A quantum fluctuation theorem for any Lindblad master equation

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We present a general quantum fluctuation theorem for the entropy production of an open quantum system whose evolution is described by a Lindblad master equation. Such theorem holds for both local and global master equations, thus settling the dispute on the thermodynamic consistency of the local quantum master equations. The theorem is genuinely quantum, as it can be expressed in terms of conservation of an Hermitian operator, describing the dynamics of the system state operator and of the entropy change in the baths. The integral fluctuation theorem follows from the properties of such an operator. Furthermore, it is valid for arbitrary number of baths and for time-dependent Hamiltonians. As such, the quantum Jarzynski equality is a particular case of the general result presented here. Moreover, our result can be extended to non-thermal baths, as long as microreversibility is preserved. We finally present some numerical examples to showcase the exact results previously obtained.

\textbf{Introduction.} In classical stochastic thermodynamics the physics of work and heat fluctuations in small, out-of-equilibrium systems is now well understood in the framework of the fluctuation theorems (FTs) extending the second law of thermodynamics to the microscopic realm \cite{1,2}. While the proof of the FT in the classical regime often relies on the stochastic trajectories that a system performs on its phase space while interacting with the external environment \cite{2}, other approaches based on the symmetries of the classical master equation \cite{3} or of the Fokker-Planck equation have been proposed \cite{5,6}.

In the quantum realm, several approaches have been put forward to generalise the FT and the impossibility of monitoring a quantum system without disturbance has generated a long debate (see for example the reviews \cite{11,12}). Several attempts to prove the quantum FT employ the formalism of quantum trajectories \cite{14,15,16,17,18,19,20}. In this context, one needs to introduce an effective non-Hermitian Hamiltonian and a set of jumps that generate a random trajectory, along which thermodynamic quantities, e.g. entropy and energy, can be sampled. Interestingly, the back action from the observation of the jump, through the emission of a photon, for instance, gives rise to a genuinely quantum heat contribution \cite{22,23,24}. Very often, the so-called two-point measurement scheme, where the system is observed at the start and end of the protocol, is used, destroying potentially useful quantum coherences. Alternatively, one can prove the FT by diagonalizing the instantaneous density matrix, thus generating a quantum counterpart of the classical trajectories \cite{25,26}. A fully coherent quantum FT in the framework of quantum resource theory has also been proposed \cite{27}.

In this paper, we present a general and unified approach that naturally extends the classical FT to open quantum systems and is only based on the quantum Lindblad master equation. We prove the FT by introducing an auxiliary quantum master equation and a Hermitian operator that accounts for the time evolution of both the system’s state and the bath entropy. Our formalism, based on the change of entropy in the baths and in the system, is general: it is valid at all times and not just at steady state, it is valid for both local and global quantum master equations (for which a heated debate has arisen in recent years), for an arbitrary number of baths, and for time-dependent system Hamiltonians.

Our quantum FT goes beyond the two-point measurement scheme: it requires an initial projection of the system in an arbitrary basis to estimate the initial system’s entropy along a specific trajectory. The initial projection may also occur in the eigenbasis of the initial density matrix, thus preventing any measurement back-action. It also requires the continuous monitoring of the baths but not the final system’s projection or the continuous measurement of the work done on the system for time-dependent Hamiltonians. As such, its experimental implementation may be easier than schemes based on two-point measurements. Moreover, a dissipative quantum Jarzynski equality (JE) \cite{28,29,30,31} can be derived in operator form, and the result of the classical stochastic thermodynamics can be immediately recovered for diagonal density matrices. Our approach is unifying as it provides a proof of the quantum FT for relevant physical situations, namely manipulated systems in contact with multiple heat baths, and allows a full description of the system’s thermodynamics.

\textbf{The fluctuation theorem.} We assume the evolution of a $d$-level system weakly coupled to $N_b$ environments to follow the Gorini-Kossakowski-Sudarshan-Lindblad (GKSL) master equation (ME)\cite{32,33} ($\hbar = 1$):

$$
\frac{d\rho(t)}{dt} = -i[H(t),\rho(t)] + \sum_{\alpha=1}^{N_b} D_{\alpha}[\rho(t)],
$$

for its density matrix $\rho(t)$ with dissipators

$$
D_{\alpha}[\rho] = \sum_{\lambda} \gamma_{\alpha,\lambda} \left( L_\lambda \rho L_\lambda^\dagger - \frac{1}{2} (L_\lambda^\dagger L_\lambda, \rho) \right),
$$

where $L_\lambda = \langle j' | j \rangle$ and $\lambda = \lambda(j \rightarrow j')$ denotes a transition between two states $|j\rangle$ and $|j'\rangle$. In the following,
in order to lighten the notation, we will omit the initial and final state of such a transition. The orthonormal basis \{\{j\}\}, though arbitrary, is motivated by the physical environments. If the states \{j\} are the eigenstates of \(H\), e.g. collective superpositions of states that are local with respect to the subparts of the system, the ME is dubbed “global” or “local” otherwise [35]. We split an operator \(X = X_D + X_{\bar{D}}\) into the sum of its diagonal and non-diagonal parts in the basis \{\{j\}\} and set \(X_{jj} = \langle j | X | j \rangle\). The dissipation rates \(\gamma_{\alpha,\lambda}\), are taken to obey the (local) detailed balance condition:

\[
\gamma_{\alpha,\lambda}(\omega) \gamma_{\lambda,\alpha}(-\omega) = e^{-\beta_\alpha \omega},
\]

where \(\omega = \omega_{j'j} = H_{j'j} - H_{jj} = \Delta H_{D,\lambda}\),

\[
\omega_{\lambda} = \omega_{j'j} = H_{j'j} - H_{jj} = \Delta H_{D,\lambda},
\]

and \(\beta_\alpha\) is the inverse temperature of the bath \(\alpha\). We consider the general case where different baths can drive the same transition \(\lambda\), if \(\gamma_{\alpha,\lambda} \neq 0\), and we will omit the dependency of \(\gamma_{\alpha,\lambda}\) on \(\omega_{\lambda}\), so as to lighten the notation.

