Work as an external quantum observable and an operational quantum Jarzynski equality

Konstantin Beyer,* Kimmo Luoma,† and Walter T. Strunz‡

Institut für Theoretische Physik, Technische Universität Dresden, D-01062, Dresden, Germany
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In this Letter we propose a framework to define work as a quantum observable on a control device which is driving a system. Motivated by the conceptual difference between well known quantum versions of the Jarzynski equality (JE), where the initial and final system Hamiltonian have to be known in advance, and their classical counterparts where such knowledge is not needed, we construct a scheme where a work increment is given by an expectation value of a quantum observable on an external system. We further show that such a definition of work satisfies a fluctuation theorem which allows the free energy difference to be estimated operationally without knowledge about the Hamiltonian of the system at the end of the driving protocol. However, knowledge about the basis of the initial Hamiltonian is in general still needed. Providing two examples we describe how bounds on free energy differences could approximately be determined in experiments.

Introduction— The classical Jarzynski equality (JE) [1, 2] connects the work W performed in non-equilibrium realizations of a driving protocol with the equilibrium free energy difference ∆F by the relation

\[ e^{-\beta W} = e^{-\beta \Delta F} \]  

(1)

The driving protocol is given by a time-dependent system Hamiltonian \( H_S(t) \). Initially, the system is in a thermal state with respect to the initial Hamiltonian \( H_S^A = H_S(0) \) at inverse temperature \( \beta \). At the end of the protocol the final Hamiltonian \( H_S^B = H_S(T) \) is reached. The JE then tells us that, by measuring the work \( W \) for many realizations of the protocol, we can obtain the free energy difference \( \Delta F = -1/\beta \ln(Z_B/Z_A) \) between the thermal states of \( H_S^A \) and \( H_S^B \) even though the system never reaches the thermal state of the final Hamiltonian.

The JE has been celebrated not only for its theoretical impact on the understanding of non-equilibrium dynamics but also because of its practical relevance for the estimation of free energy differences of complex mesoscopic systems [3–16]. The prototypical example is the forced unfolding of large molecules such as RNA [6, 7, 9, 11, 12]. The work needed to expand the molecule is measured externally by pulling one end and simultaneously measuring the force during this process (for example with an AFM). It is then possible to determine the \( \Delta F \) without any knowledge about the details of the system of interest (for example the Hamiltonian of the molecule) and without waiting a long time until the system has reached a thermal state at the end of the driving protocol.

Extending the concept of work to the quantum case has led to different proposals which are able to capture different aspects of what is classically called work [17–26]. A particularly popular ansatz to define work in the quantum case is the so called two point measurement (TPM) scheme. One of the main reasons for its broad acceptance [4, 27–32] is probably its ability to reproduce all kinds of fluctuation relations known from classical statistical physics, especially the JE in the form given by Eq. (1). The TPM scheme in its standard form is based on two projective energy measurements. The first measurement takes place at time \( t = 0 \), the second one at time \( t = T \). Assuming a finite quantum system, the energy measurements are, therefore, given by

\[ \hat{H}_S^A = \sum_a E_a |a⟩⟨a|, \quad \hat{H}_S^B = \sum_b E_b |b⟩⟨b|, \]  

(2)

where the \(|a⟩\)'s and \(|b⟩\)'s are the energy eigenstates for the first and the second measurement, respectively. Throughout this Letter we will consider closed system dynamics. Thus, the dynamics of the system between the two measurements is given by a unitary

\[ U = T e^{-i \int_0^T dt \hat{H}_S(t)}. \]  

(3)

It can easily be verified that the JE (Eq. (1)) is fulfilled for arbitrary \( U \) if the work assigned to given outcomes \( a \) and \( b \) is defined by \( W(a,b) = E_b - E_a \) [33].

Corrections and alternative formulations of the JE have been proposed for different kinds of non-unitary quantum evolution between the energy measurements, including decoherence, heat exchange and intermediate measurements [4, 23, 34–42]. For simplicity we will stick here to the case of unitary system dynamics.

