Nonequilibrium fluctuations, fluctuation theorems, and counting statistics in quantum systems

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Fluctuation theorems (FTs), which describe some universal properties of nonequilibrium fluctuations, are examined from a quantum perspective and derived by introducing a two-point measurement on the system. FTs for closed and open systems driven out of equilibrium by an external time-dependent force, and for open systems maintained in a nonequilibrium steady state by nonequilibrium boundary conditions, are derived from a unified approach. Applications to fermion and boson transport in quantum junctions are discussed. Quantum master equations and Green's functions techniques for computing the energy and particle statistics are presented.

CONTENTS

I. INTRODUCTION

Small fluctuations of systems at equilibrium or weakly driven near equilibrium satisfy a universal relation known as the fluctuation-dissipation (FD) theorem (Callen and Welton, 1951; Kubo, 1957; de Groot and Mazur, 1984; Stratonovich, 1992; Kubo *et al.*, 1998; Zwanzig, 2001). This relation that connects spontaneous fluctuations to the linear response holds for classical and quantum systems alike. The search for similar relations for systems driven far from equilibrium has been an ac-

tive area of research for many decades. A major breakthrough in this regard had taken place over the past 15 years with the discovery of exact fluctuation relations, which hold for classical systems far from equilibrium. These are collectively referred to as fluctuation theorems (FTs). In order to introduce these theorems we adopt the following terminology. A system that follows a Hamiltonian dynamics is called isolated. By default, we assume that the Hamiltonian is time independent. Otherwise, it means that some work is performed on the system and we denote it driven isolated system. A system that can only exchange energy with a reservoir will be denoted closed. If particles are exchanged as well, we say that the system is open.

The first class of FTs, and the earliest discovered, deal with irreversible work fluctuations in isolated driven systems described by a Hamiltonian dynamics where the Hamiltonian is time dependent (Bochkov and Kuzovlev, 1977, 1979, 1981a, 1981b; Stratonovich, 1994; Jarzynski, 1997a, 1997b; Cohen and Mauzerall, 2004; Jarzynski, 2004; Cleuren et al., 2006; Horowitz and Jarzynski, 2007; Jarzynski, 2007; Kawai et al., 2007; Gomez-Marin et al., 2008). An example is the Crooks relation which states that the nonequilibrium probability $p(W)$, that a certain work $w=W$ is performed by an external time-dependent driving force acting on a system initially at equilibrium with temperature β^{-1}, divided by the probability $\tilde{p}(-W)$, that a work $w=-W$ is performed by the time-reversed external driving force acting on the system which is again initially at equilibrium, satisfies $p(W)/\tilde{p}(-W)=\exp[\beta(W-\Delta F)]$, where ΔF is the free-energy difference between the initial (no driving force) and final (finite driving force) equilibrium state. The Jarzynski relation $\langle\exp[-\beta W]\rangle=\exp[-\beta\Delta F]$ follows immediately from $\int dW\tilde{p}(-W)=1$. A second class of FTs is concerned with entropy fluctuations in closed systems described by deterministic thermostatted equations of motions (Evans et al., 1993; Evans and Searles, 1994, 1995, 1996; Gallavotti and Cohen, 1995a, 1995b; Cohen and Gallavotti, 1999; Schöll-Paschinger and Dellago, 2006) and a third class treats the fluctuations of entropy (or related quantities such as irreversible work, heat, and matter currents) in closed or open systems described by a stochastic dynamics (Ross et al., 1988; Crooks, 1998, 1999, 2000; Kurchan, 1998; Lebowitz and Spohn, 1999; Searles and Evans, 1999; Hatano and Sasa, 2001; Seifert, 2005; Chernyak et al., 2006; Andrieux and Gaspard, 2007b; Esposito et al., 2007a; Taniguchi and Cohen, 2007; Chetrite and Gawędzki, 2008). As an example for the last two classes, we give the steady-state FT for the entropy production. We consider a trajectory quantity s whose ensemble average $\langle s \rangle$ can be associated with an entropy production (the specific form of s depends on the underlying dynamics). If $p(S)$ denotes the probability that $s=S$ when the system is in a nonequilibrium steady state, then for long times the FT reads $p(S)/p(-S)=\exp[S]$. FTs valid at any time such as the work FTs are called transient FTs while those who require a long-time limit are called steady-state FTs.

The FTs are all intimately connected to time-reversal symmetry and the relations between probabilities of forward and backward classical trajectories. Close to equilibrium the FTs reduce to the known fluctuation-dissipation relations such as the Green-Kubo relation for transport coefficients (Gallavotti, 1996a, 1996b; Lebowitz and Spohn, 1999; Andrieux and Gaspard, 2004, 2007a). These classical fluctuation relations have been reviewed by Maes (2003); Gaspard (2006); Gallavotti (2007, 2008); and Harris and Schutz (2007). Some of these relations were verified experimentally in mesoscopic systems where fluctuations are sufficiently large to be measurable. Work fluctuations have been studied in macromolecule pulling experiments (Liphardt et al., 2002; Collin et al., 2005) and in optically driven microspheres (Trepagnier et al., 2004), entropy fluctuations have also been measured in a similar system (Wang et al., 2005) and in spectroscopic experiments on a defect center in diamond (Schuler et al., 2005; Tietz et al., 2006). When decreasing system sizes, quantum effects may become significant. Applying the standard trajectory-based derivations of FTs to quantum regime is complicated by the lack of a classical trajectory picture when coherences are taken into account and by the essential role of measurements, which can be safely ignored in ideal classical systems. We show that the FTs follow from fundamental dynamical symmetries that apply equally to classical and quantum systems.

Earlier derivations of the Jarzynski relation for quantum systems defined a work operator (Bochkov and Kuzovlev, 1977, 1979, 1981a, 1981b; Stratonovich, 1994; Yukawa, 2000; Monnai and Tasaki, 2003; Chernyak and Mukamel, 2004; Allahverdyan and Nieuwenhuizen, 2005; Engel and Nolte, 2006; Gelin and Kosov, 2008). Since work is not in general an ordinary quantum "observable" (the final Hamiltonian does not commute with the initial Hamiltonian) (Talkner et al., 2007), attempts to define such an operator had led to quantum corrections to the classical Jarzynski result. However, the Jarzynski relation in a closed driven quantum system may be derived without quantum corrections by introducing an initial and a final projective measurement of the system energy in accordance with the quantum mechanical measurement postulate. This has been done, not always in a explicit way by Kurchan (2000), Tasaki (2000), Mukamel (2003b), Monnai (2005), Talkner and Hänggi (2007), Talkner et al. (2007), and Talkner, Hänggi, and Morillo (2008). The work is then a two-point quantity obtained by calculating the difference between the initial and final energy of the system. When the reservoir is explicitly taken into account, the Jarzynski relation has often been derived using a master equation approach (De Roeck and Mass, 2004; Esposito and Mukamel, 2006; Crooks, 2008a, 2008b). Alternative derivations can be found in Monnai (2005) and Talkner et al. (2009).

The derivation of a steady-state FT for quantum systems has been considered as well (Jarzynski and Wojcik, 2004; Tobiska and Nazarov, 2005; Andrieux and Gaspard, 2006; Esposito and Mukamel, 2006; De Roeck and

Maes, 2006; Cleuren and den Broeck, 2007; Esposito *et al.*, 2007b; Harbola *et al.*, 2007; De Roeck, 2007; Saito and Dhar, 2007; Derezinski *et al.*, 2008; Saito and Utsumi, 2008; Andrieux *et al.*, 2009). Because of the need to describe nonequilibrium fluctuations in closed or open quantum systems exchanging energy or matter with their reservoir, many similarities exist with the rapidly developing field of electron counting statistics (Levitov and Lesovik, 1993; Levitov *et al.*, 1996; Gurvitz, 1997; Nazarov, 1999; Belzig and Nazarov, 2001a, 2001b; Bagrets and Nazarov, 2003; Belzig, 2003; Kindermann and Nazarov, 2003; Nazarov and Kindermann, 2003; Pilgram *et al.*, 2003, 2006; Shelankov and Rammer, 2003; Kindermann and Pilgram, 2004; Levitov and Reznikov, 2004; Rammer *et al.*, 2004; Flindt *et al.*, 2005, 2008; Wabnig *et al.*, 2005; Braggio *et al.*, 2006; Kiesslich *et al.*, 2006; Utsumi *et al.*, 2006; Emary *et al.*, 2007; Nazarov, 2007; Schönhammer, 2007; Bednorz and Belzig, 2008; Snyman and Nazarov, 2008; Welack *et al.*, 2008), where small nanoscale electronic devices exchange electrons. Fluctuations in such systems can nowadays be experimentally resolved at the single electron level (Lu *et al.*, 2003; Fujisawa *et al.*, 2004, 2006; Bylander *et al.*, 2005; Gustavsson *et al.*, 2006). Similarities also exist with the more established field of photon counting statistics, where photons emitted by a molecule or an atom driven out of equilibrium by a laser are individually detected (Glauber, 1963; Kelley and Kleiner, 1964; Mandel, 1982; Mandel and Wolf, 1995; Gardiner and Zoller, 2000; Mukamel, 2003a; Zheng and Brown, 2003a, 2003b; Barkai *et al.*, 2004; Kulzer and Orrit, 2004; Sanda and Mukamel, 2005).

Different types of approaches have been used to derive these FTs and describe these counting experiments. The first is based on the quantum master equation (QME) (Gurvitz, 1997; Rammer *et al.*, 2004; Flindt *et al.* 2005, 2008; Wabnig *et al.*, 2005; Braggio *et al.*, 2006; Esposito and Mukamel, 2006; Kiesslich *et al.*, 2006; De Roeck and Maes, 2006; Emary *et al.*, 2007; Esposito *et al.*, 2007b; Harbola *et al.*, 2007; Welack *et al.*, 2008). Here one starts with an isolated total system containing the system and the reservoir in weak interaction. By tracing the reservoir degrees of freedom, taking the infinite reservoir limit and using perturbation theory, one can derive a closed evolution equation for the reduced density matrix of the system. The information about the reservoir evolution is discarded. However, the evolution of a quantum system described by a QME can be seen as resulting from a continuous projective measurement on the reservoir, leading to a continuous positive operator-valued measurement on the system. Such interpretation allows one to construct a trajectory picture of the system dynamics, where each realization of the continuous measurement leads to a given system trajectory (Brun, 2000, 2002; Gardiner and Zoller, 2000; Nielsen and Chuang, 2000; Breuer and Petruccione, 2002). The QME is recovered by ensemble averaging over all possible trajectories. This *unraveling* of the QME into trajectories has been originally developed in the description of photon counting statistics (Wiseman and Milburn, 1993a, 1993b;

Plenio and Knight, 1998; Gardiner and Zoller, 2000; Breuer and Petruccione, 2002). Another approach is based on a modified propagator defined on a Keldysh loop which, under certain circumstances, can be interpreted as the generating function of the electron counting probability distribution (Nazarov, 1999, 2007; Belzig and Nazarov, 2001a, 2001b; Belzig, 2003; Kindermann and Nazarov, 2003; Nazarov and Kindermann, 2003; Kindermann and Pilgram, 2004). Using a path integral formalism, the propagator of the density matrix of a "detector" with Hamiltonian $p^2/2m$ interacting with a system can be expressed in terms of the influence functional that only depends on the system degrees of freedom (Feynman and Vernon, 1963). The modified propagator is the influence functional when the system is linearly coupled to the detector (with coupling term xA, where x is the position of the detector and A is a system observable) in the limit of very large detector inertia $m \to \infty$. It is only under some specific assumptions (such as a classical detector where the detector density matrix is assumed diagonal) that the modified propagator becomes the generating function associated with the probability distribution that the detector momentum changes from a given amount, which can be interpreted as the probability to measure the time average of the system observable A: $\int_0^t d\tau A(\tau)$. If A is an electric current, then the integral gives the number of electrons transfered. An early quantum FT for electronic junctions has been derived in this context by Tobiska and Nazarov (2005) based on the time-reversal invariance of the Hamiltonian quantum dynamics. Different derivations of quantum FTs relying on this approach have been considered by Saito and Dhar (2007) and Saito and Utsumi (2008). A third semiclassical scattering approach is often used in electron counting statistics (Pilgram *et al.*, 2003, 2004; Jordan *et al.*, 2004; Nagaev *et al.*, 2004; Pilgram, 2004). This can be recovered from the modified propagator approach as recently shown by Snyman and Nazarov (2008), but will not be addressed here.

We consider fluctuations in the output of a two-point projective measurement (of energy, particle, charge, etc.). This allows us to avoid the detailed modeling of detectors and their dynamics. The projective measurement can be viewed as an effective modeling of the effect of the system-detector interaction on the system or as resulting in a fundamental way from the quantum measurement postulate. The three other approaches (unraveling of the QME, modified propagator on Keldysh loop, and the scattering approach) can be recovered in some limits of the two-point measurement approach. This provides a unified framework from which the different types of FTs previously derived for quantum systems can be obtained.

In Sec. II, we give the general expression for the probability of the output of a two-point measurement at different times on a quantum system described by the quantum Liouville equation. The calculation is repeated for a system described by the time-reversed dynamics. In Sec. III, we start by discussing the basic ingredients required for FTs to hold. We use these results to derive

three transient FTs, the Jarzynski and Crooks relation in isolated and closed driven systems and a FT for matter and heat exchange between two systems in direct contact. We also show that a steady-state FT can be derived for matter and heat exchange between two reservoirs through an embedded system. In Sec. IV, we consider a small quantum system weakly interacting with multiple reservoirs. We develop a projection superoperator formalism to derive equations of motion for the generating function associated with the system reduced density matrix conditional of the output of a two-point measurement of the energy or number of particles in the reservoirs. We apply this generalized quantum master equation (GQME) formalism to calculate the statistics of particles or heat transfer in different models of general interest in nanosciences in order to verify the validity of the steady-state FT. In Sec. V, we present a nonequilibrium Green's function formalism in Liouville space, which provides a powerful tool to calculate the particle statistics of many- body quantum systems. In Sec. VI, we show that the FTs can be used to derive generalized fluctuation-dissipation relations. Conclusions and perspectives are drawn in Sec. VII.

II. TWO-POINT MEASUREMENT STATISTICS

We consider an isolated, possibly driven, quantum system described by a density matrix $\hat{\rho}(t)$, which obeys the von Neumann (quantum Liouville) equation

$$\frac{d}{dt}\hat{\rho}(t) = -\frac{i}{\hbar}[\hat{H}(t),\hat{\rho}(t)]. \tag{1}$$

Its formal solution reads

$$\hat{\rho}(t) = \hat{U}(t,0)\hat{\rho}_0\hat{U}^\dagger(t,0). \tag{2}$$

The propagator

$$\begin{aligned}
\hat{U}(t,0) &= \exp_+\left\{-\frac{i}{\hbar}\int_0^t d\tau \hat{H}(\tau)\right\} \\
&\equiv 1 + \sum_{n=1}^{\infty}\left(-\frac{i}{\hbar}\right)^n \int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \\
&\times \int_0^{t_{n-1}} dt_n \hat{H}(t_1)\hat{H}(t_2)\cdots\hat{H}(t_n)
\end{aligned} \tag{3}$$

is unitary $\hat{U}^\dagger(t,0) = \hat{U}^{-1}(t,0)$ and satisfies $\hat{U}^\dagger(t,0) = \hat{U}(0,t)$ and $\hat{U}(t,t_1)\hat{U}(t_1,0) = \hat{U}(t,0)$. We use the subscript $+$ $(-)$ to denote an antichronological (chronological) time ordering from left to right. We call Eq. (2) the forward evolution to distinguish it from the the time-reversed evolution that will be defined below.

A. The forward probability

We consider an observable $\hat{A}(t)$ in the Schrödinger picture whose explicit time dependence solely comes from an external driving. For nondriven systems $\hat{A}(t)$

$= \hat{A}$. In the applications considered $\hat{A}(t)$ will be either an energy operator $\hat{H}$ or a particle number operator $\hat{N}$. The eigenvalues (eigenvectors) of $\hat{A}(t)$ are denoted by a_t ($|a_t\rangle$): $\hat{A}(t) = \Sigma_{a_t}|a_t\rangle a_t\langle a_t|$.

