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The Crooks relation in optical spectra - universality in work distributions for weak local quenches

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We show that work distributions and non-equilibrium 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. Due to 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 given fixed external parameters. Additionally, equilibrium thermodynamics allows for the description of transitions between different equilibrium states even if the system is not in equilibrium in the meantime. The near-equilibrium properties of systems driven only slightly out of equilibrium are determined by its equilibrium fluctuations according to linear response theory. Starting in 1997 with a seminal contribution from Jarzynski [1], the field of non-equilibrium work fluctuation theorems opened up. These relate a measurable non-equilibrium quantity, the work performed, to equilibrium free energies even if the system is driven arbitrarily far away from equilibrium. Most importantly, it is not required to wait for the system to equilibrate.

Suppose a system is initially prepared in an equilibrium state at a temperature $T = 1/k_B\beta$. If the Hamiltonian $H(t)$ of the system changes during a time interval from 0 to t_f according to an arbitrary protocol, energy is not conserved and work is performed on the system. In order to determine the work done on a system two energy measurements are necessary leading to the notion that work is not an observable [2]. The work ω rather is a random variable with a probability distribution function [2]

$$P_F(\omega) = \int \frac{dt}{2\pi}\, e^{i\omega t} G(t),\ \ G(t) = \left\langle e^{iH(0)t} e^{-iH_H(t_f)t} \right\rangle . \tag{1}$$

Here $\langle\cdots\rangle$ denotes the thermal average over the initial equilibrium configuration and $H_H(t_f) = U^\dagger(t_f)H(t_f)U(t_f)$ is the time-evolved final Hamiltonian with $U(t_f)$ the time-evolution operator obeying the differential equation $i\partial_t U(t) = H(t)U(t)$.

Let $P_B(\omega)$ denote the probability distribution function for the backward protocol. Then the Crooks relation, first shown for classical systems [3] and later extended to closed as well as open quantum systems [4–6]:

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

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 contained in Eq. (2) as a special case.

Experimental tests of the Crooks relation and of its variants have been performed in recent years. 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 [7, 8]. Moreover, the Crooks relation has been verified in electrical circuits [9], mechanical oscillators [10], for small colloidal particles [11] and for non-thermal systems, specifically a driven two-level system in a non-equilibrium steady state [12].

In this work it will be shown that work distributions and therefore the non-equilibrium work fluctuation theorems such as the Crooks relation can be measured in a large class of quantum systems. Namely, optical spectra of systems where the absorption and emission of a photon corresponds to the sudden switch on or off of a local perturbation are in fact work distributions. Among these are X-ray spectra of simple bulk metals as well as of quantum dots coupled to fermionic reservoirs. In such systems, the absorption spectra $A(\omega)$ and emission spectra $E(\omega)$ are proportional to forward and backward work distributions such that they are connected to each other via the Crooks relation. For the particular case of a weak local perturbation, they satisfy the universal relations

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

in second order renormalized perturbation theory. Here ΔF is the free energy difference between the system with and without local perturbation. 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 by plotting the spectrum, see below. Due to the correspondence between spectra and work distributions, Eq. (3) implies universal relations for work distributions of weak local quenches:

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

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

Consider a system that is coupled to a monochromatic light field of frequency ω. This coupling is assumed to be small such that it can be treated perturbatively. In the following, we will concentrate on the class of systems in which the absorption or emission of a photon corresponds to the sudden switch on or off of a local perturbation. In the remainder, H denotes the Hamiltonian with the local perturbation and H_0 without, respectively. Such systems have already been discussed extensively in the literature. In the X-ray spectra of simple metals, for example, a system of free fermions has to adapt to a suddenly created or annihilated local potential scatterer [13–15]. Quantum dots coupled to fermionic reservoirs can be initialized in such a way that the absorption of a photon implements the sudden switch on of a Kondo impurity [16].

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

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

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. Its precise value, however, is irrelevant for the derivation of Eq. (3). We consider those systems where the dynamical correlation function $G_A(t)$ appearing in Eq. (5) is of the structure

$$G_A(t) = \frac{1}{Z_A}\mathrm{Tr}\left(e^{-\beta H_0} e^{iH_0 t} e^{-iHt}\right), \;\; Z_A = \mathrm{Tr}\left(e^{-\beta H_0}\right). \qquad (6)$$

This is the case for X-ray edge type problems such as the original X-ray edge problem or the Kondo exciton. Thus, $G_A(t)$ is the characteristic function of a work distribution for a quench from H_0 to H, cf. Eq. (1). This is the origin of the connection between optical spectra and the work distribution that allows to observe the Crooks relation in an optics experiment. Recently, X-ray edge singularities have been observed in work distributions for local quenches in an Ising chain at criticality [17].