While the classical JE and its TPM quantum version are formally identical, there is an important difference from the operational point of view. The classical work values can be determined by measuring an externally applied force along a path. Such a tool is by construction missing in the TPM scheme. This issue is closely related to the fact that “work is not an observable” [22] on the system. The \( W \) is not given by a quantum expectation value but is assigned to a sequence of outcomes \( \{a,b\} \) [29].
Relative Hamiltonians— We will now construct a model which allows to define work as a quantum observable on a control system. As in the classical experimental approaches we will separate the system of interest $S$ (e.g. the RNA in the classical experiment) from the control device $C$ (e.g. the AFM which applies and measures the external force which drives the system). Usually, varying quantum Hamiltonians are modelled by an operator $\hat{H}_S(\lambda)$, where $\lambda$ is a parameter, associated with an external classical and macroscopic system, for example a varying magnetic field which is given by a vector $\vec{B}$. In such an approach the classical part, by construction, cannot be treated quantum mechanically. Therefore, in order to derive an operationally accessible description of an external force which results in a change of the system Hamiltonian we need an ansatz which includes the external device in the quantum picture in a meaningful way, that is, the global dynamics should be modelled by the standard formalism of quantum mechanics: unitary evolution and quantum measurements.

We consider a system $S$ which is coupled to a control device $C$. The coupling is given by a Hamiltonian $\hat{H}_{SC}$. In general the interaction will create entanglement between $S$ and $C$. However, we expect the control system not to be entangled but in an objective pure state, otherwise it would not be justified to consider it to be in a definite state representing a parameter of the system Hamiltonian. In order to keep the control system in a well defined state we can reset it rapidly to a definite state $|\psi_C\rangle$. In a Zeno-like limit (very fast resetting) the system does not entangle anymore with the control device. For reasons that will become clear later, we model the resetting procedure by a sequence of ancilla control systems $C_i$ all prepared in the same initial state $|\psi_C\rangle$. Each ancilla interacts once with $S$ by the interaction Hamiltonian $\hat{H}_{SC}$. We assume the coupling time $\Delta t$ to be very short such that the single-collision map for the system state $\rho_S$ is given by

$$
\rho'_S = \text{Tr}_C\{e^{-i\hat{H}_{SC}\Delta t} (\rho_S \otimes |\psi_C\rangle\langle\psi_C|) e^{i\hat{H}_{SC}\Delta t}\},
$$

$$
= \rho_S - i[\langle\psi_C|\hat{H}_{SC}|\psi_C\rangle, \rho_S] + O(\Delta t^2). \tag{4}
$$

In a continuous limit ($\Delta t \rightarrow dt$) we obtain an effective unitary von-Neumann dynamics in $S$ [43]

$$
\dot{\rho}_S = -i[\langle\psi_C|\hat{H}_{SC}|\psi_C\rangle, \rho_S] = -i[H_{SC}^{(\psi_C)}, \rho_S], \tag{5}
$$
given by the effective Hamiltonian $H_{SC}^{(\psi_C)} = \langle\psi_C|\hat{H}_{SC}|\psi_C\rangle$ which we denote the relative Hamiltonian of $S$ with respect to the control state $|\psi_C\rangle$. The analogy to the classical case is obvious. There, the potential in the Hamiltonian can depend on the setting of an external control parameter, e.g. the displacement of a spring pulling the system. It is important to note that the Zeno-like resetting applies to the control device only. The system is not measured. As shown in [44] this would lead to frozen dynamics and trivializes the work statistics.

A change of the local Hamiltonian in $S$ can now be implemented by changing the initial states $|\psi_C(t)\rangle$ of the ancillas (before their collision) in the control system which results in a time-dependent Hamiltonian $\hat{H}_S^{(\psi_C)}$.

Work— Within this collision model framework we are now able to define work operationally by an external observable. Varying the relative Hamiltonian $\hat{H}_S^{(\psi_C)}$ leads to a change of the inner energy of $S$ which can be seen as work performed on the system by the external control. Between two collisions the experimenter changes the control system $|\psi_C\rangle \mapsto |\psi'_C\rangle = |\psi_C\rangle + |\psi_C\rangle dt$. This results in a change of the effective Hamiltonian on the system $\hat{H}_S^{(\psi_C)} \mapsto \hat{H}_S^{(\psi'_C)}$. Accordingly, the energy of the system in a state $|\psi_S\rangle$ changes to first order in $dt$ as