The basic quantity in the following will be the joint probability to measure a_0 at time 0 and a_t at time t,

$$\begin{aligned}
P[a_t,a_0] &\equiv \text{Tr}\{\hat{P}_{a_t}\hat{U}(t,0)\hat{P}_{a_0}\hat{\rho}_0\hat{P}_{a_0}\hat{U}^\dagger(t,0)\hat{P}_{a_t}\} \\
&= P^*[a_t,a_0],
\end{aligned} \tag{4}$$

where the projection operators are given by

$$\hat{P}_{a_t} = |a_t\rangle\langle a_t|. \tag{5}$$

Using the properties $\hat{P}_{a_t} = \hat{P}_{a_t}^2$ and $\Sigma_{a_t}\hat{P}_{a_t} = \hat{1}$, we can verify the normalization $\Sigma_{a_t a_0}P[a_t,a_0] = 1$. Consider two complete Hilbert space basis sets $\{|i,a_0\rangle\}$ and $\{|j,a_t\rangle\}$, where i (j) are used to differentiate between the states with same a_0 (a_t). The basis $\{|i,a_0\rangle\}$ is chosen such that it diagonalizes $\hat{\rho}_0$ (this is always possible since $\hat{\rho}_0$ is Hermitian). We can also write Eq. (4) as

$$P[a_t,a_0] = \sum_{i,j} P[j,a_t;i,a_0], \tag{6}$$

where

$$P[j,a_t;i,a_0] \equiv |\langle j,a_t|\hat{U}(t,0)|i,a_0\rangle|^2\langle i,a_0|\hat{\rho}_0|i,a_0\rangle. \tag{7}$$

The probability distribution for the difference $\Delta a = a_t - a_0$ between the output of the two measurements is given by

$$p(\Delta a) = \sum_{a_t a_0} \delta(\Delta a - (a_t - a_0))P[a_t,a_0], \tag{8}$$

where $\delta(a)$ denotes the Dirac distribution. It is often more convenient to calculate the generating function (GF) associated with this probability

$$\begin{aligned}
G(\lambda) &\equiv \int_{-\infty}^{\infty} d\Delta a\, e^{i\lambda\Delta a}p(\Delta a) = G^*(-\lambda) \\
&= \sum_{a_t a_0} e^{i\lambda(a_t - a_0)}P[a_t,a_0].
\end{aligned} \tag{9}$$

The nth moment $\langle\Delta a^n\rangle$ of $p(\Delta a)$ is obtained by taking nth derivative of the GF with respect to λ evaluated at $\lambda = 0$:

$$\langle\Delta a^n\rangle = (-i)^n \left.\frac{\partial^n}{\partial\lambda^n}G(\lambda)\right|_{\lambda=0}. \tag{10}$$

We further define the cumulant GF

$$\mathcal{Z}(\lambda) = \ln G(\lambda). \tag{11}$$

The nth cumulant K_n of $p(\Delta a)$ is obtained by taking nth derivative of the cumulant GF with respect to λ evaluated at $\lambda = 0$:

$$K_n = (-i)^n \left. \frac{\partial^n}{\partial \lambda^n} \mathcal{Z}(\lambda) \right|_{\lambda=0}. \qquad (12)$$

The first cumulant coincides with the first moment which gives the average $K_1 = \langle \Delta a \rangle$. Higher order cumulants can be expressed in term of the moments. The variance $K_2 = \langle \Delta a^2 \rangle - \langle \Delta a \rangle^2$ gives the fluctuations around the average, and the skewness $K_3 = \langle (\Delta a - \langle \Delta a \rangle)^3 \rangle$ gives the leading order deviation of $p(\Delta a)$ from a Gaussian. When measuring the statistics of quantities associated to nonequilibrium fluxes, in most cases [but not always (Esposito and Lindenberg, 2008)] the cumulants grow linearly with time and it becomes convenient to define the long-time limit of the cumulant GF

$$S(\lambda) = \lim_{t \to \infty} \frac{1}{t} \mathcal{Z}(\lambda), \qquad (13)$$

which measures the deviations from the central limit theorem (Sornette, 2006).

We next turn to computing the GF. The initial density matrix can be expressed as

$$\hat{\rho}_0 = \bar{\hat{\rho}}_0 + \bar{\bar{\hat{\rho}}}_0, \qquad (14)$$

where

$$\bar{\hat{\rho}}_0 = \sum_{a_0} \hat{P}_{a_0} \hat{\rho}_0 \hat{P}_{a_0}, \quad \bar{\bar{\hat{\rho}}}_0 = \sum_{a_0 \neq a_0'} \hat{P}_{a_0} \hat{\rho}_0 \hat{P}_{a_0'}. \qquad (15)$$

$\bar{\hat{\rho}}_0$ commutes with $\hat{A}(0)$. Using the fact that $f(\hat{A}) = \sum_a \hat{P}_a f(a)$, where f is an arbitrary function, and using also

$$\sum_{a_0} e^{-i\lambda a_0} \hat{P}_{a_0} \hat{\rho}_0 \hat{P}_{a_0} = e^{-i(\lambda/2)\hat{A}(0)} \bar{\hat{\rho}}_0 e^{-i(\lambda/2)\hat{A}(0)}, \qquad (16)$$

we find, by substituting Eq. (4) into Eq. (9), that

$$G(\lambda) = \text{Tr } \hat{\rho}(\lambda, t), \qquad (17)$$

where we have defined

$$\hat{\rho}(\lambda, t) \equiv \hat{U}_{\lambda/2}(t,0) \bar{\hat{\rho}}_0 \hat{U}_{-\lambda/2}^\dagger(t,0) \qquad (18)$$

and the modified evolution operator

$$\hat{U}_\lambda(t,0) \equiv e^{i\lambda \hat{A}(t)} \hat{U}(t,0) e^{-i\lambda \hat{A}(0)}. \qquad (19)$$

For $\lambda = 0$, $\hat{\rho}(\lambda, t)$ reduces to the system density matrix and $\hat{U}_\lambda(t,0)$ to the standard evolution operator. Defining the modified Hamiltonian

$$\hat{H}_\lambda(t) \equiv e^{i\lambda \hat{A}(t)} \hat{H}(t) e^{-i\lambda \hat{A}(t)} - \hbar \lambda \partial_t \hat{A}(t), \qquad (20)$$

we find that $\hat{U}_\lambda(t,0)$ satisfies the equation of motion

$$\frac{d}{dt} \hat{U}_\lambda(t,0) = -\frac{i}{\hbar} \hat{H}_\lambda(t) \hat{U}_\lambda(t,0). \qquad (21)$$

Since $\hat{U}_\lambda(0,0) = \hat{1}$, we get

$$\hat{U}_{\lambda/2}(t,0) = \exp_+ \left\{ -\frac{i}{\hbar} \int_0^t d\tau \hat{H}_{\lambda/2}(\tau) \right\}, \qquad (22)$$

$$\hat{U}_{-\lambda/2}^\dagger(t,0) = \exp_- \left\{ \frac{i}{\hbar} \int_0^t d\tau \hat{H}_{-\lambda/2}(\tau) \right\}. \qquad (23)$$

Equations (17) and (18) together with Eqs. (22) and (23) provide an exact formal expression for the statistics of changes in $\hat{A}(t)$ derived from the two-point measurements.

We note that if and only if the eigenvalues of $\hat{A}$ are integers (as in electron counting where one considers the number operator), using the integral representation of the Kronecker delta

$$\delta_K(a - a') = \int_0^{2\pi} \frac{d\Lambda}{2\pi} e^{-i\Lambda(a-a')}, \qquad (24)$$

Eq. (18) can be written as

$$\hat{\rho}(\lambda, t) = \int_0^{2\pi} \frac{d\Lambda}{2\pi} \hat{\rho}(\lambda, \Lambda, t), \qquad (25)$$

where

$$\hat{\rho}(\lambda, \Lambda, t) \equiv \hat{U}_{\Lambda+(\lambda/2)}(t,0) \hat{\rho}_0 \hat{U}_{\Lambda-(\lambda/2)}^\dagger(t,0). \qquad (26)$$

We see that by introducing an additional Λ dependence, we were able to keep the initial density matrix $\hat{\rho}_0$ in Eq. (26) instead of $\bar{\hat{\rho}}_0$ as in Eq. (18).

The current operator associated with $\hat{A}(t)$ is given by

$$\hat{I}(t) \equiv \frac{i}{\hbar} [\hat{H}(t), \hat{A}(t)] + \partial_t \hat{A}(t). \qquad (27)$$

As a result,

$$\hat{I}^{(h)}(t) = \frac{d}{dt} \hat{A}^{(h)}(t), \qquad (28)$$

where the superscript (h) denotes the Heisenberg representation $\hat{A}^{(h)}(t) \equiv \hat{U}^\dagger(t,0) \hat{A}(t) \hat{U}(t,0)$. We can write Eq. (20) as

$$\hat{H}_\lambda(t) = \hat{H}(t) - \lambda \hbar \hat{I}(t) + \mathcal{O}(\lambda^2 \hbar^2). \qquad (29)$$

In the semiclassical approximation where terms $\mathcal{O}(\lambda^2 \hbar^2)$ are disregarded, the GF (17) [with Eqs. (18), (22), and (23)], after going to the interaction representation, becomes

$$G(\lambda) = \text{Tr} \left\{ \exp_- \left[i\frac{\lambda}{2} \int_0^t d\tau \hat{I}^{(h)}(\tau) \right] \bar{\hat{\rho}}_0 \right.$$
$$\left. \times \exp_- \left[i\frac{\lambda}{2} \int_0^t d\tau \hat{I}^{(h)}(\tau) \right] \right\}. \qquad (30)$$

This form is commonly found in the modified propagator approach, described in the introduction, to counting statistics (Kindermann and Nazarov, 2003; Nazarov and Kindermann, 2003; Kindermann and Pilgram, 2004). Note that in these publications the full initial density matrix $\hat{\rho}_0$ is used in Eq. (30) instead of $\bar{\hat{\rho}}_0$.

In most applications discussed in this review, we consider initial density matrices with no initial coherences in $\hat{A}(0)$ space

$$[\hat{A}(0),\hat{\rho}_0]=0. \tag{31}$$

This is equivalent to say that $[\hat{P}_{a_0},\hat{\rho}_0]=0$ or that $\hat{\rho}_0=\bar{\rho}_0$. In this case, Eq. (4) can be written as

$$P[a_t,a_0] = \text{Tr}\{\hat{U}^\dagger(t,0)\hat{P}_{a_t}\hat{U}(t,0)\hat{P}_{a_0}\hat{\rho}_0\}, \tag{32}$$

and using Eq. (32) in Eq. (9), the GF simplifies to

$$G(\lambda) = \text{Tr}\{e^{i\lambda\hat{U}^\dagger(t,0)\hat{A}(t)\hat{U}(t,0)}e^{-i\lambda\hat{A}(0)}\hat{\rho}_0\}. \tag{33}$$

B. The time-reversed probability

The time-reversed evolution brings the final density matrix of the forward quantum evolution (2) back to its initial density matrix. This means that if the initial condition of the time-reversed evolution is $\hat{\rho}_0^{\text{tr}}=\hat{\rho}(t)$ $=\hat{U}(t,0)\hat{\rho}_0\hat{U}^\dagger(t,0)$, the time-reversed evolution must be defined as $\hat{\rho}^{\text{tr}}(t)=\hat{U}^\dagger(t,0)\hat{\rho}_0^{\text{tr}}\hat{U}(t,0)$, so that $\hat{\rho}^{\text{tr}}(t)=\hat{\rho}_0$. The time-reversed expression of the two-point probability (4) is therefore

$$P^{\text{tr}}[a_0,a_t] \equiv \text{Tr}\{\hat{P}_{a_0}\hat{U}^\dagger(t,0)\hat{P}_{a_t}\hat{\rho}_0^{\text{tr}}\hat{P}_{a_t}\hat{U}(t,0)\hat{P}_{a_0}\}. \tag{34}$$

A more systematic discussion on time-reversal operation in quantum mechanics and its relation to the definition (34) is given in Appendix A. Without loss of generality, we choose a basis set $\{|j,a_t\rangle\}$ that diagonalizes $\hat{\rho}_0^{\text{tr}}$, to show that Eq. (34) can be rewritten as

$$P^{\text{tr}}[a_0,a_t] = \sum_{i,j} P^{\text{tr}}[i,a_0;j,a_t], \tag{35}$$

where

$$P^{\text{tr}}[i,a_0;j,a_t] \equiv |\langle j,a_t|\hat{U}(t,0)|i,a_0\rangle|^2 \langle j,a_t|\hat{\rho}_0^{\text{tr}}|j,a_t\rangle. \tag{36}$$

The probability to measure the difference $\Delta a=a_0-a_t$ between the two measurements is given by

$$p^{\text{tr}}(\Delta a) \equiv \sum_{a_t a_0} \delta(\Delta a - (a_0 - a_t))P^{\text{tr}}[a_0,a_t]. \tag{37}$$

The associated GF reads

$$G^{\text{tr}}(\lambda) \equiv \int_{-\infty}^{\infty} d\Delta a\, e^{i\lambda\Delta a}p^{\text{tr}}(\Delta a)$$
$$= \sum_{a_t,a_0} e^{-i\lambda(a_t-a_0)}P^{\text{tr}}[a_0,a_t]. \tag{38}$$

We note that for a nondriven system with $\hat{\rho}_0^{\text{tr}}=\hat{\rho}_0$, using Eqs. (4) and (34), we find that $P[a_t,a_0]=P^{\text{tr}}[a_t,a_0]$. This means, using Eqs. (6) and (35), that

$$p^{\text{tr}}(\Delta a) = p(\Delta a) \tag{39}$$

and

$$G^{\text{tr}}(\lambda) = G(\lambda). \tag{40}$$

Using again the partitioning

$$\hat{\rho}_0^{\text{tr}} = \bar{\rho}_0^{\text{tr}} + \bar{\bar{\rho}}_0^{\text{tr}}, \tag{41}$$

where

$$\bar{\rho}_0^{\text{tr}} = \sum_{a_t} \hat{P}_{a_t}\hat{\rho}_0^{\text{tr}}\hat{P}_{a_t}, \quad \bar{\bar{\rho}}_0^{\text{tr}} = \sum_{a_t\neq a_t'} \hat{P}_{a_t}\hat{\rho}_0^{\text{tr}}\hat{P}_{a_t'} \tag{42}$$

and following the same procedure as for the forward GF, we obtain

$$G^{\text{tr}}(\lambda) = \text{Tr}\,\hat{\rho}^{\text{tr}}(\lambda,t), \tag{43}$$

where

$$\hat{\rho}^{\text{tr}}(\lambda,t) \equiv \hat{U}_{\lambda/2}^\dagger(t,0)\bar{\rho}_0^{\text{tr}}\hat{U}_{-\lambda/2}(t,0). \tag{44}$$

As for Eq. (30), in the semiclassical limit we find

$$G^{\text{tr}}(\lambda) = \text{Tr}\left\{ \exp_-\left[i\frac{\lambda}{2}\int_0^t d\tau \hat{I}^{(h)}(\tau) \right] \bar{\rho}_0^{\text{tr}} \right.$$
$$\left. \times \exp_-\left[i\frac{\lambda}{2}\int_0^t d\tau \hat{I}^{(h)}(\tau) \right] \right\}. \tag{45}$$

We again note that if the initial density matrix of the time-reversed evolution contains no initial coherences in $\hat{A}(t)$ space

$$[\hat{A}(t),\hat{\rho}_0^{\text{tr}}]=0, \tag{46}$$

or equivalently if $[\hat{P}_{a_t},\hat{\rho}_0^{\text{tr}}]=0$ or $\hat{\rho}_0^{\text{tr}}=\bar{\rho}_0^{\text{tr}}$, Eq. (34) becomes

$$P^{\text{tr}}[a_0,a_t] = \text{Tr}\{\hat{U}(t,0)\hat{P}_{a_0}\hat{U}^\dagger(t,0)\hat{P}_{a_t}\hat{\rho}_0^{\text{tr}}\}, \tag{47}$$

and

$$G^{\text{tr}}(\lambda) = \text{Tr}\{e^{i\lambda\hat{U}(t,0)\hat{A}(0)\hat{U}^\dagger(t,0)}e^{-i\lambda\hat{A}(t)}\hat{\rho}_0^{\text{tr}}\}. \tag{48}$$

III. THE FLUCTUATION THEOREM

A. General derivation and connection to entropy

We now define the logarithm of the ratio of the forward and time-reversed probabilities defined in Sec. II, which in the classical theory of FTs is associated with the irreversible contribution to an entropy change

$$R[j,a_t;i,a_0] \equiv \ln \frac{P[j,a_t;i,a_0]}{P^{\text{tr}}[i,a_0;j,a_t]}. \tag{49}$$

It follows from Eqs. (7) and (36) that

$$R[j,a_t;i,a_0] = \ln \frac{\langle i,a_0|\hat{\rho}_0|i,a_0\rangle}{\langle j,a_t|\hat{\rho}_0^{\text{tr}}|j,a_t\rangle}. \tag{50}$$

An *integral FT* immediately follows from the normalization of $P^{\text{tr}}[i,a_0;j,a_t]$,

$$\langle e^{-R} \rangle \equiv \sum_{j,a_t,i,a_0} P[j,a_t;i,a_0] e^{-R[j,a_t;i,a_0]}$$

$$= \sum_{j,a_t,i,a_0} P^{\text{tr}}[i,a_0;j,a_t] = 1. \tag{51}$$

Using Jensen's inequality $\langle e^X \rangle \geq e^{\langle X \rangle}$, Eq. (51) implies

$$\langle R \rangle = \sum_{j,a_t,i,a_0} P[j,a_t;i,a_0] R[j,a_t;i,a_0] \geq 0. \tag{52}$$

Using Eq. (49), we see that $\langle R \rangle$ resembles a Kullback-Leibler (or relative) entropy (Kullback and Leibler, 1951; Nielsen and Chuang, 2000).