The emission spectrum $E(\omega)$ corresponding to the same setup formally resembles the absorption case, only the roles of H_0 and H are interchanged and the sign of ω is altered. The rate of photon emission $E(\omega)$ is given by:

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

with

$$G_E(t) = \frac{1}{Z_E}\mathrm{Tr}\left(e^{-\beta H} e^{iHt} e^{-iH_0 t}\right), \;\; Z_E = \mathrm{Tr}\left(e^{-\beta H}\right). \qquad (8)$$

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

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

as an exact result. This relation depends on experimental details through the parameters κ_A and κ_E. The linear scaling of $\ln(A(\omega)/E(\omega))$ with the frequency ω of the light beam, however, is universal with a slope β.

Two different measurements are necessary to explore this relation in experiment, one to determine the absorption and one to obtain the emission spectrum. However, the Crooks relation can also be measured in a single experiment for weak local perturbations: the emission and absorption spectra are directly related to each other such that in second order renormalized perturbation theory Eq. (3) holds. 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.

Crooks relation in a single spectrum. Suppose V is the unitary transformation that diagonalizes the Hamiltonian H. As it is well known for generic weak coupling impurity problems [18] the diagonalized Hamiltonian, $VHV^\dagger = H_0 + \Delta F$, is given by the unperturbed one in the thermodynamic limit up to a constant ΔF [19]. The shift ΔF is the free energy difference between H and H_0. More details about the unitary transformation will be given below. This relation between the diagonalized Hamiltonian H and H_0 allows to write the dynamical correlation functions $G_{A/E}(t)$ in terms of overlaps between V and $V^\dagger$:

$$\begin{aligned} G_A(t) &= \frac{1}{Z_A}\mathrm{Tr}\left(e^{-\beta H_0} V^\dagger(t) V\right) e^{-i\Delta F t}, \\ G_E(t) &= \frac{1}{Z_A}\mathrm{Tr}\left(e^{-\beta H_0} V(t) V^\dagger\right) e^{i\Delta F t} \end{aligned} \qquad (10)$$

For all the relevant cases, it is possible to represent the unitary transformation V as an ordered exponential

$$V = \mathrm{O}\exp[\chi] \tag{11}$$

where χ is antihermitian, $\chi^\dagger = -\chi$, and O denotes some ordering prescription. Thus, the adjoint is given by $V^\dagger = \overline{\mathrm{O}}\exp[-\chi]$ where $\overline{\mathrm{O}}$ is the ordering prescription opposite to O. In the X-ray edge problem no ordering prescription is needed and $\chi = i(1+g)\phi(0)$ with g the strength of the potential scatterer and $\phi(x)$ a bosonic field [15]. For generic weak coupling problems such as the Kondo model at nonzero temperature analyzed later, the flow equation approach [18] provides a general prescription for the construction of the unitary transformation V as an ordered exponential of its generator $\eta(B)$

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

where the generator is determined by a set of differential equations. Here, the symbol T_B orders an $\eta(B)$ left of an $\eta(B')$ if $B > B'$ as the usual time ordering operator. In view of Eq. (10) and Eq. (11), the dynamical correlation functions $G_{A/E}(t)$ can be written as the expectation values of a single exponential with an appropriate ordering prescription $\mathrm{P}_{A/E}$. Here, only the absorption case will be shown in detail, the emission case can be obtained analogously,

$$G_A(t) = \langle \mathrm{P}_A \exp\left[\chi - \chi(t)\right]\rangle\, e^{-i\Delta F t} \tag{13}$$

where $\langle\cdots\rangle$ denotes a thermal average with respect to H_0. The ordering prescription P_A orders all time-dependent χ's to the left of all time-independent ones, the time-independent χ's according to O, and the time-dependent ones according to $\overline{\mathrm{O}}$. For expectation values of ordered exponentials such as in the equation above, there exists a general identity [20]

$$G_A(t) = \exp\left\langle \mathrm{P}_A \exp\left[\chi - \chi(t)\right] - 1\right\rangle_c e^{-i\Delta F t} \tag{14}$$

relating them to the exponential of a cumulant average indicated by an index c. At this point we perform a cumulant expansion up to second order in χ whose validity depends on the strength of the local perturbation as we will discuss below. 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 up to second order is exact within the validity of the bosonization technique as χ is linear in bosonic operators. 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 where renormalization effects are important, not only the bare coupling has to be small but also the renormalized one.

