TOPICAL REVIEW — Statistical physics and complex systems

Nonequilibrium work equalities in isolated quantum systems*

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We briefly introduce the quantum Jarzynski and Bochkov–Kuzovlev equalities in isolated quantum Hamiltonian systems, including their origin, their derivations using a quantum Feynman–Kac formula, the quantum Crooks equality, the evolution equations governing the characteristic functions of the probability density functions for the quantum work, and recent experimental verifications. Some results are given here for the first time. We particularly emphasize the formally structural consistence between these quantum equalities and their classical counterparts, which are useful for understanding the existing equalities and pursuing new fluctuation relations in other complex quantum systems.

Keywords: nonequilibrium isolated quantum systems, work equality, probability density function of quantum work, quantum Feynman–Kac formula

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1. Introduction

According to the second law of thermodynamics,[1] for an arbitrary isothermal process that starts and ends in thermal equilibrium states, the work W done on the macroscopic system is always larger than or equal to the change of the free energy of the system, ΔG, and the equality only holds for a reversible process. With the statistical interpretation of the work, this statement is argued to be still valid even in small systems with significant fluctuation, i.e.,

$$\langle W\rangle \geq \Delta G, \tag{1}$$

where $\langle\,\rangle$ denotes an average over all nonequilibrium processes that the system has undergone during the time interval.

Although the work principle (1) was rigidly established and widely accepted in modern statistical physics and thermodynamics, the second law provides little information about the characteristics of the fluctuation of Eq. (1) far from the equilibrium regime. This situation was not changed until Jarzynski in 1997 found an important equality that is now called the Jarzynski equality (JE)[2,3]

$$\langle\, \mathrm{e}^{-\beta W}\rangle = \mathrm{e}^{-\beta\Delta G}, \tag{2}$$

where the nonequilibrium processes or trajectories of an isolated system in the phase space $\Gamma = (p,q)$ start from the thermal equilibrium state with Hamiltonian $H(\Gamma,0)$ at an inverse temperature β and then are completely controlled by a time-dependent Hamiltonian $H(\Gamma,t)$ up to the final time t_{f}. The work done by an external agent on the system is

$$W = \int_0^{t_{\mathrm{f}}} \partial_\tau H(\Gamma(\tau),\tau)\,\mathrm{d}\tau, \tag{3}$$

where $\Delta G = G(t_{\mathrm{f}}) - G(0)$, and $G(t)$ is the free energy of the system with the quenched Hamiltonian $H(\Gamma,t)$ at the same inverse temperature. Using Jensen's inequality, we can reobtain the inequality (1) from the equality (2). Several experiments including single-molecule manipulation techniques have confirmed this equality.[4–6] Intensive interest in the JE also revived another equality found by Bochkov and Kuzovlev (BKE)[7–10] in the 1970s, when they generalized the fluctuation–dissipation theorems (FDTs)[11–13] into the nonlinear case

$$\langle\, \mathrm{e}^{-\beta W_0}\rangle = 1. \tag{4}$$

In contrast to the JE, their concern is the system described by the bare Hamiltonian $H_0(\Gamma)$, which is perturbed by a dynamic driven field $X(t)$, i.e., the total Hamiltonian is $H(\Gamma,t) = H_0(\Gamma) - X(t)Q(\Gamma)$, where $Q(\Gamma)$ is a conjugate generalized coordinate.[14] Moreover, they defined an alterative work as

$$W_0 = \int_0^{t_{\mathrm{f}}} X(\tau)\dot{Q}(\Gamma(\tau))\,\mathrm{d}\tau, \tag{5}$$

where the dot denotes the time derivative $\mathrm{d}/\mathrm{d}\tau$. At time 0, the field $X(0)$ is zero and the system is at the thermal equilibrium with the Hamiltonian H_0 at the inverse temperature β. The BKE (4) immediately leads into an inequality $\langle W_0\rangle \geq 0$, which is nothing but the Kelvin–Planck statement of the second law. The two work equalities are generally not equivalent.[15,16] Following Jarzynski,[15] we denote Eqs. (3) and (5) as the inclusive work and exclusive work, respectively. These work equalities together with the celebrated fluctuation theorem found earlier by Evans *et al.*[17] in 1993 trigged the

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enthusiasm of research in the second law in small systems and the fluctuation of nonequilibrium processes, and finally led into a discovery of a series of exact and asymptotic equalities about statistics of various entropy production or dissipated work.[2,3,7–10,17–33] Now these results are all termed the fluctuation relations. Because the fluctuation relations are related to energy, dissipation, and information during the manipulation and control of small thermodynamic systems, they also attract considerable interdisciplinary interest, e.g., the molecular biophysics and nanoscience.[34–37]

With the clarification for the classical systems, in the past decade, extending the classical fluctuation relations into the nonequilibrium quantum regime has been attracting intensive interest and significant progresses have been achieved.[7–10,38–76] The major challenge of the generalization is that, the key concepts including various classical thermodynamic quantities and a classical mechanical picture have to be reconsidered very carefully in the quantum case. For instance, the meanings of the work, heat, and entropy production become ambiguous, whereas a very useful concept of the trajectory in the phase space does not even exist in quantum mechanics. Currently, these research efforts are still ongoing. By comparison, for the relatively simple isolated quantum systems, there is a clear consensus about the quantum-extended work equalities,[38,40,48,49,49,54] which is also the object of the current review.