We define the probability distributions

$$p(R) \equiv \sum_{j,a_t,i,a_0} P[j,a_t;i,a_0] \delta(R - R[j,a_t;i,a_0]), \tag{53}$$

$$p^{\text{tr}}(R) \equiv \sum_{j,a_t,i,a_0} P^{\text{tr}}[i,a_0;j,a_t] \delta(R - R^{\text{tr}}[i,a_0;j,a_t]), \tag{54}$$

where

$$R^{\text{tr}}[i,a_0;j,a_t] \equiv \ln \frac{P^{\text{tr}}[i,a_0;j,a_t]}{P[j,a_t;i,a_0]}. \tag{55}$$

Using Eqs. (50) and (55), we see that

$$R^{\text{tr}}[i,a_0;j,a_t] = - R[j,a_t;i,a_0]. \tag{56}$$

It then follows that

$$p(R) = \sum_{j,a_t,i,a_0} e^{R[j,a_t;i,a_0]} P^{\text{tr}}[i,a_0;j,a_t] \delta(R - R[j,a_t;i,a_0])$$

$$= e^R \sum_{j,a_t,i,a_0} P^{\text{tr}}[i,a_0;j,a_t] \delta(R - R[j,a_t;i,a_0])$$

$$= e^R \sum_{j,a_t,i,a_0} P^{\text{tr}}[i,a_0;j,a_t] \delta(R + R^{\text{tr}}[i,a_0;j,a_t])$$

$$= e^R p^{\text{tr}}(-R), \tag{57}$$

which gives the *detailed* FT

$$\ln \frac{p(R)}{p^{\text{tr}}(-R)} = R. \tag{58}$$

The FTs (51) and (58) are completely general but only useful when R can be exclusively expressed in terms of physical and measurable quantities [the eigenvalues of $\hat{A}(0)$ and $\hat{A}(t)$]. In Secs. III.B and III.C, we show that the i and j dependence of R, which labels states which cannot be differentiated by a projective measurement of the physical observable $\hat{A}(t)$, can be eliminated by making specific choices of $\hat{\rho}$ and $\hat{\rho}^{\text{tr}}$.

If assumptions (31) and (46) are satisfied (this will be the case in most of the following applications), Eq. (52) can be expressed in term of quantum entropies. Using Eq. (50), the general property

$$\sum_{j,a_t} P[j,a_t;i,a_0] = \langle i,a_0|\hat{\rho}_0|i,a_0\rangle, \tag{59}$$

and the fact that [using assumption (31)]

$$\sum_{i,a_0} P[j,a_t;i,a_0] = \langle j,a_t|\hat{\rho}(t)|j,a_t\rangle, \tag{60}$$

Eq. (52) can be rewritten as a quantum relative entropy (Nielsen and Chuang, 2000; Breuer and Petruccione, 2002) between $\hat{\rho}(t)$ and $\hat{\rho}_0^{\text{tr}}$:

$$\langle R \rangle = \bar{S} - S = \text{Tr}\,\hat{\rho}(t)[\ln\hat{\rho}(t) - \ln\hat{\rho}_0^{\text{tr}}] \geq 0, \tag{61}$$

where

$$S \equiv -\text{Tr}\,\hat{\rho}(t)\ln\hat{\rho}(t) = -\text{Tr}\,\hat{\rho}_0\ln\hat{\rho}_0$$

$$= -\sum_{i,a_0} \langle i,a_0|\hat{\rho}_0|i,a_0\rangle\ln\langle i,a_0|\hat{\rho}_0|i,a_0\rangle \tag{62}$$

and

$$\bar{S} \equiv -\text{Tr}\,\hat{\rho}(t)\ln\hat{\rho}_0^{\text{tr}} = -\text{Tr}\,\hat{\rho}_0\ln\hat{\rho}^{\text{tr}}(t)$$

$$= -\sum_{j,a_t} \langle j,a_t|\hat{\rho}(t)|j,a_t\rangle\ln\langle j,a_t|\hat{\rho}_0^{\text{tr}}|j,a_t\rangle. \tag{63}$$

The second line of Eq. (62) [Eq. (63)] is obtained using assumption (31) [assumption (46)]. S is a von Neumann entropy but $\bar{S}$ is not. It can be compared to the von Neumann entropy

$$S^{\text{tr}} \equiv -\text{Tr}\,\hat{\rho}^{\text{tr}}(t)\ln\hat{\rho}^{\text{tr}}(t) = -\text{Tr}\,\hat{\rho}_0^{\text{tr}}\ln\hat{\rho}_0^{\text{tr}}$$

$$= -\sum_{j,a_t} \langle j,a_t|\hat{\rho}_0^{\text{tr}}|j,a_t\rangle\ln\langle j,a_t|\hat{\rho}_0^{\text{tr}}|j,a_t\rangle, \tag{64}$$

which is obtained using the general property

$$\sum_{i,a_0} P^{\text{tr}}[i,a_0;j,a_t] = \langle j,a_t|\hat{\rho}_0^{\text{tr}}|j,a_t\rangle \tag{65}$$

together with [using assumption (46)]

$$\sum_{j,a_t} P^{\text{tr}}[i,a_0;j,a_t] = \langle i,a_0|\hat{\rho}^{\text{tr}}(t)|i,a_0\rangle. \tag{66}$$

In the following applications we show that $\langle R \rangle$ is always associated to the irreversible contribution of an entropy change. Equation (61) is therefore the quantum analog of the classical relation derived by Kawai *et al.* (2007) and Gomez-Marin *et al.* (2008) and of the stochastic relation by Gaspard (2004b) and Andrieux *et al.* (2007).

In Appendix B, following the work of Callens *et al.* (2004) and Yacobas and Maes (2005), we show that if one allows for a coarse graining of $\hat{\rho}_0$ and $\hat{\rho}_0^{\text{tr}}$ in their measured subspaces, one can derive FTs for R's which can be expressed exclusively in terms of measurable probabilities (no i and j index) and such that $\langle R \rangle$ is the difference between the Gibbs–von Neumann entropy associated to the coarse-grained $\hat{\rho}_0^{\text{tr}}$ and $\hat{\rho}_0$.

We now examine the detailed FT from the GF perspective. We define the GFs associated with $p(R)$ and $p^{\text{tr}}(R)$:

$$G(\lambda) \equiv \int_{-\infty}^{\infty} dR\, e^{i\lambda R} p(R),$$

$$G^{\mathrm{tr}}(\lambda) \equiv \int_{-\infty}^{\infty} dR e^{i\lambda R} p^{\mathrm{tr}}(R). \tag{67}$$

By combining Eq. (58) with Eq. (67), we get

$$G(\lambda) = G^{\mathrm{tr}}(i-\lambda). \tag{68}$$

For a nondriven system with $\hat{\rho}_0^{\mathrm{tr}} = \hat{\rho}_0$, we have seen that Eq. (40) is satisfied. Combining this with Eq. (68), the detailed FT (58) implies the fundamental symmetry $G(\lambda) = G(i-\lambda)$ on the GF. This type of symmetry is used in Sec. VI to derive generalized fluctuation-dissipation relations.

B. Transient fluctuation theorems

In this section, we show that the FT (58) can be used to derive the Crooks (Crooks, 1999, 2000; Horowitz and Jarzynski, 2007) and Jarzynski relations (Jarzynski, 1997a, 1997b, 2004) in either isolated or closed driven quantum systems as well as a FT for heat and particle exchange between two finite systems.

1. Work fluctuation theorem for isolated driven systems

We consider an isolated system initially described by the Hamiltonian $\hat{H}(0)$ and at equilibrium $e^{-\beta\hat{H}(0)}/Z(0)$, where $Z(0) = \mathrm{Tr}\, e^{-\beta\hat{H}(0)}$ is the partition function. We can imagine that the system was in contact with a reservoir at temperature β^{-1} for $t < 0$. At $t=0$ the reservoir is removed and the system energy is measured for the first time. After the first measurement, the system is then subjected to an external and arbitrary driving (the Hamiltonian is time dependent). The second energy measurement occurs at time t, where the Hamiltonian is $\hat{H}(t)$. From the two measurements of this forward process we can calculate $P[E_t, E_0]$.

In the backward process, the isolated system is initially described by the Hamiltonian $\hat{H}(t)$ and at equilibrium $e^{-\beta\hat{H}(t)}/Z(t)$, where $Z(t) = \mathrm{Tr}\, e^{-\beta\hat{H}(t)}$. We can imagine that at the end of the forward process, the system described by the Hamiltonian $\hat{H}(t)$ is put in contact with a reservoir at temperature β^{-1} until it thermalizes, and that the reservoir is then removed at time zero when the energy of the system is measured for the first time in the backward process. After this first measurement, an external driving, which is the time-reversed driving of the forward process, is applied. The second energy measurement occurs at time t, where the Hamiltonian is $\hat{H}(0)$.

In Appendix A, we show that the time-reversed evolution (as defined in Sec. II.B) of an isolated system driven externally according to a given protocol corresponds to the forward evolution of the isolated system externally driven according to the time-reversed protocol. This means that the backward process just described is identical to the time reversal of our forward process, so that the two measurements occurring during the backward process can be used to calculate $P^{\mathrm{tr}}[E_0, E_t]$.

To make the connection with the results of Sec. II, we define the initial density matrices for the forward and backward processes

$$\hat{\rho}_0 = \frac{e^{-\beta\hat{H}(0)}}{Z(0)}, \quad \hat{\rho}_0^{\mathrm{tr}} = \frac{e^{-\beta\hat{H}(t)}}{Z(t)}. \tag{69}$$

We further set $a_t = E_t$ ($a_0 = E_0$), where $\hat{H}(t)|E_t,j\rangle = E_t|E_t,j\rangle$ [$\hat{H}(0)|E_0,i\rangle = E_0|E_0,i\rangle$]. The index j (i) distinguishes between degenerate eigenstates so that $\{|E_t,j\rangle\}$ ($\{|E_0,i\rangle\}$) constitutes a complete basis in Hilbert space. We also define the free-energy difference $\Delta F(t) = F(t) - F(0)$ between the initial and final state, where $F(t) = -\beta^{-1} \ln Z(t)$. Since the system is isolated, no heat exchange occurs and the change in the system energy can be interpreted as the work done by the driving force on the system

$$w = \Delta a = E_t - E_0. \tag{70}$$

Equations (7) and (36) become

$$P[j, E_t; i, E_0] = |\langle j, E_t|\hat{U}(t,0)|i, E_0\rangle|^2 e^{-\beta[E_0 - F(0)]},$$

$$P^{\mathrm{tr}}[i, E_0; j, E_t] = |\langle j, E_t|\hat{U}(t,0)|i, E_0\rangle|^2 e^{-\beta[E_t - F(t)]},$$

so that Eq. (50) becomes

$$R[j, E_t; i, E_0] = \beta[w - \Delta F(t)] = R[E_t, E_0]. \tag{71}$$

The essential property that R is independent of i and j and only expressed in terms of observable quantities is therefore satisfied.

Equations (62) and (63) become

$$\bar{S} = \beta[\mathrm{Tr}\, \hat{H}(t)\hat{\rho}(t) - F(t)],$$

$$S = \beta[\mathrm{Tr}\, \hat{H}(0)\hat{\rho}_0 - F(0)], \tag{72}$$

and

$$\langle R \rangle = \bar{S} - S = \beta(\langle w \rangle - \Delta F) \geqslant 0, \tag{73}$$

where

$$\langle w \rangle = \mathrm{Tr}\, \hat{H}(t)\hat{\rho}(t) - \mathrm{Tr}\, \hat{H}(0)\hat{\rho}_0. \tag{74}$$

$\langle w \rangle$ is the average work so that $\beta^{-1}\langle R \rangle$ is the irreversible work (the irreversible contribution to the entropy change). Using Eq. (58), we get the Crooks relation

$$\frac{p(w)}{p^{\mathrm{tr}}(-w)} = e^{\beta(w - \Delta F)}. \tag{75}$$

The Jarzynski relation follows immediately from Eq. (75) [by integrating $p^{\mathrm{tr}}(-w)$ over w which is equal to 1 because of normalization],

$$\langle e^{-\beta w} \rangle = e^{-\beta \Delta F}. \tag{76}$$

Equations (76) and (75) have been first derived by Kurchan (2000) for a periodic driving (where $\Delta F = 0$) and by Tasaki (2000) for finite ΔF. Further studies of Eq. (76) have been done by Mukamel (2003b), Talkner *et al.* (2007), and Talkner, Burada, and Hänggi (2008a) and of

Eq. (75) by Talker and Hänggi (2007). It was generalized to the microcanonical ensemble by Campisi (2008) and Talkner, Hänggi, and Morillo (2008).

2. Work fluctuation theorem for closed driven systems

We consider the same forward and backward processes as described above, except that during the driving the system now remains in weak contact with a reservoir at equilibrium. The total Hamiltonian is therefore of the form $\hat{H}(t) = \hat{H}_S(t) + \hat{H}_B + \hat{V}$, where $\hat{H}_S(t)$ ($\hat{H}_B$) is the system (reservoir) Hamiltonian and $\hat{V}$ is the weak interaction between the two. The work done by the driving force on the system is now given by the difference between the system and the reservoir energy change (this last one represents heat) according to the first law of thermodynamics.

In this case, the connection with the results of Sec. II is done with

$$\hat{\rho}_0 = \frac{e^{-\beta \hat{H}_S(0)}}{Z_S(0)} \frac{e^{-\beta \hat{H}_B}}{Z_B}, \quad \hat{\rho}_0^{\mathrm{tr}} = \frac{e^{-\beta \hat{H}_S(t)}}{Z_S(t)} \frac{e^{-\beta \hat{H}_B}}{Z_B}, \quad (77)$$

as well as $a_0 = E_s(0) + E_b$ and $a_t = E_{s'}(t) + E_{b'}$, where $E_s(0)$ [$E_s(t)$] are the eigenvalues of $\hat{H}_S(0)$ [$\hat{H}_S(t)$] and E_b are the eigenvalues of $\hat{H}_B$. We define $i = (i_s, i_b)$ and $j = (j_s, j_b)$, where i_s and j_s are used to distinguish between degenerate eigenstates of $\hat{H}_S(0)$ and $\hat{H}_S(t)$ and i_b and j_b between degenerate eigenstates of $\hat{H}_B$. The work is therefore

$$w = \Delta a = U_{s's} + Q_{b'b}, \quad (78)$$

where $U_{s's} = E_{s'}(t) - E_s(0)$ is the change in the system energy and $Q_{b'b} = E_{b'} - E_b$ is the heat transferred from the system to the reservoir. Since the eigenstates of the Hamiltonian constitute a complete basis set, Eqs. (7) and (36) become

$$P[j, E_{s'}(t) + E_{b'}; i, E_s(0) + E_b]$$
$$= |\langle js'b'|\hat{U}(t,0)|isb\rangle|^2 \langle sb|\hat{\rho}_0|sb\rangle, \quad (79)$$

$$P^{\mathrm{tr}}[i, E_s(0) + E_b; j, E_{s'}(t) + E_{b'}]$$
$$= |\langle js'b'|\hat{U}(t,0)|isb\rangle|^2 \langle s'b'|\hat{\rho}_0^{\mathrm{tr}}|s'b'\rangle. \quad (80)$$

Equation (50) therefore gives

$$R[j, E_{s'}(t) + E_{b'}; i, E_s(0) + E_b]$$
$$= \beta(w - \Delta F) = R[E_{s'}(t) + E_{b'}, E_s(0) + E_b], \quad (81)$$

where $\Delta F(t) = F(t) - F(0)$ is the free-energy difference between the initial and final system state [$F(t) = -\beta^{-1} \ln Z_S(t)$]. The essential property that R is independent of i and j and expressed solely in terms of observable quantities is therefore again satisfied. Using Eq. (58), we get the same Crooks (75) and Jarzynski (76) relation as in the isolated case. The two relations were derived for quantum open driven systems in many different ways by Kurchan (2000), De Roeck and Maes (2004), Monnai (2005), Esposito and Mukamel (2006),

Crooks (2008a, 2008b), and Talkner *et al.* (2009). Using Eqs. (62) and (63), we also find that Eq. (73) still holds with

$$\langle w \rangle = \mathrm{Tr}(\hat{H}_S(t) + \hat{H}_B)\hat{\rho}(t) - \mathrm{Tr}(\hat{H}_S(0) + \hat{H}_B)\hat{\rho}_0. \quad (82)$$

3. Fluctuation theorem for direct heat and matter exchange between two systems

We consider two finite systems A and B with Hamiltonians $\hat{H}_A$ and $\hat{H}_B$, each initially at equilibrium with its own temperature and chemical potential. The two systems are weakly interacting, allowing heat and matter exchange between them. The total Hamiltonian is of the form $\hat{H}_{\mathrm{tot}} = \hat{H}_A + \hat{H}_B + \hat{V}$, where $\hat{V}$ is the coupling term between A and B. The joint Hilbert space is $\mathcal{H}_A \times \mathcal{H}_B$. The energy E_A and the number of particles n_A of system A is measured at time zero and again at time t. We assume

$$\hat{\rho}_0 = \hat{\rho}_0^{\mathrm{tr}} = \hat{\rho}_A^{\mathrm{eq}}(\beta_A, \mu_A)\hat{\rho}_B^{\mathrm{eq}}(\beta_B, \mu_B), \quad (83)$$

where

$$\hat{\rho}_X^{\mathrm{eq}}(\beta_X, \mu_X) = e^{-\beta_X(\hat{H}_X - \mu_X \hat{N}_X)}/\Xi_X \quad (84)$$

and $X = A, B$. Ξ_X is the grand canonical partition function. The index i_X is used to distinguish between eigenstates of $\hat{H}_X$ with same energy E_X and number of particles n_X. We define $i = (i_A, i_B)$ and $\alpha = (E_A, n_A, E_B, n_B)$. Using Eqs. (7) and (36), we find

$$P[i', \alpha'; i, \alpha] = |\langle i', \alpha'|\hat{U}_t|i, \alpha\rangle|^2 \langle \alpha|\hat{\rho}_0|\alpha\rangle, \quad (85)$$

$$P^{\mathrm{tr}}[i, \alpha; i', \alpha'] = |\langle i', \alpha'|\hat{U}_t|i, \alpha\rangle|^2 \langle \alpha'|\hat{\rho}_0|\alpha'\rangle. \quad (86)$$