In the classical case the FT reads [27]

\[
\langle e^{-\Delta S_B - \Delta S_B} \rangle = 1,
\]

where \(\Delta S_B = -\sum_\alpha \beta_\alpha Q_\alpha\) is the total entropy change in the baths due to the heat \(Q_\alpha\), and \(\Delta S_S\) is the entropy change of the system along a given stochastic trajectory, and where the average runs over all the possible stochastic trajectories in the phase space, given the system dynamics and the time protocol \(H(t)\). We adopt the convention \(Q_\alpha > 0\) when the heat flows from the bath into the system. In order to evaluate the entropy change in the baths, one has to characterize the statistics of the energy absorbed/ emitted by the baths. To this end, we will follow closely the approach discussed in [28] for classical stochastic systems. The “jumps” between two states occur at the rates \(\gamma_{j'j}\) because of the interaction with the baths which in turn absorb/emit quanta of energy. The corresponding energy flowing into the system is \(\beta_\alpha^{-1} \log(\gamma_{j'j}/\gamma_{jj})\) and the entropy change in the bath \(\alpha\) reads

\[
\Delta s_{\alpha,j'j} = -\log(\gamma_{\alpha,j'j}/\gamma_{\alpha,jj}).
\]

We would like to characterize the joint probability distribution \(\Phi_j(\Delta S_B, t)\) of finding the system in the state \(|j\rangle\) with a total entropy \(\Delta S_B\) flowed into the reservoirs up to the time \(t\). This can be done by introducing an extended quantum ME that takes into account the dynamic evolution of both the density operator and of the entropy change in the baths. In practice we introduce a modified density matrix \(\tilde{\rho}(\Delta S_B, t)\), such that its diagonal elements describe the desired joint probability \(\tilde{\rho}_{jj} = \Phi_j(\Delta S_B, t)\), and a modified ME:

\[
\partial_t \tilde{\rho}_{jj}(\Delta S_B, t) = -i[H, \tilde{\rho}_{jj}(\Delta S_B, t)] + \sum_{\alpha,j} \left\{ \gamma_{\alpha,j'j} \left[ \sum_{n=0}^{\infty} \frac{(\Delta s_{\alpha,j'j})}{n!} \frac{\partial^n \tilde{\rho}_{jj}}{\partial S_B^n} \right] - \gamma_{\alpha,j'j} \tilde{\rho}_{jj} \right\},
\]

\[
\partial_t \tilde{\rho}_{ik}(\Delta S_B, t) = -i[H, \tilde{\rho}_{ik}(\Delta S_B, t)] + \sum_{\alpha} D_{ND,\alpha}(\tilde{\rho}_{ND}(\Delta S_B, t)), \quad l \neq k,
\]

where \(D_{ND,\alpha}[\cdot]\) is a super-operator such that \(D_{ND}[\tilde{\rho}_{ND}(\Delta S_B, t)]\) has vanishing diagonal terms and only couples non-diagonal terms of the density matrix in the chosen basis, see appendix A for the derivation. Next, we introduce the operator \(\Psi(\xi, t)\) akin to the generating function in classical physics, defined as

\[
\Psi(\xi, t) = \int d\Delta S_B \tilde{\rho}(\Delta S_B, t)e^{-\xi \Delta S_B},
\]

and applying this integral transform to both sides of Eqs. (7) and (8), one obtains the equations for \(\Psi(\xi, t)\)

\[
\partial_t \Psi_{jj}(\xi, t) = -i[H, \Psi_{jj}(\xi, t)] + \sum_{\alpha,j} \left\{ \gamma_{\alpha,j'j} \left( \frac{\gamma_{\alpha,j'j}}{\gamma_{\alpha,jj}} \right) \Psi_{jj}(\xi, t) - \gamma_{\alpha,j'j} \Psi_{jj'}(\xi, t) \right\},
\]

\[
\partial_t \Psi_{ik}(\xi, t) = -i[H, \Psi_{ik}(\xi, t)] + D_{ND}[\Psi_{ND}(\xi, t)], \quad l \neq k.
\]

We shall now discuss the physical initial condition for Eqs. (7-8) and Eqs. (10-11). Let \(\rho^{(0)}\) be the initial state at \(t = 0\). Since no entropy has yet flowed into the baths: \(\tilde{\rho}(\Delta S_B, t = 0) = \rho^{(0)}(\Delta S_B)\). Given the definition of \(\Psi\), Eq. (9), its initial condition becomes \(\Psi(\xi, t = 0) = \rho^{(0)}(\xi)\), \(\forall \xi\) and in the following \(\Psi(\xi, t|\rho^{(0)})\) will indicate the solution to Eqs. (10-11) with this specific initial condition. The following equalities hold

\[
\langle e^{-\xi \Delta S_B} \rangle_{\Pi_j, \rho^{(0)}} = \text{Tr} \left[ \Pi_j \Psi(\xi, t|\rho^{(0)}) \right] = \Psi_{jj}(\xi, t|\rho^{(0)}) \tag{12}
\]

\[
\langle e^{-\xi \Delta S_B} \rangle_{\rho^{(0)}} = \text{Tr} \left[ \Psi(\xi, t|\rho^{(0)}) \right] \tag{13}
\]

where \(\langle \ldots \rangle_{\Pi_j, \rho^{(0)}}\) in Eq. (12) denotes the expectation value constrained by the initial state \(\rho^{(0)}(\xi)\) and the state at time \(t\) taken to be \(\Pi_j = |j\rangle\langle j|\) and in Eq. (13) we summed over all possible final states.