There have existed many excellent reviews on the work equalities.[34,63,77–82] In particular, Campisil *et al.*[82] systematically reviewed the quantum work equalities just two years ago. Hence, it is very challenging for us to present another one with a very fresh perspective for the simple isolated quantum systems. Even though, we do so on the basis of the following several considerations. First, we want to introduce this very active field to the readers who are not experts but are still very interested. The isolated Hamiltonian systems are always the prime example for them.[83] Second, we organize this review by emphasizing the mathematical consistence of the work equalities in classical and quantum isolated systems. In our opinion, it is not only a formal interest, which is complementary to the review by Campisil *et al.*,[82] but also it provides a plausible scheme for finding new work equalities in other quantum systems.[67,69,70] Finally, the experimental verifications of quantum work equalities have obtained important progresses[85] very recently. We clearly see that this advancement brings the quantum work equalities and quantum measurement and information[85] together and creates a new research direction.[86–89]

The organization of this review is as follows. In Section 2, we rederive the classical work equalities from a point of view of irreversibility rather than by directly using the definitions of the work. We extend this idea into the isolated quantum systems in Section 3. In order to establish a quantum analogy with the classical trajectory-version work equalities, in Section 4 we present a quantum Feynman–Kac formula and obtain new expressions for the existing quantum work equalities. Section 5 is about the quantum Crooks equality. In Section 6, we introduce a method of computing the characteristic functions of the probability density functions (PDFs) of the quantum work by solving the evolution equations. In Section 7 we review recent experimental progresses in verifying the quantum work equalities. We conclude this review in Section 8.

2. Classical work equalities

There are usually two steps in deriving the classical JE and BKE,[2,3,7] namely, defining the work first and then proving that it satisfies some equalities. This scheme was also used in quantum regimes.[38–41,48,49,54,55] Although defining work is not a fundamental problem in the classical systems, the situation becomes very subtle in quantum mechanics.[41,55] It is worth pointing out that the work equalities including other fluctuation relations essentially arise from the irreversible characteristic of the nonequilibrium processes. Hence, defining the irreversibility rather than pursuing the definition of the work will be universal either in the classical systems or in the quantum systems. This idea has existed in the literature for a long time.[23,24,29,31,32,77,90–96] Here we use the idea to reobtain the equalities (2) and (4).

For the Jarzynski equality, as we mentioned previously, the system is initially at thermal equilibrium with the heat bath with the inverse temperature β. After time 0, the system is immediately disconnected from the bath (or keeps very weak interaction with the bath) and evolves under the Hamiltonian $H(\Gamma,t)$ up to the final time $t_{\rm f}$. We call this process the forward process. We may introduce the backward process with the time-reversed Hamiltonian

$$H_{\rm R}(\Gamma,s)=H(\tilde{\Gamma},t_{\rm f}-s)=H(\Gamma,t_{\rm f}-s), \tag{6}$$

where $\tilde{\Gamma}=(-p,q)$ and the new time parameter s is used to distinguish from the forward time t. We have assumed that the Hamiltonian is time-reversible at arbitrary time point as stated by the second equation of Eq. (6). For simplicity, we do not consider the case in the presence of magnetic field. Very importantly, we specifically assume that the backward process starts from another thermal equilibrium state with the Hamiltonian $H(\Gamma,t_{\rm f})$ at the inverse temperature β. Let the density functions of the forward and backward processes be ρ and $\rho_{\rm R}$, respectively. Since both the processes follow the Hamiltonian dynamics, according to the Liouville theorem, we have

$$\begin{aligned}\rho_{\rm R}(\tilde{\Gamma},t_{\rm f}) &= \rho_{\rm R}(\tilde{\Gamma}_{t_{\rm f}}(\Gamma),0)=\frac{{\rm e}^{-\beta H(\Gamma_{t_{\rm f}}(\Gamma),t_{\rm f})}}{Z(t_{\rm f})}\\ &= {\rm e}^{-\beta[H(\Gamma_{t_{\rm f}}(\Gamma),t_{\rm f})-H(\Gamma,0)]}\rho(\Gamma,0)\frac{Z(0)}{Z(t_{\rm f})},\end{aligned} \tag{7}$$

where $\Gamma_{t_f}(\Gamma)$ is the solution of Hamilton's equations at time t_f starting from the initial phase point Γ, and $Z(t)=\int e^{-\beta H(\Gamma,t)}d\Gamma=e^{-\beta G(t)}$ is the instantaneous partition function at time t. We may clearly see that the whole exponential term except for β, which can also be rewritten as Eq. (3), is the change of the energy of the isolated system along the specific process $\Gamma_\tau(\Gamma)$. Hence, it is the inclusive work done on the whole system described by $H(\Gamma,t)$.[15] Integrating both sides of Eq. (7) on Γ, we reobtain the classical JE (2).