$$
dW = \langle\psi'_C|\langle\psi_S|\hat{H}_{SC}|\psi_S\rangle|\psi'_C\rangle - \langle\psi_C|\langle\psi_S|\hat{H}_{SC}|\psi_S\rangle|\psi_C\rangle
= \langle\psi'_C|\hat{H}_S^{(\psi'_C)}|\psi'_C\rangle - \langle\psi_C|\hat{H}_S^{(\psi_C)}|\psi_C\rangle
= dt\langle\psi'_C|\hat{H}_S^{(\psi'_C)}|\psi'_C\rangle + \langle\psi_C|\hat{H}_S^{(\psi_C)}|\psi_C\rangle dt + O(dt^2)
= i dt\langle\psi'_C|\hat{H}_S^{(\psi'_C)}|\psi'_C\rangle - i dt\langle\psi'_C|\psi_C\rangle
= -2dt \text{Im}\{\langle\psi_C|\psi'_C\rangle\}, \tag{6}
$$

where we have used that the state of a single ancilla after its collision with the system in state $|\psi_S\rangle$ is given by $|\psi'_C\rangle = |\psi_C\rangle - i H_{SC}^{(\psi'_C)}|\psi_C\rangle dt = |\psi_C\rangle + |\psi'_C\rangle dt$, and, therefore, $\hat{H}_S^{(\psi'_C)}|\psi_C\rangle = i|\psi_C\rangle$. From Eq. (6) we can see that the work increment done on $S$ is encoded in the change of the ancilla’s initial state $|\psi_C\rangle$, which is controlled by the experimenter, and the change of the ancilla state due to an interaction with the system $|\psi'_C\rangle$, which can be measured by the experimenter. Crucially, knowledge about the Hamiltonian $\hat{H}_{SC}$ is not needed to determine $dW$. Furthermore, no measurement is performed on $S$.

In order to determine the work $dW$, an observable on the state of the ancilla $|\psi'_C\rangle$ after its collision with $S$ has to be measured. It should be clear that this measurement yields, in general, random outcomes. Thus, we are looking for an observable on $C$ whose expectation value is the performed work $dW$. We can build the work increment observable for a single step in the collision model with the following orthogonal vectors which only con-
tain states known to the experimenter:

\[ |\phi_+\rangle = |\psi_C\rangle + i \alpha |\dot{\psi}_C\rangle, \]
\[ |\phi_-\rangle = |\psi_C\rangle - i \alpha |\dot{\psi}_C\rangle, \]
\[ \alpha = \sqrt{\frac{\langle \psi_C | \psi_C \rangle}{\langle \dot{\psi}_C | \dot{\psi}_C \rangle}}. \quad (7) \]

The work increment observable reads

\[ \Omega = \frac{1}{2\alpha} (\langle \psi_+ \rangle \langle \psi_+ \rangle - \langle \psi_- \rangle \langle \psi_- \rangle) + \zeta \mathds{1} \]
\[ = \mathcal{I} (\langle \psi_C^\ast \rangle |\psi_C\rangle - |\psi_C\rangle \langle \psi_C^\ast \rangle) + \zeta \mathds{1}, \quad (8) \]
with \( \zeta = -2i \text{Im} \{ \langle \psi_C | \psi_C \rangle \} \). The correction \( \zeta \) is also known to the experimenter since it does not depend on the state of the system \( S \) but only on the control \( C \). The observable \( \Omega \) yields the correct average work increment (to the first order in \( dt \)) for the single step

\[ \langle \psi_C^\ast | \Omega | \psi_C \rangle = dW. \]

Therefore, concatenating the work increments \( dW \), in our scheme we are able to operationally determine work performed on a system \( S \) by measuring a control system \( C \) without knowing the Hamiltonians. This is in strong analogy to classical pulling experiments for the verification of the JE, where the work can be measured by measurements of an external force along a path of the control system.

Let us assume that the system \( S \) starts in an initial state \( \rho_S \). Applying the external driving by means of the collision model approach leads to a unitary evolution \( \rho'_S = U \rho_S U^\dagger \). The work supplied by the control system has to be measured over many runs with the same initial state and the same protocol \( |\psi_C(t)\rangle \), since the quantum observables \( \Omega \) yield the correct \( dW \) as their expectation values. Total \( \langle W \rangle \) along the protocol is the change of the energy expectation value during the evolution \( \langle W \rangle = \text{Tr} \{ \hat{H}^B \rho'_S \} - \text{Tr} \{ \hat{H}^A \rho_S \} \). Starting in a mixed state \( \rho_S \), the observable will only give the average change of energy. This is crucial for the development of a JE as we will see later on.

