz energy is an important quantity that links thermodynamics and statistical physics. In the thermodynamics case, the Helmholtz energy is defined as the Legendre transform of the internal energy U as $F = U - TS$, where S is the entropy and T is the absolute temperature. In the statistical physics case, the Helmholtz energy is evaluated from the partition function (PF) Z by $F = -k_B T \ln Z$, where k_B is the Boltzmann constant. The thermodynamic variables such as U, S, and magnetization M for an external magnetic field B can be obtained from the Helmholtz energy. Note that the free energy defined from the partition function is ubiquitously referred to as the Helmholtz energy. In the thermodynamic sense, the Helmholtz energy for B should be called the Gibbs energy because they appear as the Legendre transformation of F with respect to B and its conjugate property M ($dG = -SdT - MdB$).[4] However, following convention, we refer to F as the Helmholtz energy.

While investigations based on the partition function are limited in the equilibrium case, the free energy-based investigation has been extensively extended to the non-equilibrium condition, particularly after the discovery of the Jarzynski equality. The non-equilibrium work is related to the equilibrium free energy as $-\ln(\langle \exp[-\beta W(t)] \rangle)/\beta = \Delta F_A(t)$.[5–7] Here, $\beta \equiv 1/k_B T$ is the inverse temperature, $\Delta F_A(t)$ is the change in the free energy of the system, $W(\tau)$ is the non-equilibrium work, and $\langle \cdots \rangle$ is the ensemble average over all phase-space trajectories under the time-dependent

external perturbation from time t_0 to t. More generally, the fluctuation theorem that can treat non-isothermal cases has been developed.[8–17]

Although investigating such thermodynamic systems in the classical regime is straightforward (e.g., using classical molecular dynamics simulations),[18] doing so in the quantum regime remains challenging.[12–17,19–27] For example, the dynamics of a microscopic subsystem (main system) is reversible in time and cannot reach its thermal equilibrium state by itself. Thus, system–bath (SB) models in which a small main system is coupled to a bath are employed to describe the time irreversibility of the dynamics of a reduced system evolving toward the thermal equilibrium state.[28–30] The temperature of the bath does not change because its heat capacity is infinite; meanwhile, the canonical distribution of the main system on its own cannot be assumed as an equilibrium state due to the presence of the system–bath interaction.[31–34]

This scenario differs significantly from the classical case where the main system reaches its canonical distribution on its own spontaneously when the system is sufficiently large. While the Jarzynski equality and fluctuation theorem utilize the ensemble average over all phase-space trajectories under time-dependent external perturbation, such a trajectory-based approach is invalid in a small quantum system because of the measurements of the quantum trajectories.[14,35]

Recently, it was found that the thermodynamic system A coupled to a heat bath B can be described using the quasi-equilibrium Helmholtz energy (qHE) in a physically consistent manner with classical thermodynamics. The qHE is defined as $\Delta F_A(t) = W^{qst}(t)$, where $W^{qst}(t)$ is the quasi-static work done on the system during the isothermal operation at time t.[35,36] Note that in this paper, the work is defined by the change in energy from one state to another under a time-dependent perturbation; when the change is quasi-static, it is regarded as thermodynamic work. From $\Delta F_A(t)$, a variety of thermodynamic variables that include the change in the internal energy and entropy can be obtained. The previous investigation was limited to the isothermal case;[35,36] in this study, we extend it to treat thermal transitions between the adiabatic and isothermal states (adiabatic transitions). For this purpose, we introduce a time-dependent SB interaction that describes a manipulation of an adiabatic wall between the system and the bath. The key to investigating this quasi-static thermodynamic problem is the hierarchical equations of motion (HEOM) formalism, which enables the evaluation of the internal energies of not only the system but also the bath and the SB interactions, even in low-temperature, non-Markovian, and nonperturbative conditions.[31–42]

The qHE treatment for the determination of thermodynamic properties, including entropy change in the adiabatic wall, shall be useful for the study of a quantum heat machine[43–56] because the thermodynamic effects of the heat bath play a significant role in an investigation of this kind.[57–64] In addition, a thermodynamic work diagram of external forces (such as stresses) and their conjugate variables (such as strains), similar to Clapeyron's P–V diagram,[65] can be introduced to analyze the work done in the system. Such an extension can be useful for analyzing the experimental results in the quantum regime, where the quantized work and heat are to be manipulated.[66–75]

As a demonstration, we simulate a three-stroke heat machine with a single heat bath that consists of the isothermal process, the adiabatic transition process, and the combination of these processes by using the thermodynamic work diagrams. Then, we show that our numerical results are consistent with the Kelvin–Planck statement (or heat engine statement) of the second law of thermodynamics.[76] The simulations of this cycle can be a critical check on the accuracy of thermodynamic formulations and the description of equations of motion in the quantum regime since the thermodynamic laws will break down if the work done for the entire system, including the adiabatic wall operation, is not properly evaluated.

This paper is organized as follows: In Sec. II, we present the definition of the qHE for an arbitrary SB model that satisfies the first and second laws of thermodynamics. In Sec. III, we introduce a harmonic oscillator heat bath and present a spin–boson model with a time-dependent SB interaction. The HEOM for this system are also introduced. Section IV presents and discusses the numerical results. Finally, concluding remarks are provided in Sec. V.

II. TOTAL ENERGY AND INTERNAL ENERGY

A. Total energy

We start from a situation where the dynamics of a system are described by a time-dependent Hamiltonian expressed as $\hat{H}_{tot}(t)$. The total density operator is then expressed as

$$\hat{\rho}_{tot}(t) = \exp_+\left[-\frac{i}{\hbar}\int_{t_0}^{t}dt'\hat{H}_{tot}(t')\right]\hat{\rho}_{tot}(t_0)\exp_-\left[\frac{i}{\hbar}\int_{t_0}^{t}dt'\hat{H}_{tot}(t')\right], \quad (1)$$

where $\exp_\pm[\cdots]$ are the time-ordered exponentials in which the operators in $[\cdots]$ are arranged in chronological order and $\hat{\rho}_{tot}(t_0)$ is an initial state normalized as $\text{tr}\{\hat{\rho}_{tot}(t_0)\} = 1$. The expectation value for any operator $\hat{A}$ is defined as $\langle\hat{A}\rangle = \text{tr}\{\hat{A}\hat{\rho}_{tot}(t)\}$. The change in the total energy is expressed as

$$\Delta U_{tot}(t) = \langle\hat{H}_{tot}(t)\rangle - \langle\hat{H}_{tot}(t_0)\rangle. \quad (2)$$

Because we have $\text{tr}\{[\hat{H}_{tot}(t),\hat{H}_{tot}(t)]\hat{\rho}_{tot}(t)\} = 0$, the time derivative of the above equation is evaluated as

$$\frac{d}{dt}\Delta U_{tot}(t) = P_{tot}(t), \quad (3)$$

where $P_{tot}(t) \equiv \text{tr}\{(\partial\hat{H}_{tot}(t)/\partial t)\hat{\rho}_{tot}(t)\}$. Thus, the conservation law of the total energy is expressed as

$$\Delta U_{tot}(t) = W_{tot}(t), \quad (4)$$

where

$$W_{tot}(t) = \int_{t_0}^{t}dt'\text{tr}\left\{\frac{\partial\hat{H}_{tot}(t')}{\partial t'}\hat{\rho}_{tot}(t')\right\}. \quad (5)$$

The work here is defined as the change in energy from one state to another under a time-dependent perturbation. This work is attributed to external perturbations. The above equality represents

the relationship between the work and the total energy in any Hamiltonian $\hat{H}_{tot}(t)$ and is not restricted to thermodynamic systems characterized by temperature.

