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Derivation of quantum work equalities using a quantum Feynman-Kac formula

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On the basis of a quantum mechanical analog of the famous Feynman-Kac formula, we present a method to derive nonequilibrium work equalities for isolated quantum systems, which include the Jarzynski equality and Bochkov-Kuzovlev equality. Compared with other methods in the literature, our method shows a higher similarity in form to the method deriving the fluctuation relations in the classical systems.

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Introduction. The Feynman-Kac (FK) formula, originally found by Feynman in quantum mechanics [1] and extended by Kac [2], establishes an important connection between partial differential equations and classical stochastic processes. Briefly, assume that in a continuous diffusion process the probability of a stochastic trajectory X started from a state x' at time t' is $P[X|x',t']$. The solution $u(x',t')$ of the following partial differential equation,

$$\begin{aligned}&\partial_{t'}u(x',t') = -\mathcal{L}^{+}(x',t')u(x',t') - g(x',t')u(x',t'),\\ &u(x',t'=t) = q(x'),\end{aligned} \tag{1}$$

has a concise path integral representation [3]:

$$u(x',t') = \int \mathcal{D}X e^{\int_{t'}^{t} g(x_\tau,\tau)d\tau} q(x_t,t)P[X|x',t'], \tag{2}$$

where $\mathcal{L}^{+}$ is the Markovian generator of the diffusion process. This is the famous FK formula in classical stochastic processes.

Recently, the FK formula was also found to be very useful in studying fluctuation relations [4–9]. In the past two decades, these important relations have greatly deepened our understanding of the second law of thermodynamics and nonequilibrium physics of small systems [4,10–20]. With the fluctuation relations clarified in the classical systems, considerable research interest is turning to their quantum cases and fruitful theoretical and experimental results [21–30] have been obtained. To our best knowledge, however, there is no work explicitly using the FK formula. At first glance, the reason is very obvious, because the classical trajectory picture on which the FK is based is not available in quantum physics. Contrary to intuition, in this Rapid Communication we use an isolated quantum system as an example to show that there indeed exists a quantum-mechanical analog of the classical FK formula and it is very useful to derive the quantum nonequilibrium work relations, including the Jarzynski [21,23,24] and Bochkov-Kuzovlev equalities [29]. Additionally, we also demonstrate that the involvement of the quantum FK formula is a consequence of the difference between the original quantum system and its time reversal.

The Kolmogorov picture and backward invariable. We start by introducing essential notations and a picture that is a quantum-mechanical analog of Kolmogorov's idea [31] in classical stochastic theory. Although the picture is virtually equivalent to other well-known pictures, e.g., the Heisenberg picture, we will see later that it is very relevant to the time-reversal concept. We assume that the closed quantum system is described by a time-dependent Hamiltonian $H(t)$. The system's density operators ρ at two different times t and t' $(<t)$ are connected by the time-evolution operators U at the two times as

$$\rho(t) = U(t)U^{\dagger}(t')\rho(t')U(t')U^{\dagger}(t). \tag{3}$$

Given an arbitrary observable F that does not depend explicitly on time, we define its Kolmogorov picture as

$$F(t,t') = U(t')F^{\mathrm{H}}(t)U^{\dagger}(t'), \tag{4}$$

where the superscript H denotes the Heisenberg picture: $F^{\mathrm{H}}(t) = U^{\dagger}(t)FU(t)$. On the basis of Eqs. (3) and (4), the expectation value $\langle F\rangle(t)$ at time t in the picture is

$$\mathrm{Tr}[F\rho(t)] = \mathrm{Tr}[F(t,t')\rho(t')], \tag{5}$$

and the equation of motion for $F(t,t')$ with respect to the backward time t' is simply

$$\begin{aligned}&i\hbar\partial_{t'}F(t,t') = -[F(t,t'),H(t')],\\ &F(t,t'=t) = F.\end{aligned} \tag{6}$$

We see that it is a terminal condition rather than an initial condition problem. It is worth pointing out that Eq. (6) is very distinct from the equation of motion for the same $F(t,t')$ with respect to the forward time t if the Hamiltonian explicitly depends on time.