**TPM-JEs are mathematical identities** — Before we continue to apply our observable definition of work to a JE we have to discuss some conceptual issues of the standard TPM-JE. The latter has no predictive power for the free energy difference \( \Delta F \), which is in very contrast to the usual classical approach. In a TPM-JE the free energy difference is already known before the experiment starts. By construction, in order to perform the projective energy measurements, the two Hamiltonians \( \hat{H}_S^A \) and \( \hat{H}_S^B \) need to be known in advance. This, however, allows to calculate the free energy difference \( \Delta F \) directly from the partition functions \( Z_A \) and \( Z_B \). In other words, the left and right hand side of a quantum JE are determined from the same inputs, namely \( \hat{H}_S^A \) and \( \hat{H}_S^B \). Interestingly enough, this issue is usually not mentioned in the literature about quantum fluctuation relations [45], although other problems like coherences and measurement backactions in the quantum case are usually explicitly stressed and addressed [40, 46–53].

It is insightful to consider a TPM scenario in the classical pulling RNA experiment. At time \( t = 0 \) the experimenter needs to determine the microstate of the molecule, that is, she measures position and momentum of each single atom (in principle this is possible in a classical experiment). Then, she only needs to input this phase space state into the (classical) Hamiltonian of the whole molecule, which she of course needs to have at hand in order to determine the energy of the particular microstate in this run. After applying the driving protocol she measures the new microstate and plugs it into the new Hamiltonian in order to get the energy at the end of the protocol. Such a classical TPM scheme could in principle be implemented and it would of course lead to the verification of the JE, but it would hardly be considered as a breakthrough for the experimental accessibility of equilibrium quantities through non-equilibrium processes. It is important to emphasize that the issue addressed here is not an insufficiency of the possible experimental realizations, such as finite number of runs, noise, energy stored in the control system or problems with the convergence of the average over the exponentiated work [6, 54–58] but a conceptual problem of the TPM scheme.

Several alternative approaches avoiding the TPM scenario have been proposed and experimentally implemented in recent years. They rely, for example, on interferometric, ancilla-assisted schemes [59–65], work reservoirs [40, 46], or use quantum trajectory techniques to define work [36, 66–73]. The knowledge of the initial and final Hamiltonians are again necessary in these scenarios, though. However, it has to be emphasized that this conceptual issue only applies to the operational determination of free energy differences and does not affect quantum thermodynamics in general.

How does the situation change in our framework proposed above? The work can be measured externally without knowing the Hamiltonian \( \hat{H}_{SC} \). On the other hand, since \( \Omega \) is a quantum observable only its expectation value is in general a meaningful quantity which has to be determined in many runs of the same experiment. Thus, starting in a thermal state with respect to the initial Hamiltonian \( \hat{H}_{SC}^0 \), the approach can only measure the average work \( \langle W \rangle \) without any knowledge about the Hamiltonians. Nevertheless, while in the TPM scheme both Hamiltonians \( \hat{H}_S^A \) and \( \hat{H}_S^B \) are known, the externally observed work allows to construct a one-point measurement scheme which can determine free energy differences \( \Delta F \) in an operationally meaningful way.
Operational Quantum One-Point Measurement JE— In order to obtain a work distribution which satisfies a JE, the experimenter needs to prepare on objective ensemble of energy eigenstates which represents the initial thermal state. She can do so by measuring the initial state in the basis of $\hat{H}_S^A$ which of course means that also in this scenario the basis of the initial Hamiltonian has to be known. However, from the operational point of view, there is a difference between $\hat{H}_S^A$ and $\hat{H}_S^B$ in a quantum JE experiment. While the initial Hamiltonian can be operationally determined by state tomography, the final one could only be obtained by process tomography since the system never thermalizes in $\hat{H}_S^B$.

