Quantum Work Relations and Response Theory

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A universal quantum work relation is proved for isolated time-dependent Hamiltonian systems in a magnetic field as the consequence of microreversibility. This relation involves a functional of an arbitrary observable. The quantum Jarzynski equality is recovered in the case this observable vanishes. The Green-Kubo formula and the Casimir-Onsager reciprocity relations are deduced thereof in the linear response regime.

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Nonequilibrium work relations have recently attracted much interest [1,2]. They provide relations for the work dissipated in time-dependent driven systems, independently of the form of the driving. They are of great interest to evaluate free energies under general nonequilibrium conditions and they provide new methods to study nanosystems. In the nanoscopic world, the extension of these classical relations to quantum systems is of particular importance and different approaches have been proposed.

A first scheme was introduced by Kurchan [3]. In this framework, a measurement of the system state is performed at the initial time. In the sequel, the system is perturbed by a time-dependent Hamiltonian before performing another measurement at the final time. The random work performed on the system is associated with the energy difference between the final and initial eigenstates. This setup leads to the quantum extension of Jarzynski equality and Crooks fluctuation theorem [4–7]. Another possibility is to introduce a quantum work operator which measures the energy difference [8], in which cases quantum corrections to the fluctuation theorem must be taken into account. On the other hand, quantum fluctuation theorems have been obtained in suitable limits where the dynamics admits a Markovian description, allowing, in particular, the applications to nonequilibrium steady states [9–14]. Yet, the connection between the quantum work relations and response theory is still an open question even in the linear regime.

The purpose of the present Letter is to derive a new type of work relations which involves a functional of an arbitrary observable. This generating functional can be related to another functional but averaged over the time-reversed process. This new work relation turns out to be of great generality since we can recover known results such as Jarzynski equality as special cases. Furthermore, this universal work relation allows us to formulate the response theory, to derive the quantum linear response functions, the quantum Green-Kubo relations [15,16], as well as the Casimir-Onsager reciprocity relations [17,18] in the regime close to the thermodynamic equilibrium.

Functional symmetry relations.—We suppose that the system is described by a Hamiltonian operator $H(t;\mathcal{B})$ which depends on the time t and the magnetic field $\mathcal{B}$. The time-reversal operator Θ is an antilinear operator such that $\Theta^2 = I$ and which has the effect of changing the sign of all odd parameters such as magnetic fields:

$$\Theta H(t;\mathcal{B})\Theta = H(t;-\mathcal{B}). \tag{1}$$

We first introduce the *forward process*. The system is initially in thermal equilibrium at the inverse temperature $\beta = 1/k_B T$. The initial state of the system is described by the canonical density matrix

$$\rho(0) = \frac{e^{-\beta H(0;\mathcal{B})}}{Z(0)}, \tag{2}$$

where the partition function is given in terms of the corresponding free energy $F(0)$ by $Z(0) = \mathrm{tr} e^{-\beta H(0;\mathcal{B})} = e^{-\beta F(0)}$. Starting from this equilibrium situation at the initial time $t = 0$, the system evolves until some final time $t = T$ under the Hamiltonian dynamics. The corresponding forward time evolution is defined as

$$i\hbar \frac{\partial}{\partial t} U_F(t;\mathcal{B}) = H(t;\mathcal{B}) U_F(t;\mathcal{B}), \tag{3}$$

with the initial condition $U_F(0;\mathcal{B}) = I$ [19]. In the Heisenberg representation, the observables evolve according to

$$A_F(t) = U_F^\dagger(t) A U_F(t), \tag{4}$$

which also concerns the time-dependent Hamiltonian

$$H_F(t) = U_F^\dagger(t) H(t;\mathcal{B}) U_F(t). \tag{5}$$

The average of an observable is thus obtained from

$$\langle A_F(t)\rangle = \mathrm{tr}\rho(0) A_F(t). \tag{6}$$

We note that the dependence on the magnetic field is implicit in these expressions.