Equations (50) with (83) give

$$R[\alpha', \alpha] = -\beta_A[(E_A - E_A') - \mu_A(n_A - n_A')]$$
$$- \beta_B[(E_B - E_B') - \mu_B(n_B - n_B')]. \quad (87)$$

Conservation laws imply that changes in matter and energy in one system are accompanied by the opposite changes in the other system so that

$$E_A - E_A' \approx -(E_B - E_B'), \quad (88)$$

$$n_A - n_A' = n_B - n_B'. \quad (89)$$

The weak-interaction assumption is required for Eq. (88) to hold. Using Eqs. (88) and (89) and defining the heat and matter nonequilibrium constraints

$$\mathcal{A}_h \equiv -\beta_A + \beta_B,$$

$$\mathcal{A}_m \equiv \beta_A \mu_A - \beta_B \mu_B, \quad (90)$$

we find that Eq. (87) can be expressed exclusively in terms of measured quantities E_A and n_A:

$$R[E_A', n_A'; E_A, n_A] \approx -\mathcal{A}_h(E_A' - E_A) - \mathcal{A}_m(n_A' - n_A). \quad (91)$$

Using Eqs. (62) and (63), we find

$$S = - \sum_{X=A,B} \beta_X (\operatorname{Tr} \hat{H}_X \hat{\rho}_0 - \mu_X \operatorname{Tr} \hat{N}_X \hat{\rho}_0), \qquad (92)$$

$$\bar{S} = - \sum_{X=A,B} \beta_X [\operatorname{Tr} \hat{H}_X \hat{\rho}(t) - \mu_X \operatorname{Tr} \hat{N}_X \hat{\rho}(t)]. \qquad (93)$$

From Eq. (61), the ensemble average of Eq. (91) is the time-integrated entropy production which has the familiar force-flux form of nonequilibrium thermodynamics (de Groot and Mazur, 1984; Kondepudi and Prigogine, 1998; Mehta and Andrei, 2008)

$$\langle R \rangle \approx - \mathcal{A}_h [\operatorname{Tr} \hat{H}_A \hat{\rho}(t) - \operatorname{Tr} \hat{H}_A \hat{\rho}(0)]$$
$$- \mathcal{A}_m [\operatorname{Tr} \hat{N}_A \hat{\rho}(t) - \operatorname{Tr} \hat{N}_A \hat{\rho}(0)]. \qquad (94)$$

The detailed FT follows from Eqs. (58) and (91)

$$\frac{p(\Delta E_A, \Delta n_A)}{p(-\Delta E_A, -\Delta n_A)} \approx e^{-(\mathcal{A}_h \Delta E_A + \mathcal{A}_m \Delta n_A)}. \qquad (95)$$

Positive $\mathcal{A}_h$ ($\mathcal{A}_m$) means that $T_A > T_B$ ($\beta_A \mu_A > \beta_B \mu_B$) so that the probability for an energy transfer ΔE_A (of a particle transfer Δn_A) from A to B is exponentially more likely than from B to A.

Such a FT for heat has been derived by Jarzynski and Wojcik (2004). A similar FT for exchange of bosons has been derived by Kawai *et al.* (2007). This FT for particles can also be derived from the GF of Shelankov and Rammer (2003) and Levitov and Reznikov (2004). Derivations of this detailed FT for specific models are presented in Secs. IV.B.4 and V.B.2.

C. Steady-state fluctuation theorems

We give simple qualitative and general arguments to show that the FT (58) can be used to obtain a quantum steady-state FT for heat and matter exchange between two reservoirs through an embedded system.

We consider two reservoirs A and B, with Hamiltonians $\hat{H}_A$ and $\hat{H}_B$, each initially at equilibrium with its own temperature and chemical potential. A heat and matter exchange occurs between the two reservoirs through a weakly coupled embedded system (e.g., a molecule or a quantum dot). The total Hamiltonian is $\hat{H}_{\text{tot}} = \hat{H}_A + \hat{H}_B + \hat{V}$, where $\hat{V} = \hat{H}_S + \hat{V}_{AS} + \hat{V}_{BS}$ contains the free Hamiltonian of the system $\hat{H}_S$ and the coupling term between each of the reservoirs and the system $\hat{V}_{AS}$ and $\hat{V}_{BS}$. The total Hilbert space is $\mathcal{H}_A \times \mathcal{H}_B \times \mathcal{H}_S$. We use the index i_X to distinguish between eigenstates of $\hat{H}_X$ with same energy E_X and number of particles n_X, where $X = A, B, S$. We define the abbreviated notation $i = (i_A, i_B, i_S)$ and $\alpha = (E_A, n_A, E_B, n_B, E_S, n_S)$. The energy E_A and the number of particles n_A is measured in reservoirs A at time zero and again at time t. We assume

$$\hat{\rho}_0 = \hat{\rho}_0^{\text{tr}} = \hat{\rho}_A^{\text{eq}}(\beta_A, \mu_A) \hat{\rho}_B^{\text{eq}}(\beta_B, \mu_B) \hat{\rho}_S^{\text{eq}}(\beta_S, \mu_S), \qquad (96)$$

where $\hat{\rho}_S^{\text{eq}}$ is the equilibrium system reduced density matrix. Since

$$P[i', \alpha'; i, \alpha] = |\langle i', \alpha' | \hat{U}_t | i, \alpha \rangle|^2 \langle i, \alpha | \hat{\rho}_0 | i, \alpha \rangle, \qquad (97)$$

$$P^{\text{tr}}[i, \alpha; i', \alpha'] = |\langle i', \alpha' | \hat{U}_t | i, \alpha \rangle|^2 \langle i', \alpha' | \hat{\rho}_0 | i', \alpha' \rangle, \qquad (98)$$

Eq. (50) reads

$$R[\alpha', \alpha] = - \beta_A [(E_A - E'_A) - \mu_A(n_A - n'_A)]$$
$$- \beta_B [(E_B - E'_B) - \mu_B(n_B - n'_B)]$$
$$- \beta_S [(E_S - E'_S) - \mu_S(n_S - n'_S)]. \qquad (99)$$

Since the system-reservoir couplings are weak, conservation laws of the total unperturbed system ($\hat{H}_{\text{tot}}$ with $\hat{V}_{AS} + \hat{V}_{BS} = 0$) imply that

$$E_B - E'_B \approx - (E_A - E'_A) - (E_S - E'_S), \qquad (100)$$

$$n_B - n'_B = n'_A - n_A + n'_S - n_S. \qquad (101)$$

This means that Eq. (99) is equal to

$$R[E'_A, n'_A; E_A, n_A] \approx - \mathcal{A}_h(E'_A - E_A) - \mathcal{A}_m(n'_A - n_A)$$
$$+ \mathcal{O}(E'_S - E_S) + \mathcal{O}(n'_S - n_S). \qquad (102)$$

Since A and B are assumed macroscopic (i.e., reservoirs), the change in energy $E'_A - E_A$ and matter $n_A - n'_A$ in reservoir A is not bounded. However, because system S is assumed small and finite, $E'_S - E_S$ and $n'_S - n_S$ are always bounded and finite. This means that in the long-time limit these contribution to R will become negligible in Eq. (102). For long times, the FT (58) with Eq. (102) becomes a universal (independent of system quantities) steady-state FT for the heat and matter currents,

$$\lim_{t \to \infty} \frac{1}{t} \ln \frac{p(\Delta E_A, \Delta N_A)}{p(-\Delta E_A, -\Delta N_A)} = \mathcal{A}_h I_h + \mathcal{A}_m I_m, \qquad (103)$$

where $I_h = \Delta E_A / t$ and $I_m = \Delta N_A / t$ are the heat and matter current between the system and the reservoir A. The right-hand side of Eq. (103) can thus be interpreted as an entropy production. A rigorous proof of Eq. (103) has been recently given by Andrieux *et al.* (2009). In the long-time limit, the steady-state FT (103) is similar to the detailed FT (95). We note that the long-time limit is related to the existence of a large deviation function (see Appendix C). We also note that when the system S is not finite, $\mathcal{O}(E'_S - E_S)$ and $\mathcal{O}(n'_S - n_S)$ terms in Eq. (102) may not be negligible in the long-time limit, as observed by van Zon and Cohen (2003, 2004). Similar problems are expected if A and B are not "good" reservoirs. A good reservoir should allow the system to reach a steady state. Since it is known that such reservoirs cannot be properly described within the Hamiltonian formalism, it should be no surprise that more systematic derivations of quantum steady-state FT (103) require to use some effective (and irreversible) description of the embedded system dynamics. A common way to do this is the quantum master equation approach, which consists in deriving an approximate equation of motion for the system reduced density matrix containing the effects of reservoir

through its correlation functions. As required for a "true" reservoir, the back action of the system on the reservoir is neglected (Born approximation). Such a derivation of the steady-state FTs is presented in Sec. IV [see Eq. (141) and (149)]. Another approach is based on a system Green's function description. Here the effect of the reservoirs appear through the self-energies. These derivations will be presented in Sec. V.C. It has been recently suggested that finite thermostats (commonly used to model thermostatted classical dynamics) could also be used to describe thermostatted quantum dynamics (Gallavotti, 2008).

IV. HEAT AND MATTER TRANSFER STATISTICS IN WEAKLY COUPLED OPEN SYSTEMS

We now consider a small quantum system weakly interacting with a reservoir. Heat and matter exchanges are measured by a projective measurement in the reservoir. We derive a generalized quantum master equation (GQME) for the GF associated to the system density matrix conditional to a given transfer with the reservoir. The statistics is therefore obtained from the solution of the GQME. When summing the GQME over all possible transfer processes, one recovers the standard quantum master equation (QME).

A. Generalized quantum master equation

We consider a single reservoir, but the extension to multiple reservoirs is straightforward. The total Hamiltonian is the sum of the system S Hamiltonian $\hat{H}_S$, the reservoir R Hamiltonian $\hat{H}_R$, and the weak interaction between the two $\hat{V}$:

$$\hat{H} = \hat{H}_0 + \hat{V} = \hat{H}_S + \hat{H}_R + \hat{V}. \tag{104}$$

We use the index s (r) to label the eigenstates of the Hamiltonian of system S (R). The reservoir is initially assumed to be at equilibrium $\hat{\rho}_R^{\mathrm{eq}} = e^{-\beta(\hat{H}_R - \mu \hat{N}_R)} / \Xi_R$. The measured observable is the energy $\hat{H}_R$ and number of particle $\hat{N}_R$ in the reservoir. Since the measured observables commutes with the initial density matrix $\hat{\rho}_0 = \hat{\rho}_S(0) \hat{\rho}_R^{\mathrm{eq}}$, using Eq. (17) we obtain

$$G(\lambda, t) = \mathrm{Tr}\, \hat{\rho}(\lambda, t), \tag{105}$$

where $\lambda = \{\lambda_h, \lambda_m\}$,

$$\hat{\rho}(\lambda, t) \equiv e^{-(i/\hbar)\hat{H}_\lambda t} \hat{\rho}_0 e^{(i/\hbar)\hat{H}_{-\lambda} t} \tag{106}$$

and

$$\hat{H}_\lambda = e^{(i/2)(\lambda_h \hat{H}_R + \lambda_m \hat{N}_R)} \hat{H} e^{-(i/2)(\lambda_h \hat{H}_R + \lambda_m \hat{N}_R)} = \hat{H}_0 + \hat{V}_\lambda. \tag{107}$$

Obviously, $\hat{\rho}(t) = \hat{\rho}(\lambda = 0, t)$.

We define the system GF

$$\hat{\rho}_S(\lambda, t) \equiv \mathrm{Tr}_R\, \hat{\rho}(\lambda, t), \tag{108}$$

which is an operator in the system space. Since $\hat{\rho}_S(t) = \hat{\rho}_S(\lambda = 0, t)$ is the reduced density matrix of the system, $\hat{\rho}_S(\lambda, t)$ is a reduced density matrix of the system conditional to a certain energy and matter transfer between S and R. We can now rewrite Eq. (105) as

$$G(\lambda, t) = \mathrm{Tr}_S\, \hat{\rho}_S(\lambda, t). \tag{109}$$

We derive a closed evolution equation for $\hat{\rho}_S(\lambda, t)$ using the projection operator technique and second-order perturbation theory in $\hat{V}$ on $\hat{\rho}(\lambda, t)$. By solving this equation one can obtain $G(\lambda, t)$. Details are given in Appendix D. The final result reads

$$\begin{aligned}
\dot{\hat{\rho}}_S(\lambda, t) = &-\frac{i}{\hbar}[\hat{H}_S, \hat{\rho}_S(\lambda, t)] \\
&+ \frac{1}{\hbar^2} \sum_{\kappa\kappa'} \int_0^t d\tau [-\mathrm{Tr}_R\{\hat{V}_\lambda^\kappa \hat{V}_\lambda^{\kappa'}(-\tau) \hat{\rho}_R^{\mathrm{eq}} \hat{\rho}_S(\lambda, t)\} \\
&- \mathrm{Tr}_R\{\hat{\rho}_R^{\mathrm{eq}} \hat{\rho}_S(\lambda, t) \hat{V}_{-\lambda}^\kappa(-\tau) \hat{V}_{-\lambda}^{\kappa'}\} \\
&+ \mathrm{Tr}_R\{\hat{V}_\lambda^\kappa \hat{\rho}_R^{\mathrm{eq}} \hat{\rho}_S(\lambda, t) \hat{V}_{-\lambda}^{\kappa'}(-\tau)\} \\
&+ \mathrm{Tr}_R\{\hat{V}_\lambda^\kappa(-\tau) \hat{\rho}_R^{\mathrm{eq}} \hat{\rho}_S(\lambda, t) \hat{V}_{-\lambda}^{\kappa'}\}], \tag{110}
\end{aligned}$$

where

$$\hat{V}_\lambda^\kappa(t) = e^{(i/\hbar)\hat{H}_0 t} \hat{V}_\lambda^\kappa e^{-(i/\hbar)\hat{H}_0 t}. \tag{111}$$

1. Generalized reservoir correlation functions

We now consider an interaction of the form

$$\hat{V} = \sum_\kappa \hat{S}^\kappa \hat{R}^\kappa, \tag{112}$$

where $\hat{S}^\kappa$ ($\hat{R}^\kappa$) is a coupling operator of system S (B). It follows from Eq. (107) that $\hat{V}_\lambda \equiv \Sigma_\kappa \hat{S}^\kappa \hat{R}_\lambda^\kappa$, where

$$\hat{R}_\lambda^\kappa \equiv e^{(i/2)(\lambda_h \hat{H}_R + \lambda_m \hat{N}_R)} \hat{R}^\kappa e^{-(i/2)(\lambda_h \hat{H}_R + \lambda_m \hat{N}_R)}. \tag{113}$$

For such an interaction, Eq. (110) becomes

$$\dot{\hat{\rho}}_S(\lambda,t) = -\frac{i}{\hbar}[\hat{H}_S,\hat{\rho}_S(\lambda,t)]$$

$$+\frac{1}{\hbar^2}\sum_{\kappa\kappa'}\int_0^t d\tau\{-\alpha_{\kappa\kappa'}(\tau)\hat{S}^\kappa\hat{S}^{\kappa'}(-\tau)\hat{\rho}_S(\lambda,t)$$

$$-\alpha_{\kappa\kappa'}(-\tau)\hat{\rho}_S(\lambda,t)\hat{S}^\kappa(-\tau)\hat{S}^{\kappa'}$$

$$+\alpha_{\kappa'\kappa}(-\lambda,-\tau)\hat{S}^\kappa\hat{\rho}_S(\lambda,t)\hat{S}^{\kappa'}(-\tau)$$

$$+\alpha_{\kappa'\kappa}(-\lambda,\tau)\hat{S}^\kappa(-\tau)\hat{\rho}_S(\lambda,t)\hat{S}^{\kappa'}\}. \qquad (114)$$

Here we have defined the generalized reservoir correlation functions

$$\alpha_{\kappa\kappa'}(\lambda,t) \equiv \mathrm{Tr}_R\,\hat{\rho}^{\mathrm{eq}}\hat{R}_{2\lambda}^\kappa(t)\hat{R}^{\kappa'}$$

$$=\sum_{rr'}\frac{e^{-\beta(E_r-\mu N_r)}}{Z_G}e^{(i/\hbar)(E_r-E_{r'})t}$$

$$\times e^{i\{\lambda_h(E_r-E_{r'})+\lambda_m(N_r-N_{r'})\}}R_{rr'}^\kappa R_{r'r}^{\kappa'}, \qquad (115)$$

where $\hat{R}_\lambda^\kappa(t)=e^{(i/\hbar)\hat{H}_R t}\hat{R}_\lambda^\kappa e^{-(i/\hbar)\hat{H}_R t}$. The reservoir correlation functions are given by $\alpha_{\kappa\kappa'}(t)\equiv\alpha_{\kappa\kappa'}(\lambda=0,t)$. For $\lambda=0$, Eq. (114) therefore reduces to the non-Markovian Redfield QME of Gaspard and Nagaoka (1999b).