B. Internal energy

To introduce thermodynamic temperature in the framework of open quantum dynamics theory, we next consider a quasi-static process in which the system changes slowly under weak external perturbation while maintaining a quasi-equilibrium state. Thus, we assume that the total system is described by the quasi-equilibrium partition function (qPF), which is defined as $Z_{tot}(t) = tr\{\exp[-\beta\hat{H}_{tot}(t)]\}$.[11–17] We then have

$$\frac{\partial \ln Z_{tot}(t)}{\partial t} = -\beta tr\left\{\frac{\partial \hat{H}_{tot}(t)}{\partial t}\hat{\rho}_{tot}(\beta;t)\right\}, \tag{6}$$

where $\hat{\rho}_{tot}(\beta;t) \equiv \exp[-\beta\hat{H}_{tot}(t)]/Z_{tot}(t)$. Thus, we define

$$\ln\left(\frac{Z_{tot}(t)}{Z_{tot}(t_0)}\right) = -\beta\Delta F_{tot}(\beta;t), \tag{7}$$

where

$$\Delta F_{tot}(\beta;t) \equiv \int_{t_0}^{t}dt'\, tr\left\{\frac{\partial \hat{H}_{tot}(t')}{\partial t'}\hat{\rho}_{tot}(\beta;t')\right\} \tag{8}$$

is the qHE.[35,36] The significant difference between the qHE and the conventional free energy is that the qHE involves time-dependent work done for the system and is thus a time-dependent function. Therefore, the qHE vanishes when there is no work.

For the inverse bath temperature β, the qHE and the work defined by Eq. (5) satisfy the minimum work principle expressed as[4,8,77]

$$W_{tot}(\beta;t) \geq \Delta F_{tot}(\beta;t), \tag{9}$$

which corresponds to the second law of thermodynamics. Although the above inequality has been derived for an isolated quantum system, it can also be applied to an SB system because the total system of an SB model is regarded as an isolated system (see Appendix A). As we will show below, we can utilize the above inequality for open quantum dynamics systems because the HEOM formalism allows us to evaluate the work and free energy not only for a reduced system but also for a bath.

In general, work is not a state variable, but as has been shown, it is the state variable in quasi-static processes where the equality sign holds.[35,36] Using the qPF-based density operator, we can evaluate the change in the total internal energy as

$$\Delta U_{tot}(\beta;t) = tr\{\hat{H}_{tot}(t)\hat{\rho}_{tot}(\beta;t)\} - tr\{\hat{H}_{tot}(t_0)\hat{\rho}_{tot}(\beta;t_0)\}, \tag{10}$$

which agrees with $\Delta U_{tot}(\beta;t) = \partial(\beta\Delta F_{tot}(\beta;t))/\partial\beta$. We can also evaluate the change in heat as $Q_{tot}(\beta;t) = \beta\partial\Delta F_{tot}(\beta;t)/\partial\beta$. From the above relations, the first law of thermodynamics can be expressed as

$$\Delta U_{tot}(\beta;t) = Q_{tot}(\beta;t) + W_{tot}(\beta;t), \tag{11}$$

where we used $W_{tot}(\beta;t) \equiv \Delta F_{tot}(\beta;t)$ from the definition in Eq. (5). From Eq. (4) under the quasi-equilibrium condition, we have

$$\Delta U_{tot}^{qeq}(\beta;t) = \Delta U_{tot}(\beta;t) - Q_{tot}(\beta;t), \tag{12}$$

which indicates that the difference between the system energy and the internal energy is the heat $Q_{tot}(\beta;t)$.

III. OPEN QUANTUM DYNAMICS THEORY FOR THERMODYNAMICS

A. System–bath model for isothermal–adiabatic transitions

To proceed one step, we consider an SB model to compute the thermodynamic variables. The total Hamiltonian is expressed as $\hat{H}_{tot}(t) = \hat{H}_A(t) + \hat{H}_I(t) + \hat{H}_B$, where $\hat{H}_A(t)$ and $\hat{H}_I(t)$ are the time-dependent Hamiltonians of the main system and the SB interaction, respectively, and $\hat{H}_B$ is the Hamiltonian of the bath. The time dependences of $\hat{H}_A(t)$ and $\hat{H}_I(t)$ are, respectively, described by the isothermal driving field (IDF) and the adiabatic transition field (ATF), which are represented by $B(t)$ and $A(t)$, respectively. By choosing $B(t)$ and $A(t)$, a real experimental situation can be simulated.[66–75] Later, IDF and ATF are given explicit forms when conducting numerical simulations.

We employ a heat bath modeled by an ensemble of harmonic oscillators,

$$\hat{H}_B = \sum_{j=1}^{N}\left(\frac{\hat{p}_j^2}{2m_j} + \frac{1}{2}m_j\omega_j^2\hat{x}_j^2\right), \tag{13}$$

with the momentum, position, mass, and frequency of the jth bath oscillator given by $\hat{p}_j$, $\hat{x}_j$, m_j, and ω_j, respectively. To describe the transition between the isothermal and adiabatic processes, we consider the SB interaction expressed as

$$\hat{H}_I(t) = A(t)\hat{V}\sum_{j=1}^{N}c_j\hat{x}_j, \tag{14}$$

where $\hat{V}$ is the system part of the interaction and c_j is the jth coupling constant. With a proper choice of $A(t)$, $\hat{V}$, and the spectral distribution of the bath coupling, a variety of isothermal–adiabatic manipulations (e.g., the insertion and exertion of the adiabatic wall or attaching or removing the quantum system to the bath) can be performed.