The *backward process* is introduced similarly but in the magnetic field reversed. The system is perturbed according to the time-reversed protocol $H(T-t;-\mathcal{B})$, starting at the initial time $t = 0$ from the density matrix

$$\rho(T) = \frac{e^{-\beta H(T;-\mathcal{B})}}{Z(T)}, \tag{7}$$

where the free energy $F(T)$ is given in terms of the partition function according to $Z(T) = \mathrm{tr} e^{-\beta H(T;-\mathcal{B})} = e^{-\beta F(T)}$. The system ends at time $t = T$ with the Hamiltonian $H(0; -\mathcal{B})$. The evolution operator of the backward process is defined as

$$i\hbar \frac{\partial}{\partial t} U_R(t; \mathcal{B}) = H(T - t; \mathcal{B}) U_R(t; \mathcal{B}), \tag{8}$$

with the initial condition $U_R(0; \mathcal{B}) = I$ [19], and is related to the one of the forward process by the following:

Lemma.—The forward and backward time evolution operators are related to each other according to

$$\Theta U_F(T - t; \mathcal{B}) U_F^\dagger(T; \mathcal{B}) \Theta = U_R(t; -\mathcal{B}), \tag{9}$$

where t is an arbitrary time $0 \le t \le T$.

This lemma is proved by first substituting $T - t$ for t in Eq. (3) to get

$$-i\hbar \frac{\partial}{\partial t} U_F(T - t; \mathcal{B}) = H(T - t; \mathcal{B}) U_F(T - t; \mathcal{B}). \tag{10}$$

Multiplying this equation by $U_F^\dagger(T; \mathcal{B})\Theta$ from the right and by Θ from the left, we find

$$i\hbar \frac{\partial}{\partial t} \Theta U_F(T - t; \mathcal{B}) U_F^\dagger(T; \mathcal{B}) \Theta = H(T - t; -\mathcal{B}) \Theta U_F(T - t; \mathcal{B}) U_F^\dagger(T; \mathcal{B}) \Theta, \tag{11}$$

where we used the antilinearity $\Theta i = -i\Theta$ of the time-reversal operator and its further property (1). This shows that the expression $\Theta U_F(T - t; \mathcal{B}) U_F^\dagger(T; \mathcal{B}) \Theta$ obeys the same evolution Eq. (8) as $U_R(t; -\mathcal{B})$. Since they also satisfy the same initial condition, $\Theta U_F(T; \mathcal{B}) U_F^\dagger(T; \mathcal{B}) \Theta = U_R(0; -\mathcal{B}) = I$, we have proven Eq. (9) QED.

With this lemma, we can now demonstrate the following:

Theorem.—Let us consider an arbitrary time-independent observable A with a definite parity under time reversal: $\Theta A \Theta = \epsilon_A A$, with $\epsilon_A = \pm 1$. It satisfies the following functional relation:

$$\langle e^{\int_0^T dt \lambda(t) A_F(t)} e^{-\beta H_F(T)} e^{\beta H(0)} \rangle_{F,\mathcal{B}} = e^{-\beta \Delta F} \langle e^{\epsilon_A \int_0^T dt \lambda(T-t) A_R(t)} \rangle_{R,-\mathcal{B}}, \tag{12}$$

where $\lambda(t)$ is an arbitrary function, while the subscripts F and R stand for the forward or backward protocol, respectively. $\Delta F = F(T) - F(0)$ is the difference of the free energies of the initial equilibrium states (7) and (2) of the backward and forward processes.

In order to prove Eq. (12), we first consider the quantity $A_F(t)$, which can be written as

$$\begin{aligned} A_F(t) &= U_F^\dagger(t) A U_F(t) \\ &= U_F^\dagger(T) U_F(T) U_F^\dagger(t) A U_F(t) U_F^\dagger(T) U_F(T) \\ &= \epsilon_A U_F^\dagger(T) \Theta A_R(T - t) \Theta U_F(T), \end{aligned} \tag{13}$$

where we have inserted the identity $U_F^\dagger(T) U_F(T) = I$ to go at the second equality. At the third equality, we inserted $\Theta^2 = I$ between the evolution operators and we used $\Theta A \Theta = \epsilon_A A$ along with Eq. (9). The connection is thus established with the backward process. Integrating over time with an arbitrary function $\lambda(t)$ and taking the exponential of both sides, the previous expression becomes

$$\exp\left(\int_0^T dt \lambda(t) A_F(t)\right) = U_F^\dagger(T) \Theta \exp\left(\epsilon_A \int_0^T dt \times \lambda(T - t) A_R(t)\right) \Theta U_F(T), \tag{14}$$

after the change of integration variables $t \to T - t$ in the right-hand side.