The same procedure is also available for obtaining the classical BKE (4), where the Hamiltonian is $H(\Gamma,t) = H_0(\Gamma) - X(t)Q(\Gamma)$. The only change is that, although the backward process in this case is still under the control of the Hamiltonian defined by Eq. (6), its initial condition is the same as that of the forward process, i.e., the thermal equilibrium state with the Hamiltonian $H_0(\Gamma)$. Let the density function of the backward process be ρ_R^0, we have

$$\begin{aligned}\rho_R^0(\tilde{\Gamma},t_f) &= \rho_R^0(\tilde{\Gamma}_{t_f}(\Gamma),0) = \frac{e^{-\beta H_0(\Gamma_{t_f}(\Gamma))}}{Z(0)} \\ &= e^{-\beta[H_0(\Gamma_{t_f}(\Gamma))-H_0(\Gamma,0)]}\rho(\Gamma,0). \end{aligned} \quad (8)$$

It is not difficult to see that the exponential term except β, which can be rewritten as Eq. (5), is the change of the energy of the system described by the Hamiltonian $H_0(\Gamma)$. Hence, it is named the exclusive work W_0.[15] Integrating both sides of Eq. (8) on Γ leads to the classical BKE (4). The relationship between these two work definitions and work equalities for the classical systems have been discussed in detail.[15,16]

The careful reader may note that there is no sign of irreversibility in the above discussion. However, the irreversibility indeed comes from the preparation of the thermal equilibrium initial states.[79] For instance, in the JE case, in order to prepare the initial state of the backward process, at the final time of the forward process we have to fix the Hamiltonian function at time t_f and reconnect the system to the heat bath. A relaxation then occurs irreversibly up to the establishment of the thermal equilibrium state. One may prove that the dissipated work,[2] $\langle W\rangle - \Delta G$, is the total entropy production of the whole process including the relaxation.[95]

3. Quantum work equalities

The above derivations of the classical work equalities can be straightforwardly extended into the isolated quantum systems even if we do not know exactly what a quantum work means. Because we now consider the quantum physics, the classical Hamiltonian functions and the density functions are replaced by the Hamiltonian operators H and density operators ρ. In order to avoid too many notations, we use the same notations but without the phase coordinate Γ, which will not cause confusion in understanding. Analogous to the classical case, we first introduce the backward quantum process of the forward process with the Hamiltonian operator $H(t)$. Its Hamiltonian reads

$$H_R(s) = \Theta H(t_f - s)\Theta^{-1} = H(t_f - s), \quad (9)$$

where Θ is the time-reversal operator. Because the evolutions of both processes are unitary, according to the quantum Liouville theorem, we have

$$\begin{aligned}\rho_R(t_f) &= U_R(t_f)\rho_R(0)U_R^\dagger(t_f) \\ &= \Theta U^\dagger(t_f)\Theta^{-1}\frac{e^{-\beta H(t_f)}}{Z(t_f)}\Theta U(t_f)\Theta^{-1} \\ &= \Theta U^\dagger(t_f)e^{-\beta H(t_f)}U(t_f)e^{\beta H(0)}\rho(0)\Theta^{-1}\frac{Z(0)}{Z(t_f)}, \end{aligned} \quad (10)$$

where $U(t)$ and $U_R(s)$ are the time evolution operators of the forward and backward quantum processes, respectively. They satisfy a general relationship: $U_R(s) = \Theta U(t_f - s)U^\dagger(t_f)\Theta^{-1}$,[56,68] i.e., the microreversibility of the isolated quantum system.[82] Making traces of both sides, we reobtain the quantum Jarzynski equality (QJE) for the isolated system as[38–40]

$$\begin{aligned} e^{-\beta\Delta G} &= \mathrm{Tr}[U^\dagger(t_f)e^{-\beta H(t_f)}U(t_f)e^{\beta H(0)}\rho(0)] \\ &= \langle e^{-\beta H^H(t_f)}e^{\beta H(0)}\rangle, \end{aligned} \quad (11)$$

where the superscript H denotes the Heisenberg picture. The reasons why it is called an equality about the quantum work and why it is physically important will become explicit after we rewrite the right-hand side of the equality in the energy representation[97]

$$\begin{aligned}&\sum_{m_0,n_{t_f}} p_{eq}(m_0,0)\left|\langle n_{t_f}|U(t_f)|m_0\rangle\right|^2 e^{-\beta[\varepsilon_n(t)-\varepsilon_m(0)]} \\ &= \sum_{m_0,n_{t_f}} p_{eq}(m_0,0)p(n_{t_f},t_f|m_0,0)e^{-\beta w} = E[e^{-\beta w}], \end{aligned} \quad (12)$$

where the Hamiltonian $H(t)$ is assumed to have discrete transient eigenstates and eigenvalues: $H(t)|n_t\rangle = \varepsilon_n(t)|n_t\rangle$. Equation (12) presents a two energy measurement interpretation of Eq. (11). In the first measurement of the system, the outcome of the energy is one of the eigenvalues $\varepsilon_m(0)$ with the probability $p_{eq}(m_0,0) = e^{-\beta[\varepsilon_m(0)-G(0)]}$. According to the postulates of quantum mechanics,[85,98] the system is projected into the eigenstate $|m_0\rangle$. With time increasing, the system evolves up to the second energy measurement performed at the final time t_f, which produces an eigenvalue $\varepsilon_n(t_f)$ with the conditional probability $p(n_{t_f},t_f|m_0,0)$. Note that the condition probability is of quantum feature and is absent in the classical isolate systems. Due to energy conservation, w is very reasonably interpreted as the inclusive work for the specific quantum process. Using Jensen's inequality, one immediately recovers the work principle $E[w] \geq \Delta G$. The definition of the work in quantum case using the two-energy measurement scheme was originally proposed independently by Piechocinska[38] and Kurchan[39]

in 2000. The idea was further generalized[40] and then was highly developed in a series of articles by Talkner, Hänggi, and their coauthors.[48–54] A summary of the latter reference may refer to their review article.[82] Even so, our derivation (10) shows that the quantum measurement concept is not always essential for finding the work equality.