The open quantum dynamics theory utilizes the reduced density operator (RDO) assuming that the heat bath is in the thermal equilibrium state at β. When the bath part of the SB interaction is a linear function of the bath coordinates, as in Eq. (14), we can eliminate the bath degrees of freedom by performing the Gaussian integrations involved in the bath Hamiltonian. This leads to the following reduced description of the system operator:

$$\hat{\rho}_A^{rd}(t) = \frac{tr_B\{\hat{\rho}_{tot}(t)\}}{Z_B^0(\beta)}, \tag{15}$$

where the denominator $Z_B^0(\beta) = tr_B\{\exp[-\beta\hat{H}_B]\}$ is introduced to maintain the reduced operator in a finite value and the RDO is normalized as $tr_A\{\hat{\rho}_A^{rd}(t)\} = 1$.

Due to the bosonic nature of the bath, all bath effects on the system are determined by the bath correlation function $C(t) \equiv \langle \hat{X}(t)\hat{X}(0)\rangle_B$, where $\hat{X} \equiv \sum_j c_j \hat{x}_j$ is the collective coordinate of the bath and $\langle \cdots \rangle_B$ represents the average taken with respect to the canonical density operator of the bath. The bath correlation function is expressed in terms of the bath spectral density $J(\omega)$ as

$$C(t) = \int_0^\infty d\omega J(\omega)\left[\coth\left(\frac{\beta\hbar\omega}{2}\right)\cos(\omega t) - i\sin(\omega t)\right], \quad (16)$$

where $J(\omega) \equiv \sum_{j=1}^N (\hbar c_j^2/2m_j\omega_j)\delta(\omega - \omega_j)$. The real part of Eq. (16) is analogous to the classical correlation function of the bath and represents the fluctuations, while its imaginary part represents the dissipation. The fluctuation term is related to the dissipation term through the quantum version of the fluctuation—dissipation theorem.[31,34,78] For the heat bath to be an unlimited heat source with an infinite heat capacity, the number of heat bath oscillators N can be made infinitely large by replacing $J(\omega)$ with a continuous distribution.

We should note that in the framework of regular open quantum dynamic theories, the energy conservation law in Eq. (4) does not hold due to the reduced description of the density operator $\hat{\rho}_{tot}(t)$. For example, without the external force [i.e., $\hat{H}_{tot}(t) = \hat{H}_{tot}$], the total system reaches the equilibrium state $\hat{\rho}_{tot}^{eq} = \exp[-\beta\hat{H}_{tot}]$ for sufficiently long t, even if we start from a non-equilibrium initial condition expressed as $\hat{\rho}_{tot}(t_0) = \hat{\rho}_A(t_0)\exp[-\beta\hat{H}_B]$, where $\hat{\rho}_A(t_0)$ is a highly excited initial state of the system. This indicates that we have $\Delta U_{tot}(t) \neq 0$ for a dissipative system; in contrast, from Eq. (2), we have $\Delta U_{tot}(t) = 0$ for the total system. In open quantum dynamics theory, this phenomenon arises because we have reduced the degrees of freedom of the heat bath prior to the total system evolving in time. Thus, to apply the qPF theory introduced in Sec. II B to the SB model, we must extend the reduced dynamics theory to separately evaluate the energy flow to the bath.

B. HEOM

We now introduce the HEOM formalism that plays a key role in the present quantum thermodynamic investigations. In the HEOM formalism, the set of equations of motion consists of the auxiliary density operators (ADOs).[31–38,78–80] Here, we consider the case that the bath correlation function [Eq. (16)] is written as a linear combination of exponential functions, $C(t) = \sum_{l=0}^K \zeta_l e^{-\nu_l|t|}$, where ν_l and ζ_l are, respectively, the frequency and the strength obtained from a Padé spectral decomposition scheme to reduce the hierarchy size.[81] The ADOs introduced in the HEOM are defined by the index $\vec{n} = (n_0, n_1, \ldots, n_K)$, where n_l takes an integer value zero and above. The zeroth ADO for which all elements are zero, $\vec{0} = (0, 0, \ldots, 0)$, corresponds to the actual RDO, $\hat{\rho}_A^{rd}(t) = \hat{\rho}_{\vec{0}}(t)$, and we normalize the RDO as $\mathrm{tr}_A\{\hat{\rho}_{\vec{0}}(t)\} = 1$. The SB coupling strength of the equations of motion for the ADOs depends on time. The HEOM are then expressed as

$$\frac{\partial}{\partial t}\hat{\rho}_{\vec{n}}(t) = \left(-\frac{i}{\hbar}\hat{H}_A^\times(t) - \sum_{l=0}^K n_l\nu_l\right)\hat{\rho}_{\vec{n}}(t)$$
$$- \frac{iA(t)}{\hbar}\sum_{l=0}^K n_l\hat{\Theta}_l\hat{\rho}_{\vec{n}-\vec{e}_l}(t) - \frac{iA(t)}{\hbar}\hat{V}^\times\sum_{l=0}^K \hat{\rho}_{\vec{n}+\vec{e}_l}(t), \quad (17)$$

where $\vec{e}_l$ is the $(K+1)$-dimensional unit vector. The operators are defined as

$$\hat{\Theta}_0 = \left(\frac{\gamma}{\beta} + \sum_{l=1}^K \frac{\zeta_l}{\gamma^2}\beta\frac{2\gamma}{\gamma^2 - \nu_l^2}\right)\hat{V}^\times - \frac{i\hbar\gamma^2}{2}\hat{V}^\circ, \quad (18)$$

and

$$\hat{\Theta}_l = -\frac{\zeta_l\gamma^2}{\beta}\frac{2\nu_l}{\gamma^2 - \nu_l^2}\hat{V}^\times \quad (l \in \{1, 2, \ldots, K\}), \quad (19)$$

where $\hat{\mathcal{O}}^\times\hat{\mathcal{P}} = [\hat{\mathcal{O}}, \hat{\mathcal{P}}]$ and $\hat{\mathcal{O}}^\circ\hat{\mathcal{P}} = \{\hat{\mathcal{O}}, \hat{\mathcal{P}}\}$ for arbitrary operators $\hat{\mathcal{O}}$ and $\hat{\mathcal{P}}$.

In principle, the HEOM provide an asymptotic approach to calculate various physical quantities with any desired accuracy by adjusting the number of hierarchal elements determined by K, and the error introduced by the truncation is negligibly small in the case that K is sufficiently large.[34]

C. Physical variables

1. System energy and work

First, we evaluate the change in the energy of each part of the Hamiltonian, which is defined as $U_\alpha(t) = \mathrm{tr}\{\hat{H}_\alpha(t)\hat{\rho}_{tot}(t)\}$ for $\alpha = A, I$, and B, with $\hat{\rho}_{tot}(t)$ given by Eq. (1).