Starting from the left-hand side of Eq. (12), we get

$$\begin{aligned} \mathrm{tr}\rho(0) \exp\left(\int_0^T dt \lambda(t) A_F(t)\right) \exp[-\beta H_F(T)] \exp[\beta H(0)] &= \frac{1}{Z(0)} \mathrm{tr} \exp\left(\epsilon_A \int_0^T dt \lambda(T - t) A_R(t)\right) \Theta \exp[-\beta H(T; \mathcal{B})] \Theta \\ &= \frac{Z(T)}{Z(0)} \mathrm{tr} \exp\left(\epsilon_A \int_0^T dt \lambda(T - t) A_R(t)\right) \rho(T) \\ &= e^{-\beta \Delta F} \langle \exp\left(\epsilon_A \int_0^T dt \lambda(T - t) A_R(t)\right) \rangle_{R,-\mathcal{B}}. \end{aligned} \tag{15}$$

We used the invariance of the trace over cyclic permutations as well as the exponential of Eq. (13) at the first equality. In the second equality, we introduced the equilibrium density matrix (7) which is precisely the initial condition of the backward process. To obtain the last equality, we used that the partition functions have been expressed in terms of the corresponding free energies. This completes the proof of the theorem QED.

We notice that related results have previously been considered in the restricted case where there is no change in free energy $\Delta F = 0$ [20,21]. The present theorem allows us to recover, in particular, the quantum Jarzynski equality as a special case of Eq. (12) if $\lambda = 0$:

$$\langle e^{-\beta H_F(T)} e^{\beta H(0)} \rangle_{F,\mathcal{B}} = e^{-\beta \Delta F}. \tag{16}$$

The factor inside the bracket can indeed be interpreted in the quantum setting in terms of the work performed on the system during the forward process [3,4,6,9] in spite of the noncommutativity of the energy operators $H_F(T)$ and $H(0)$ and thanks to the protocol with von Neumann quantum measurements of the energy at the initial and final times. It is only in the classical limit that both energies commute and the classical work can be formed as $W_{\rm cl} = [H_F(T) - H(0)]_{\rm cl}$. In this case, both exponentials in the left-hand side of the relation (12) becomes $\exp(-\beta W_{\rm cl})$ which is the classical version of this relation.

Response theory.—We can obtain different correlation functions by taking functional derivatives of the relation (12) with respect to the arbitrary function $\lambda(t)$. In this way, we can obtain the expression of linear response theory from the generalized symmetry relation (12). For this purpose, we consider a perturbation of the form

$$H(t) = H_0 - X(t)B, \tag{17}$$

where the perturbation $X(t)$ is such that $X(t) = 0$ for $t \leq 0$ and $X(t) = 0$ for $T \leq t$. The observable B is here arbitrary and should not be confused with the magnetic field $\mathcal{B}$. In order to obtain the linear response of an observable A with respect to the perturbation $-X(t)B$, we take the functional derivative of Eq. (12) with respect to $\lambda(T)$, around $\lambda = 0$. This yields

$$\langle A_F(T) e^{-\beta H_F(T)} e^{\beta H_0} \rangle_{F,\mathcal{B}} = \epsilon_A \langle A_R(0) \rangle_{R,-\mathcal{B}} = \epsilon_A \langle A \rangle_{{\rm eq},-\mathcal{B}}, \tag{18}$$