In the following we will mostly be interested in the case \(\xi = 1\) to evaluate the expectation value of exp(\(-\Delta S_B\)). Let \(\Psi^{(1)}(t) = \Psi(\xi = 1, t)\), a straightforward calculation (see appendix A) gives

\[
\partial_t \Psi^{(1)}(t) = -i[H, \Psi^{(1)}(t)] + \sum_{\alpha} D_{\alpha}^{*}[\Psi^{(1)}(t)],
\]

where \(D_{\alpha}^{*}\) is the dual of the dissipator \(D_{\alpha}^{*}[\cdot] = \sum_\lambda \gamma_{\alpha,\lambda} \left( L_{\lambda} \cdot L_{\lambda} - \frac{1}{2} \left\{ L_{\lambda} L_{\lambda}, \cdot \right\} \right).\) Thus the time evolution of \(\Psi^{(1)}\), as given by Eq. (14), has the same conservative part as in Eq. (1), but the dissipative part (the
dual of $D$) is the same as the one found in the time evolution of an operator in the Heisenberg picture: this observation reflects the fact that the operator $\Psi^{(1)}$ bears information on both the system state $\rho(t)$ and on the quantity $\exp(-\Delta S_B)$. As such, the operator $\Psi^{(1)}$ is Hermitian at any time if it is Hermitian at $t = 0$. Modified MEs of the type \cite{10} emerge quite naturally through the large deviation approach used to study the long-time limit of thermodynamic currents. Such an approach was first introduced in \cite{36}, and became later quite consolidated in the field of stochastic thermodynamics, see e.g., \cite{37,38}. A modified quantum ME was first introduced in \cite{15} and later in \cite{39} to study the long-time counting statistics in dissipative quantum systems. The entropy production reflects the fact that the operator $\Psi^{(1)}(t)$ is Hermitian at any time if it is Hermitian at $t = 0$, and therefore the modified ME \cite{10}-\cite{11} turns out to be the right tool to study its statistics.

Let us now introduce the operator $\Psi^{(1)}(t)$

$$\Psi^{(1)}(t) = \sum_{j_0} \Psi^{(1)}(t|\Pi_{j_0}).$$

\label{eq:15}

Given that $\Psi^{(1)}(t)$ is a linear combination of solutions of Eqs. \cite{10}-\cite{11} with $\xi = 1$, it is a solution itself, with initial condition $\Psi^{(1)}(0) = \sum_{j_0} \Pi_{j_0} = \mathbb{I}$. Thus, inspection of Eqs. \cite{10}-\cite{11} with $\xi = 1$ (or of Eq. \cite{14}), suggests that $\Psi^{(1)}(t)$ is a stationary solution at any time, such that

$$\Psi^{(1)}(t) = \Psi^{(1)}(t|\Pi) = \mathbb{I}, \ \forall t \geq 0. \quad \text{(16)}$$

The last equality for $\Psi^{(1)}(t)$ is the first important result of the present paper. It is the operatorial counterpart of the integral theorem \cite{5}, and involves the Hermitian operators $\Psi^{(1)}(t|\Pi_{j_0})$ expressing the joint dynamics of the system density operator and of the baths’ entropy change. It does not depend on the choice of the initial basis. Remarkably by introducing an arbitrary basis $\{|b_0\rangle\}$, and noticing that Eqs. \cite{10}-\cite{11} are linear, we can write their solution at time $t$, with the specific initial condition $\Pi_{b_0}$ as

$$\Psi^{(1)}(t|\Pi_{b_0}) = \sum_{j_0,j_0'} \langle j_0|b_0\rangle \langle b_0|j_0'\rangle \Psi^{(1)}(t|j_0|j_0'). \quad \text{(17)}$$

Notice that here $\langle b_0|j_0\rangle$ are $c$-numbers, while $\Psi^{(1)}(t|j_0)\langle j_0'|j_0\rangle$ are Hermitian operators. From Eq. \cite{17} one obtains

$$\sum_{b_0} \Psi^{(1)}(t|\Pi_{b_0}) = \sum_{j_0} \Psi^{(1)}(t|\Pi_{j_0}) = \Psi^{(1)}(t),$$

where we have used the completeness relation for $\{|b_0\rangle\}$: $\sum_{b_0} \langle b_0|b_0\rangle = \mathbb{I}$. Furthermore Eq. \cite{16} implies $\sum_{j_0} \exp(-\Delta S_B)|_{\Pi_{j_0}} = d$ where we have used Eq. \cite{13} and \cite{15}.