Although the evaluations of $U_I(t)$ and $U_B(t)$ are not easy within the framework of the open quantum dynamics theory because the bath degrees of freedom have been reduced, we can obtain their values indirectly by using the hierarchical elements in the HEOM formalism. This is because, in the HEOM formalism, the higher hierarchical elements store information about the higher cumulant of the bath coordinates, as previously demonstrated.[35–39]

We express the HEOM elements obtained from Eq. (17) under any form of external field as $\hat{\rho}_{\vec{n}}(t)$. Using the zeroth member of the hierarchy $\hat{\rho}_{\vec{0}}(t)$, the expectation value of the system energy at time t is evaluated as

$$U_A(t) = \mathrm{tr}_A\{\hat{H}_A(t)\hat{\rho}_{\vec{0}}(t)\}. \quad (20)$$

In the HEOM formalism, the first-order hierarchical elements $\hat{\rho}_{\vec{e}_l}(t)$ $(0 \leq l \leq K)$ are defined as the expectation value of the collective bath coordinate $\hat{X}$. Thus, from Eq. (14), the SB interaction energy is expressed as[35–38]

$$U_I(t) = A(t)\sum_{l=0}^K \mathrm{tr}_A\{\hat{V}\hat{\rho}_{\vec{e}_l}(t)\}, \quad (21)$$

where $\vec{e}_l$ is the index for the first-order hierarchical member. To evaluate the bath energy, we consider the expectation value of bath energy defined as $U_B(t) \equiv \mathrm{tr}\{\hat{H}_B\hat{\rho}_{tot}(t)\}$ and evaluate the change in the bath energy from $\partial U_B(t)/\partial t = i\int_{t_0}^t \mathrm{tr}\{[\hat{H}_I, \hat{H}_B]\hat{\rho}_{tot}(t)\}dt/\hbar$, which is obtained from $\partial\hat{\rho}_{tot}(t)/\partial t = [\hat{H}_{tot}(t), \hat{\rho}_{tot}(t)]/i\hbar$. The bath energy is then evaluated as (see Appendix B)

$$\frac{\partial}{\partial t}U_B(t) = A(t)\sum_{l=0}^K \nu_l\mathrm{tr}_A\{\hat{V}\hat{\rho}_{\vec{e}_l}(t)\} + A^2(t)\gamma^2\mathrm{tr}_A\{\hat{V}^2\hat{\rho}_{\vec{0}}(t)\}. \quad (22)$$

The total work is evaluated as

$$W_{tot}(t) = W_A(t) + W_I(t), \tag{23}$$

where

$$W_A(t) = \int_{t_0}^{t} dt' \, \text{tr}_A \left\{ \frac{\partial \hat{H}_A(t')}{\partial t} \hat{\rho}_{\vec{0}}(t') \right\} \tag{24}$$

and

$$W_I(t) = \int_{t_0}^{t} dt' \frac{dA(t')}{dt'} \sum_{l=0}^{K} \text{tr}_A \{ \hat{V} \hat{\rho}_{\vec{e}_l}(t') \}. \tag{25}$$

Thus, we have $\Delta U_{tot}(t) = \Delta U_A(t) + \Delta U_I(t) + \Delta U_B(t)$, where $\Delta U_\alpha(t) \equiv U_\alpha(t) - U_\alpha(t_0)$ for $\alpha = A, B, I$, and tot. The change in the total energy and the work evaluated from the HEOM now satisfy the energy conservation law in Eq. (4).

2. Free energies and partition functions

For the SB Hamiltonian, the RDO is expressed as Eq. (15). By using the above definition with the HEOM, the work and internal energy changes are calculated numerically and rigorously for any thermal cycle driven by the IDF and ATF regardless of the condition in Eq. (9). Nevertheless, we limit our discussion to the quasi-static case and attempt to quantify the quantum thermodynamic variables by comparing physical quantities calculated in the HEOM with thermodynamic quantities evaluated in the qHE formalism. Then, the reduced qPF operator is assumed to be of the form $\hat{Z}_{A+I}^{rd}(\beta;t) = tr_B \{ \exp[-\beta \hat{H}_{tot}(t)] \} / Z_B^0(\beta)$, which has been evaluated as $\hat{Z}_{A+I}^{rd}(\beta;t) = \exp[-\beta \hat{H}^*(t)]$, with $\hat{H}^*(t)$ being referred to as the Hamiltonian of mean force or effective Hamiltonian.[15–17] Then, we have $Z_{tot}(\beta;t) = Z_{A+I}^{rd}(\beta;t) Z_B^0(\beta)$, where $Z_{A+I}^{rd}(\beta;t) = tr_A \{ \hat{Z}_{A+I}^{rd}(\beta;t) \}$. In this study, we evaluate Z_{tot} from the HEOM approach, including a contribution from the SB coupling using Eq. (25). We define the RDO for the PF as $\hat{\rho}_{tot}(\beta;t) \equiv \exp[-\beta \hat{H}_{tot}(t)] / Z_{tot}(\beta;t)$ and $\hat{\rho}_A^{rd}(\beta;t) \equiv tr_B \{ \exp[-\beta \hat{H}_{tot}(t)] \} / Z_{tot}(\beta;t)$. Accordingly, we evaluate Eq. (7) as

$$\ln \left(\frac{Z_{A+I}^{rd}(\beta;t)}{Z_{A+I}^{rd}(\beta;t_0)} \right) = -\beta \Delta F_{A+I}^{rd}(\beta;t), \tag{26}$$

where $\Delta F_{A+I}^{rd}(\beta;t)$ is the reduced free energy. From Eqs. (24) and (25), we have

$$\Delta F_{A+I}^{rd}(\beta;t) = \Delta F_A^{qst}(\beta;t) + \Delta F_I^{qst}(\beta;t), \tag{27}$$

where

$$\Delta F_A^{qst}(\beta;t) = \int_{t_0}^{t} dt' \, \text{tr}_A \left\{ \frac{\partial \hat{H}_A(t')}{\partial t} \hat{\rho}_{\vec{0}}^{qst}(t') \right\} \tag{28}$$

and

$$\Delta F_I^{qst}(\beta;t) = \int_{t_0}^{t} dt' \frac{dA(t')}{dt'} \sum_{l=0}^{K} \text{tr}_A \{ \hat{V} \hat{\rho}_{\vec{e}_l}^{qst}(t') \}. \tag{29}$$