Using the same procedure, we can reobtain the quantum BKE (QBKE) as[54]

$$\begin{aligned} 1 &= \langle \mathrm{e}^{-\beta H_0^{\mathrm{H}}(t_{\mathrm{f}})}\mathrm{e}^{\beta H_0}\rangle = \sum_{m,n} p_{\mathrm{eq}}(m,0)\,|\langle n|U(t_{\mathrm{f}})|m\rangle|^2\,\mathrm{e}^{-\beta[\varepsilon_n-\varepsilon_m]} \\ &= \sum_{m,n} p_{\mathrm{eq}}(m,0)p(n,t_{\mathrm{f}}|m,0)\,\mathrm{e}^{-\beta w_0} = E[\,\mathrm{e}^{-\beta w_0}], \end{aligned} \tag{13}$$

where the Hamiltonian H_0 is also assumed to have discrete eigenstates and eigenvalues: $H_0|n\rangle = \varepsilon_n|n\rangle$. We see that the two-energy measurement scheme is available as well and the work principle $E[w_0] > 0$ is easily derived.

In the efforts of establishing the quantum work equalities, there were several alternative definitions about the work in a quantum regime. Bochkov and Kuzovlev[7,8] first attempted to define a work operator $\hat{W}_0(t_{\mathrm{f}}) = H_0^{\mathrm{H}}(t_{\mathrm{f}}) - H_0$ in order to extend their equality to quantum case. Yukawa,[41] Allahverdyan and Nieuwenhuizen[55] defined another quantum work operator $\hat{W}(t_{\mathrm{f}}) = H^{\mathrm{H}}(t_{\mathrm{f}}) - H(0)$. Although the averages of both definitions consist with the average of the work definitions using the two energy measurement scheme, they do not always lead into correct predictions about the fluctuations of the work and explicit equalities. The fundamental reason is that work is a quantity of process rather than of the state of the system. Hence, "work is not an observable".[48]

4. Quantum Feynman–Kac formula

When we compare the classical and quantum JEs, we note that there is no trajectory version like (2) for the latter. It is not surprising since the classical phase space does not play a role in quantum mechanics because of Heisenberg's uncertainty principle.[98] Even so, we are still curious about whether there exists an unknown mathematical formula that is equivalent to Eq. (11), but might be more fundamental. Recalling the derivations of the classical JE, a method on the basis of the celebrated Feynman–Kac formula[99,100] is very intriguing.[3,15,91,93–95,101,102] The formula is valid for the very general Markovian processes[103] including the Hamiltonian mechanics that we are discussing. Importantly, the Feynman–Kac formula is essential for the abstract Dyson series[98] represented in the phase or configuration spaces.[104] Hence, we may expect that the method has a quantum-mechanical counterpart, which has been demonstrated by Chetrite and Mallick[67] and one of the authors of Ref. [68] independently. Here we briefly review their results.

Let us consider the following operator equation:

$$\rho_{\mathrm{R}}(s) = \Theta R(t',t_{\mathrm{f}})\rho_{\mathrm{eq}}(t')\Theta^{\dagger}, \tag{14}$$

where the parameter $t'+s = t_{\mathrm{f}}$, and the instantaneous thermal equilibrium density matrix $\rho_{\mathrm{eq}}(t') = \mathrm{e}^{-\beta H(t')}\mathrm{e}^{\beta G(t')}$. Not strictly speaking, the operator $R(t',t_{\mathrm{f}})$ measures the difference between the two density matrixes (see an analogy in the classical system).[92] If $s = t_{\mathrm{f}}$, equation (14) reduces to Eq. (10) due to $\rho_{\mathrm{eq}}(0) = \rho(0)$. It is not difficult to prove that $R(t',t_{\mathrm{f}})$ satisfies an evolution equation given by

$$\begin{cases} \mathrm{i}\hbar\partial_{t'}R(t',t_{\mathrm{f}}) \\ \quad = [H(t'),R(t',t_{\mathrm{f}})] - \mathcal{W}_{t'}R(t',t_{\mathrm{f}}) \\ \quad = [H(t'),R(t',t_{\mathrm{f}})] - \mathrm{i}\hbar R(t',t_{\mathrm{f}})\partial_{t'}\rho_{\mathrm{eq}}(t')\rho_{\mathrm{eq}}^{-1}(t'), \\ R(t_{\mathrm{f}},t_{\mathrm{f}}) = I, \end{cases} \tag{15}$$

where $\boldsymbol{I}$ is the identity matrix. We introduce a superoperator $\mathcal{W}$, the action of which on an operator is a multiplication from its right-hand side. Using the Dyson series and time evolution operator $U(t)$, we obtain the formal solution for Eq. (15) as[67–69]

$$\begin{aligned} & R(t',t_{\mathrm{f}}) \\ &= [G^{\star}(t',t_{\mathrm{f}}) + \sum_{n=1}^{\infty}\int_{t'}^{t_{\mathrm{f}}}\mathrm{d}t_1\cdots\int_{t_{n-1}}^{t_{\mathrm{f}}}\mathrm{d}t_n \\ &\quad \times\prod_{i=1}^{n}G^{\star}(t_{i-1},t_i)\mathcal{W}_{t_i}G^{\star}(t_n,t_{\mathrm{f}})]R(t_{\mathrm{f}},t_{\mathrm{f}}) \\ &= U(t')\mathcal{T}_{+}\,\mathrm{e}^{(\mathrm{i}\hbar)^{-1}\int_{t'}^{t_{\mathrm{f}}}\mathrm{d}\tau U^{\dagger}(\tau)\partial_{\tau}\rho_{\mathrm{eq}}(\tau)\rho_{\mathrm{eq}}^{-1}(\tau)U(\tau)}U^{\dagger}(t'), \end{aligned} \tag{16}$$