Equation (5) has a trivial property: The derivatives on both sides with respect to t' vanish, or equivalently, $\mathrm{Tr}[F(t,t')\rho(t')]$ is a backward time invariable. The property is very analogous to that of the Chapman-Kolmogorov equation in the classical diffusion theory [32]. According to our previous experience, which, constructing a more general backward time invariable, may lead into the classical fluctuation relations [9], it would be very interesting to explore whether the same idea is still true here. Imitating Eq. (5) in Ref. [8], we find there is a very analogous backward time invariable in the quantum case

$$\mathrm{Tr}[F\bar{\rho}(t)] = \mathrm{Tr}[\overline{F}(t,t')\bar{\rho}(t')], \tag{7}$$

if the operator $\overline{F}(t,t')$ satisfies

$$\begin{aligned}i\hbar\partial_{t'}\overline{F}(t,t') = &-[\overline{F}(t,t'),H(t')] - \overline{F}(t,t')\{i\hbar\partial_{t'}\bar{\rho}(t')\\ &+[\bar{\rho}(t'),H(t')]\}\bar{\rho}^{-1}(t') + \{[\overline{F}(t,t'),A(t')]B(t')\\ &+\overline{F}(t,t')[B(t'),A(t')]\}\bar{\rho}^{-1}(t'),\end{aligned} \tag{8}$$

and its terminal condition at t is still assumed to be F, where the operators $A(t')$, $B(t')$, and the invertible density operator

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$\bar{\rho}(t')$ are arbitrary. The proof of Eq. (7) is straightforward. The meaning of the last two terms on the right hand side will appear when we choose $\bar{\rho}(t')$ to be the system's density operator $\rho(t')$, i.e., the term $i\hbar\partial_{t'}\bar{\rho}+[\bar{\rho},H]$ vanishes. The general equation (8) seems uncommon in the quantum mechanics except for a specific case:

$$\begin{aligned} i\hbar\partial_{t'}\overline{F}(t,t') &= -[\overline{F}(t,t'),H(t')] - \overline{F}(t,t')O(t'),\\ \overline{F}(t,t'=t) &= F, \end{aligned} \tag{9}$$

where $O(t')$ is an arbitrary operator. We may easily write down its solution given by

$$\overline{F}(t,t') = U(t')F^{\rm H}(t)\mathcal{T}_+ e^{(i\hbar)^{-1}\int_{t'}^{t} d\tau U^\dagger(\tau)O(\tau)U(\tau)}U^\dagger(t') \tag{10}$$

$$= U(t')F^{\rm H}(t)Q(t,t')U^\dagger(t'), \tag{11}$$

where $\mathcal{T}_+$ is the time-ordering operator. We simply name Eq. (10) the quantum FK formula because of its highly formal similarity to the classical FK formula (2). However, we must remind the reader that the whole time-ordering term, which we especially denote by an operator $Q(t,t')$ for convenience, only indicates that the operator satisfies

$$i\hbar\partial_{t'}Q(t,t') = -Q(t,t')[U^\dagger(t')O(t')U(t')] \tag{12}$$

with a terminal condition $Q(t,t'=t)=1$. So far, we mainly concentrate on a formal development; the physical relevance of the quantum FK formula (10) and the backward time invariable (7) is not obvious. In the following we show that these results would lead into the quantum Jarzynski and Bochkov-Kuzovlev equalities if one chooses a specific $\bar{\rho}(t')$, $A(t')$, and $B(t')$.

Quantum Jarzynski equality. We assume that the closed quantum system is initially in thermal equilibrium with a density operator $\rho_{\rm eq}(0)=e^{-\beta H(0)}/Z(0)$, where the partition function $Z(0)={\rm Tr}[e^{-\beta H(0)}]=e^{-\beta G(0)}$, β is the inverse temperature, and $G(0)$ is the initial free energy. At later times the system evolves under the time-dependent Hamiltonian $H(t)$. We choose $A=B=0$, $\bar{\rho}(t')$ to be the instant equilibrium state $\rho_{\rm eq}(t')=e^{-\beta H(t')}/Z(t')$ with the instant partition function $Z(t')={\rm Tr}[e^{-\beta H(t')}]=e^{-\beta G(t')}$. Equation (8) then becomes

$$i\hbar\partial_{t'}\overline{F}(t,t') = -[\overline{F}(t,t'),H(t')] - i\hbar\overline{F}(t,t')\partial_{t'}\rho_{\rm eq}(t')\rho_{\rm eq}^{-1}(t'). \tag{13}$$

Obviously, the above equation follows the structure of Eq. (9) and especially

$$O(t') = i\hbar[\partial_{t'}e^{-\beta H(t')}e^{\beta H(t')} + \beta\partial_{t'}G(t')] \tag{14}$$

when we substitute the expression of $\rho_{\rm eq}(t')$ into the "source" term of Eq. (13). Intriguingly, in this case Eq. (12) in fact has a very simple analytical solution,

$$Q(t,t') = [U^\dagger(t)e^{-\beta H(t)}U(t)][U^\dagger(t')e^{\beta H(t')}U(t')]e^{\beta[G(t)-G(t')]}. \tag{15}$$

