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Crooks Relation in Optical Spectra: Universality in Work Distributions for Weak Local Quenches

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We show that work distributions and nonequilibrium work fluctuation theorems can be measured in optical spectra for a wide class of quantum systems. We consider systems where the absorption or emission of a photon corresponds to the sudden switch on or off of a local perturbation. For the particular case of a weak local perturbation, the Crooks relation establishes a universal relation in absorption as well as in emission spectra. Because of a direct relation between the spectra and work distribution functions this is equivalent to universal relations in work distributions for weak local quenches. As two concrete examples we treat the x-ray edge problem and the Kondo exciton.

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Equilibrium thermodynamics provides the framework for the description of the equilibrium properties of macroscopically large systems. This includes the properties of systems in equilibrium states as well as the description of transitions between different equilibrium states even if the system is not in equilibrium in the meantime. Starting in 1997 with a seminal contribution from Jarzynski [1], the field of nonequilibrium work fluctuation theorems [2] opened up. These relate a measurable nonequilibrium quantity, the work performed, to equilibrium free energies even if the system is driven arbitrarily far away from equilibrium.

Suppose a system is prepared in a thermal state at inverse temperature β . If the Hamiltonian $H(t)$ of the system changes during a time interval from 0 to t_f according to a prescribed protocol, work is performed on the system. In order to determine the work done two energy measurements are necessary leading to the notion that work is not an observable [3]; the work W rather is a random variable with a probability distribution function [3]

$$P_F(W) = \int \frac{ds}{2\pi} e^{iWs} G(s), \quad G(s) = \langle e^{iH(0)s} e^{-iH_H(t_f)s} \rangle. \quad (1)$$

Here $\langle \cdots \rangle$ denotes the thermal average over the initial state and $H_H(t_f) = U^\dagger(t_f) H(t_f) U(t_f)$ with $U(t_f)$ the time-evolution operator obeying the differential equation $i\partial_t U(t) = H(t)U(t)$. In this Letter we set $\hbar = 1$.

Let $P_B(W)$ be the probability distribution function for the backward protocol. Then the Crooks relation, first shown for classical systems [4] and later extended to closed as well as open quantum systems [5–7]:

$$\frac{P_F(W)}{P_B(-W)} = e^{\beta(W - \Delta F)}, \quad (2)$$

establishes a universal connection between the forward and backward processes that only depends on the equilibrium free energy difference ΔF of the final and initial state independent of the details of the protocol. The Jarzynski relation [1] is a consequence of Eq. (2), see, e.g., Ref. [4].

Experimental tests of the Crooks relation have been performed in recent years for classical systems. Among these are folding-unfolding experiments of small RNA-hairpins where the free energy difference between the folded and unfolded state has been extracted using the Crooks relation [8,9]. Moreover, it has been verified in electrical circuits [10], for mechanical oscillators [11], small colloidal particles [12], and nonthermal systems [13].

In the quantum case a measurement of work distributions has not been performed up to now. Recently, a measurement scheme in optical traps has been proposed [14] that has not been realized yet. In the present Letter we show that work distributions of quantum systems have been measured for decades in terms of x-ray spectra of simple metals. We point out that there exists a large class of quantum systems associated with the x-ray edge problem where absorption spectra $A(\omega)$ and emission spectra $E(\omega)$ can be identified with forward and backward work distributions for a sudden switch on or off of a local perturbation. This allows for an experimental observation of nonequilibrium work fluctuation theorems such as the Crooks relation. For the particular case of a weak local perturbation, the Crooks relation manifests in the universal relations

$$\frac{A(\omega + \Delta F)}{A(-\omega + \Delta F)} = e^{\beta\omega}, \quad \frac{E(\omega + \Delta F)}{E(-\omega + \Delta F)} = e^{-\beta\omega} \quad (3)$$

that hold in second order renormalized perturbation theory. This is the central result of this Letter that will be proven below. Here ΔF is the free energy difference between the system with and without local perturbation at the same inverse temperature β . Notice that an independent measurement of ΔF is not required to establish Eq. (3) in an experiment. Actually, Eq. (3) permits a determination of ΔF similar to experiments in biophysics [8,9]. Because of the correspondence between spectra and work distributions, Eq. (3) implies universal relations for work distributions of weak local quenches:

$$\frac{P_F(W + \Delta F)}{P_F(-W + \Delta F)} = e^{\beta W}, \quad \frac{P_B(W - \Delta F)}{P_B(-W - \Delta F)} = e^{\beta W}. \quad (4)$$

Here, $P_F(W)$ is the work distribution for a protocol where the local perturbation is suddenly switched on and $P_B(W)$ the work distribution for the backward protocol.