From the above equations, we define $\Delta U_\alpha^{rd}(\beta;t) \equiv \partial(\beta \Delta F_\alpha^{qst}(\beta;t)) / \partial \beta$ and $\Delta S_\alpha^{rd}(\beta;t) \equiv k_B \beta^2 \partial \Delta F_\alpha^{qst}(\beta;t) / \partial \beta$ for $\alpha = A$ and I. Note that we introduced the suffix rd in addition to qst because $\Delta U_A^{rd}(\beta;t)$ involves the contribution from the system part of the SB interaction, as we briefly explain in Sec. III C 3.[36] Using the qHE, we can introduce the conjugate variables of the IDF and ATF as

$$M(\beta;t) \equiv -\frac{\partial \Delta F_A^{qst}(\beta;t)}{\partial B(t)} \tag{30}$$

and

$$D(\beta;t) \equiv -\frac{\partial \Delta F_I^{qst}(\beta;t)}{\partial A(t)}, \tag{31}$$

where $B(t)$ and $A(t)$ represent, for example, the magnetic field and stress, respectively, whereas $M(\beta; t)$ and $D(\beta; t)$ represent, for example, the magnetization and strain, respectively. From the definition of the total work Eq. (5), we can evaluate the above variables in terms of the ADOs as

$$M(\beta;t) = \text{tr}_A \{ \hat{\sigma}_z \hat{\rho}_{\vec{0}}(t) \} \tag{32}$$

and

$$D(\beta;t) = -\sum_{l=0}^{K_k} \text{tr}_A \left\{ \hat{V} \hat{\rho}_{\vec{e}_l^k}(t) \right\}. \tag{33}$$

Note that $M(\beta; t)$ and $D(\beta; t)$ are the state variables in the quasi-static case because they are uniquely determined by the state specified by the quasi-equilibrium distribution at t and are independent of the pathway of work. As described in Eq. (11), we have the first law of thermodynamics for each component $\alpha = A$ and I as

$$\Delta U_\alpha^{rd}(\beta;t) = T \Delta S_\alpha^{rd}(\beta;t) + W_\alpha^{qst}(\beta;t), \tag{34}$$

where

$$W_A^{qst}(\beta;t) = -\int_{t_0}^{t} \frac{dB(t')}{dt'} M(\beta;t') dt' \tag{35}$$

and

$$W_I^{qst}(\beta;t) = -\int_{t_0}^{t} \frac{dA(t')}{dt'} D(\beta;t') dt'. \tag{36}$$

For $\Delta U_{A+I}^{rd}(\beta;t) = \Delta U_A^{rd}(\beta;t) + \Delta U_I^{rd}(\beta;t)$, $Q_{A+I}^{rd}(\beta;t) = T \Delta S_{A+I}^{rd}(\beta;t)$ with $\Delta S_{A+I}^{rd}(\beta;t) = \Delta S_A^{rd}(\beta;t) + \Delta S_I^{rd}(\beta;t)$, and $W_{tot}(\beta;t) = W_A^{qst}(\beta;t) + W_I^{qst}(\beta;t)$, we have

$$\Delta U_{A+I}^{rd}(\beta;t) = Q_{A+I}^{rd}(\beta;t) + W_{tot}(\beta;t). \tag{37}$$

Here, work is defined by the quasi-static change in the total energy under time-dependent perturbation. This work is regarded as thermodynamic work. When the main system consists of n non-interacting spins that are independently coupled to the heat bath, the magnitude of $\Delta U_{A+I}^{rd}(\beta;t)$, $Q_{A+I}^{rd}(\beta;t)$, $\Delta S_{A+I}^{rd}(\beta;t)$, $W_{tot}(\beta; t)$,

$M(\beta; t)$, and $D(\beta; t)$ are proportional to n. Thus, they are extensive properties, whereas $B(t)$, $A(t)$, and T are intensive properties.

Using the qHE, we can also define the reduced PF for $\alpha = A$ and I as

$$Z_\alpha^{qst}(\beta; t) = \exp[-\beta \Delta F_\alpha^{qst}(\beta; t)]Z_\alpha^{qst}(\beta; t_0). \tag{38}$$

The total PF is then expressed as $Z_{tot}(\beta; t) = Z_{A+I}^{rd}(\beta; t)Z_B^0(\beta)$, where $Z_{A+I}^{rd}(\beta; t) = Z_A^{qst}(\beta; t)Z_I^{qst}(\beta; t)$, which is consistent with Eq. (37) for $W_{tot}(t) = \Delta F_{A+I}^{rd}(t)$. However, from the above, we have $\Delta U_{tot}(\beta; t) = \Delta U_{A+I}^{rd}(\beta; t)$ and $Q_{tot}(\beta; t) = Q_{A+I}^{rd}(\beta; t)$, which contradicts the first law of thermodynamics for the total system presented in Eq. (11). To illustrate this point, we consider the change in the internal energy of each Hamiltonian component defined as

$$\Delta U_\alpha^{qst}(\beta; t) \equiv U_\alpha^{qst}(\beta; t) - U_\alpha^{qst}(\beta; t_0), \tag{39}$$

where $U_\alpha^{qst}(\beta; t)$ is evaluated from Eqs. (20)–(22) with the use of $\hat{\rho}_{\bar{n}}^{qst}(t)$ for $\alpha = A, B$, and I. The total internal energy is then given by

$$\Delta U_{tot}(\beta; t) = \Delta U_A^{qst}(\beta; t) + \Delta U_I^{qst}(\beta; t) + \Delta U_B^{qst}(\beta; t), \tag{40}$$

whereas we obtain $\Delta U_{tot}^{rd}(\beta; t) = \Delta U_A^{rd}(\beta; t) + \Delta U_I^{rd}(\beta; t)$ from $Z_{tot}(\beta; t) = Z_{A+I}^{rd}(\beta; t)Z_B^0(\beta)$, with $\Delta U_{tot}^{rd}(\beta; t) = -\partial \ln Z_{tot}(\beta; t)/\partial \beta$. What is missing here is the change in the bath internal energy evaluated from Eq. (22). This difference arises because the reduced description of the system cannot evaluate the change in the bath energy, whereas the HEOM formalism can include the change in bath energy from Eq. (22).

3. Reduced heat bath energy

To illustrate the above point, we consider the isothermal and the adiabatic transition processes for $B(t)$ and $A(t)$.[35,36] Then, we have $Z_{tot}(\beta; t) = Z_A^{qst}(\beta; t)Z_I^{qst}(\beta; t)Z_B^0(\beta)$, which leads to $\Delta U_{tot}(\beta; t) = \Delta U_{A+I}^{rd}(\beta; t)$ when we differentiate both sides with regard to β. This indicates that there is no heat flow between the system and the bath, due to the constraints of the reduced description of the system, even when we consider the non-equilibrium situation. Then, as illustrated in Eq. (40), we must compensate for the change in the SB interaction energy using the HEOM formalism.