where we used that $\Delta F = 0$ since $X(0) = X(T) = 0$. Since the reversed process also starts at equilibrium, the average in the right-hand side is an equilibrium average, albeit with a reversed magnetic field. Nevertheless, we have that $\epsilon_A \langle A \rangle_{{\rm eq},-\mathcal{B}} = \langle A \rangle_{{\rm eq},\mathcal{B}}$ by using time reversal. We now have to calculate the exponentials of the initial and final Hamiltonians. Since, in the Heisenberg representation, the total time derivative of the Hamiltonian equals its partial derivative, $dH_F/dt = (\partial H/\partial t)_F$, we can write

$$\exp[-\beta H_F(T)] = \exp[-\beta(H_0 + E)] \tag{19}$$

with

$$E = \int_0^T dt \left(\frac{\partial H}{\partial t}\right)_F = -\int_0^T dt \dot{X}(t) B_F(t) = \int_0^T dt X(t) \dot{B}_F(t), \tag{20}$$

where the last equality follows from an integration by parts. We now use the expression

$$\exp[\beta(P+Q)]\exp(-\beta P) = 1 + \int_0^\beta du \times \exp[u(P+Q)] Q \exp(-uP), \tag{21}$$

which can be proved by differentiating with respect to β. To first order in Q, we may neglect Q in the last exponential function, $\exp[u(P+Q)]$. Taking $P = -H_0$ and $Q = -E$ and developing to first order in X, we get

$$\begin{aligned} e^{-\beta H_F(T)} e^{\beta H_0} &= 1 - \int_0^T dt X(t) \int_0^\beta du e^{-uH_0} \dot{B}(t) e^{uH_0} + O(X^2) \\ &= 1 - \int_0^T dt X(t) \int_0^\beta du \dot{B}(t + i\hbar u) + O(X^2), \end{aligned}$$

where $B(t) = \exp(iH_0 t/\hbar) B \exp(-iH_0 t/\hbar)$ since, at first order in the driving force, the time evolution proceeds under the unperturbed Hamiltonian H_0. Inserting this expansion into Eq. (18) and after some manipulations using the time invariance of correlation function as well as the KMS-like property $\rho A = A(i\hbar\beta)\rho$ [22], we finally find

$$\langle A_F(T) \rangle_{\mathcal{B}} = \langle A \rangle_{{\rm eq},\mathcal{B}} + \int_0^T dt X(T-t) \phi_{AB}(t) + O(X^2), \tag{22}$$

with the response function

$$\phi_{AB}(t) = \int_0^\beta du \langle \dot{B}(-i\hbar u) A(t) \rangle_{{\rm eq},\mathcal{B}}. \tag{23}$$

Equations (22) and (23) are the well-known expressions of linear response theory in the canonical ensemble, also known as the Green-Kubo formula [15,16]. The Casimir-Onsager reciprocity relations for the conductivities [17,18] are obtained by taking $A = J_\mu / V$ and $\dot{B} = J_\nu$ in terms of the current $J_\mu = \sum_n e_n \dot{x}_{n\mu}$ and the volume V, in which case the time-reversal symmetry implies $\phi_{\mu\nu}(t; \mathcal{B}) = \phi_{\nu\mu}(t; -\mathcal{B})$ and $\sigma_{\mu\nu}(\omega; \mathcal{B}) = \sigma_{\nu\mu}(\omega; -\mathcal{B})$ for the tensor of conductivities $\sigma_{\mu\nu}(\omega; \mathcal{B}) = \int_0^\infty dt e^{i\omega t} \phi_{\mu\nu}(t; \mathcal{B})$. Higher-order terms in the expansion can be obtained as well.

Conclusions.—In this Letter, we have obtained a universal quantum work relation which involves arbitrary observables at arbitrary times. This result relates an average over the forward process ponderated by the quantum analogue of the work to an average over the reversed process. By taking functional derivatives, we can obtain relations for arbitrary correlation functions, which are the consequence of microreversibility. In the simplest case, it can be used to recover the well-known Jarzynski equality. On the other hand, we can also straightforwardly derive from the universal relation the linear response theory of an arbitrary observable. In this regard, this relation unifies in a common framework the work relations and the response theory, thereby opening the possibility to obtain further general relations which are valid not only close to equilibrium but also in the far-from-equilibrium regime.

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