The ordinary reservoir correlation functions satisfy the standard Kubo-Martin-Schwinger (KMS) condition (Kubo *et al.*, 1998)

$$\alpha_{\kappa\kappa'}(t) = \alpha_{\kappa'\kappa}(-t-i\hbar\beta). \qquad (116)$$

In the frequency domain

$$\tilde{\alpha}_{\kappa\kappa'}(\lambda,\omega) = \int_{-\infty}^\infty \frac{dt}{2\pi}e^{i\omega t}\alpha_{\kappa\kappa'}(\lambda,t), \qquad (117)$$

the KMS relation reads

$$\tilde{\alpha}_{\kappa\kappa'}(\omega) = e^{\beta\hbar\omega}\tilde{\alpha}_{\kappa'\kappa}(-\omega). \qquad (118)$$

The generalized reservoir correlation functions satisfy the symmetry

$$\alpha_{\kappa\kappa'}(\{\lambda_h,\lambda_m\},t) = \alpha_{\kappa'\kappa}(\{-\lambda_h-i\beta,-\lambda_m+i\beta\mu\},-t). \qquad (119)$$

We note also that if $\hat{R}^\kappa$ and $\hat{S}^\kappa$ are Hermitian, we further have

$$\alpha_{\kappa\kappa'}(\lambda,t) = \alpha_{\kappa'\kappa}^*(-\lambda,-t). \qquad (120)$$

2. The Markovian and the rotating wave approximation

Two approximations commonly used to simplify the QME may also be used on the GQME. The Markovian approximation consist of setting the upper bound of the time integral in Eq. (114) to infinity. The rotating wave approximation (RWA) (Gardiner and Zoller, 2000; Breuer and Petruccione, 2002) [also known as secular approximation (Cohen-Tannoudji *et al.*, 1996; Schaller and Brandes, 2008) or Davis procedure (Spohn, 1980; van Kampen, 1997) is often used to impose a Lindblad

form (Lindblad, 1976; Spohn, 1980; Breuer and Petruccione, 2002) to the Markovian QME generator in order to guarantee the complete positivity of the subsystem density matrix time evolution. Without RWA, the Markovian QME generator can lead to a positivity breakdown for certain set of initial conditions due to small errors introduced on the initial short-time dynamics by the Markovian approximation (Suarez *et al.*, 1992; Pechukas, 1994; Kohen *et al.*, 1997; Gaspard and Nagaoka, 1999b; Cheng and Silbey, 2005; Jordan *et al.*, 2008). One has to note, however, that the use of the RWA is not always physically justified and might miss important effects (Suarez *et al.*, 1992; Kohen *et al.*, 1997; Gaspard and Nagaoka, 1999b; Cheng and Silbey, 2005). The RWA is equivalent to define a coarse-grained time derivative of the system density matrix on times long compared to the free system evolution (Cohen-Tannoudji *et al.*, 1996; Schaller and Brandes, 2008). One easy way to perform the RWA consists in time averaging $\lim_{T\to\infty}(1/2T)\int_{-T}^T dt$ the generator of the QME in the interaction picture and in the system eigenbasis, using

$$\int_0^\infty d\tau e^{\pm i\omega\tau} = \pi\delta(\omega)\pm iP\frac{1}{\omega} = \lim_{\eta\to 0^+}\frac{1}{\eta\mp i\omega}. \qquad (121)$$

Using these two approximations on the GQME (114), we find that coherences $\rho_{ss'}(t)\equiv\langle s|\hat{\rho}_S(t)|s'\rangle$, with $s\neq s'$, follow the dynamics

$$\dot{\rho}_{ss'}(\lambda,t) = (-\Gamma_{ss'}-i\Omega_{ss'})\rho_{ss'}(\lambda,t), \qquad (122)$$

where the relaxation rates are given by

$$\Gamma_{ss'} = \frac{1}{\hbar^2}\sum_{\kappa\kappa'}\left\{-2\pi\tilde{\alpha}_{\kappa\kappa'}(0)S_{ss}^{\kappa'}S_{s's'}^\kappa\right.$$

$$\left.+\pi\sum_{\bar{s}}[\tilde{\alpha}_{\kappa\kappa'}(\omega_{s\bar{s}})S_{s\bar{s}}^\kappa S_{\bar{s}s}^{\kappa'} + \tilde{\alpha}_{\kappa'\kappa}(\omega_{s'\bar{s}})S_{s'\bar{s}}^{\kappa'}S_{\bar{s}s'}^\kappa]\right\} \qquad (123)$$

and the modified system frequencies are

$$\Omega_{ss'} = \omega_{ss'} - \frac{1}{\hbar^2}\sum_{\kappa\kappa'}\sum_{\bar{s}}\left[\int_{-\infty}^\infty d\omega P\frac{\tilde{\alpha}_{\kappa\kappa'}(\omega)}{\omega+\omega_{s\bar{s}}}S_{s\bar{s}}^\kappa S_{\bar{s}s}^{\kappa'}\right.$$

$$\left.-\int_{-\infty}^\infty d\omega P\frac{\tilde{\alpha}_{\kappa\kappa'}(\omega)}{\omega+\omega_{s'\bar{s}}}S_{s's}^\kappa S_{\bar{s}s'}^{\kappa'}\right]. \qquad (124)$$

The coherences evolve independently from the populations [diagonal elements $\rho_{ss}(t)$] and also independently from of each other. They simply undergo exponentially damped oscillations which are independent of λ. Populations, on the other hand, evolve according to the equation

$$\dot{\rho}_{ss}(\lambda,t) = \frac{1}{\hbar^2}\sum_{\kappa\kappa'}\sum_{\bar{s}}\{-2\pi\tilde{\alpha}_{\kappa\kappa'}(-\omega_{\bar{s}s})S_{s\bar{s}}^\kappa S_{\bar{s}s}^{\kappa'}\rho_{ss}(\lambda,t)$$

$$+2\pi\tilde{\alpha}_{\kappa'\kappa}(\lambda,\omega_{\bar{s}s})S_{s\bar{s}}^\kappa S_{\bar{s}s}^{\kappa'}\rho_{\bar{s}\bar{s}}(\lambda,t)\}. \qquad (125)$$

The population dynamics depends on λ.

B. Applications to particle counting statistics

We now calculate the particle statistics for different models and derive various steady-state FTs using the GQME.

1. Fermion transport

We consider a many electron quantum system attached to two metal leads which act as particle reservoirs. We denote the singe-particle eigenstates of the system and leads by indices s and i, respectively. The total Hamiltonian is $\hat{H} = \hat{H}_A + \hat{H}_B + \hat{H}_S + \hat{V}$, where

$$\hat{H}_X = \sum_{i \in X=A,B} \epsilon_i \hat{c}_i^\dagger \hat{c}_i, \quad \hat{H}_S = \sum_s \epsilon_s \hat{c}_s^\dagger \hat{c}_s. \quad (126)$$

The coupling between the lead $X = A, B$ and the system is $\hat{V}_X = \hat{J}_X + \hat{J}_X^\dagger$, where $\hat{J}_X = \Sigma_{s,i \in X} J_{si}^X \hat{c}_s^\dagger \hat{c}_i$ and J_{si}^X are the coupling elements between the system and the leads X. The total coupling is then

$$\hat{V} = \hat{J}_A + \hat{J}_B + \hat{J}_A^\dagger + \hat{J}_B^\dagger. \quad (127)$$

There is no direct coupling between the two leads, and an electron transfer is only possible by charging or discharging the quantum system. The operators $\hat{c}$ ($\hat{c}^\dagger$) represent the annihilation (creation) operators which satisfy the Fermi anticommutation relations

$$\hat{c}_s \hat{c}_{s'}^\dagger + \hat{c}_{s'}^\dagger \hat{c}_s = \delta_{ss'},$$

$$\hat{c}_s^\dagger \hat{c}_{s'}^\dagger + \hat{c}_{s'}^\dagger \hat{c}_s^\dagger = \hat{c}_s \hat{c}_{s'} + \hat{c}_{s'} \hat{c}_s = 0. \quad (128)$$

To connect with the notation of the Hamiltonian (104), we have $\hat{H}_R = \hat{H}_A + \hat{H}_B$ and $\hat{V} = \hat{V}_A + \hat{V}_B$. Apart from the difference in chemical potentials μ_A and μ_B with $eV = \mu_A - \mu_B$, the two leads are assumed be identical.

To count the change in the number of electrons in the lead A, the projection is done on A. Therefore Eq. (111) for this model reads

$$\hat{V}_\lambda = e^{(i/2)\lambda \hat{N}_A} (\hat{J}_A + \hat{J}_A^\dagger) e^{-(i/2)\lambda \hat{N}_A} + \hat{V}_B$$

$$= e^{-(i/2\lambda)} \hat{J}_A + e^{(i/2)\lambda} \hat{J}_A^\dagger + \hat{V}_B. \quad (129)$$

To obtain the second line, we used the relation $\hat{J}_A \hat{N}_A = (\hat{N}_A + 1) \hat{J}_A$. Substituting Eq. (129) into Eq. (110), the GQME becomes

$$\dot{\hat{\rho}}_S(\lambda, t) = -\frac{i}{\hbar} [\hat{H}_S, \hat{\rho}_S(\lambda, t)] + \frac{1}{\hbar^2} \sum_{ss'} \int_0^t d\tau [\{e^{i\lambda} \alpha_{ss'}^A(-\tau) + \alpha_{ss'}^B(-\tau)\} \hat{c}_{s'} \hat{\rho}_S(\lambda, t) \hat{c}_s^\dagger(-\tau) + \{e^{i\lambda} \alpha_{ss'}^A(\tau) + \alpha_{ss'}^B(\tau)\}$$

$$\times \hat{c}_{s'}(-\tau) \hat{\rho}_S(\lambda, t) \hat{c}_s^\dagger + \{e^{-i\lambda} \beta_{ss'}^A(-\tau) + \beta_{ss'}^B(-\tau)\} \hat{c}_s^\dagger \hat{\rho}_S(\lambda, t) \hat{c}_{s'}(-\tau) + \{e^{-i\lambda} \beta_{ss'}^A(\tau) + \beta_{ss'}^B(\tau)\} \hat{c}_s^\dagger(-\tau) \hat{\rho}_S(\lambda, t) \hat{c}_{s'}$$

$$- \alpha_{ss'}(\tau) \hat{c}_s^\dagger \hat{c}_{s'}(-\tau) \hat{\rho}_S(\lambda, t) - \beta_{ss'}(\tau) \hat{c}_{s'} \hat{c}_s^\dagger(-\tau) \hat{\rho}_S(\lambda, t) - \alpha_{ss'}(-\tau) \hat{\rho}_S(\lambda, t) \hat{c}_s^\dagger(-\tau) \hat{c}_{s'} - \beta_{ss'}(-\tau) \hat{\rho}_S(\lambda, t) \hat{c}_{s'}(-\tau) \hat{c}_s^\dagger], \quad (130)$$

where

$$\alpha_{ss'}^X(\tau) = \sum_{ii' \in X} J_{si}^X (J_{s'i'}^X)^* \text{Tr}\{\hat{c}_i(\tau) \hat{c}_{i'}^\dagger \hat{\rho}_B\},$$

$$\beta_{ss'}^X(\tau) = \sum_{ii' \in X} J_{si}^X (J_{s'i'}^X)^* \text{Tr}\{\hat{c}_i^\dagger(\tau) \hat{c}_{i'} \hat{\rho}_B\} \quad (131)$$

are the equilibrium correlation functions for leads X and where $\alpha_{ss'}(\tau) = \alpha_{ss'}^A(\tau) + \alpha_{ss'}^B(\tau)$ and $\beta_{ss'}(\tau) = \beta_{ss'}^A(\tau) + \beta_{ss'}^B(\tau)$.

For $\lambda = 0$, Eq. (130) reduces to the QME derived by Harbola *et al.* (2006). After applying the Markovian approximation described in Sec. IV.A.2 [the upper limit of the time integral in Eq. (130) is extended to infinity], we perform the RWA approximation which is equivalent to assume that the lead correlation functions are diagonal in s (Harbola *et al.*, 2006). Equation (130) then becomes

$$\dot{\hat{\rho}}_S(\lambda, t) = -\frac{i}{\hbar} [\hat{H}_S, \hat{\rho}_S(\lambda, t)] + \sum_s [\{e^{-i\lambda} \alpha_{ss}^A$$

$$+ \alpha_{ss}^B\} \hat{c}_s^\dagger \hat{\rho}_S(\lambda, t) \hat{c}_s + \{e^{i\lambda} \beta_{ss}^A + \beta_{ss}^B\} \hat{c}_s \hat{\rho}_S(\lambda, t) \hat{c}_s^\dagger$$

$$- \alpha_{ss} \hat{c}_s \hat{c}_s^\dagger \hat{\rho}_S(\lambda, t) - \beta_{ss} \hat{c}_s^\dagger \hat{c}_s \hat{\rho}_S(\lambda, t)]. \quad (132)$$

The rates α_{ss}^X and β_{ss}^X are calculated by assuming a constant density of states σ for the leads over the energy range around the Fermi level

$$\alpha_{ss}^X = \frac{2\pi}{\hbar^2} \sigma |J_s^X|^2 [1 - f_X(\epsilon_s)],$$

$$\beta_{ss}^X = \frac{2\pi}{\hbar^2} \sigma |J_s^X|^2 f_X(\epsilon_s), \quad (133)$$

where $f_X(\epsilon) = [1 + e^{-\beta(\epsilon - \mu_X)}]^{-1}$ is the Fermi function of lead X and $\beta = 1/k_B T$. These rates satisfy the relation

$$\frac{\alpha_{ss}^A \beta_{ss}^B}{\alpha_{ss}^B \beta_{ss}^A} = e^{\beta eV}. \tag{134}$$

The solution of Eq. (132) allows one to compute the time-dependent electron statistics between lead A and the system at any time. For $\lambda = 0$, Eq. (132) is the Lindblad QME derived by Harbola et al. (2006). Equation (132) was first derived by Esposito et al. (2007b) by unraveling this QME. This derivation used that the QME is interpreted as resulting from a continuous positive operator-valued measurement (Nielsen and Chuang, 2000; Breuer and Petruccione, 2002) on the system by the leads. This allows one to construct probabilities for histories of electron transfers, and to use them to derive equations of motion for the GF associated with the probability distribution of a net transfer of electrons during a given time interval, which are identical to Eq. (132). We thus find that the two-point projection method and the positive operator-valued measurement lead to the same electron statistics result in the weak coupling regime (with Markovian and RWA). A similar conclusion was reached by De Roeck (2007) and Derezinski et al. (2008).

In Eq. (132), the GF factorizes in terms of single orbital GF of the system $\hat{\rho}_S(\lambda, t) = \Pi_{s=1}^M \hat{\rho}_s(\lambda, t)$, where M is the total number of orbital and $\hat{\rho}_s(\lambda, t)$ is the single orbital GF, so that

$$\dot{\hat{\rho}}_s(\lambda, t) = -\frac{i}{\hbar} \epsilon_s [\hat{c}_s^\dagger \hat{c}_s, \hat{\rho}_s] + [\{e^{-i\lambda} \alpha_{ss}^A + \alpha_{ss}^B\} \hat{c}_s^\dagger \hat{\rho}_s(\lambda, t) \hat{c}_s$$
$$+ \{e^{i\lambda} \beta_{ss}^A + \beta_{ss}^B\} \hat{c}_s \hat{\rho}_s(\lambda, t) \hat{c}_s^\dagger - \alpha_{ss} \hat{c}_s \hat{c}_s^\dagger \hat{\rho}_s(\lambda, t)$$
$$- \beta_{ss} \hat{c}_s^\dagger \hat{c}_s \hat{\rho}_s(\lambda, t)]. \tag{135}$$

As discussed in Sec. IV.A.2, the GQME (132), when expressed in the eigenbasis of the system, describes an independent dynamics for coherences and populations. The coherences simply decay in time following damped oscillations while populations follow a classical rate equation. If the eigenstates of each orbital are denoted by $|n_s\rangle$, where $n_s = 0, 1$, the vector made of the population of $\hat{\rho}_s(\lambda, t)$ in this basis denoted by $\tilde{\rho}_s(\lambda, t)$ $\equiv \{\langle 0 | \hat{\rho}_s(\lambda, t) | 0 \rangle, \langle 1 | \hat{\rho}_s(\lambda, t) | 1 \rangle\}$ evolves according to

$$\dot{\tilde{\rho}}_s(\lambda, t) = \Gamma_s(\lambda) \tilde{\rho}_s(\lambda, t), \tag{136}$$

where $\Gamma_s(\lambda)$ is a 2×2 matrix

$$\Gamma_s(\lambda) = \begin{pmatrix} -\alpha_{ss} & e^{i\lambda} \beta_{ss}^A + \beta_{ss}^B \\ e^{-i\lambda} \alpha_{ss}^A + \alpha_{ss}^B & -\beta_{ss} \end{pmatrix}. \tag{137}$$

The eigenvalues of this matrix are given by

$$\gamma_{s\pm}(\lambda) = -\frac{\alpha_{ss} + \beta_{ss}}{2} \pm \sqrt{f(\lambda)}, \tag{138}$$

where

$$f(\lambda) = (e^{i\lambda} \beta_{ss}^A + \beta_{ss}^B)(e^{-i\lambda} \alpha_{ss}^A + \alpha_{ss}^B) + \frac{1}{4}(\alpha_{ss} - \beta_{ss})^2.$$

Since $G(\lambda, t) = \Pi_s G_s(\lambda, t)$, where $G_s(\lambda, t) = \langle 0 | \hat{\rho}_s(\lambda, t) | 0 \rangle + \langle 1 | \hat{\rho}_s(\lambda, t) | 1 \rangle$, the long-time limit of the cumulant GF is given by the dominant eigenvalue

$$\mathcal{S}(\lambda) = \lim_{t \to \infty} \frac{1}{t} \ln G(\lambda, t) = \sum_s \gamma_{s+}(\lambda). \tag{139}$$

Using Eqs. (134) and (138), we find that $\gamma_{s\pm}(\lambda) = \gamma_{s\pm}(-i\beta eV - \lambda)$, which implies that

$$\mathcal{S}(\lambda) = \mathcal{S}(-i\beta eV - \lambda). \tag{140}$$

In Appendix C, we show that this symmetry implies the steady-state fluctuation theorem

$$\lim_{t \to \infty} \frac{p(k, t)}{p(-k, t)} = e^{\beta eVk}, \tag{141}$$

where $p(k, t)$ is the probability of transferring a net number k of electrons in time t from lead A to the system. Similar FTs have been derived by Tobiska and Nazarov (2005), Andrieux and Gaspard (2006), Esposito et al. (2007), and Saito and Utsumi (2008).