We now present the mathematical statement of the integral FT which is the second main result of this paper, and later on we discuss its physical significance. Such a FT reads:

$$\text{Tr} \left[ \sum_{b_0} \rho_0^{(b_0)} \Psi^{(1)}(t|\Pi_{b_0}) e^{-\log \rho_0^{(b_0)}} e^{\log \rho^{(f)}} \right] = \text{Tr}[\Psi^{(1)}(t)\rho^{(f)}] = 1, \quad \text{(18)}$$

where we have used Eq. \cite{15}-\cite{17} and introduced an arbitrary final state $\rho^{(f)}$. Notice that the only requirement on the final state is $\text{Tr} \rho^{(f)} = 1$. This feature of the FT was already noticed in \cite{7} for the classical case: Eq. \cite{18} holds for any normalised quantum final state $\rho^{(f)}$, not necessarily the solution of Eq. \cite{1} at time $t$.

We now turn our attention to the physical significance of this result. First, Eq. \cite{18} has the form of the expectation value of the Hermitian operator $\Psi^{(1)}$ over the final state of the system. We then recall the physical interpretation of the operator $\Psi^{(1)}(t)\rho^{(0)}$: its $j$-th diagonal element represents the expectation value of $\exp(-\Delta S_B)$ constrained by the initial $\rho^{(0)}$ and final state $\Pi_f$, Eq. \cite{12}. We make no specific assumption on the coherence in the initial and the final state $\rho^{(0)}$ and $\rho^{(f)}$: they can both exhibit coherence in the jump-operators’ basis $\{|\alpha\rangle\}$ as well as in the energy eigenbasis. Let $\{|k_0\rangle\}$ and $\{|r_\ell\rangle\}$ be the eigenbases of $\rho^{(0)}$ and $\rho^{(f)}$, respectively. Changing basis, from $\{|\alpha\rangle\}$ to $\{|r_\ell\rangle\}$ and recalling the definition \cite{9}, we can rewrite Eq. \cite{18} as

$$1 = \sum_{r_\ell,j_0} \langle e^{-\Delta S_B}\rho^{(f)}_r \Pi_f \rho^{(0)}_j \rangle e^{-\log \rho^{(j)}_0} e^{\log \rho^{(r)}_r} = \quad \text{(19)}$$

$$\sum_{r_\ell,k_0} \int \text{d}\Delta S_B e^{-\Delta S_B + \log \rho^{(r)}_r - \log \rho^{(k)}_k} \Phi_{r,\ell} (\Delta S_B,t|\Pi_{k_0}) \rho^{(k_0)}_k = \quad \text{(20)}$$

We notice that the last expression for the FT has the form of the classical counterpart Eq. \cite{5}, with an average over the joint probability distribution $\Phi_{r,\ell} (\Delta S_B)$. Moreover, Eqs. \cite{18}-\cite{19} exhibit the structure of a double trace, one over the initial state $\rho^{(0)}$ and one over the final one $\rho^{(f)}$, and as such their values do not depend on the chosen basis. Notice that performing the initial projection of $\rho^{(0)}$ in its eigenbasis preserves its quantum coherence in other bases, e.g. in the energy eigenbasis.

Using Jensen’s inequality, one recovers the second law:

$$\langle \Delta S_B \rangle - \langle \text{Tr}[\rho^{(f)} \log \rho^{(f)}] - \text{Tr}[\rho^{(0)} \log \rho^{(0)}] \rangle \geq 0. \quad \text{(21)}$$

Furthermore, by noticing that the heat flowing into a bath as a consequence of a jump is $-\omega_{j_\ell}$, and that such a quantity only involves the diagonal part of the system Hamiltonian (see Eq. \cite{1}), expressing $\langle \Delta S_B \rangle = -\sum \alpha \beta_\alpha Q_{D,\alpha}$ we can rewrite Eq. \cite{20} as

$$\Delta S_S = -\langle \text{Tr}[\rho^{(f)} \log \rho^{(f)}] - \text{Tr}[\rho^{(0)} \log \rho^{(0)}] \rangle \geq \sum \alpha \beta_\alpha Q_{D,\alpha} \quad \text{(21)}$$

in accordance with the findings of \cite{35}, where it was found that, in the local ME, only the diagonal part of the heat currents, defined as $Q_{D,\alpha} = \text{Tr} \{ \rho D_0^\alpha [H_D] \}$, enters the differential version of the second law: $dS_S/dt \geq \sum \alpha \beta_\alpha Q_{D,\alpha}$.

Comparing \cite{19} and \cite{21} we reach the conclusion (and the third important result in this paper) that the change in entropy in the bath, within the local ME framework, is only determined by the diagonal part of the system’s Hamiltonian, and only $H_D$ enters the FT \cite{19} and the
second law \(21\). When the ME is global, \(H_D = H\), one recovers the standard definition \(Q_{D,\alpha} = \text{Tr}\{D_\alpha[\rho]H\}\).

In this respect, it is interesting to consider the case of absence of coherence at \(t = 0\) and \(t\). This situation occurs when the ME \(1\) is global, and the initial state \(\rho^{(0)}\) has no coherence (i.e. the system is classical at any time), or when one performs a measurements of the system state at \(t = 0\) and \(t\), as in the two-point measurement scheme. In this case, it makes sense to introduce the concept of classical trajectories starting from the state \(|j_0\rangle\) at \(t = 0\) and ending in the state \(|j\rangle\). From Eq. \(18\) or \(19\), one then recovers immediately the classical FT \(5\) with \(\Delta S_B + \Delta S_S = -\sum_\alpha \beta_\alpha Q_\alpha + \log \rho^{(f)}_{jj} - \log \rho^{(0)}_{jj}\).