Hence, on the basis of Eqs. (7), (10), and (15) we obtain

$$\begin{aligned} &{\rm Tr}[F\rho_{\rm eq}(t)]\\ &= {\rm Tr}[U(t')F^{\rm H}(t)\mathcal{T}_+e^{\int_{t'}^{t} d\tau U^\dagger(\tau)\partial_\tau\rho_{\rm eq}(\tau)\rho_{\rm eq}^{-1}(\tau)U(\tau)}U^\dagger(t')\rho_{\rm eq}(t')] \end{aligned} \tag{16}$$

$$= {\rm Tr}[F^{\rm H}(t)e^{-\beta H^{\rm H}(t)}e^{\beta H^{\rm H}(t')}U^\dagger(t')\rho_{\rm eq}(t')U(t')]\; e^{\beta[G(t)-G(t')]}. \tag{17}$$

If $F=1$ and $t'=0$, Eq. (17) is just the quantum Jarzynski equality on the inclusive work [24]

$$\langle e^{-\beta H^{\rm H}(t)}e^{\beta H(0)}\rangle_{\rm eq}(0) = e^{-\beta\Delta G(t)}, \tag{18}$$

where $\Delta G(t)=G(t)-G(0)$, and we have used $\langle\rangle_{\rm eq}(0)$ to denote an average over the initial density operator $\rho_{\rm eq}(0)$. Additionally, Eq. (17) at $t'=0$ is also a specific case of the general functional relation given earlier by Andrieux and Gaspard [26]; see Eq. (12) therein.

Bochkov-Kuzovlev equality. Here we consider a special realization of the time-dependent Hamiltonian [33]: A dynamic perturbation $H_1(t)$ ($t\geqslant 0$) is applied on a system that is initially in thermal equilibrium with a time-independent H_0, that is, the total Hamiltonian at later times is $H(t)=H_0+H_1(t)$. Obviously, the system's initial density operator is $\rho(0)=\rho_0=e^{-\beta H_0}/Z_0$, where the partition function $Z_0={\rm Tr}[e^{-\beta H_0}]=e^{-\beta G_0}$. Choosing $H(t')=H_0$, $A(t')=-H_1(t')$, $B(t')=\bar{\rho}(t')=\rho_0$ in Eq. (8), we obtain the following equation:

$$i\hbar\partial_{t'}\widetilde{F}(t,t') = -[\widetilde{F}(t,t'),H_0+H_1(t')] - \widetilde{F}(t,t')[\rho_0,H_1(t')]\rho_0^{-1}. \tag{19}$$

We have used a symbol $\widetilde{F}$ to distinguish it from the previous $\overline{F}$ because they satisfy different equations. We see that the above equation also follows the structure of Eq. (9) and especially

$$O(t') = [e^{-\beta H_0},H_1(t')]e^{\beta H_0}. \tag{20}$$

It would be interesting to check whether there is a simple analytical solution to Eq. (12) under this circumstance. We find that it indeed has

$$Q(t,t') = [U^\dagger(t)e^{-\beta H_0}U(t)][U^\dagger(t')e^{\beta H_0}U(t')]. \tag{21}$$

Using Eqs. (7), (10), and (21) we establish another equality given by

$$\begin{aligned} &{\rm Tr}[F\rho_0]\\ &= {\rm Tr}\big[U(t')F^{\rm H}(t)\mathcal{T}_+e^{(i\hbar)^{-1}\int_{t'}^{t} d\tau U^\dagger(\tau)[\rho_0,H_1(\tau)]\rho_0^{-1}U(\tau)}U^\dagger(t')\rho_0\big] \end{aligned} \tag{22}$$

$$= {\rm Tr}\big[F^{\rm H}(t)e^{-\beta H_0^{\rm H}(t)}e^{\beta H_0^{\rm H}(t')}U^\dagger(t')\rho_0U(t')\big]. \tag{23}$$

If $F=1$ and $t'=0$, Eq. (23) is the quantum Bochkov-Kuzovlev equality on the exclusive work

$$\big\langle e^{-\beta H_0^{\rm H}(t)}e^{\beta H_0}\big\rangle_0 = 1 \tag{24}$$

that was proposed very recently in Ref. [29], where $\langle\ \rangle_0$ indicates an average over the initial density operator ρ_0.