Therefore, we propose the following operational One-Point Measurement scheme. In each run, the system starts in a thermal state with respect to the initial Hamiltonian $\hat{H}_S^A$ at inverse temperature $\beta$. At $t = 0$ the system is measured in the energy eigenbasis with outcome $a$ and the work is measured externally by the observables $\Omega$. After sufficiently many runs the work associated with outcome $a$ can be determined and we get

$$\langle W_a \rangle = \text{Tr}\{\hat{H}_S^B U |a\rangle \langle a| U^\dagger\} - \text{Tr}\{\hat{H}_S^B |a\rangle \langle a|\}. \quad (9)$$

These work values do not satisfy the standard JE (1) but it has been shown in [74] that they fulfil a modified equality

$$E_a [e^{-\beta\langle W_a \rangle}] = e^{-\beta \Delta F} e^{-S(\hat{\rho}_T||\rho_T^{\text{th}})} = e^{-\beta \Delta F}, \quad (10)$$

where $S(\hat{\rho}_T||\rho_T^{\text{th}})$ is the quantum relative entropy between a fictitious “best guess” state and the thermal state of the final Hamiltonian for the given inverse temperature $\beta$. $\langle W_a \rangle$ denotes the quantum expectation value for the work performed whenever the initial measurement yields $a$, whereas $E_a$ denotes the classical average over $a$. The state $\hat{\rho}_T$ is given by

$$\hat{\rho}_T = \frac{1}{Z_T} \sum_a e^{-\beta\langle a| U^\dagger \hat{H}_S^B U |a\rangle } U |a\rangle \langle a| U^\dagger, \quad (11)$$

with $Z_T = \sum_a e^{-\beta\langle a| U^\dagger \hat{H}_S^B U |a\rangle }$. The right hand side of this modified JE (10) was originally derived to show the thermodynamic cost of the second measurement in a standard TPM scheme. It clearly depends on the time evolution $U$ generated by the driving. It is crucial to note that both states $\hat{\rho}_T$ and $\rho_T^{\text{th}}$ remain unknown in our operational approach. Thus, Eq. (10) cannot directly be used to obtain the $\Delta F$ in an operational sense. However, the relative entropy $S(\hat{\rho}_T||\rho_T^{\text{th}})$ is always non-negative and only vanishes if $\hat{\rho}_T = \rho_T^{\text{th}}$. So we have

$$\Delta F = \Delta \hat{F} - \frac{1}{\beta} S(\hat{\rho}_T||\rho_T^{\text{th}}) \leq \Delta \hat{F} \leq \langle W \rangle. \quad (12)$$

Therefore, optimizing over possible protocols which start in $\hat{H}_S^A$ and end in $\hat{H}_S^B$ can provide tighter bounds on $\Delta F$ because the resulting unknown $U$ might lead to a lower relative entropy. The true $\Delta \hat{F}$ is obtained for $S(\hat{\rho}_T||\rho_T^{\text{th}}) = 0$ which is the case whenever $[U^\dagger \hat{H}_S^B U, \hat{H}_S^B] = 0$. Therefore, in principle, $\Delta F$ is operationally obtainable without knowledge about the final Hamiltonian $\hat{H}_S^B$.

**Example: Qubit System, Qubit Control**— To illustrate the concept we consider a simple example. System $S$ and control $C$ are qubits. The change of the Hamiltonian in $S$ is given by a sequence of ancilla qubit systems $C_i$ initialized in states $|\psi_i(t)\rangle$ with coupling

$$\hat{H}_{SC}^1 = \sigma_x \otimes |0\rangle\langle 0| - \frac{1}{2} \sigma_y \otimes |1\rangle\langle 1|. \quad (13)$$

We parametrize the initial ancilla states by two functions $\theta(t)$ and $\phi(t)$ with

$$|\psi_C(t_i)\rangle = \cos \frac{\theta(t_i)}{2} |0\rangle + e^{i\phi(t)} \sin \frac{\theta(t_i)}{2} |1\rangle. \quad (14)$$

The relative Hamiltonian on $S$ only depends on $\theta$ and is given by

$$\hat{H}_S^1(\theta) = \cos^2 \frac{\theta(t_i)}{2} \sigma_x - \frac{1}{2} \sin^2 \frac{\theta(t_i)}{2} \sigma_y. \quad (15)$$

Starting the protocol at $\theta(0) = 0$ and ending with $\theta(T) = \pi$ leads to a change of the free energy $\Delta F = -\langle 1/\beta \rangle \ln[\cosh(\beta A)/\cosh(\beta B)]$. In Fig. 1 (a) we plot $\Delta F$, $\Delta F_1$ and $\langle W \rangle_1$ for different switching times $T$. The switching function is $\theta(t) = (\pi/T) t$ and we approximate the protocol by $N = 40000$ collisions each of length $\Delta t = T/N$.