Our results also hold when the system’s Hamiltonian is time-dependent. In the special case of a single bath at inverse temperature \(\beta\) and choosing the final and initial state to be the Gibbs states \(\rho^{(f)} = \exp(-\beta H(t))/Z_t\), and \(\rho^{(0)} = \exp(-\beta H(0))/Z_0\), Eq. \(18\) becomes

\[
\text{Tr}\{\sum_j \rho^{(0)}_{j,j_0} \Psi^{(1)}(t | j_0)_j e^{\beta H_{j,j_0}(0)} e^{-\beta H(t)}\} = Z_t/Z_0 = e^{-\beta \Delta F},
\]

where \(\Delta F\) is the difference in equilibrium free energy between the final and the initial thermal state, corresponding to the JE. Following the same procedure that leads to Eq. \(19\) we find

\[
\sum_{j,j_0} \int dQ e^{\beta(Q_D - H_{j,j_0}(t) + H_{j,j_0}(0))} \Phi_j(Q_D, t | j_0)_j p^{(0)}_{j_0} = \int dW_D P(W_D) e^{-\beta W_D} = e^{-\beta \Delta F},
\]

where we have set \(\Delta S_B = -\beta Q_D\), and have defined work as \(W_D \equiv \Delta H_D - Q_D\).

**Numerical examples.** While results \(18\) and \(19\) are exact, we resort to numerical simulations to exemplify them and gain physical insight into their implications. Specifically, we consider a system of spin-1/2 particles, characterised by Pauli operators \(\sigma_{x,y,z}\), with Hamiltonian \(H = -J\sigma_{x,a}\sigma_{x,b} + H_{\text{ext}}\) where each spin is connected to an equilibrium reservoir at temperatures \(T_a\) and \(T_b\), respectively. The jump operators “flip” the individual spins: \(L_\lambda = \sigma_{-,\lambda} \otimes 1_b \) or \(L_\lambda = 1_a \otimes \sigma_{-,\lambda}\). When \(J \neq 0\) the quantum ME \(1\) is local, see appendix \(3\) for further details for the numerical simulations.

We numerically evolve the system’s state using the quantum Monte Carlo (QMC) algorithm for the unraveling of the ME \(10\) provided by Qutip \(11, 12\). The QMC algorithm evolves the system’s state from \(|\psi(0)\rangle\) to \(|\psi(t)\rangle\) with an alternation of continuous dynamics and stochastic jumps \(10\). Along each trajectory, we monitor the individual jumps, driven by one of the two baths, and collect the statistics for the bath’s entropy:

\[
-\Delta S_B = \beta_\alpha Q_{a,D} + \beta_\beta Q_{b,D} = \sum_{l=1}^{n_a} \beta_\alpha \omega_{j,l+1,j_l}(t_l) + \sum_{m=1}^{n_\beta} \beta_\beta \omega_{j,m+1,j_m}(t_m) \tag{24}
\]

where \(t_l\) is the time at which the \(l\)-th jump (out of \(n_\alpha\) total jumps) induced by the bath \(\alpha = a, b\) occurs.

We evaluate the quantum FT in the form of Eq. \(18\) where now the average is taken over the trajectories generated by QMC. For the system’s entropy change we employ the definition (see also appendix \(3\)):

\[
\Delta S_S = -\log \langle \psi(t) | \rho(t) | \psi(t) \rangle/\langle \psi(0) | \rho^{(0)} | \psi(0) \rangle \tag{25}
\]

Within QMC, one can evaluate the solution \(\rho(t)\) to the ME \(1\) as \(\rho(t) = \langle \psi(t) | \psi(t) \rangle_{\text{tr}}\), where \(\langle \ldots \rangle_{\text{tr}}\) is the average over the QMC trajectories. Analogously, from the definition of \(\Psi(\xi, t)\) Eq. \(9\), we obtain

\[
\Psi^{(1)}(t | j_{k_0}) = \langle e^{-\beta S_B} | \psi(t) \rangle | j_{k_0} \rangle \langle \psi(t) | \psi(t) \rangle_{\text{tr}} \tag{26}
\]

which again can be sampled with QMC, and where we have chosen \(\{|k_0\}\) as initial basis in Eq. \(18\).

Our numerical results in Fig. \(1\) confirm the quantum FT \(18\). Our FT holds for initially diagonal and non-diagonal states in contact with baths at the same temperatures \((T_a = T_b)\) or different ones. Moreover, in Fig. \(1\) (d) we consider the case of a time-dependent Hamiltonian, where the external field is changed according to \(h(t) = h_0 + (h_1 - h_0)t/t_i\). In the same figure, we also show that \(\langle \exp(-\Delta S_B) \rangle \geq 1\), thus demonstrating the relevance of the system entropy variation for the FT to hold.

**Conclusions.** We have proved a quantum fluctuation theorem valid for a quantum system evolving with any Lindblad master equation and with a time-dependent Hamiltonian. Our theorem goes beyond the two-point measurement scheme by preserving quantum correlations created by the non-equilibrium dynamics. Our results conclude the debate on the “inadequacy” of local master equations for quantum thermodynamics restoring their physical consistency. Our theorem provides a convenient tool for the numerical and experimental exploration of irreversible quantum coherent thermodynamics. We finally notice that in case of non-thermal baths, where the local detailed balance condition \(3\) does not hold, our results \(18\)–\(19\) are still valid for the quantity \(\Delta S_B\) as defined at microscopic level in Eq. \(6\) with the only requirement of micro reversibility between jumps. However in this case the quantity \(\Delta S_B\) cannot be identified as the entropy change in the baths.