It is important to note that we have $|\Delta U_{A+I}^{rd}(\beta; t) - \Delta U_{A+I}^{qst}(\beta; t)| \neq 0$ because $\Delta U_{A+I}^{rd}(\beta; t)$ does not include the contribution from the bath part of the SB interaction due to the reduced description of the system.[36] Then, we separate the system part of the SB interaction as $\Delta U_I^A(\beta; t) \equiv \Delta U_{A+I}^{rd}(\beta; t) - \Delta U_A^{qst}(\beta; t)$. The bath part of the internal energy in the SB interaction is expressed as $\Delta U_I^B(\beta; t) \equiv \Delta U_I^{qst}(\beta; t) - \Delta U_I^A(\beta; t)$. Thus, we have the change in the internal energy of the reduced bath system, which is expressed as

$$\Delta U_B^{rd}(\beta; t) = \Delta U_I^B(\beta; t) + \Delta U_B^{qst}(\beta; t). \tag{41}$$

Because there is no external force on the bath, the qHE for the reduced bath vanishes [i.e., $\ln(Z_B^{rd}(t)/Z_B^{rd}(t_0)) = 0$]. Thus, we have

$$\Delta U_B^{rd}(\beta; t) = Q_B^{rd}(\beta; t). \tag{42}$$

Since $Q_{tot}(\beta; t) = Q_{A+I}^{rd}(\beta; t) + Q_B^{rd}(\beta; t) = 0$, the first law of thermodynamics for the total system is expressed as

$$\Delta U_{tot}(\beta; t) = W_{tot}(t), \tag{43}$$

where $\Delta U_{tot}(\beta; t) = \Delta U_{A+I}^{rd}(\beta; t) + \Delta U_B^{rd}(\beta; t)$ and $W_{tot}(\beta; t) = W_{A+I}^{qst}(\beta; t) = \Delta F_{A+I}^{rd}(\beta; t)$. Although a similar expression has been employed in a perturbative Markovian case in which $\Delta U_B^{rd}(\beta; t) \approx \Delta U_B(\beta; t)$,[12,13] the present expression is valid even in a non-Markovian and nonperturbative case. For the bath part of heat $Q_B(\beta; t) = \Delta U_I^B(\beta; t) + \Delta U_B(\beta; t)$, we thus obtain the total entropy production as

$$\Sigma_{tot}(\beta; t) = \Delta S_A^{rd}(\beta; t) + \beta Q_B^{rd}(\beta; t). \tag{44}$$

It should be noted that when considering the thermodynamic properties of A, we can ignore the effects of the bath.

Note that for the situation that describes a thermal transition from an adiabatic state to an isothermal state described by the fixed IDF $B(t) = B_0$ with the ATF $A(t)$, the work $W_I^{qst}(\beta; t)$ of inserting or removing the adiabatic wall that applies to both the system and the bath plays a role. The heat $Q_{tot}(\beta; t)$ is generated during the manipulation of the adiabatic wall, indicating that Maxwell's demon[82,83] for thermal processes also obeys the thermodynamic law.

IV. NUMERICAL RESULTS

To demonstrate the roles of the isothermal and adiabatic transition processes, we conducted numerical simulations for a spin system expressed as

$$\hat{H}_A(t) = -B(t)\hat{\sigma}_z, \tag{45}$$

where $B(t)$ is the IDF and $\hat{\sigma}_\alpha$ ($\alpha = x, y$, and z) are the Pauli matrices. In the case of nuclear magnetic resonance spectroscopy, $B(t)$ corresponds to the longitudinal magnetic field. The time-dependent SB interaction is controlled by the ATF $[A(t)]$.

To construct the HEOM presented in Eq. (17), we assume the Drude spectral distribution function given by

$$J(\omega) = \frac{\hbar}{\pi} \frac{\gamma^2 \omega}{\gamma^2 + \omega^2}, \tag{46}$$

where γ is the inverse noise correlation time of the bath, and we set $\hat{V} = \hat{\sigma}_x$. We fix the inverse of the noise correlation time to $\gamma = 1.0$ and use this as the frequency unit for the system. Then, we employ a Padé spectral decomposition scheme to obtain the expansion coefficients of the noise correlation functions.

Next, we consider three cases: (a) the high-temperature case ($\beta\hbar = 0.2$), (b) the intermediate-temperature case ($\beta\hbar = 1.0$), and (c) the low-temperature case ($\beta\hbar = 5.0$). We then choose the truncation number of hierarchy, which represents the depth of the HEOM computation, as $N = 6$. We set the maximum number of

hierarchy levels to $K = 4$ for $\beta\hbar = 0.2$ and 1.0 and $K = 7$ for $\beta\hbar = 5.0$. Starting from a temporal initial state, we integrate Eq. (17) until the cycle of the simulation reaches the steady state with the time-dependent functions $B(t)$ and $A(t)$. We set the period of one stroke as $\tau = 10\,000$ so that the motion of the system is quasi-static. We use the fourth-order Runge–Kutta method with a time step of $\delta t = 1.0 \times 10^{-2}$.

We conducted the simulation for a three-stroke engine (a Kelvin–Planck cycle) consisting of (i) isothermal expansion, (ii) isothermal–adiabatic transition, and (iii) the combination of isothermal compression and adiabatic–isothermal transition [described by $B(t)$ and $A(t)$ in Table I with amplitudes of $B_0 = 0.5$ and $A_0 = 1.0$, respectively]. To elucidate the characteristics of the cyclic process, we constructed thermodynamic work diagrams for external forces and their conjugate variables as the B–M and A–D diagrams analogous to the P–V diagram. Figure 1 depicts the B–M (left) and A–D (right) diagrams for different inverse temperatures. The processes in the B–M diagrams evolve in a clockwise fashion over time, whereas those in the A–D diagrams evolve in a counter-clockwise manner. In comparison with the P–V diagram for an ideal gas, the rotational directions in the B–M and A–D diagrams are opposite because the ideal gas is described by $dU = TdS - PdV$, whereas here we have $dU = TdS + BdM + AdD$. The area enclosed by the curves corresponds to the work, but a counterclockwise cycle represents positive work, which is also opposite to the P–V case.

In this model, $B(t)$ represents the excitation energy of the spin. Then, as $B(t)$ increases, the spin is aligned with the ground state, so the magnetization $M(\beta; t)$ increases. Since the SB interaction with $\hat{V} = \hat{\sigma}_x$ excites the spins, as $A(t)$ increases, $M(\beta; t)$ decreases, even if $B(t)$ does not change, as shown by the blue horizontal line in the B–M diagram. Similarly, an increase in $B(t)$ suppresses the spin excitation effect of $A(t)$, so $D(\beta; t)$ decreases even if $A(t)$ does not change, as shown by the red horizontal line in the A–D diagram.