Consider a system weakly coupled to a monochromatic light field of frequency ω where the absorption or emission of a photon corresponds to the sudden switch on or off of a local perturbation. Such systems have been discussed extensively in the literature. In the x-ray spectra of simple metals a system of free fermions has to adapt to a suddenly created or annihilated local potential scatterer [15–18]. For metals with incomplete shells the local perturbation is related to localized orbitals [18,19]. As has been shown recently, spectra of quantum dots allow for an idealized implementation of x-ray edge type problems [20,21]. In the remainder, H denotes the Hamiltonian with the local perturbation and H_0 without, respectively.

Crooks relation in absorption and emission spectra.— First, we concentrate on the absorption case, the related emission spectra will be discussed below. The absorption spectrum for incident light of frequency ω in second order of the system-light field coupling (Fermi's golden rule) is related to a dynamical correlation function via Fourier transformation

$$A(\omega) = \kappa_A \int \frac{dt}{2\pi} e^{i\omega t} G_A(t). \quad (5)$$

The constant κ_A contains parameters depending on the experimental details such as the intensity of the incident light beam or the system-light field coupling. Note that the photon energy ω in Eq. (5) is not the bare one, it is usually measured relative to a constant offset ω_0 , e.g., the core-hole binding energy in the x-ray edge problem. We consider those systems where the dynamical correlation function $G_A(t)$ appearing in Eq. (5) is of the structure

$$G_A(t) = \frac{1}{Z_A} \text{Tr}(e^{-\beta H_0} e^{iH_0 t} e^{-iH t}), \quad Z_A = \text{Tr}(e^{-\beta H_0}) \quad (6)$$

as in the case of x-ray edge type problems [15–21]. For a particular problem at hand, the question of whether $G_A(t)$ can be brought into the form in Eq. (6) has to be studied on a case by case basis. Regarding Eq. (6) $G_A(t)$ is the characteristic function of a work distribution for a quench from H_0 to H , cf. Eq. (1). This identification allows for an observation of the Crooks relation in an optics experiment. Recently, x-ray edge singularities have been found in work distributions for local quenches in an Ising chain at criticality [22].

The emission spectrum $E(\omega)$ corresponding to the same setup is given by

$$E(\omega) = \kappa_E \int \frac{dt}{2\pi} e^{-i\omega t} G_E(t) \quad (7)$$

with

$$G_E(t) = \frac{1}{Z_E} \text{Tr}(e^{-\beta H} e^{iH t} e^{-iH_0 t}), \quad Z_E = \text{Tr}(e^{-\beta H}). \quad (8)$$

Hence, $E(-\omega)$ is proportional to the work distribution for a protocol where the local perturbation is switched off, that is precisely the backward process to absorption. A direct application of the Crooks relation in Eq. (2) therefore yields

$$\frac{A(\omega)}{E(\omega)} = \frac{\kappa_A}{\kappa_E} e^{\beta(\omega - \Delta F)} \quad (9)$$

as an exact result. This relation depends on experimental details through the parameters κ_A and κ_E . The linear scaling of $\ln(A(\omega)/E(\omega))$ as a function of the frequency ω of the light beam, however, is universal with a slope β . Note that Eq. (9) is valid for an arbitrary strength of the local perturbation, we only assume a small coupling to the external light field.

Two different measurements, absorption and emission, are necessary to explore this relation in experiment. However, the Crooks relation can also be measured in a single experiment in case of weak local perturbations where Eq. (3) holds as will be shown below. This has the additional advantage as opposed to the exact relation in Eq. (9) that also the experiment specific constants κ_A and κ_E drop out.

Equations (1), (6), and (8), show the formal equivalence between work distribution functions and optical x-ray edge spectra. In conventional experiments the work distribution function is sampled by recording in each realization the work performed. The full distribution function is successively built up jointly over all work values. Optical spectra, however, are recorded differently. The outcome of a measurement is not the work performed. Instead one obtains directly the probability for photon absorption (or emission) at a given frequency ω (work performed). The full distribution function is then constructed by sweeping the laser through all relevant frequencies.

The advantage of measuring work distributions via optical spectra is that the absorbed photon carries out the sequence of measuring the energy in the initial state, applying the perturbation, and measuring the energy of the final state, in a single step. It can be absorbed or emitted only in case when its frequency ω matches precisely the energy difference between the system's initial and final state. The disadvantage is that only specific local perturbations and only specific protocols (sudden switchings) can be implemented.