Implementing the same procedure for the emission case $G_E(t)$ one observes that $G_A(t)$ and $G_E(t)$ are directly related to each other within the cumulant expansion up to second order via $G_A(t)e^{i\Delta F t} = G_E(t)e^{-i\Delta F t}$. For the spectra this result implies:

$$E(\omega + \Delta F) = \frac{\kappa_E}{\kappa_A} A(-\omega + \Delta F). \tag{15}$$

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 [14]. Hence, we have $H_0 = \sum_k \varepsilon_k\!: c_k^\dagger c_k\!:$ and $H = H(g) = H_0 + (2\pi/L)g\sum_{kk'}\!: c_k^\dagger c_{k'}\!:$. 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 [14]

$$S(t) = \frac{1}{Z_A}\mathrm{Tr}\left(e^{-\beta H_0} e^{H_0 t}\psi(0) e^{-iH(g)t}\psi^\dagger(0)\right) \tag{16}$$

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 $\psi(x) = a^{-1/2}Fe^{-i\phi(x)}$ with a^{-1} an ultra-violet cutoff [21]. 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 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 threshold frequency and $G_A(t)$ is in the desired form:

$$G_A(t) = \frac{1}{Z_A}\mathrm{Tr}\left(e^{-\beta H_0} e^{iH_0 t} e^{-iH(1+g)t}\right). \tag{17}$$

The diagonalizing transformation V of $H(1+g)$ equals $V = e^{i(1+g)\phi(0)}$ [15]. 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 [15] with the exact treatment [14], it yields the correct result up to second order in g. This restriction stems from the linearization of the free fermionic spectrum [15].

In view of Eq. (16) it is an interesting question if correlation functions in other systems can be transformed

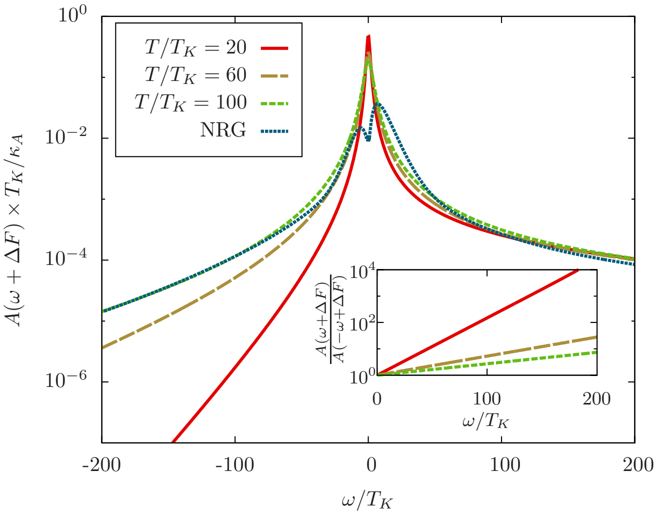

Figure 1: Absorption spectrum of a Kondo exciton for different temperatures as a function of the light frequency $\omega+\Delta F$. As a reference, a NRG curve for $T = 100\,T_K$ is shown taken from Türeci *et al.* [16]. In the regime $|\omega| > T$ where the NRG data is accurate the agreement is excellent. The inset exemplifies the validity of the Crooks relation in the absorption spectrum of the Kondo exciton.

into the form as in Eq. (6). This may allow to determine similar relations or to gain an additional point of view by realizing the equivalence to a work distribution. One example is the local density of states in a Luttinger liquid.

The Kondo exciton. Recently, Türeci *et al.* [16] proposed an experimental setup for a quantum dot where the absorption of a photon corresponds to the sudden switch on of a Kondo impurity. Hence, we have $H_0 = \sum_{k\sigma} \varepsilon_k\!:\!c^\dagger_{k\sigma} c_{k\sigma}\!:$ and $H = H_0 + \sum_{kk'} J_{kk'}\!:\!\vec{S}\cdot\vec{s}_{kk'}\!:$. For details about the Kondo problem see for example Ref. [22]. 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 [18], 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 [23]. 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 $T \gg T_K$ [24]. A plot of the absorption spectrum is shown in Fig. 1 for different temperatures. As a reference, a NRG-curve for $T = 100\,T_K$ obtained by Türeci *et al.* [16] for an Anderson impurity model in the Kondo regime is included in this figure [25]. 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. [16]. For frequencies $|\omega| > T$, however, where the NRG data is accurate we observe excellent agreement with the results of the flow equation formalism. 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 the non-equilibrium 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). Due to the correspondence between optical spectra and work distributions this translates directly into universal relations for work distributions of weak local quenches, see Eq. (4).

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