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FIG. 1. QMC simulations of the two-spin system: \( \langle \exp(\Delta S_{\text{tot}}) \rangle_{\text{tr}} \) and \( \langle \exp(\Delta S_B) \rangle_{\text{tr}} \) as functions of \( t \), with with \( \Delta S_{\text{tot}} = \Delta S_B + \Delta S_S \). Averages over \( 10^6 \) trajectories, \( g = 0.1 \), \( T_a = 1 \). (a): diagonal \( \rho^{(0)} \), \( J = 0 \), \( h = 0.2 \), \( T_b = 1 \) (classical case at equilibrium). (b): diagonal \( \rho^{(0)} \), \( J = 0.1 \), \( h = 0.2 \), \( T_b = 1.2 \). (c): non-diagonal \( \rho^{(0)} \), \( J = 0.1 \), \( h = 0.2 \), \( T_b = 1.2 \). (d): non-diagonal \( \rho^{(0)} \), \( J = 0.2 \), \( T_b = 1.2 \), and time dependent field \( h(t) = 0.4t/t_f \), with \( t_f = 15 \). See appendix [2] for further details on the numerical simulations.

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Appendix A: The modified quantum master equation

Here we discuss the derivation of Eq. (7) in the main text. Such a derivation follows the corresponding derivation of the modified ME for classical stochastic systems discussed in Ref. [3]. The time evolution of $\rho(t)$ is described by the GKSME (1). We notice that the diagonal terms of the density matrix $\rho(t)$ express the time evolution of the populations, i.e., the probability $p_j(t) = \rho_{jj}(t)$ of observing the system in the state $|j\rangle$ at time $t$. We are interested in the joint probability distribution $\Phi_j(\Delta S_B, t)$ of finding the system in the state $j$ with a total entropy $\Delta S_B$ which has flowed into the reservoirs at time $t$ as a consequence of the jumps between states in the system. In the main text we have already introduced the modified density matrix $\tilde{\rho}(\Delta S_B, t)$, such that its diagonal elements describe the desired joint probability $\tilde{\rho}_{jj} = \Phi_j(\Delta S_B, t)$. We first observe that the dissipators in the ME, as defined in Eq. (2), only couple diagonal elements of the density matrix with diagonal elements and non-diagonal elements with non-diagonal elements. The coupling between the diagonal and non-diagonal elements of $\rho$ occurs through the coherent part of the dynamics, expressed by the commutator in Eq. (1).

Thus we can write

$$D_\alpha[\rho] = D_D[\rho_D] + D_{ND,\alpha}[\rho_{ND}],$$

(A1)

where $D_D[\rho_D]$ and $D_{ND}[\rho_{ND}]$ contain only diagonal and non-diagonal entries in their matrix representation, respectively, and $D_D[\rho_{ND}] = D_{ND}[\rho_D] = 0$. This becomes evident when one rewrites Eq. (1) as

$$\frac{d\rho(t)}{dt} = -i [H(t), \rho(t)] + \sum_{\alpha,\lambda} \gamma_{\alpha,\lambda} \left( |j\rangle \langle j| \rho(t) |j\rangle \langle j| - \frac{1}{2} \left( \Pi_j \rho + \rho \Pi_j \right) \right).$$

(A2)

where we remind the reader that $\lambda = \lambda(j \rightarrow j')$ denotes a transition between two states $|j\rangle$ and $|j'\rangle$. Thus isolating the diagonal part of (A2), one obtains

$$\partial_t \rho_{jj'} = -i [H, \tilde{\rho}_{jj'}] + \sum_{\alpha, j} \left( \gamma_{\alpha,j'j} \rho_{jj} - \gamma_{\alpha,jj'} \rho_{jj'} \right).$$

(A3)

The jump between the states $|j\rangle$ and $|j'\rangle$ occurs with rate $\gamma_{\alpha,j'j}$, and the corresponding entropy change in the bath $\alpha$ is given by Eq. (6) in the main text. Such jumps in the ME (1) are described by $D_D[\rho_D]$ implicitly introduced in Eq. (A3), thus only the coupling between the diagonal elements in the ME contributes to the change in the bath entropy $\Delta S_B$. Let us now suppose that we know the modified density matrix $\tilde{\rho}(\Delta S_B, t)$ at time $t$, and let us consider the time evolution of its diagonal and non-diagonal part. For the diagonal part, at time $t + \delta t$, we have

$$\tilde{\rho}_{jj'}(\Delta S_B, t + \delta t) \simeq \tilde{\rho}_{jj'}(\Delta S_B, t) - i[H, \tilde{\rho}(\Delta S_B)]_{jj'} \delta t + \delta t \sum_{\alpha,j} \gamma_{\alpha,j'j} \tilde{\rho}_{jj} (\Delta S_B - \Delta s_{\alpha,j'}, t) - \gamma_{\alpha,j'j} \tilde{\rho}_{jj'} (\Delta S_B, t) \tag{A4}$$