where the adjoint propagator

$$G^{\star}(t_1,t_2)\mathcal{O} = U(t_1)U^{\dagger}(t_2)\mathcal{O}U(t_2)U^{\dagger}(t_1), \quad (t_1 < t_2),$$

and $\mathcal{T}_{+}$ denotes the antichronological time-ordering operator. We named Eq. (16) the quantum Feynman–Kac formula.[68] Substituting the solution into Eq. (14) at $t' = 0$ and making traces on both sides, we have

$$\begin{aligned} 1 &= \mathrm{Tr}[R(0,t_{\mathrm{f}})\rho_{\mathrm{eq}}(0)] \\ &= \langle\mathcal{T}_{+}\,\mathrm{e}^{\int_0^{t_{\mathrm{f}}}\mathrm{d}\tau U^{\dagger}(\tau)\partial_{\tau}\rho_{\mathrm{eq}}(\tau)\rho_{\mathrm{eq}}^{-1}(\tau)U(\tau)}\rangle. \end{aligned} \tag{17}$$

Although the equivalence of Eqs. (11) and (17) is undoubted, a more insightful way of corroborating it is to perform a series expansion of $R(0,t_{\mathrm{f}})$ except for the term $\mathrm{e}^{-\beta\Delta G}$ therein in terms of the inverse temperature β. Such a kind of expansion does not essentially matter with a high-temperature series expansion. For instance, the coefficients of the first two orders are

$$\begin{aligned} & \int_0^{t_{\mathrm{f}}}\mathrm{d}t_1\mathrm{Tr}[\partial_{t_1}H(t_1)G(t_1,0)\rho_{\mathrm{eq}}(0)] \\ &= \int_0^{t_{\mathrm{f}}}\mathrm{d}t_1\langle\partial_{t_1}H^{\mathrm{H}}(t_1)\rangle = E[w], \\ & \int_0^{t_{\mathrm{f}}}\int_{t_1}^{t_{\mathrm{f}}}\mathrm{d}t_1\,\mathrm{d}t_2\mathrm{Tr}[\partial_{t_2}H(t_2)G(t_2,t_1)\partial_{t_1}H(t_1)G(t_1,0)\rho_{\mathrm{eq}}(0)] \\ & +\frac{1}{2}\int_0^{t_{\mathrm{f}}}\mathrm{d}t_1\mathrm{Tr}[[H(t_1),\partial_{t_1}H(t_1)]G(t_1,0)\rho_{\mathrm{eq}}(0)] \end{aligned} \tag{18}$$

$$= \int_0^{t_f}\int_{t_1}^{t_f} \mathrm{d}t_1\,\mathrm{d}t_2\langle\partial_{t_2}H^{\mathrm{H}}(t_2)\partial_{t_1}H^{\mathrm{H}}(t_1)\rangle + \frac{1}{2}\int_0^{t_f}\mathrm{d}t_1\langle[H^{\mathrm{H}}(t_1),\partial_{t_1}H^{\mathrm{H}}(t_1)]\rangle = \frac{1}{2}E[w^2], \quad (19)$$

respectively, where $G(t_2,t_1)\mathcal{O} = U(t_2)U^\dagger(t_1)\mathcal{O}U(t_1)U^\dagger(t_2)$ is the propagator of the system. We see that the double integral of Eq. (19) is about the correlation of the operators at two times. Additionally, this equation clearly explains the reason why defining the work operator $\hat{W}(t_f) = \int_0^{t_f}\partial_\tau H^{\mathrm{H}}(\tau)\,\mathrm{d}\tau$ alone[41,55] cannot lead into the correct prediction about the second moment of the quantum work except for the specific canonical initial density matrix. Finally, the expansion does not matter with the initial canonical density matrix. Hence, equations (18) and (19) will be generally valid, e.g., for the microcanonical initial condition.[50]

The quantum Feynman–Kac formula (16) is also useful to obtain the new expression of the QBKE (13). In this case, equation (14) is replaced by

$$\rho_{\mathrm{R}}^0(s) = \Theta R_0(t',t_f)\rho_{\mathrm{eq}}(0)\Theta^\dagger. \quad (20)$$

The reader is reminded that here $\rho_{\mathrm{eq}}(0) = \mathrm{e}^{-\beta H_0}\mathrm{e}^{\beta G(0)}$. We find that the equation of motion for the new operator $R_0(t',t_f)$ still has a form like Eq. (15) except that $\mathcal{W}_{t'}$ is changed into $\mathcal{W}_{t'}^0 = [\rho_{\mathrm{eq}}(0),H_1(t')]\rho_{\mathrm{eq}}^{-1}(0)$ and $H_1(t) = X(t)Q$, where Q is now an operator.[68] Then we have

$$1 = \mathrm{Tr}[R_0(0,t_f)\rho_{\mathrm{eq}}(0)] = \langle\mathcal{T}_+\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\int_0^{t_f}\mathrm{d}\tau U^\dagger(\tau)[\rho_{\mathrm{eq}}(0),H_1(\tau)]\rho_{\mathrm{eq}}^{-1}(0)U(\tau)}\rangle. \quad (21)$$