Here, the areas surrounded by the counter-clockwise curves are positive work (a heat engine), whereas those surrounded by the clockwise curves are negative work (a refrigerator). This indicates that the IDF and ATF described in Table I drive the system as a refrigerator and heat engine, respectively. The size of each area is determined mainly by the adiabatic transition (the horizontal blue line) in the case of the B–M diagrams and by the isothermal transition (the horizontal red line) in the case of the A–D diagrams. As the temperature decreases, the area becomes larger because the efficiency of the energy change under a given external force improves as the internal energy decreases. Thus, we find that the areas in the B–M and A–D diagrams are identical at each temperature, and
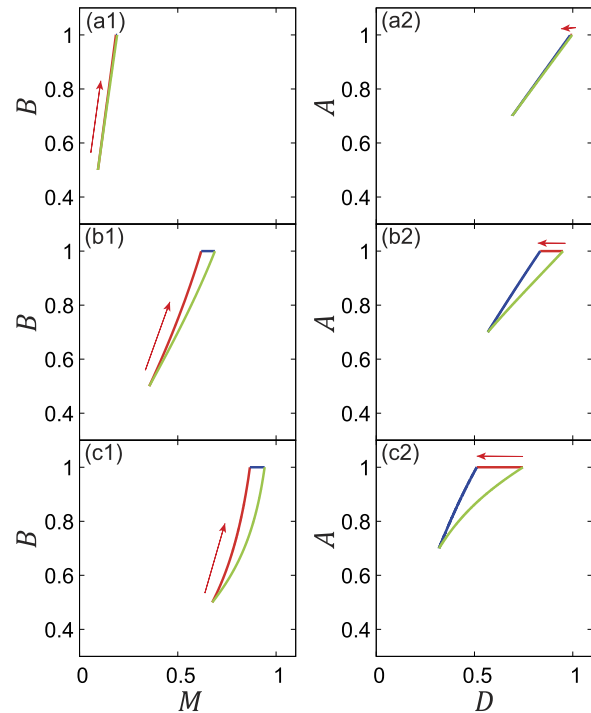

FIG. 1. B–M diagrams (left) and A–D diagrams (right) for the three-stroke heat-machine (a Kelvin–Planck cycle) described by the ATF $[A(t)]$ and IDF $[B(t)]$ in Table I at different temperatures: (a) $\beta\hbar = 0.2$ (high), (b) $\beta\hbar = 1.0$ (intermediate), and (c) $\beta\hbar = 5.0$ (low). In each figure, the cycle starts from the red arrow, and the three curves represent (i) isothermal expansion (red curves), (ii) adiabatic transition (blue curves), and (iii) the combination of isothermal compression and diabatic transition (green curves). The processes in the B–M diagrams evolve in a clockwise fashion over time (refrigerator), whereas the processes in the A–D diagrams evolve in a counter-clockwise fashion over time (heat engine). The areas in each B–M and A–D diagram are identical; thus, the work done for the system is zero (see Table II).

the work done for the system is zero within the numerical accuracy (see Table II) because we cannot subtract the energy from the heat machine with a single heat bath. This result demonstrates the Kelvin–Planck statement (or heat engine statement) of the second law of thermodynamics[4] in open quantum dynamics theory—it is impossible for any substance to derive the mechanical effects from a single heat source.

TABLE I. Time evolutions of IDF $[B(t)]$ and ATF $[A(t)]$ for a three-stroke heat machine (a Kelvin–Planck cycle) with equal time intervals τ. The cycle consists of (i) isothermal expansion, (ii) adiabatic transition, and (iii) the combination of isothermal compression and diabatic transition.

	$B(t)/|B_0|$	$A(t)/|A_0|$
(i)	$1.0 + t/\tau$	1.0
(ii)	2.0	$1.3 - 0.3t/\tau$
(iii)	$4.0 - t/\tau$	$0.1 + 0.3t/\tau$

TABLE II. System, interaction, and total quasi-static works per cycle (W_A^{qst}, W_I^{qst}, and $W_{tot}^{qst} = W_A^{qst} + W_I^{qst}$, respectively) at different inverse temperatures $\beta\hbar$.

$\beta\hbar$	W_A^{qst}	W_I^{qst}	W_{tot}^{qst}
0.2	1.34×10^{-3}	-1.33×10^{-3}	1.04×10^{-5}
1.0	1.71×10^{-2}	-1.71×10^{-2}	1.28×10^{-5}
5.0	2.68×10^{-2}	-2.69×10^{-2}	-1.19×10^{-4}

V. CONCLUSIONS

We investigated the thermodynamic properties of quantum dissipative systems based on the SB model by identifying the quasi-static work as the qHE. The key to investigating the non-equilibrium thermodynamic problem is the HEOM formalism, which enables the evaluation of the internal energies of not only the system but also the bath and the SB interaction, even under low-temperature, non-Markovian, and nonperturbative conditions, where the quantum effects become important. While the qHE was originally developed for an isothermal process, we extended it to treat an adiabatic transition process in a unified manner.

As a demonstration, we numerically simulated a three-stroke heat machine consisting of an isothermal process, an adiabatic process, and their combination. To analyze the results, the work diagrams with external fields and their conjugated variables were used. The results are consistent with the Kelvin–Planck statement of the second law of thermodynamics. This indicates that the thermodynamic rule is broken if the work of adiabatic wall manipulation described by the ATF is not taken into account, suggesting its importance. In the case of Markov limits, where the γ is large and the heat bath is hot, or in the case of perturbative approximations, where the interaction is weak, the effects of the ATF are expected to be less pronounced.

Although our demonstration was restricted to a simple model, this approach can be applied to investigate a variety of heat engines and refrigerators that consist of the isothermal and adiabatic processes. Moreover, while we analyzed only a quasi-static case, the present formalism can be applied to non-equilibrium situations by regarding the work as the non-equilibrium free energy. Numerically rigorous HEOM experiments on such systems can be a versatile means to formulate and verify quantum thermodynamics far from equilibrium. In the future, we plan to extend the present research to a study of the quantum Carnot cycle.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Shoki Koyanagi: Data curation (lead); Investigation (equal); Methodology (equal); Writing – original draft (lead). **Yoshitaka Tanimura:** Conceptualization (lead); Funding acquisition (lead); Investigation (lead); Methodology (equal); Project administration (lead); Resources (lead); Software (supporting); Supervision (lead); Validation (lead); Visualization (equal); Writing – original draft (supporting); Writing – review and editing (lead).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

APPENDIX A: THE MINIMUM WORK PRINCIPLE [EQ. (9)]

For an isolated quantum system described by the Hamiltonian $\hat{H}_0$ and the perturbed Hamiltonian $\hat{H}_{\delta t} = \hat{H}_0 + \delta\hat{H}$, we have an identity that leads to a quantum version of the Jarzynski equality expressed as[8,10,11,14]

$$\left\langle e^{-\beta\hat{H}_0^{(H)}(\delta t)} e^{\beta\hat{H}_0} \right\rangle = \frac{Z_{\delta t}}{Z_0}, \tag{A1}$$

where $\langle\cdots\rangle$ implies an average of appropriate sampling states; $Z_{\delta t}$ and Z_0 are the partition functions for $\hat{H}_{\delta t}$ and $\hat{H}_0$, respectively, at the inverse temperature β; and $\hat{H}_0^{(H)}(\delta t)$ is the Heisenberg operator of $\hat{H}_0$ whose time dependence is described by $\hat{H}_{\delta t}$.