For the non-diagonal part of the dynamics, that do not contribute to $\Delta S_B$, we have

$$\tilde{\rho}_{lk}(\Delta S_B, t + \delta t) \simeq -i[H, \tilde{\rho}_{lk}] \delta t + \delta t \sum_{\alpha} D_{ND}[\tilde{\rho}_{ND}(\Delta S_B, t)]_{lk}, \quad l \neq k. \tag{A5}$$

Taking the limit $\delta t \rightarrow 0$ in both (A4) and (A5), and expanding the right-hand side of Eq. (A4) in Taylor series of the microscopic entropy change $\Delta s_{\alpha,j'}$, we obtain the modified quantum ME Eqs. (7) and (8) in the main text.
We now consider Eqs. (10–11), and take \( \xi = 1 \). Such equations become
\[
\partial_t \Psi_j^{(1)}(\xi,t) = -i[H,\Psi_j^{(1)}](\xi,t) + \sum_{\alpha,j} \gamma_{\alpha,j} \left\{ \Psi_j^{(1)}(\xi,t) - \Psi_j^{(1)*}(\xi,t) \right\},
\]
(A6)
\[
\partial_t \Psi_k^{(1)}(\xi,t) = -i[H,\Psi_k^{(1)}](\xi,t) + D_{ND}[\Psi_k^{(1)}](\xi,t), \quad l \neq k.
\]
(A7)

The dual dissipator applied on an operator \( X \) reads
\[
D_{\alpha}^{*}[X] = \sum_{j \rightarrow j''} \gamma_{\alpha,j''j} \left( X_{j''j''} - \frac{1}{2} \left\{ \Pi_j, X \right\} \right),
\]
(A8)
and considering the diagonal element
\[
D_{\alpha}^{*}[X]_{j,j'} = \sum_{j''} \gamma_{\alpha,j''j'} \left( X_{j''j''} - X_{j'j'} \right),
\]
(A9)
one finds that it corresponds to the term on the right-hand side of Eq. (A6). For the non-diagonal part, one finds \( D_{\alpha,ND}^{*}[X_{ND}] = D_{\alpha,ND}[X_{ND}] \).

Appendix B: Additional information on the numerical results

The QMC algorithm evolves the system’s state from an initial pure state \( |\psi(0)\rangle \) to a final \( |\psi(t)\rangle \). To initiate a QMC trajectory one thus needs to choose an initial state \( |\psi(0)\rangle \) compatible with the initial density matrix \( \rho(0) \). One special choice is to take \( |\psi(0)\rangle \) to be one of the \( \{|k_0\rangle\} \), i.e. the eigenstates of \( \rho(0) \), with probability \( p_{k_0} \), such that:
\[
\rho(0) = \sum_{k_0} p_{k_0} |k_0\rangle\langle k_0|.
\]
(B1)

This choice corresponds to a non-invasive measurement that does not induce any back-action on the system. This is the approach that we followed for the simulations whose results are shown in Fig. 1 in the main text, and in Fig. 2 in this appendix. Given that the FT, Eq. (18), is independent of the initial basis, we also consider below the case where the system is initially projected on the basis \( \{|j\rangle\} \) defining the jump operators introduced in Eq. (2). In contrast to the previous choice, in this case the measurement is indeed invasive and induces measurement back-action. Nonetheless, our fluctuation theorem is still valid.

We now discuss the evaluation of the system’s entropy change with the QMC. We write the FT, Eq. (18), in the form, see Eq. (5),
\[
\langle e^{-\Delta S_B - \Delta S_S}\rangle_{tr} = 1,
\]
(B2)
where now \( \langle \ldots \rangle_{tr} \) is the average over the QMC trajectories.

Given that the entropy change of the baths along a trajectory is well defined, see Eq. (24), we are left with the question of how to sample the system’s entropy change \( \Delta S_S \) along the quantum trajectories.

Inspired by what one does in the classical case one can possibly sample two different quantities along a single trajectory
\[
\Delta S_{sys,x} = -\langle \psi(t)| \log \rho(t)|\psi(t)\rangle + \langle \psi(0)| \log \rho(0)|\psi(0)\rangle,
\]
(B3)
\[
\Delta S_{sys,y} = -\log \left( \langle \psi(t)| \rho(t)|\psi(t)\rangle \right) + \log \left( \langle \psi(0)| \rho(0)|\psi(0)\rangle \right).
\]
(B4)
where \( \rho(t) \) is the solution of the ME \( \{B1\} \). In the classical case, these two quantities are equivalent, as \( \rho(t) \) is diagonal, and the state \( |\psi(t)\rangle \) is one of the states of the chosen basis. However, these two possible definitions for the system entropy provide a completely different result for a quantum non-diagonal state. This is also evident in our numerical demonstration of the FT, and we anticipate that the second definition is the correct one. We can also provide a theoretical argument for this result. With the QMC, one can evaluate the solution \( \rho(t) \) to the ME as
\[
\rho(t) = \langle |\psi(t)\rangle|\psi(t)\rangle_{tr}.
\]
(B5)

Strictly speaking, the equality is exact when one considers the whole ensemble of possible trajectories. In a QMC trajectory, from \( |\psi(0)\rangle = |k_0\rangle \) to \( |\psi(t)\rangle \), one can sample \( \Delta S_B \), Eq. (24). Let us now consider the FT in the form of Eq. (18) and address the question of how we can evaluate \( \Psi^{(1)}(t)\{\Pi_{k_0}\} \) with an average over the MC trajectories. Inspection of Eq. (B5), and of the definition of \( \Psi(\xi,t) \), Eq. (9), suggests
\[
\Psi^{(1)}(t\{\Pi_{k_0}\}) = \langle e^{-\Delta S_B} |\psi(t),|k_0\rangle |\psi(t)\rangle\langle \psi(t)|_{tr}.
\]
(B6)

Comparison of the last equality with the FT in the form of \( \{B3\} \) and \( \{B4\} \), suggests that \( \Delta S(t)_{sys,y} \) as given by Eq. (B4) must be used in the numerical evaluation of the FT. This corresponds to Eq. (25) introduced in the main text.