In addition, very similar results like Eqs. (18) and (19) exist as well, where

$$\partial_\tau H(\tau)\to\frac{\mathrm{i}}{\hbar}[H_1(\tau),H_0],\ H(\tau)\to H_0,\ w\to w_0. \quad (22)$$

Before closing this section, we want to point out several observations. First, if we interpret these operators as ordinary functions, $-\mathrm{i}[\cdots]/\hbar$ as the Poisson bracket, and the propagators under the classical meaning, equations (17) and (21) automatically reduce into their classical trajectory versions. Note that the time-ordering operator will disappear because of the c-number characteristics of the functions. Second, the equations of motion for $R(t',t_f)$ and $R_0(t',t_f)$ inspire us to find the equations governing the evolution of the characteristic functions of the quantum work (see the following discussion). Finally and most importantly, the definitions of $R(t',t_f)$ and $R_0(t',t_f)$, their equations of motion, and the solutions on the basis of the Dyson series do not depend much on whether the system is isolated or not. Hence, the currently developed formal apparatus provides us with a plausible path beyond the isolated quantum systems.[67,69,70]

5. Quantum Crooks equality

The QJE (11) and QBKE (13) impose strong restrictions on the PDFs of the quantum work. On the basis of previous arguments, for instance, it is easy to see that the PDF of observing a certain value of the inclusive work W is

$$p(W) = \sum_{m_0,n_{t_f}} p_{\mathrm{eq}}(m_0,0)p(n_{t_f},t_f|m_0,0)\delta(W-w). \quad (23)$$

Using the microreversibility of the isolated quantum system,[82] the quantum Crook equality[23,24] for the inclusive quantum work was obtained as[38–40]

$$p(W) = p_{\mathrm{R}}(-W)\,\mathrm{e}^{-\beta(\Delta G-W)}, \quad (24)$$

where $p_{\mathrm{R}}(W)$ is the PDF of observing the certain value W for the backward process (9). The presence of the delta-function in Eq. (23) is not always convenient for computing the PDF. An elegant way that bypasses it[7–10,48,49] is to calculate the characteristic function of the PDF[105]

$$G(u) = \int\mathrm{d}W p(W)\mathrm{e}^{\mathrm{i}uW} = \langle\mathrm{e}^{\mathrm{i}uH^{\mathrm{H}}(t_f)}\mathrm{e}^{-\mathrm{i}uH(0)}\rangle, \quad (25)$$

where u is a real number. The Crooks equality (24) indicates a symmetry about the characteristic function

$$G(u)Z(0) = G_{\mathrm{R}}(-u+\mathrm{i}\beta)Z(t_f), \quad (26)$$

where G_{R} is the characteristic function for the backward process.[39,49]

Equations (23)–(26) have their counterparts in the QBKE case.[54] Here we list the results without explanations. Firstly, the PDF of the exclusive work is defined as

$$p_0(W_0) = \sum_{m,n} p_{\mathrm{eq}}(m,0)p(n,t_f|m,0)\delta(W_0-w_0). \quad (27)$$

Its characteristic function $G_0(u) = \langle\mathrm{e}^{\mathrm{i}uH_0^{\mathrm{H}}(t_f)}\mathrm{e}^{-\mathrm{i}uH_0}\rangle$ possesses a symmetry like Eq. (26), namely,

$$G_0(u) = G_{\mathrm{R}}^0(-u+\mathrm{i}\beta), \quad (28)$$

where G_{R}^0 is the characteristic function of the exclusive work for the backward process. This symmetry implies

$$p_0(W_0) = p_{\mathrm{R}}^0(-W_0)\,\mathrm{e}^{\beta W_0}, \quad (29)$$

where $p_{\mathrm{R}}^0(W_0)$ is the PDF of the exclusive quantum work for the backward process.

The intriguing quantum work equalities and Crooks equality stimulated the interest for calculating the PDFs of the quantum work for concrete physical models.[106–110] Because of the involvement of exponential operators and the time-dependent Hamiltonian, however, this job is very challenging and fewer cases can be solved analytically, e.g., the harmonic oscillator with a specific time-dependent angular frequency[107] or driven by a classical external force.[108]

6. Evolution equations for the characteristic functions

When we compare the right-hand side of the characteristic function (25) with that of the QJE (11), their only distinction is that the inverse temperature β in the latter is changed into $-\mathrm{i}u$. This observation immediately reminds us that $G(u)$ can be calculated alternatively by firstly solving an operator $K(t',t_\mathrm{f};u)$ that satisfies

$$\begin{cases} \mathrm{i}\hbar\partial_{t'}K(t',t_\mathrm{f};u) = [H(t'),K(t',t_\mathrm{f};u)] \\ \quad -\mathrm{i}\hbar K(t',t_\mathrm{f};u)\partial_{t'}\,\mathrm{e}^{\mathrm{i}uH(t')}\,\mathrm{e}^{-\mathrm{i}uH(t')}, \\ K(t_\mathrm{f},t_\mathrm{f};u) = I, \end{cases} \tag{30}$$

and

$$G(u) = \langle K(0,t_\mathrm{f};u)\rangle. \tag{31}$$

This situation is very analogous to the evaluation of an operator's Heisenberg picture: one may either obtain the picture by the definition or solve the Heisenberg's equation.[98] To our knowledge, this result is new in the literature. Similarly, the characteristic function $G_0(u)$ for the case of QBKE also has an alternative expression

$$G_0(u) = \langle K_0(0,t_\mathrm{f};u)\rangle, \tag{32}$$

where the equation of motion for the operator $K_0(t',t_\mathrm{f};u)$ is

$$\begin{cases} \mathrm{i}\hbar\partial_{t'}K_0(t',t_\mathrm{f};u) = [H(t'),K_0(t',t_\mathrm{f};u)] \\ \quad -K_0(t',t_\mathrm{f};u)[\mathrm{e}^{\mathrm{i}uH_0},H_1(t')]\,\mathrm{e}^{-\mathrm{i}uH_0}, \\ K_0(t_\mathrm{f},t_\mathrm{f};u) = I. \end{cases} \tag{33}$$