2. Boson transport

We consider a single oscillator mode at frequency $\epsilon_0 / \hbar \hat{H}_S = \epsilon_0 \hat{a}_0^\dagger \hat{a}_0$ coupled to two baths $X = A, B$ at different temperatures β_A^{-1} and β_B^{-1} ($k_B = 1$) that consist in a collection of noninteracting bosons (e.g., phonons) $\hat{H}_R = \hat{H}_A + \hat{H}_B$, where $\hat{H}_X = \Sigma_{i \in X} \epsilon_i \hat{a}_i^\dagger \hat{a}_i$. The coupling is assumed to take the form $\hat{V} = \hat{V}_A + \hat{V}_B$, where $\hat{V}_X = \Sigma_{i \in X} J_{i0}^X (\hat{a}_0 + \hat{a}_0^\dagger)(\hat{a}_i^\dagger + \hat{a}_i)$. The subscript 0 denotes the system oscillator and i is for the ith oscillator in the bath. J_{i0}^X is the coupling between the system and the ith bath oscillator from X. All operators satisfy the boson commutation relations

$$\hat{a}_s \hat{a}_{s'}^\dagger - \hat{a}_{s'}^\dagger \hat{a}_s = \delta_{ss'},$$

$$\hat{a}_s^\dagger \hat{a}_{s'}^\dagger - \hat{a}_{s'}^\dagger \hat{a}_s^\dagger = \hat{a}_s \hat{a}_{s'} - \hat{a}_{s'} \hat{a}_s = 0. \tag{142}$$

The system eigenstates have an energy $N_S \epsilon_0$, where $N_S = 1, 2, \ldots$. We are interested in the statistics of the energy transfers between the system and the A reservoir, so that the two energy measurements are performed on system A. It can be shown that performing the RWA on the GQME is equivalent to assume from the beginning that the coupling term is of the simplified form $\hat{V}_X = \Sigma_{i \in X} J_{i0}^X (\hat{a}_i^\dagger \hat{a}_0 + \hat{a}_0^\dagger \hat{a}_i)$. We thus have

$$\hat{V}_\lambda = e^{(i/2)\lambda \hat{H}_A}(\hat{V}_A + \hat{V}_B)e^{-(i/2)\lambda \hat{H}_A} = \hat{J}_A(\lambda) + \hat{J}_A^\dagger(\lambda) + \hat{V}_B, \tag{143}$$

where

$$\hat{J}_A(\lambda) = \sum_i J_{i0}^A \hat{a}_0^\dagger \hat{a}_i e^{(i/2)\lambda \epsilon_i}. \tag{144}$$

We have used $\hat{a}_i \hat{H}_A = (\epsilon_i + \hat{H}_A) \hat{a}_i$. Note that unlike fermions, Eq. (129), in this case we have a factor ϵ_i in the exponential in the coupling because we now measure energy. However, in the present model the energy change is directly proportional to particle change, i.e., their statistics is the same.

Substituting Eq. (143) into Eq. (110), we get

$$\dot{\hat{\rho}}_S(\lambda,t) = -\frac{i}{\hbar}[\hat{H}_S,\hat{\rho}_S(\lambda,t)] - \alpha_d \hat{a}_0 \hat{a}_0^\dagger \hat{\rho}_S(\lambda,t)$$
$$- \alpha_u \hat{a}_0^\dagger \hat{a}_0 \hat{\rho}_S(\lambda,t) + (\alpha_u^A e^{i\lambda\epsilon_0} + \alpha_u^B)\hat{a}_0 \hat{\rho}_S(\lambda,t)\hat{a}_0^\dagger$$
$$+ (\alpha_d^A e^{-i\lambda\epsilon_0} + \alpha_d^B)\hat{a}_0^\dagger \hat{\rho}_S(\lambda,t)\hat{a}_0, \qquad (145)$$

where the rates α_u and α_d correspond to the "up" and "down" jumps between the system states

$$\alpha_u^X = \frac{2\pi\sigma}{\hbar^2}|J_0^X|^2[1 + n_X(\epsilon_0)],$$

$$\alpha_d^X = \frac{2\pi\sigma}{\hbar^2}|J_0^X|^2 n_X(\epsilon_0). \qquad (146)$$

$n_X(\epsilon_0)=[e^{\beta_X\epsilon_0}-1]^{-1}$ is the Bose distribution function and $\alpha_{d(u)}=\alpha_{d(u)}^A+\alpha_{d(u)}^B$. The rates satisfy

$$\frac{\alpha_u^A \alpha_d^B}{\alpha_d^A \alpha_u^B} = e^{\epsilon_0(\beta_A-\beta_B)}. \qquad (147)$$

For $\lambda=0$, Eq. (145) is the Lindblad form QME derived by Segal and Nitzan (2005) and Harbola et al. (2007). In the system eigenbasis $\{|N_S\rangle\}$, Eq. (145) describes a populations dynamics which follows as

$$\dot{\rho}_{N_S}(\lambda,t) = (\alpha_u^A e^{i\lambda\epsilon_0} + \alpha_u^B)(N_S + 1)\rho_{N_S+1}(\lambda,t)$$
$$- \{\alpha_d(N_S + 1) + \alpha_u N_S\}\rho_{N_S}(\lambda,t)$$
$$+ (\alpha_d^A e^{-i\lambda\epsilon_0} + \alpha_d^B)N_S \rho_{N_S-1}(\lambda,t), \qquad (148)$$

where $\rho_{N_S}(\lambda,t) \equiv \langle N_S|\hat{\rho}_S(\lambda,t)|N_S\rangle$. Like Eq. (136), Eq. (148) may also be recast into a matrix form. However, unlike fermions, in this case since the matrix is infinite. $\tilde{\rho}$ is an infinite dimensional vector and $\Gamma(\lambda)$ is a tridiagonal infinite dimensional matrix. The determinant of a tridiagonal matrix can be expressed as a sum of terms where the nondiagonal terms always appear in pair with its symmetric nondiagonal term with respect to the diagonal. With the help of Eq. (147), this pair is symmetric with respect to $\lambda \to -i\epsilon_0(\beta_A-\beta_B)-\lambda$, so that $\det\{\Gamma(\lambda)\} = \det\{\Gamma(-i\epsilon_0(\beta_A-\beta_B)-\lambda)\}$. This implies that the eigen-

values have the same symmetry and therefore that the following steady-state FT hold:

$$\lim_{t\to\infty} \frac{p(k,t)}{p(-k,t)} = e^{\epsilon_0(\beta_A-\beta_B)k}. \qquad (149)$$

$p(k,t)$ is the probability that a net number of bosons are transferred from the reservoir A to the system in a time t. Similar FTs have been derived by Harbola et al. (2007), Saito and Dhar (2007), and Derezinski et al. (2008). The transport statistics of bosons and fermions is different and was compared by Harbola et al. (2007). However, both satisfy the same type of FT [Eqs. (141) and (149)].

3. Modulated tunneling

In the above discussion, fermion and bosons are transferred from one lead to another by charging or discharging an embedded system. We now consider electron tunneling between two coupled leads, where the tunneling elements are modulated by the state of an embedded system. Contrary to the model of Sec. IV.B.1, the system never gets charged; however, it affects the electron tunneling between the leads. This can happen, for example, if an impurity at the leads interface interacts with the spin of the tunneling electrons. The effect of this interaction is to modulate the tunneling elements between the two leads. This model of electron transfer was proposed by Rammer et al. (2004). Here we treat this model using the GQME approach.

The Hamiltonian of the junction is of the form (104), where $\hat{H}_S$ is the system Hamiltonian and $\hat{H}_R=\hat{H}_A+\hat{H}_B$ with $\hat{H}_X=\Sigma_{i\in X}\epsilon_i \hat{c}_i^\dagger \hat{c}_i$ ($X=A,B$) are the two leads Hamiltonian. The coupling between the two leads is of the form $\hat{V}=\hat{J}+\hat{J}^\dagger$, where $\hat{J}=\Sigma_{i\in A,j\in B}\hat{J}_{ij}\hat{c}_i^\dagger \hat{c}_j$. The tunneling elements between the leads $\hat{J}_{ij}^\dagger=\hat{J}_{ji}$ are now operators in the system space. We measure the number of particles in the lead A. We then have

$$\hat{V}_\lambda = e^{(i/2)\lambda\hat{N}_A}\hat{V}e^{(-i/2)\lambda\hat{N}_A} = e^{(i/2)\lambda}\hat{J} + e^{-(i/2)\lambda}\hat{J}^\dagger. \qquad (150)$$

Substituting this into Eq. (110), we obtain

$$\dot{\hat{\rho}}_S(\lambda,t) = -\frac{i}{\hbar}[\hat{H}_S,\hat{\rho}_S(\lambda,t)] - \sum_{i\in A,j\in B}[f_A(\epsilon_i)[1-f_B(\epsilon_j)][\hat{J}_{ij}\{\hat{J}_{ij}^\dagger(t)\}\hat{\rho}_S(\lambda,t) + \text{H.c.}] + f_B(\epsilon_j)[1-f_A(\epsilon_i)][\hat{J}_{ij}^\dagger\{\hat{J}_{ij}(t)\}\hat{\rho}_S(\lambda,t)$$
$$+ \text{H.c.}] - f_B(\epsilon_j)[1-f_A(\epsilon_i)]e^{i\lambda}(\hat{J}_{ij}\hat{\rho}_S(\lambda,t)\{\hat{J}_{ij}^\dagger(t)\} + \text{H.c.}) - f_A(\epsilon_i)[1-f_B(\epsilon_j)]e^{-i\lambda}(\{\hat{J}_{ij}^\dagger(t)\}\hat{\rho}_S(\lambda,t)\hat{J}_{ij} + \text{H.c.})], \qquad (151)$$

where

$$\{\hat{J}_{ij}(t)\} = \frac{1}{\hbar^2}\int_0^t d\tau e^{i\epsilon_{ij}\tau}e^{-i\hat{H}_S\tau}\hat{J}_{ij}e^{i\hat{H}_S\tau}. \qquad (152)$$

For $\lambda=0$, Eq. (151) reduces to a Redfield equation for the reduced density matrix of the system. A QME for

the charge specific reduced density matrix of the system was derived by Rammer et al. (2004). Equation (151) is the evolution equation for the GF associated to it.

When applying the Markovian approximation and the RWA to Eq. (151) in the system eigenbasis $\{|s\rangle\}$, the populations $\rho_{ss}(\lambda,t)=\langle s|\hat{\rho}_S(\lambda,t)|s\rangle$ evolve independently

from the exponentially damped coherences according to

$$\dot{\rho}_{ss}(\lambda,t) = \sum_{s'} [\Gamma_{s's}(\lambda)\rho_{s's'}(\lambda,t) - \Gamma_{s's}(\lambda = 0)\rho_{ss}(\lambda,t)].$$

(153)

The rates are given by

$$\Gamma_{ss'}(\lambda) = e^{-i\lambda}\alpha_{s's} + e^{i\lambda}e^{\beta(E_{ss'} - eV)}\alpha_{ss'},$$

(154)

where

$$\alpha_{ss'} = \frac{2\pi}{\hbar^2}\sum_{ij} f_A(\epsilon_i)[1 - f_B(\epsilon_j)]|\langle s|\hat{J}_{ij}|s'\rangle|^2\delta(\epsilon_{ij} - E_{ss'}).$$

(155)

They satisfy the symmetry

$$\Gamma_{s's}(-\lambda - i\beta eV) = e^{\beta E_{s's}}\Gamma_{ss'}(\lambda).$$

(156)

We define $\Gamma(\lambda)$ as the matrix generating the dynamics (153). Using the Leibniz formula, the determinant reads

$$\det\{\Gamma(\lambda)\} = \sum_\sigma \text{sgn}(\sigma)\prod_s^N \Gamma_{s\sigma(s)}(\lambda),$$

(157)

where N is the order of matrix Γ and the sum is computed over all permutations σ of the numbers $\{1,2,\dots,N\}$. $\text{sgn}(\sigma)$ denotes the sign of the permutation, $\text{sgn}(\sigma)=+1$ if σ is an even permutation and $\text{sgn}(\sigma)=-1$ if it is odd. Using Eq. (156), it can be shown that

$$\det\{\Gamma(\lambda)\} = \sum_\sigma \text{sgn}(\sigma)\prod_{s=1}^N e^{\beta E_{s\sigma(s)}}\Gamma_{\sigma(s)s}(-\lambda - i\beta eV)$$

$$= \sum_\sigma \text{sgn}(\sigma)\prod_{s=1}^N \Gamma_{\sigma(s)s}(-\lambda - i\beta eV)$$

$$= \sum_\sigma \text{sgn}(\sigma)\prod_{s=1}^N \Gamma_{s\sigma(s)}(-\lambda - i\beta eV)$$

$$= \det\{\Gamma(-\lambda - i\beta eV)\}.$$

(158)

In going from the first to second line, we used the fact that $\Pi_{s=1}^N e^{\beta E_{s\sigma(s)}} = 1$ due to $\Sigma_{s=1}^N E_{s\sigma(s)} = 0$. This property follows from the bijective nature of permutations, which implies that for a given $E_{s\sigma(s)}$ in the sum such that $\sigma(s) = s'$ there will always be a $E_{s'\sigma(s')}$ in the sum that cancels the $E_{s'}$. Since the eigenvalues of $\Gamma(\lambda)$ satisfy the same symmetry property as the determinant, we get the same steady-state FT as Eq. (141), where $p(k,t)$ is the probability for a net number k of electron transfer from the lead A to the lead B. This shows that the FT (141) is not model specific but rather a generic property of the nonequilibrium distribution of electron transfers between the two leads.

4. Direct-tunneling limit

When the system is decoupled from the junction, the tunneling elements between the two leads are given by $\hat{J}_{ij} = J_{ij}\hat{1}$. Using the Markov approximation, $t \to \infty$ in Eq. (152), we get

$$\{\hat{J}_{ij}\} = \frac{J_{ij}\hat{1}}{\hbar^2}\left(\pi\delta(\epsilon_i - \epsilon_j) - iP\frac{1}{\epsilon_i - \epsilon_j}\right),$$

(159)

where $P\frac{1}{x}$ is the principal part of x which we neglect. Under these approximations, it is possible to obtain the explicit form of the GF for the particle transfer statistics between the two leads. Substituting Eq. (159) into Eq. (151) and tracing over the system degrees of freedom [Eq. (109)], we obtain

$$\dot{G}(\lambda,t) = \frac{2\pi}{\hbar^2}\sum_{ij} |J_{ij}|^2\delta(\epsilon_i - \epsilon_j)[\{f_A(\epsilon_i) + f_B(\epsilon_j)\}$$

$$- f_A(\epsilon_i)f_B(\epsilon_j)\}(\cos\lambda - 1) + i\{f_B(\epsilon_i)$$

$$- f_A(\epsilon_j)\}\sin\lambda]G(\lambda,t).$$

(160)

The solution of this equation with the initial condition $G(\lambda,0)=1$ is

$$G(\lambda,t) = \exp\{t\mu_1(e^{i\lambda} - 1) + t\mu_2(e^{-i\lambda} - 1)\},$$

(161)

where

$$\mu_1 = \frac{2\pi}{\hbar^2}\sum_{ij} |J_{ij}|^2\delta(\epsilon_i - \epsilon_j)f_B(\epsilon_j)\{1 - f_A(\epsilon_i)\},$$

$$\mu_2 = \frac{2\pi}{\hbar^2}\sum_{ij} |J_{ij}|^2\delta(\epsilon_i - \epsilon_j)f_A(\epsilon_i)\{1 - f_B(\epsilon_j)\}.$$

(162)

We show in Appendix E that the probability distribution associated to the GF (161) is a bidirectional Poisson process: the difference of two Poisson processes with moments μ_1 and μ_2. Since the moments μ_1 and μ_2 satisfy $\mu_1 = e^{-\beta eV}\mu_2$, the GF has the symmetry (see Appendix E)

$$G(\lambda,t) = G(-\lambda - i\beta eV, t).$$

(163)

This immediately implies the FT

$$\frac{p(k,t)}{p(-k,t)} = e^{\beta eVk},$$

(164)

which is satisfied at all times (transient FT) unlike Eq. (141), which only hold at long times (steady-state FT). The entire distribution $p(k,t)$ is calculated in Appendix E.

V. MANY-BODY APPROACH TO PARTICLE COUNTING STATISTICS

In previous sections, we formulated the counting statistics using a kinetic equation approach. This simple and intuitive approach makes some key assumptions. It assumes an initially factorized density matrix of the interacting systems so that initial Fock space coherences are ignored. Moreover, the approach is valid only in the weak coupling limit and it is not obvious how to include many-body interactions such as electron-electron and electron-phonon. In this section, we present a formulation of counting statistics based on superoperator nonequilibrium Green's functions (SNGF) (Harbola and Mukamel, 2008) which allows us to relax these approximations.