The orthonormal basis set of $\hat{H}_0$ is expressed as $\{|i\rangle\}$ of $\hat{H}_0$. Then, we have inequality expressed as[4]

$$\langle i|e^{-\beta\hat{H}}|i\rangle \geq e^{\langle i|\hat{H}|i\rangle} \tag{A2}$$

for any Hermitian operator $\hat{H}$. This leads to

$$\left\langle e^{-\beta\hat{H}_0^{(H)}(\delta t)} e^{\beta\hat{H}_0} \right\rangle \geq \sum_i p_i e^{-\beta(\langle i|\hat{H}_0^{(H)}(\delta t)|i\rangle - E_i)}, \tag{A3}$$

where $E_i = \langle i|\hat{H}_0|i\rangle$ and $p_i = e^{-\beta E_i}/Z_0$. Using Jensen's inequality $\langle\exp[-\beta\hat{X}]\rangle \geq \exp[-\beta\langle\hat{X}\rangle]$, we have[8,16,77]

$$-\beta\left(\langle\hat{H}_0^{(H)}(\delta t)\rangle - \langle\hat{H}_0\rangle\right) \leq \ln Z_{\delta t} - \ln Z_0. \tag{A4}$$

Because our SB system is also an isolated system, the above inequality holds for $\hat{H}_{tot}(t)$ with the heat bath Eq. (13) consisting of N harmonic oscillators. Thus, we obtain

$$W_{tot}(\beta; t) \geq \Delta F_{tot}(\beta; t), \tag{A5}$$

which is the minimum work principle given by Eq. (9). Finally, taking the limit of $N \to \infty$, we obtain the description for the case of open quantum dynamics systems. In general, the above inequalities may not hold for reduced systems because both work and free energy are evaluated from a reduced system rather than from an isolated whole system; by using the HEOM formalism, the above inequality

TABLE III. The IDF $[B(t)]$ and ATF $[A(t)]$ as functions of t. Here, τ is the time duration, and the process approaches a quasi-static state when τ becomes large.

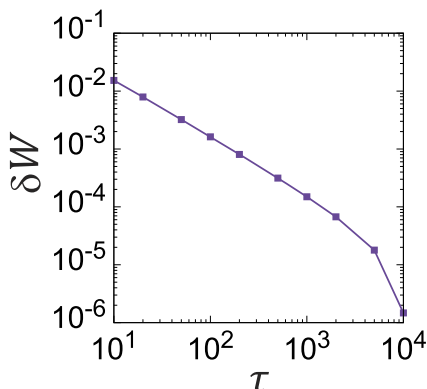| Time	$B(t)$	$A(t)$
$t < 0$	1.0	1.0
$0 \leq t < \tau$	$1.0 + t/\tau$	$1.0 - 0.3t/\tau$
$\tau \leq t$	2.0	0.7

FIG. 2. $\delta W(\tau) \equiv W_{tot}(\tau) - \Delta F_{tot}(\tau)$ plotted as a function of time duration τ. For any τ, $\delta W(\tau)$ is positive, indicating that the inequality Eq. (9) holds.

can be applied because contributions from the bath part of work and free energy can also be evaluated.

In Eq. (A5), the equal sign holds if the process is reversible (the minimum work principle). The quantity $\delta W(\beta; t) = W_{tot}(\beta; t) - \Delta F_{tot}(\beta; t)$ produced in the irreversible case is the work discarded as dissipative heat; in a quasi-static process, the energy loss due to dissipation is suppressed and $W_{tot}(\beta; t)$ approaches $\Delta F_{tot}(\beta; t)$.

Although Eq. (A5) for quantum finite systems has been proved, the mathematical proof for infinite systems is not complete at this time. Here, we conduct numerical calculations by using the HEOM, which are derived by reducing a heat bath with infinite degrees of freedom, and verified the results within the error range.

For the SB Hamiltonian, Eq. (9) has been examined numerically in the isothermal case.[36] Here, we extend it to the case of a mixture of isothermal and adiabatic transitions by using the system discussed in Sec. IV. To conduct the simulation, we set the IDF and ATF as in Table III. The non-equilibrium work $W_{tot}(\tau)$ is evaluated from Eq. (17) for various values of τ and fixed parameter values ($\gamma = 1.0, \beta\hbar = 1.0, N = 8, K = 4$, and $\delta t = 0.01$). Meanwhile, the equilibrium free energy $\Delta F_{tot}(\tau)$ is evaluated from the partition function obtained from the imaginary HEOM with $N = 6$ and $K = 10$ and the imaginary time step $\delta t = 0.0001$.[32] We plot $\delta W(\tau) \equiv W_{tot}(\tau) - \Delta F_{tot}(\tau)$ for different time scales of driving fields τ in Fig. 2. As shown in this figure, δF is always positive.

APPENDIX B: DERIVATION OF EQ. (22)

The time differentiation of the expectation value $\text{tr}_{tot}\{\hat{H}_{tot}(t)\hat{\rho}_{tot}(t)\}$ is expressed as

$$\frac{\partial U_B(t)}{\partial t} = W_{tot}(t) - \frac{\partial U_A(t)}{\partial t} - \frac{\partial U_I(t)}{\partial t}, \quad \text{(B1)}$$

where $W_{tot}(t)$ is defined in Eq. (23). Applying Eqs. (20) and (21) in Eq. (B1), we can rewrite Eq. (B1) as

$$\frac{\partial U_B(t)}{\partial t} = -\text{tr}_A\left\{\hat{H}_A(t)\frac{\partial \hat{\rho}_{\vec{0}}(t)}{\partial t}\right\} - A(t)\sum_{l=0}^{K}\text{tr}_A\left\{\hat{V}\frac{\partial \hat{\rho}_{\vec{e}_l}(t)}{\partial t}\right\}. \quad \text{(B2)}$$

The second term on the right-hand side of the above equation can be evaluated from Eq. (17). Thus, we obtain Eq. (22).

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