In the limit of short switching time $T$ the reduced state stays diagonal in the initial Hamiltonian and, since
\[ \langle H_0^A + H_0^B \rangle \neq 0, \] the modified Jarzynski equality does not give the correct free energy \( \Delta F \) because of the contribution of the relative entropy in Eq. (12). Nevertheless, the obtained value is better than the bound given by \( \langle W \rangle_1 \).

For large \( T \) we are in the regime of quantum adiabatic evolution. The system approximately stays diagonal in the eigenbasis of the instantaneous Hamiltonian during the whole protocol. Thus, \( \langle S(\rho_f || \rho^b_f) \rangle = 0 \) and \( \Delta \tilde{F} = \Delta F \).

The quantum adiabatic evolution must not be confused with a thermodynamically adiabatic process. The system does not evolve through thermal equilibrium states and \( \langle W \rangle \neq \Delta F \).

The Hamiltonian \( \hat{H}_1^1(\theta) \) only depends on a single parameter of the control system. Taking another interaction Hamiltonian \( \hat{H}_2^2_{\text{SC}} = 2(\sigma_+ \otimes \sigma_+ + \sigma_- \otimes \sigma_-) \) we get a dependence on both \( \theta \) and \( \phi \).

\[
\hat{H}_2^2(\theta, \phi) = e^{i\phi} \sin(\theta) \sigma_+ + e^{-i\phi} \sin(\theta) \sigma_-,
\]

where \( \theta \) determines the spread of the energy levels and \( \phi \) defines the direction of the Hamiltonian in the \( x - y \) plane of the Bloch sphere. We set \( \theta(0) = \pi/2, \theta(T) = \pi/6, \phi(0) = 0, \) and \( \phi(T) = \pi/2 \) which leads to same initial and final Hamiltonians and, therefore, also to the same \( \Delta F \) as in the example above. As we can see in Fig. 1 (a) the quantities \( \Delta \tilde{F}_2 \) and \( \langle W \rangle_2 \) show a different behavior under this protocol and the correct free energy difference \( \Delta F \) can now be reached even if the evolution cannot be considered to be approximately quantum adiabatic.

**Example: Displaced Harmonic Oscillator**—To illustrate the relevance of the entropic contribution for the external determination of free energy differences we consider a harmonic oscillator system \( S \). The control device \( C \) is again given by a qubit. The global Hamiltonian is chosen to be

\[
\hat{H}_{\text{SC}} = \omega(a^\dagger a + 1/2) + g(a \otimes \sigma_+ + a^\dagger \otimes \sigma_-),
\]

where \( g \) is a real coupling constant. The relative Hamiltonian on \( S \) depending on the the control state \( |\psi_C(t)\rangle \) is then given by

\[
\hat{H}_S(\theta, \phi) = \omega(a^\dagger a + 1/2) + \frac{g}{2} \sin(\theta)(e^{i\phi} a^\dagger + e^{-i\phi} a),
\]

which describes a harmonic oscillator displaced by a complex force. The free energy is independent of \( \phi \) and the free energy difference for an initial \( \theta_A \) and a final \( \theta_B \) is \( \Delta F = -|g^2/(4\omega)| \sin^2(\theta_B) - \sin^2(\theta_A) \). The external forcing only leads to an energy offset but does not influence the level spacing in the oscillator.

The chosen Hamiltonian has the property that the work performed on the system does not depend on the initial energy eigenstate [75]. Therefore, the initial energy measurement is superfluous and we have \( \Delta \tilde{F} = \langle W \rangle \). In a classical system such a situation would be rather boring since all energies are shifted by the same amount. In the quantum case, however, it allows to directly study the contribution of the relative entropy by measuring the average work externally. In Fig. 1 (b) we show the measurable \( \Delta \tilde{F} \) for different protocols \( \theta(t) \) and \( \phi(t) \) with the same initial and final Hamiltonians for different switching times \( T \). Most importantly, the correct free energy \( \Delta F \) can be determined not only in the quantum adiabatic limit but at finite times if the switching protocol is suitably chosen.