Crooks relation in a single spectrum.—Suppose V is the unitary transformation that diagonalizes the Hamiltonian H . In the following we normal order Hamiltonians relative to the finite temperature initial mixed state [23]. For generic weak coupling impurity problems the diagonalized Hamiltonian can be represented as [24]

$$VHV^\dagger = H_0 + \Delta F \quad (10)$$

in the thermodynamic limit [25] where ΔF denotes the free energy difference between the systems described by H and H_0 at the same temperature T . The appearance of temperature in this equation can be understood from the normal ordering procedure [24]. As a consequence of Eq. (10), the dynamical correlation functions $G_{A/E}(t)$ can be written as

$$\begin{aligned} G_A(t) &= \frac{1}{Z_A} \text{Tr}(e^{-\beta H_0} V^\dagger(t) V) e^{-i\Delta F t}, \\ G_E(t) &= \frac{1}{Z_A} \text{Tr}(e^{-\beta H_0} V(t) V^\dagger) e^{i\Delta F t} e^{-\beta \Delta F}, \end{aligned} \quad (11)$$

where $V(t) = e^{iH_0 t} V e^{-iH_0 t}$ and $\Delta F = -\beta^{-1} \log(Z_E/Z_A)$. For all the relevant cases, it is possible to represent the unitary transformation V as an ordered exponential $V = \text{Oexp}[\chi]$ where χ is anti-Hermitian, $\chi^\dagger = -\chi$, and O denotes some ordering prescription. For generic weak coupling problems such as the Kondo model at nonzero temperature analyzed later, the flow equation approach provides a general prescription for the construction of the unitary transformation V as an ordered exponential of its generator $\eta(B)$ [26]

$$V = \mathcal{T}_B \exp \left[\int_0^\infty dB \eta(B) \right], \quad (12)$$

where $\eta(B)$ is determined by a set of differential equations. For $B > B'$, \mathcal{T}_B orders an $\eta(B)$ left of an $\eta(B')$. Expectation values of ordered exponentials such as in Eq. (11) can be related to the exponential of a cumulant average [27] that can be expanded in a power series in powers of χ . The first cumulant vanishes as χ can be chosen normal ordered relative to the initial state. For the x-ray edge problem the cumulant expansion stops at second order within the validity of the bosonization technique, see below. For more complicated problems such as the Kondo exciton the diagonalizing unitary transformation can be obtained by the flow equation framework, see Eq. (12). In this case, the generator $\eta(B)$ and thus the

operator χ is proportional to the strength of the local perturbation such that in the case of a weak local perturbation the expansion is controlled by a small parameter. For systems with significant renormalization effects, couplings have to stay small over the whole renormalization flow.

Performing this cumulant expansion up to second order one observes that $G_A(t)$ and $G_E(t)$ are directly related to each other via $G_A(t) e^{i\Delta F t} = G_E(t) e^{-i\Delta F t} e^{-\beta \Delta F}$. For the spectra this result implies $\kappa_A E(\omega + \Delta F) e^{-\beta \Delta F} = \kappa_E A(-\omega + \Delta F)$. Plugging this relation into the Crooks relation, see Eq. (9), one directly proves the main result, Eq. (3), in second order renormalized perturbation theory.

In the remainder of this Letter, we will discuss two examples for the Crooks relation in absorption spectra: the x-ray edge problem and the Kondo exciton.

The x-ray edge problem.—In the x-ray edge problem the absorption of a photon is accompanied by the sudden creation of a local potential scatterer in a sea of noninteracting fermions [16]. Hence, we have $H_0 = \sum_k \varepsilon_k : c_k^\dagger c_k :$ and $H = H(g) = H_0 + (2\pi/L)g \sum_{kk'} : c_k^\dagger c_{k'} :$ where the colons denote normal ordering, see [24]. We consider a linearized dispersion $\varepsilon_k = v_F k$ and set $v_F = 1$. The Fourier transform of the absorption spectrum is given by [16]

$$S(t) = \frac{1}{Z_A} \text{Tr}(e^{-\beta H_0} e^{iH_0 t} \psi(0) e^{-iH(g)t} \psi^\dagger(0)) \quad (13)$$

that is yet not in the desired form as in Eq. (6). Using the bosonization technique, the fermionic fields $\psi(x)$ can be represented in terms of bosonic ones, $\phi(x)$, via $\psi(x) = a^{-1/2} F e^{-i\phi(x)}$ with a^{-1} an ultraviolet cutoff [28]. The Klein factor F commutes with $H(g)$ and does not contribute to $S(t)$ due to its property $FF^\dagger = 1$. The bosonization identity allows us to regard the fermionic fields as a unitary transformation acting on $H(g)$ such that $S(t) \propto G_A(t) e^{-i\Delta t}$ with a constant energy shift Δ that can be absorbed into a redefinition of the constant offset ω_o and $G_A(t)$ is in the desired form:

$$G_A(t) = \frac{1}{Z_A} \text{Tr}(e^{-\beta H_0} e^{iH_0 t} e^{-iH(1+g)t}). \quad (14)$$

The diagonalizing transformation V of $H(1+g)$ equals $V = e^{i(1+g)\phi(0)}$ [17]. Although the effective strength of the scatterer $1+g$ is not small, the cumulant expansion stops at second order as the operator in the exponent is linear in bosonic operators. Hence, in the range of validity of the bosonization treatment, the Crooks relation in Eq. (3) holds exactly for the x-ray edge absorption spectrum. Comparing bosonization [17] with the exact treatment [16], it yields the correct result up to second order in g . This restriction originates from the linearization of the free fermionic spectrum [17].