A. Liouville space formulation of particle counting statistics

We consider particle transfer between two coupled systems A and B described by the Hamiltonian

$$\hat{H} = \hat{H}_A + \hat{H}_B + \hat{V}, \tag{165}$$

where the coupling is $\hat{V} = \hat{J} + \hat{J}^\dagger$. By choosing a suitable form for $\hat{J}$, we can recover the different models studied in Sec. IV.B. For the present discussion, we do not need to specify the explicit form of $\hat{J}$.

The measurement of the net number of particles transferred from A to B is performed using a two-point measurement as described in Sec. II. Here the measured observable is the number of particles in A. A measurement is done at time $t=0$. If right before this measurement the system is described by a density matrix $|\rho(0)\rangle\rangle$, the measurement destroys all Fock space coherences and immediately after the measurement the density matrix becomes diagonal in the Fock basis. A second measurement is performed at time t. A difference of the two measurements gives the net number of particles transferred between A and B. However, if the particle transfer between A and B occurs though an embedded system, the two-point measurement of particle numbers in A measures the net particle transfer between A and the embedded system rather than between A and B.

It will be convenient to work with superoperators in Liouville space (Fano, 1963; B.-Reuven, 1975; Mukamel, 1995; Harbola and Mukamel, 2006, 2008). These are defined in Appendix F. We denote Liouville space superoperators by a breve and Hilbert space operators by a hat: $\breve{H}_\alpha$, $\breve{V}_\alpha$, and $\breve{H}_{0\alpha}$, where $\alpha = L, R$, are the left and right superoperators corresponding to $\hat{H}$, $\hat{V}$ and $\hat{H}_0 = \hat{H}_A + \hat{H}_B$. The probability of the net transfer of k electrons from A to B during the time interval t is [see Eq. (G6)]

$$p(k,t) = \sum_n \langle\langle I | \breve{P}_{n-k} \breve{U}(t,0) \breve{P}_n | \rho(0)\rangle\rangle, \tag{166}$$

where $\breve{U}(t,0) = e^{-i\sqrt{2}\breve{H}_- t}$ is the time evolution operator in Liouville space and $\breve{P}_n$ is the projection operator associated with the measurement of n electrons in A. $|\rho(0)\rangle\rangle$ is the interacting density matrix when the counting starts and contains coherences in the number operator basis. It is constructed by switching on the interaction $\hat{V}$ from the infinite past, where the density matrix $|\rho(-\infty)\rangle\rangle$ is given by a direct product of the density matrices of systems A and B, to $t=0$,

$$|\rho(0)\rangle\rangle = \breve{U}_I(0,-\infty)|\rho(-\infty)\rangle\rangle, \tag{167}$$

where

$$\breve{U}_I(0,-\infty) = \exp_+\left\{ -\frac{i}{\hbar}\int_{-\infty}^0 d\tau \sqrt{2}\breve{V}_-(\tau) \right\}, \tag{168}$$

with $\sqrt{2}\breve{V}_-(\tau) = \breve{V}_L(\tau) - \breve{V}_R(\tau)$ [see Eq. (F8)] and

$$\breve{V}_\alpha(\tau) = \breve{U}_0^\dagger(\tau,0)\breve{V}_\alpha \breve{U}_0(\tau,0), \quad \alpha = L,R, \tag{169}$$

where

$$\breve{U}_0(\tau,0) = \theta(\tau)e^{-(i/\hbar)\sqrt{2}\breve{H}_{0-}\tau}. \tag{170}$$

The GF associated to $p(k,t)$ is defined by

$$G(\lambda,t) = \sum_k e^{i\lambda k} p(k,t). \tag{171}$$

Substituting Eq. (171) into Eq. (166), we obtain (see Appendix G)

$$G(\lambda,t) = \int_0^{2\pi} \frac{d\Lambda}{(2\pi)^3} G(\lambda,\Lambda,t), \tag{172}$$

with

$$\begin{aligned}
G(\lambda,\Lambda,t) = \langle\langle I | e^{-(i/\hbar)\sqrt{2}\breve{H}_{0-}t} \\
\times \exp_+\left\{ -(i/\hbar)\int_{-\infty}^t d\tau \sqrt{2}\breve{V}_-[\gamma(\tau),\tau] \right\} \\
\times |\rho(-\infty)\rangle\rangle,
\end{aligned} \tag{173}$$

where $\breve{V}_-(\gamma(t)) = \breve{V}_L(\gamma_L(t)) - \breve{V}_R(\gamma_R(t))$ with $\gamma_L(t) = \theta(t)(\Lambda + \lambda/2)$ and $\gamma_R(t) = \theta(t)(\Lambda - \lambda/2)$. The GF (173) includes the initial $t=0$ correlations between systems A and B in the density matrix. These correlations are built through the switching of the coupling $\hat{V}$ from $t=-\infty$ to $t=0$. In the absence of such correlations, the initial density matrix is diagonal in the number basis and $G(\lambda,t) = G(\lambda,\Lambda=0,t)$ [i.e., $\rho(0)$ commutes with $\hat{N}_A$]. Next we show how $G(\lambda,\Lambda,t)$ can be computed.

B. Electron counting statistics for direct tunneling between two systems

We next apply Eq. (173) to calculate the electron current statistics for the direct tunneling model of Sec. IV.B.4. The Hamiltonian is given by Eq. (165), where

$$\hat{J} = \sum_{i\in A, j\in B} J_{ij}\hat{c}_i^\dagger \hat{c}_j, \tag{174}$$

with $J_{ij}^* = J_{ji}$. The Hamiltonians $\hat{H}_A$ and $\hat{H}_B$ are general and can include many-body interactions. The exact form for $\hat{H}_A$ and $\hat{H}_B$ is not necessary in the present discussion. A noninteracting electron model, as studied in Sec. IV.B.4, will be considered next.

We now define the superoperators $\breve{J}$, $\breve{J}^\dagger$, and $\breve{N}$ corresponding to the operators $\hat{J}$, $\hat{J}^\dagger$, and the number operator N_A for the system A. These satisfy the commutation relations

$$[\breve{J}_L, \breve{N}_L] = -\breve{J}_L, \quad [\breve{J}_L^\dagger, \breve{N}_L] = \breve{J}_L^\dagger,$$

$$[\breve{J}_R, \breve{N}_R] = \breve{J}_R, \quad [\breve{J}_R^\dagger, \breve{N}_R] = -\breve{J}_R^\dagger. \tag{175}$$

Using these commutation relations in Eq. (G14), we can write

$$\check{V}_\alpha(\gamma_\alpha(t)) = \exp\{-i\gamma_\alpha(t)\}\check{J}_\alpha + \exp\{i\gamma_\alpha(t)\}\check{J}_\alpha^\dagger. \quad (176)$$

We define

$$\mathcal{Z}(\lambda,\Lambda,t) \equiv \ln G(\lambda,\Lambda,t). \quad (177)$$

Expanding the time-ordered exponential in Eq. (173) we can compute the GF and the cumulant GF perturbatively in the coupling J_{ab}. Since $\langle\langle I|\check{V}_-|\rho(-\infty)\rangle\rangle = 0$, to second order we obtain

$$\mathcal{Z}(\lambda,\Lambda,t) = -\frac{1}{2\hbar^2}\int_{-\infty}^t d\tau_1 \int_{-\infty}^t d\tau_2$$

$$\times \langle\langle I|\check{\mathcal{T}}\check{V}_-(\gamma(\tau_1),\tau_1)\check{V}_-(\gamma(\tau_2),\tau_2)|\rho(-\infty)\rangle\rangle. \quad (178)$$

Substituting Eq. (176) into Eq. (178) we obtain

$$\mathcal{Z}(\lambda,\Lambda,t) = \mathcal{Z}^{(0)}(\lambda,t) + \mathcal{Z}^{(1)}(\lambda,\Lambda,t), \quad (179)$$

where

$$\mathcal{Z}^{(1)}(\lambda,\Lambda,t) = 2(e^{i\lambda/2} - e^{-i\lambda/2})\mathrm{Re}\{e^{i\Lambda}W(t)\}, \quad (180)$$

and

$$\mathcal{Z}^{(0)}(\lambda,t) = (e^{-i\lambda} - 1)W_{BA}^{(0)}(t) + (e^{i\lambda} - 1)W_{AB}^{(0)}(t) \quad (181)$$

are the contributions coming from time evolution from $t=-\infty$ to $t=0$ and from $t=0$ to time t, respectively, and $W(t) \equiv W_{BA}^{(1)}(t) - W_{AB}^{(1)}(t)$ with

$$W_{AB}^{(0)}(t) = \frac{1}{\hbar^2}\int_0^t dt_1 \int_0^t dt_2 \langle\langle I|\check{J}_R(t_1)\check{J}_L^\dagger(t_2)|\rho(-\infty)\rangle\rangle,$$

$$W_{BA}^{(0)}(t) = \frac{1}{\hbar^2}\int_0^t dt_1 \int_0^t dt_2 \langle\langle I|\check{J}_L(t_1)\check{J}_R^\dagger(t_2)|\rho(-\infty)\rangle\rangle,$$

$$W_{AB}^{(1)}(t) = \frac{1}{\hbar^2}\int_{-\infty}^0 dt_1 \int_0^t dt_2 \langle\langle I|\check{J}_R(t_1)\check{J}_L^\dagger(t_2)|\rho(-\infty)\rangle\rangle,$$

$$W_{BA}^{(1)}(t) = \frac{1}{\hbar^2}\int_{-\infty}^0 dt_1 \int_0^t dt_2 \langle\langle I|\check{J}_L(t_1)\check{J}_R^\dagger(t_2)|\rho(-\infty)\rangle\rangle. \quad (182)$$

From Eq. (177) and (179) we obtain

$$G(\lambda,\Lambda,t) = e^{\mathcal{Z}^{(0)}(\lambda,t)}e^{\mathcal{Z}^{(1)}(\lambda,\Lambda,t)}. \quad (183)$$

Substituting this into Eq. (172) the GF is obtained as

$$G(\lambda,t) = G^{(0)}(\lambda,t)G^{(1)}(\lambda,t), \quad (184)$$

where

$$G^{(0)}(\lambda,t) = \exp\{\mathcal{Z}^{(0)}(\lambda,t)\}, \quad (185)$$

$$G^{(1)}(\lambda,t) = \int_0^{2\pi}\frac{d\Lambda}{2\pi}\exp\{\mathcal{Z}^{(1)}(\lambda,\Lambda,t)\}. \quad (186)$$

The cumulant GF is finally obtained as

$$\mathcal{Z}(\lambda,t) = \mathcal{Z}^{(0)}(\lambda,t) + \ln\int_0^{2\pi}\frac{d\Lambda}{2\pi}\exp\{\mathcal{Z}^{(1)}(\lambda,\Lambda,t)\}. \quad (187)$$

The second term on the rhs of Eq. (187) is the contribution due to the initial correlations that exist between systems A and B right before the first measurement. When these initial correlations are ignored, i.e., initial density matrix is a direct product of the density matrix of A and B (or equivalently $[\hat{N}_A, \hat{\rho}(0)] = 0$), $\mathcal{Z}^{(1)} = 0$.

1. Effects of initial correlations

Here we discuss the corrections to the electron statistics due to correlations between A and B in the initial density matrix. We show that these contributions do not affect the first moment (the current) but only higher moments.

Using Eq. (180) and expanding in λ, we find that

$$\exp\{\mathcal{Z}^{(1)}(\lambda,\Lambda,t)\} = \sum_{n=0}^\infty \frac{(2i)^n}{n!}\sin^n\left(\frac{\lambda}{2}\right)$$

$$\times[e^{-i\Lambda}W(t) + e^{i\Lambda}W^*(t)]^n$$

$$= \sum_{n(\geq k),k=0}^\infty \frac{(2i)^n}{k!(n-k)!}\sin^n\left(\frac{\lambda}{2}\right)$$

$$\times W^{n-k}(t)W^{k*}(t)e^{-i\Lambda(n-2k)}. \quad (188)$$

Integrating over Λ, Eq. (186) becomes

$$G^{(1)}(\lambda,t) = 1 + \sum_{n=1}^\infty \frac{(-4)^n}{(n!)^2}|W(t)|^{2n}\sin^{2n}\left(\frac{\lambda}{2}\right). \quad (189)$$

By differentiating Eq. (184) with respect to λ, we can factorize the moments in two parts, $\langle k^n\rangle_0$ which does not depend on the initial correlations and $\Delta^{(n)}$ which does,

$$\langle k^n(t)\rangle = \langle k^n(t)\rangle_0 + \Delta^{(n)}(t), \quad (190)$$

where

$$\langle k^n(t)\rangle_0 = (-i)^n\left.\frac{\partial^n}{\partial\lambda^n}G^{(0)}(\lambda,t)\right|_{\lambda=0},$$

$$\Delta^{(n)}(t) = \sum_{k=1}^n\sum_{l=1}^\infty\sum_{m=0}^{2l} i^{2l-m+k}(-1)^k \,{}^{2l}C_m\,{}^nC_k$$

$$\times\langle k^{n-k}(t)\rangle_0|W(t)|^{2l}. \quad (191)$$

${}^nC_k = n!/k!(n-k)!$ are the binomial coefficients.

We find that $\Delta^{(1)}(t) = 0$, i.e., initial correlations do not contribute to the first moment, which is the net current from $A \rightarrow B$. However, they do contribute to higher moments. The correction to the second moment is

$$\Delta^{(2)}(t) = -32|W(t)|^2. \quad (192)$$

We see that initial correlations always tend to decrease the second moment.

2. The thermodynamic limit

We consider now the limit where A and B can be assumed to have continuous spectra. We treat them as noninteracting electron leads and show that initial correlations do not contribute to the long-time statistics.

This corresponds to the model discussed in Sec. IV.B.4. In this limit, the rates W_{AB} and W_{BA} given in Eq. (182) can be calculated explicitly. The Hamiltonian for two systems ($X = A, B$) is

$$\hat{H}_X = \sum_{i \in X} \epsilon_i \hat{c}_i^\dagger \hat{c}_i. \tag{193}$$

Using the fact that the density matrix at $t = -\infty$ is a direct product $|\rho(-\infty)\rangle\rangle = |\rho_A^{eq}\rangle\rangle \otimes |\rho_B^{eq}\rangle\rangle$, we get

$$\langle\langle I|\check{J}_R(\tau_1)\check{J}_L^\dagger(\tau_2)|\rho(-\infty)\rangle\rangle = \sum_{ij} |J_{ij}|^2 f_A(\epsilon_i)[1 - f_B(\epsilon_j)]$$
$$\times e^{i\omega_{ij}(\tau_1 - \tau_2)}, \tag{194}$$

$$\langle\langle I|\check{J}_L(\tau_1)\check{J}_R^\dagger(\tau_2)|\rho(-\infty)\rangle\rangle = \sum_{ij} |J_{ij}|^2 f_B(\epsilon_j)[1 - f_A(\epsilon_i)]$$
$$\times e^{i\omega_{ij}(\tau_1 - \tau_2)}\}, \tag{195}$$

where $\omega_{ij} = \epsilon_i - \epsilon_j$ and $f_X(\epsilon) = [\exp\{\beta(\epsilon - \mu_X)\} + 1]^{-1}$ is the Fermi function for the system A (B) with μ_A and μ_B denoting the chemical potential of systems A and B.

Remembering that

$$\int_0^t d\tau_1 \int_0^t d\tau_2 e^{\pm i\omega_{ij}(\tau_1 - \tau_2)} = \left(\frac{\sin(\omega_{ij}t/2)}{\omega_{ij}/2}\right)^2 \overset{t \to \infty}{=} 2\pi\delta(\omega_{ij})t \tag{196}$$

and that

$$\int_{-\infty}^0 d\tau_1 \int_0^t d\tau_2 e^{\pm i\omega_{ij}(\tau_1 - \tau_2)} = -\frac{(e^{\mp i(\omega_{ij} \mp i\eta^+)t} - 1)}{(\eta^+ \mp i\omega_{ij})^2},$$

using Eq. (181) we find that

$$\mathcal{Z}^{(0)}(\lambda, t) = (e^{-i\lambda} - 1)\mu_2 t + (e^{i\lambda} - 1)\mu_1 t, \tag{197}$$

where μ_1 and μ_2 are given by Eq. (162). $G^{(0)}(\lambda)$ is therefore identical to the GF for a bidirectional Poisson process obtained in Eq. (161) within the GQME.

The rate $W(t)$ which appears in the expression for $\mathcal{Z}^{(1)}$ in Eq. (180) is given by

$$W(t) = \sum_{ij} |J_{ij}|^2 \left[[f_A(\omega_j) - f_B(\omega_i)] \frac{e^{-i(\omega_{ij} - i\eta^+)t} - 1}{(\omega_{ij} - i\eta^+)^2} \right]. \tag{198}$$

Taking the continuous limit of the leads' density of states, we find that for long times $W(t)$ becomes time independent (Shelankov and Rammer, 2003). Therefore

$$\mathcal{S}(\lambda) = \lim_{t \to \infty} \frac{1}{t} \mathcal{Z}(\lambda, t) = \lim_{t \to \infty} \frac{1}{t} \mathcal{Z}^{(0)}(\lambda, t), \tag{199}$$

which shows that the long-time statistics is not affected by the initial correlations between A and B.