**Conclusion**—In this Letter we address the question how to construct a quantum observable for externally measuring work in analogy to the classical case of a forced system. In the framework, the control system is included in the quantum domain. Since the control parameter for the system Hamiltonian is usually assumed to be well defined, the control system needs to be in a well defined quantum state, known to the experimenter, at all times. We implement this by a repeated measure-and-prepare approach in a Zeno-like limit with a suitable work increment observable which provides a strong analogy to external work measurements in the classical case.

In contrast to standard TPM schemes for quantum work which presume that both the initial and final Hamiltonian are known to the experimenter and, therefore, have no practical relevance for the determination of free energy differences, we define an operational one point measurement scheme for work which satisfies a modified JE which only needs knowledge about the basis of the initial Hamiltonian.

Making use of this JE we illustrate in some basic examples that the model is suitable for the operational determination of bounds on free energy differences which include a relative entropy contribution if the final reduced state has coherences in the eigenbasis of the final Hamiltonian. This contribution vanishes in a quantum adiabatic limit but can also be avoided by a suitable optimization of the driving protocol.

An experimental implementation would in principle allow to obtain the left and right hand side of a quantum JE independently of each other. The one by a external measurement of different work trajectories in a quantum adiabatic regime, the other one by a thermodynamical adiabatic process including a heat bath and measuring the average work.

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* konstantin.beyer@tu-dresden.de
† kimmo.luoma@tu-dresden.de
‡ walter.strunz@tu-dresden.de
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Work as an external quantum observable and an operational quantum Jarzynski equality -
Supplemental Material

Konstantin Beyer,* Kimmo Luoma,† and Walter T. Strunz‡
Institut für Theoretische Physik, Technische Universität Dresden, D-01062, Dresden, Germany

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As in the classical case, one assumes the system to be initially in a thermal state of Hamiltonian $H_A$
\[
\rho_S = \frac{1}{Z_A} \sum_a e^{-\beta E_a} |a\rangle\langle a|, \quad Z_A = \sum_a e^{-\beta E_a}. \tag{1}
\]

Therefore, the probability to measure outcome $a$ and $b$ in first and second measurement, respectively, is then given by
\[
p(a,b) = \text{Tr}\{ |b\rangle\langle b| U |a\rangle\langle a| \rho_S |a\rangle\langle a| U^\dagger\}, \tag{2}
\]
where we have assumed that the first measurement is implemented by a Lüders instrument [? ? ]. The classical form of the JE can then directly be verified for the quantum TPM scheme [? ? ]
\[
\langle e^{-\beta W} \rangle = \sum_{a,b} p(a,b) e^{-\beta (E_b - E_a)}
= \sum_b \text{Tr}\{ Q_b U P_a \rho_S P_a U^\dagger \} e^{-\beta (E_b - E_a)}
= \sum_b e^{-\beta E_b} \text{Tr}\{ Q_b U \sum_a (e^{\beta E_a} P_a \rho_S P_a) U^\dagger \}
= \sum_b e^{-\beta E_b} \text{Tr}\{ Q_b U \frac{1}{Z_A} I U^\dagger \}
= \frac{1}{Z_A} \sum_b e^{-\beta E_b} = \frac{Z_B}{Z_A} = e^{-\beta \Delta F}. \tag{3}
\]

As one can see from the forth line, the TPM-JE in this form works for any unital dynamics and is not restricted to unitary ones [? ? ? ].

**THE WORK INCREMENT OBSERVABLE**

The vectors needed to construct the work are
\[
|\phi_+\rangle = |\psi_C\rangle + i \alpha |\psi_C\rangle,
|\phi_-\rangle = |\psi_C\rangle - i \alpha |\psi_C\rangle,
\]
\[
\alpha = \sqrt{\frac{\langle \psi_C | \psi_C \rangle}{\langle \psi_C | \psi_C \rangle}}. \tag{4}
\]

They are orthogonal and can therefore be used to define a suitable measurement on the ancillas after their collis-