The Kondo exciton.—Recently, Türeci *et al.* [21] proposed an experimental setup for a quantum dot where the absorption of a photon corresponds to the sudden

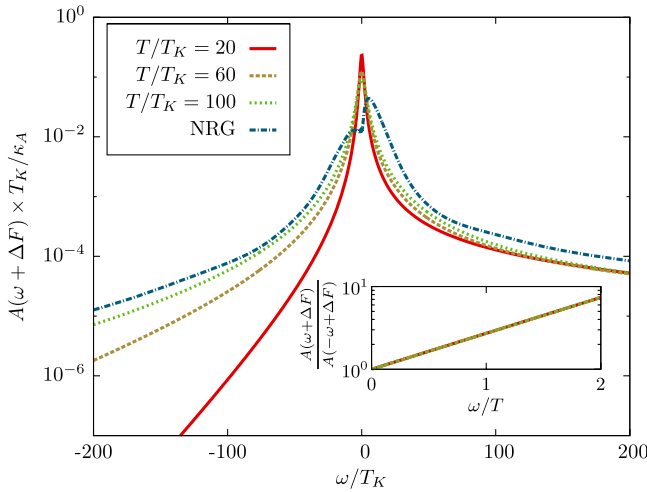


FIG. 1 (color online). Absorption spectrum of a Kondo exciton for different temperatures as a function of the light frequency. As a reference, a NRG curve for $T = 100T_K$ is shown taken from Türeci *et al.* [21]. In the regime $|\omega| \geq T$ where the NRG data are accurate the agreement is excellent within the numerical accuracy. The inset exemplifies the validity of the Crooks relation in the absorption spectrum of the Kondo exciton, all curves for $T/T_K = 20, 60, 100$ lie on top of each other when plotted against ω/T .

switch on of a Kondo impurity. Hence, we have $H_0 = \sum_{k\sigma} \varepsilon_k : c_{k\sigma}^\dagger c_{k\sigma} :$ and $H = H_0 + \sum_{kk'} J_{kk'} : \vec{S} \cdot \vec{s}_{kk'} :$. For details about the Kondo problem, see, for example, Ref. [29]. The dynamical correlation function $G_A(t)$ for the absorption spectrum is given by Eq. (6). The diagonalizing unitary transformation V can be obtained by the flow equation approach [26], cf. Eq. (12), with $\eta(B) = \sum_{kk'} (\varepsilon_k - \varepsilon_{k'}) J_{kk'}(B) : \vec{S} \cdot \vec{s}_{kk'} :$ in 1-loop order. The couplings $J_{kk'}(B)$ are determined by a set of differential equations [30]. Importantly, the flow equation framework includes all the renormalization effects such as the emergence of a low-energy scale T_K , the Kondo temperature. The absorption spectrum is obtained via the cumulant expansion up to second order in the coupling strength. Its validity is restricted to weak coupling problems such that we have to require $T \gg T_K$ [31]. A plot of the absorption spectrum is shown in Fig. 1 for different temperatures. As a reference, a NRG curve for $T = 100T_K$ obtained by Türeci *et al.* [21] for an Anderson impurity model in the Kondo regime is included in this figure [32]. In the vicinity of the main peak at small $|\omega| < T$, the NRG calculation contains an unphysical double peak structure. For more details we refer to Ref. [21]. For frequencies $|\omega| \geq T$, however, where the NRG data are accurate we observe excellent agreement with the results of the flow equation formalism. Asymptotic formulas for $A(\omega)$ in the limit $\omega \rightarrow \pm\infty$ can be found in Ref. [21]. The inset shows the validity of Eq. (3). The ratio $A(\omega + \Delta F)/A(-\omega + \Delta F)$ is the universal function $e^{\beta\omega}$ independent of any details.

Conclusions.—We have shown that work distributions and thus nonequilibrium work fluctuation theorems can be measured in optical spectra of quantum systems such as the x-ray edge problem or the Kondo exciton. For weak local perturbations, the Crooks relation establishes a universal relation within a single spectrum, absorption or emission, cf. Eq. (3).

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