This conclusion is confirmed by the results for the two-spin system shown in Fig. 2 where the trajectory average in Eq. (22) is shown for different values of the system parameters and of the initial state \( \rho(0) \), and the two possible definitions of system entropy change \( \{B3\} \)–\( \{B4\} \) are used. In particular, in Fig. 2(d) we consider the case of a time-dependent Hamiltonian, where the external field is changed according to \( h(t) = h_0 + (h_1 - h_0)t/t_t \).

We can also check that the FT holds for an arbitrary initial basis, as predicted by Eq. (18). In Fig. 2 we start the simulations from (i) the basis \( \{|k_0\rangle\} \) that diagonalises the initial state \( \rho(0) \), and (ii) the basis \( \{|j\rangle\} \) defining the jump operators introduced in Eq. (2). We see that the FT is numerically satisfied for both choices.
1. Other information on the numeric results

We remind the reader that in the main text we consider a system of two spin-1/2 particles with Hamiltonian

\[ H = -J \sigma_{x,a} \otimes \sigma_{x,b} - h(\sigma_{z,a} \otimes I_2 + \otimes I_2 \otimes \sigma_{z,b}) \]  

(B7)

where each spin is connected to an equilibrium reservoir at temperatures \( T_a \) and \( T_b \), respectively. The jump operators “flip” the individual spins: \( L_\lambda = \sigma_{-\lambda} \otimes I_b \) or \( L_\lambda = I_a \otimes \sigma_{-\lambda} \).

The diagonal initial state for Fig. 1 in the main text and Fig. 2 in this appendix (panels (a), (b), and (d)) reads \( \rho_D^{(0)} = (0.4, 0.275, 0.175, 0.15) \) in the basis \( \{ |↑↑⟩, |↑↓⟩, |↓↑⟩, |↓↓⟩ \} \).

The non-diagonal initial state in the same figures (panel (c)) was obtained as follows. We introduced the operator

\[ H_0 = -\frac{1}{2} \Pi_{|↑↑⟩} - \frac{1}{4} \Pi_{|↑↓⟩} - \frac{1}{3} \Pi_{|↓↓⟩} \]

\[ -h\sigma_{x,a} \otimes I_2 + h I_2 \otimes \sigma_{x,b} \]  

(B8)

then

\[ \rho^{(0)} = e^{-H_0/2} / \text{Tr}[e^{-H_0/2}] \]  

(B9)

The bosonic bath dissipation rates used to solve numerically the quantum ME (1) and in the QMC algorithm read \( 43 \)

\[ \gamma_{\alpha,\lambda} = \frac{g |\omega_\lambda|}{1 - e^{\beta_\alpha |\omega_\lambda|}} \begin{cases} e^{\beta_\alpha |\omega_\lambda|} & \omega_\lambda \geq 0, \\ 1 & \omega_\lambda \leq 0, \end{cases} \]  

(B10)

where \( g \) is a microscopic frequency and \( \omega_\lambda \) is defined in Eq. (4) in the main text.

**FIG. 2.** QMC simulations of the two-spin system (B7): \( \langle \exp(-\Delta S_{\text{tot}}) \rangle_{\text{tr}} \) and \( \langle \exp(-\Delta S_B) \rangle_{\text{tr}} \) as functions of \( t \), with \( \Delta S_{\text{tot}} = \Delta S_B + \Delta S_S \). For the system’s entropy variation we use the two possible definitions Eq. (B3) and (B4). Averages over \( 10^6 \) trajectories, \( g = 0.1, T_a = 1 \). (a): diagonal \( \rho^{(0)} \), \( J = 0, h = 0.2, T_b = 1 \) (classical case at equilibrium). (b): diagonal \( \rho^{(0)} \), \( J = 0.1, h = 0.2, T_b = 1.2 \). (c): non-diagonal \( \rho^{(0)} \), \( J = 0.1, h = 0.2, T_b = 1.2 \). (d): non-diagonal \( \rho^{(0)} \), \( J = 0.2, T_b = 1.2 \), and time dependent field \( h(t) = 0.4t/t_f \), with \( t_f = 15 \). See section B1 for the detailed description of \( \rho^{(0)} \).
FIG. 3. QMC simulations of the two-spin system: $\langle \exp(-\Delta S_{\text{tot}}) \rangle_{\text{tr}}$ and $\langle \exp(-\Delta S_{B}) \rangle_{\text{tr}}$ as functions of $t$, with $\Delta S_{\text{tot}} = \Delta S_{B} + \Delta S_{S}$. Non-diagonal $\rho^{(0)}$, $J = 0.1$, $h = 0.2$, $T_b = 1.2$. See section B1 for the detailed description of $\rho^{(0)}$. We start the simulations with (i) the basis $\{|k_0\rangle\}$ that diagonalises the initial state $\rho^{(0)}$, and (ii) the basis $\{|j\rangle\}$ defining the jump operators introduced in (2).