Time-reversal interpretation. In the remaining part we want to demonstrate that Eqs. (13) and (19) arise from the equations of motion of two distinct time-reversed density operators, which is necessary to understand the origin of these equations and the physical meaning of the backward time t'. We use Eq. (13) as an illustration. Multiplying both sides with $\rho_{\rm eq}(t')$ and introducing a parameter $s=t-t'(0<s<t)$, we rewrite the equation as

$$\begin{aligned} &i\hbar\partial_s[\overline{F}(t,t-s)\rho_{\rm eq}(t-s)]\\ &\quad = [\overline{F}(t,t-s)\rho_{\rm eq}(t-s),H(t-s)]. \end{aligned} \tag{25}$$

Note that this is an initial condition rather than a terminal condition problem. Equation (25) seems very analogous to the equation of motion of a density operator, which is indeed true if we multiply both sides of the equation by the antiunitary time-reversal operator Θ and its conjugation to obtain

$$i\hbar\partial_s\bar{\rho}_{\rm R}(s) = [\overline{H}_{\rm R}(s),\bar{\rho}_{\rm R}(s)], \tag{26}$$

where the time-reversed density operator and time-reversed Hamiltonian are

$$\bar{\rho}_{\rm R}(s) = \frac{1}{{\rm Tr}[F\rho_{\rm eq}(t)]}\Theta\overline{F}(t,t-s)\rho_{\rm eq}(t-s)\Theta^\dagger, \tag{27}$$

$$\overline{H}_{\rm R}(s) = \Theta H(t-s)\Theta^\dagger, \tag{28}$$

respectively, and the coefficient is essential for the normalization of $\bar{\rho}_{\rm R}(s)$. Hence, we may interpret the minus of the backward time t' to be the forward time of the time-reversed system. Moreover, Eq. (27) also explains the backward time invariable in the Jarzynski equality, because the trace of its left side is a t'-independent constant. In fact, the same equation is equivalent to the key lemma in Ref. [26] that was used to prove a functional relation; see the Appendix. Doing very analogous calculations, one can also prove that Eq. (19) is equivalent to the equations of motion of a different time-reversed density operator $\widetilde{\rho}_{\rm R}(s)$ with a time-reversed Hamiltonian $\widetilde{H}_{\rm R}(s)$, which are

$$\widetilde{\rho}_{\rm R}(s) = \frac{1}{{\rm Tr}[F\rho_{\rm o}]}\Theta\widetilde{F}(t,t-s)\rho_0\Theta^\dagger, \tag{29}$$

$$\widetilde{H}_{\rm R}(s) = \Theta H(t-s)\Theta^\dagger = H_0 + \Theta H_1(t-s)\Theta^\dagger, \tag{30}$$

respectively. For the same dynamic perturbation problem, though the original and time-reversed Hamiltonian for the quantum Jarzynski equality are the same as those for the quantum Bochkov-Kuzovlev equality, respectively, their time-reversed density operators are usually very distinct because of their different initial conditions, i.e., $\bar{\rho}_{\rm R}(0) = \rho_{\rm eq}(t)$ and $\widetilde{\rho}_{\rm R}(0) = \rho_{\rm o}$.

Conclusions. In this work, we have used a quantum-mechanical analog of the classical FK formula to derive known quantum nonequilibrium work relations in isolated quantum systems. Compared with previous methods in the literature, our method is highly similar in form to the method which we developed earlier to derive the classical fluctuation relations [9]. We think that it is insightful because one may find the backward time invariable first and then give its physical interpretation rather than vice versa. Previous work has shown that directly defining nonequilibrium physical quantities was very nontrivial in the quantum case [28]. Extending our method into more complicated quantum systems, e.g., the open quantum systems, would be a challenge for our future research.

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APPENDIX

Equation (27) could be further simplified. The time-reversed density operator at a later time s is connected to the initial condition by

$$\begin{aligned}\bar{\rho}_{\rm R}(s) &= U_{\rm R}(s)\bar{\rho}_{\rm R}(0)U_{\rm R}^\dagger(s)\\ &= \frac{1}{{\rm Tr}[F\rho_{\rm eq}(t)]}U_{\rm R}(s)\Theta F\rho_{\rm eq}(t)\Theta^\dagger U_{\rm R}^\dagger(s),\end{aligned} \tag{A1}$$

where $U_{\rm R}(s)$ is the time-evolution operator for the time-reversed Hamiltonian $\overline{H}_{\rm R}(s)$. Substituting the above equation and the solution of Eq. (13),

$$\overline{F}(t,t') = U(t')F^{\rm H}(t)e^{-\beta H^{\rm H}(t)}e^{\beta H^{\rm H}(t')}U^\dagger(t')e^{\beta[G(t)-G(t')]}, \tag{A2}$$

into Eq. (27) and doing a simple calculation, we obtain

$$U_{\rm R}(s) = \Theta U(t-s)U^\dagger(t)\Theta^\dagger. \tag{A3}$$

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