Interestingly, when we recall the characteristic function of the PDF for the classical work, parallel evolution equations were established early by Imparato and Peliti for the stochastic processes.[111–113] Their previous efforts will be capable of guiding us to further explore the properties of the characteristic functions of the quantum work.

We close this section by numerically solving the PDF of the quantum work for a simple two-level system (TLS) driven by a periodic force, whose Hamiltonian is

$$H(t) = \frac{1}{2}\hbar\omega\sigma_+\sigma_- + \lambda_0\sin(\omega t)(\sigma_+ + \sigma_-), \tag{34}$$

where $\sigma_\pm = (\sigma_x \pm \mathrm{i}\sigma_y)/2$, and σ_x and σ_y are the Pauli spin matrices. We specifically choose t_f as the integer number of cycles so that we do not need to distinguish the exclusive or inclusive quantum work. We find the predictions of Eqs. (23), (25), and (31) are the same, as shown in Fig. 1.

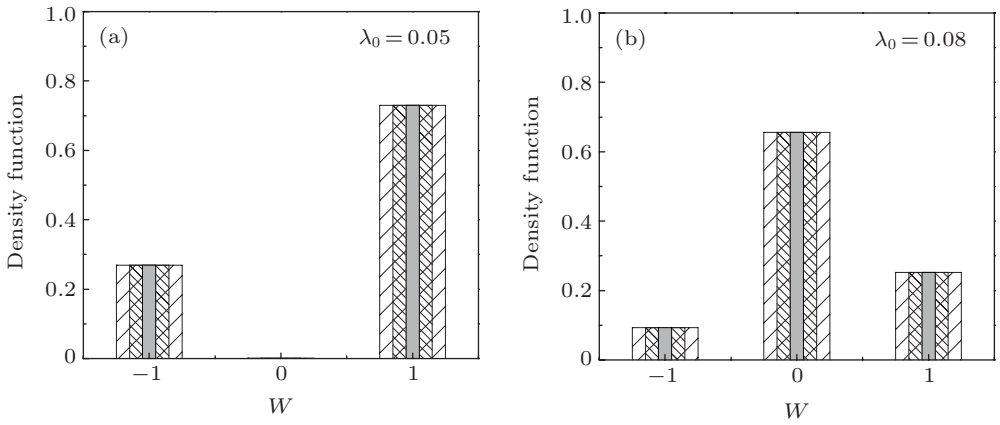


Fig. 1. The PDFs of the quantum work (in units of $\hbar\omega$) for the TLS model (34). The spare dashed bars, solid gray bars, and dense dashed bars are calculated by Eqs. (23), (25), and (31), respectively, where $\beta\hbar\omega = 1.0$, and $t_\mathrm{f}\omega/2\pi = 10$.

7. Measurement of the quantum work

Experimental measurement of the quantum work and verification of the quantum work equalities are very challenging. The crucial requirements include a preparation of an ideally isolated quantum system and two energy measurements at the beginning and the end of a quantum process. Huber *et al.*[114] argued that single ions in the linear Paul trap[115] will be a remarkable quantum system for testing the QJE. Ions in the Paul trap can be well modeled as a quantum harmonic oscillator,[116] and a time-dependent Hamiltonian can be implemented experimentally, e.g., by varying the control voltage of the trap in time.[117] Additionally, there have been well-established experimental schemes to create the desired initial thermal equilibrium state, e.g., by performing Doppler cooling.[118] The real experimental obstacle using the trapped ion is how to faithfully read out the energy eigenstates and their occurring frequencies at the beginning and ending times, respectively. Huber *et al.*[114] proposed a filtering scheme to implement this task. Its fundamental idea is that the degree of freedom of the oscillator's motion is coupled with the inner electronic state. The latter can be detected by an electron shelving method.[119] However, such kinds of experiments have not been carried out so far.

A distinct alternative method was independently proposed by Dorner *et al.* and Mazzola *et al.*,[86,87] which is based

on a Ramsey-like interferometric scheme and bypasses the direct energy projective measurements. Let us take the QJE as an example. First, the characteristic function (25) is rewritten as

$$G(u) = \mathrm{Tr}[(\mathrm{e}^{-\mathrm{i}uH(t_\mathrm{f})}U(t_\mathrm{f}))^\dagger U(t_\mathrm{f})\mathrm{e}^{-\mathrm{i}uH(0)}\rho_\mathrm{eq}(0)]. \quad (35)$$

Hence, one may regard the terms in the adjoint part as a time evolution operator of a quantum process at time $t_\mathrm{f}+u$, the Hamiltonian of which is $H(t)$ and $H(t_\mathrm{f})$ before and after time point t_f, respectively. Similarly, the latter part is regarded as the time evolution operator of another quantum process at time $t_\mathrm{f}+u$. Different from the former, the Hamiltonian is now $H(0)$ and $H(t)$ before and after time point u, respectively. Importantly, Dorner *et al.*[87] and Mazzola *et al.*[86] pointed out that these two distinct processes could in fact merge into one quantum process by coupling the quantum system with the ancillary qubit A, whose whole time evolution operator is

$$\begin{aligned}\bar{U}(u+t_\mathrm{f}) \;=\; & \mathrm{e}^{-\mathrm{i}uH(t_\mathrm{f})}U(t_\mathrm{f})\otimes|1\rangle\langle 1|_\mathrm{A} \\ & + U(t_\mathrm{f})\mathrm{e}^{-\mathrm{i}uH(0)}\otimes|0\rangle\langle 0|_\mathrm{A}, \end{aligned} \quad (36)$$

where $\{|1\rangle_\mathrm{A},|0\rangle_\mathrm{A}\}$ are the bases of the qubit. By preparing an initial joint density matrix $\rho_\mathrm{eq}(0)\otimes|+\rangle\langle+|_\mathrm{A}$, where $|+\rangle$=$(|0\rangle+|1\rangle)\sqrt{2}$, applying the time evolution operator (36) on the composite system, and performing a Hadamard transform at time $t+t_\mathrm{f}$, one can extract the characteristic function by reading out the state of the ancillary qubit, i.e.,

$$\begin{aligned}\rho_\mathrm{A} \;&=\; \mathrm{Tr}_\mathrm{S}[H_\mathrm{A}\bar{U}(u+t_\mathrm{f})(\rho_\mathrm{eq}(0)\otimes|+\rangle\langle+|_\mathrm{A})\bar{U}^\dagger(u+t_\mathrm{f})H_\mathrm{A}] \\ &=\; \frac{1}{2}(1+\mathrm{Re}[G(u)]\sigma_z+\mathrm{Im}[G(u)]\sigma_y), \end{aligned} \quad (37)$$

where the trace Tr_S is over the concerned quantum system. This scheme has been attracting much attention, and particularly, it has been complemented in a spin-1/2 system using a liquid-state NMR device.[84] Finally, we want to mention that, in addition to the above two schemes, their generalizations[88,89] and other possible experimental schemes[120,121] were also reported in the literature.

8. Conclusion

We close this review by explicitly listing the three key ingredients for establishing the quantum work equalities in the isolated quantum systems. The first ingredient is the microreversibility, which allows us to introduce the time-reversed or the backward quantum processes. We must emphasize that the microreversibility does not always conflict with the irreversible behaviors of nonequilibrium processes at the ensemble level. The isolated systems are very special, since they are reversible at both levels. The second one is that there exists an instantaneous thermal equilibrium state. In the classical systems, this condition is equivalent to the existence of the instantaneous detailed balance condition. Hence, if the condition is not satisfied, the work equalities may not exist, although one could still define the work. Self-consistently describing the quantum systems by the evolution equations for the density matrices of the systems is the last piece of the ingredients. Combining it and the second one, we can derive equations like Eq. (16) and the quantum Feynman–Kac formula is then obtained. We expect that, for some open quantum systems that interact with its environment through energy and matter exchanges, if they possess these three ingredients, new work equalities could be established accordingly.

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Appendix A: Derivation of quantum FDTs

The QJE (11) can be used to derive the famous FDTs[11–13] in quantum regime.[58,67] Here we want to show that a derivation using the QBKE (13) is simpler. Rather than the previous terminal condition $R_0(t_\mathrm{f},t_\mathrm{f})=I$, we may suppose other conditions, e.g., $R_0(t_\mathrm{f},t_\mathrm{f})=\mathcal{O}/\mathrm{Tr}[\mathcal{O}\rho_0]$, where $\mathcal{O}$ is an arbitrary physical observable. Under this circumstance, we may obtain another equality given by[68]

$$\begin{aligned}&\mathrm{Tr}[\mathcal{O}\rho_0] \\ &= \langle\mathcal{O}^\mathrm{H}(t_\mathrm{f})\mathcal{T}_+\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\int_0^{t_\mathrm{f}}\mathrm{d}\tau U^\dagger(\tau)[\rho_\mathrm{eq}(0),H_1(\tau)]\rho_\mathrm{eq}^{-1}(0)U(\tau)}\rangle. \end{aligned} \quad (38)$$

Expanding the right-hand side of the above equality up to the first order of H_1, we immediately find that

$$\begin{aligned}\langle\mathcal{O}\rangle(t_\mathrm{f})-\langle\mathcal{O}\rangle_0 \;\simeq\; & \frac{\mathrm{i}}{\hbar}\int_0^{t_\mathrm{f}}\mathrm{d}t_1\mathrm{Tr}\Bigg[\mathcal{O}^\mathrm{H}(t_\mathrm{f}) \\ & \times\left(\int_0^\beta \mathrm{d}u\frac{\mathrm{d}}{\mathrm{d}u}H_1^\mathrm{H}(t_1+\mathrm{i}\hbar u)\right)\rho_0\Bigg]. \end{aligned} \quad (39)$$

If one further specifies the expression of $H_1(t)$ such as $X(t)Q$, the celebrate quantum FDT[11–13] will be obtained. In some sense, this is expected since the BKE originally aims at the extension of the FDT.[7–10]

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