C. Electron counting statistics for transport through a quantum junction

We next apply Eq. (172) to calculate the current statistics in the transport model of Sec. IV.B.1 where a quantum system (e.g., a molecule, chain of atoms, or quantum dots) is embedded between two much larger systems A and B. Note that here the two-point measurement of the particle number in A does not measure the net particle transfer between A and B as in Sec. V.A but rather the net particle transfer between A and the embedded system. The particle transfer statistics for this model was studied in Sec. IV.B.1 using the GQME approach. Here we express the transfer statistics in terms of the SNGF (Harbola and Mukamel, 2006, 2008) of the quantum system. By connecting this powerful many-body formalism with the two-point measurement, we can study more complicated models. The effect of eigenbasis coherences in the quantum system (which requires to go beyond the RWA in the GQME approach) and the effect of many-body interactions in the quantum system can be easily incorporated into the SNGF approach via the self-energy matrix. In presence of many-body interactions, the SNGF theory involves a self-consistent calculation for the Green's functions together with their self-energies. This goes beyond the weak coupling limit of the GQME. The simple form for the lead-system interactions (127) allows us to obtain analytical results for the corresponding self-energy and hence the GF. Electron-electron interactions will provide an extra (additive) self-energy matrix computed by Harbola and Mukamel (2006).

The Hamiltonian of the model is given by Eq. (126) and (127). The superoperators $\check{H}_{0\alpha}$ and $\check{V}_\alpha$ corresponding to $\hat{H}_0 = \hat{H}_A + \hat{H}_B + \hat{H}_S$ and $\hat{V}_{A(B)}$ can be obtained using Eqs. (F11) in Eqs. (126) and (127). We get

$$\check{H}_{0L} = \sum_{x \in A,B,S} \epsilon_x \check{c}_{xL}^\dagger \check{c}_{xL},$$

$$\check{H}_{0R} = \sum_{x \in A,B,S} \epsilon_x \check{c}_{xR} \check{c}_{xR}^\dagger, \tag{200}$$

and

$$\check{V}_\alpha = \check{J}_{A,\alpha} + \check{J}_{A,\alpha}^\dagger + \check{J}_{B,\alpha} + \check{J}_{B,\alpha}^\dagger, \tag{201}$$

where

$$\check{J}_{X,L} = \sum_{s,i \in X} J_{si} \check{c}_{iL}^\dagger \check{c}_{sL},$$

$$\check{J}_{X,R} = \sum_{s,i \in X} J_{si} \check{c}_{sR} \check{c}_{iR}^\dagger. \tag{202}$$

The superoperators $\check{J}_{X,L}$ and $\check{J}_{X,L}^\dagger$ satisfy the commutation relations (Harbola and Mukamel, 2008)

$$[\check{J}_{A,L}, \check{N}_L] = -\check{J}_{A,L}, \quad [\check{J}_{A,R}, \check{N}_R] = \check{J}_{A,R}, \tag{203}$$

$$[\check{J}^{\dagger}_{A,L}, \check{N}_L] = \check{J}^{\dagger}_{A,L}, \quad [\check{J}^{\dagger}_{A,R}, \check{N}_R] = -\check{J}^{\dagger}_{A,R}, \tag{204}$$

and $[\check{N}_\alpha, \check{J}_{B,\alpha}] = [\check{N}_\alpha, \check{J}^{\dagger}_{B,\alpha}] = 0$. Using these in Eq. (G14), we obtain

$$\hat{V}_\alpha(\gamma_\alpha(t), t) = \exp\{-i\gamma_\alpha(t)\}\check{J}_{A,\alpha}(t) + \exp\{i\gamma_\alpha(t)\}\check{J}^{\dagger}_{A,\alpha}(t)$$
$$+ \check{J}_{B,\alpha} + \check{J}^{\dagger}_{B,\alpha}, \tag{205}$$

where $\check{J}_{X,\alpha} = \check{J}_{X,\alpha}(\gamma_\alpha = 0)$. Note that in Eq. (205) the exponential factors are associated only with superoperators of the lead A since the measurement (projection) is done only on A.

We can now use Eq. (205) in Eq. (173) to compute the GF. $|\rho(-\infty)\rangle\rangle$ in Eq. (173) is given by the direct product of equilibrium density matrices of the system and the leads,

$$|\rho(-\infty)\rangle\rangle = |\rho_S\rangle\rangle \otimes |\rho_A\rangle\rangle \otimes |\rho_B\rangle\rangle, \tag{206}$$

$$|\rho_x\rangle\rangle = \frac{1}{\Xi_x}|e^{-\beta\hat{H}_x - \mu_x\hat{N}_x}\rangle\rangle, \tag{207}$$

where μ_x and Ξ_x are the chemical potential and the partition function for system x, respectively.

Using Grassmann variables and a path-integral formulation, the GF (172) can be expressed in terms of the Green's functions of the quantum system. In Appendix H, we present a derivation in terms of Liouville space superoperators. For a Hilbert space derivation see Kamenev (2002). Some useful properties of Grassmann variables used in the derivation are summarized in Appendix I. The final result for the GF, Eq. (173), is

$$G(\lambda, \Lambda, t) = e^{\mathcal{Z}(\lambda, \Lambda, t)}, \tag{208}$$

with

$$\mathcal{Z}(\lambda, \Lambda, t) = \int_{-\infty}^{t} d\tau \ln \text{Det}[g^{-1}(\tau = 0) - \Sigma(\tau, \tau, \gamma(\tau))], \tag{209}$$

where $g(t - t')$ and $\Sigma(t, t')$ are Green's function and self-energy (due to system-lead interaction) matrices in $\nu, \nu' = +, -$ representation. The Green's function matrix satisfies

$$\left(i\hbar\frac{\partial}{\partial t} - \epsilon_s\right)g^{\nu\nu'}_{ss'}(t - t') = \delta(t - t')\delta_{\nu\nu'}\delta_{ss'}, \tag{210}$$

and the self-energy matrix is

$$\Sigma^{\nu\nu'}_{ss'}(t, t', \gamma(t), \gamma(t')) = \sum_X \sum_{ii' \in X} J^{\nu\nu_1}_{si}(\gamma(t))g^{\nu_1\nu_2}_{ii'}(t - t')$$
$$\times J^{\nu_2\nu'}_{i's'}(\gamma(t')), \tag{211}$$

where

$$J^{++}_{is}(\gamma) = J^{--}_{is}(\gamma) = J_{is}(e^{i\gamma_L} + e^{i\gamma_R})/2,$$

$$J^{+-}_{is}(\gamma) = J^{-+}_{is}(\gamma) = J_{is}(e^{i\gamma_L} - e^{i\gamma_R})/2 \tag{212}$$

for $i \in A$ and

$$J^{++}_{is}(\gamma) = J^{--}_{is}(\gamma) = J_{is},$$

$$J^{+-}_{is}(\gamma) = J^{-+}_{is}(\gamma) = 0 \tag{213}$$

for $i \in B$. One important point to note is that while $g^{+-}(t, t')$ (zeroth-order system Green's function without interactions with leads) is causal and $g^{-+}(t, t') = 0$ (Harbola and Mukamel, 2006, 2008), this is no longer the case for Σ^{+-} and Σ^{-+} which depend on γ. This is due to the fact that when $\gamma_L \neq \gamma_R$, the ket and the bra evolve with a different Hamiltonian. The cumulant GF is then given by

$$\mathcal{Z}(\lambda, t) = \ln \int_0^{2\pi} \frac{d\Lambda}{2\pi} G(\lambda, \Lambda, t). \tag{214}$$

Equation (214) with Eqs. (208) and (209) give the statistics for the net particle transfer between lead A and the quantum system embedded between A and B.

1. Long-time statistics

At steady state the two-time functions, such as $g(t, t')$ and $\Sigma(t, t')$, depend only on the difference of their time arguments. We factorize the time integration in Eq. (209) in two regions, one from $-\infty$ to 0 and the other from 0 to t. Since $\gamma(t) = 0$ for negative times, Eq. (G15), we obtain

$$\mathcal{Z}(\lambda, \Lambda, t) = G_0 + \int_0^t d\tau \ln \text{Det}[g^{-1}(\tau = 0)$$
$$- \Sigma(\tau, \tau, \gamma(\tau))]. \tag{215}$$

The term G_0, which is independent on time and γ, comes from integration $t = -\infty$ to $t = 0$ and contains all initial correlations between the system and the leads. Substituting for the self-energy (211), we note that since the matrix elements $J^{\nu\nu'}_{is}$ and $J^{\nu\nu'}_{si}$ appear at the same time the Λ dependence drops out. We can recast Eq. (209) for long times as

$$\mathcal{Z}(\lambda, t) = t\int \frac{d\omega}{2\pi} \ln \text{Det}[g^{-1}(\omega) - \Sigma(\omega, \lambda)] + G_0. \tag{216}$$

At long times the first term in Eq. (216) dominates, and the current GF is given solely by the first term in Eq. (216):

$$S(\lambda) = \lim_{t \to \infty} \frac{1}{t}\mathcal{Z}(\lambda, t) = \int \frac{d\omega}{2\pi} \ln \text{Det}[g^{-1}(\omega) - \Sigma(\omega, \lambda)]$$
$$\equiv \int \frac{d\omega}{2\pi} \ln \text{Det}[\chi^{-1}(\omega)]. \tag{217}$$

Thus, as in Sec. V.B.2, we conclude that contributions coming from the initial correlations between the system and the leads do not effect the long-time statistics.

We now compute the self-energy in the frequency domain. Since the leads are made of noninteracting electrons, their zeroth-order Green's functions in the frequency domain are

$$g_{ii'}^{--}(\omega) = \frac{\delta_{ii'}}{\hbar\omega - \epsilon_i + i\eta}, \quad g_{ii'}^{++}(\omega) = [g^{--}]_{ii'}^{\dagger}(\omega),$$

$$g_{ii'}^{-+}(\omega) = -2\pi i \delta_{ii'}(2f_i(\omega) - 1)\delta(\hbar\omega - \epsilon_i). \tag{218}$$

Substituting this into Eq. (211), the self-energy matrix in the wide-band approximation is obtained as

$$\Sigma_{ss'}^{++}(\omega,\lambda) = \frac{i}{2}\Gamma_{ss'}^B + \frac{i}{2}\Gamma_{ss'}^A[e^{i\lambda}(1 - f_A(\omega)) + e^{-i\lambda}f_A(\omega)], \tag{219}$$

$$\Sigma_{ss'}^{--}(\omega,\lambda) = -\frac{i}{2}\Gamma_{ss'}^B - \frac{i}{2}\Gamma_{ss'}^A[e^{i\lambda}(1 - f_A(\omega)) + e^{-i\lambda}f_A(\omega)], \tag{220}$$

$$\Sigma_{ss'}^{+-}(\omega,\lambda) = -\frac{i}{2}\Gamma_{ss'}^A[(e^{i\lambda} - 1)\{1 - f_A(\omega) \\ - (e^{-i\lambda} - 1)f_A(\omega)\}], \tag{221}$$

$$\Sigma_{ss'}^{-+}(\omega,\lambda) = -i\Gamma_{ss'}^B(2f_B(\omega) - 1) + \frac{i}{2}\Gamma_{ss'}^A \\ \times[(e^{i\lambda} + 1)\{1 - f_A(\omega)\} - (e^{-i\lambda} + 1)f_A(\omega)], \tag{222}$$

where $\Gamma_{ss'}^X = 2\pi\Sigma_{i \in X}J_{is}J_{s'i}\delta(\omega - \epsilon_i)$.

Note that when $\lambda = 0$, $\Sigma^{+-} = 0$ as it should be (causality) (Harbola and Mukamel, 2006), and Σ^{--}, Σ^{++}, and Σ^{-+} reduce to usual retarded, advanced, and correlation (Keldysh) self-energies, respectively,

$$\Sigma_{ss'}^{--}(\omega) = -\frac{i}{2}\Gamma_{ss'}, \quad \Sigma_{ss'}^{++}(\omega) = \frac{i}{2}\Gamma_{ss'},$$

$$\Sigma_{ss'}^{-+}(\omega) = i\Gamma_{ss'} - 2[\Gamma_{ss'}^A f_A(\omega) + \Gamma_{ss'}^B f_B(\omega)], \tag{223}$$

where $\Gamma = \Gamma^A + \Gamma^B$.

The retarded Green's function for the molecule is then given by

$$R_{ss'}^{--}(\omega) = \left[(\hbar\omega - \epsilon)\hat{1} - i\frac{\Gamma}{2}\right]_{ss'}^{-1}, \tag{224}$$

where $\hat{1}$ is the identity matrix and $R^{++} = [R^{--}]^{\dagger}$ is the advanced Green's function.

Finally, we transform the self-energy matrix from the $+,-$ (Σ) to the L, R ($\tilde{\Sigma}$) representation. This can be achieved by the matrix transformation $\tilde{\Sigma} = Q^{-1}\Sigma Q$ (Harbola and Mukamel, 2006), where

$$Q = \frac{1}{\sqrt{2}}\begin{pmatrix} -1 & -1 \\ 1 & -1 \end{pmatrix}. \tag{225}$$

This gives the matrix $\tilde{\Sigma}_{\alpha\beta}(\omega,\lambda)$ with elements

$$\tilde{\Sigma}_{RR}^{ss'}(\omega) = \frac{i}{2}\Gamma_{ss'} - i[\Gamma_{ss'}^A f_A(\omega) + \Gamma_{ss'}^B f_B(\omega)], \tag{226}$$

$$\tilde{\Sigma}_{LL}^{ss'}(\omega) = -\frac{i}{2}\Gamma_{ss'} + i[\Gamma_{ss'}^A f_A(\omega) + \Gamma_{ss'}^B f_B(\omega)], \tag{227}$$

$$\tilde{\Sigma}_{LR}^{ss'}(\omega,\lambda) = i\Gamma_{ss'}^B f_B(\omega) + i\Gamma_{ss'}^A f_A(\omega)e^{-i\lambda}, \tag{228}$$

$$\tilde{\Sigma}_{RL}^{ss'}(\omega,\lambda) = -i\Gamma_{ss'}^B(f_B(\omega) - 1) - i\Gamma_{ss'}^A(f_A(\omega) - 1)e^{i\lambda}, \tag{229}$$

where the λ dependence occurs only in $\tilde{\Sigma}_{LR}$ and $\tilde{\Sigma}_{RL}$.

Equation (217) together with Eqs. (218)–(222) gives the long-time current statistics within the two-point measurement approach. This approach contains the full information about the coherences in the system eigenbasis through the self-energy matrix Σ and can therefore be used to study effects of coherences on the current statistics.

2. Recovering the generalized quantum master equation

The GF (217) is different from the GF obtained using the GQME approach (139). We now show in what limit Eq. (217) reduces to Eq. (139).

Assuming that the Σ matrix is diagonal, $\Sigma_{ss'} = \delta_{ss'}\Sigma_{ss}$, the determinant $|\chi^{-1}| = |g^{-1} - \Sigma|$ in Eq. (217) factorizes into a product of determinants corresponding to each orbital s, $|\chi^{-1}| = \Pi_s|\chi_{ss}^{-1}|$, and $\mathcal{Z}(\lambda,t) = \Sigma_s\mathcal{Z}_s(\lambda,t)$ becomes the sum of GF for individual orbitals. We note that the assumption of a diagonal Σ matrix amounts to ignoring the coherences in the quantum system eigenbasis and is therefore the analog of the RWA in the GQME approach. In the following we compute $\mathcal{Z}_s$. For clarity, we omit the orbital index s in the self-energies. Since from Eq. (226)–(229) $\tilde{\Sigma}_{LL} = [\tilde{\Sigma}_{RR}]^*$, we can write

$$|\chi_{ss}^{-1}| = (\omega - \epsilon_s)^2 - |\tilde{\Sigma}_{LL}|^2 - \tilde{\Sigma}_{LR}\tilde{\Sigma}_{RL}. \tag{230}$$

Substituting this into Eq. (217), we get for the long-time cumulant GF

$$S_s(\lambda) = \int \frac{d\omega}{2\pi} \ln[(\omega - \epsilon_s)^2 + |\tilde{\Sigma}_{LL}|^2 - \tilde{\Sigma}_{LR}\tilde{\Sigma}_{RL}]. \tag{231}$$

In order to compute the frequency integral we first obtain the λ-dependent current by taking the derivative with respect to λ,

$$I_s(\lambda) = -\int \frac{d\omega}{2\pi} \frac{\partial_\lambda(\tilde{\Sigma}_{LR}\tilde{\Sigma}_{RL})}{(\omega - \epsilon_s)^2 + |\tilde{\Sigma}_{LL}|^2 - \tilde{\Sigma}_{LR}\tilde{\Sigma}_{RL}}. \tag{232}$$

Using Eqs. (226)–(229), we get

$$I_s(\lambda) = i\Gamma^A\Gamma^B \int \frac{d\omega}{2\pi} \frac{f_B(\omega)[1-f_A(\omega)]e^{i\lambda} - f_A(\omega)[1-f_B(\omega)]e^{-i\lambda}}{(\omega-\epsilon_s)^2 + M(\lambda,\omega)}, \tag{233}$$

where

$$M(\lambda,\omega) = \tfrac{1}{4}\Gamma^2 + \Gamma^A\Gamma^B\{f_B(\omega)[1-f_A(\omega)](e^{i\lambda}-1)$$
$$+ f_A(\omega)[1-f_B(\omega)](e^{-i\lambda}-1)\}. \tag{234}$$

Assuming that the couplings with the leads are weak $k_B T \gg \Gamma^X$ so that resulting broadening is small compared to ϵ_s, the contribution to the integral comes mainly from the center of the Lorentzian. This allows us to replace $\omega = \epsilon_s$ in the Fermi functions inside the integrand. We therefore need to consider the poles $\omega = \epsilon_s \pm i\sqrt{M(\lambda,\epsilon_s)}$. Computing the residues at the poles, we obtain

$$I_s(\lambda) = \frac{-i\Gamma^A\Gamma^B}{2\sqrt{M(\lambda,\epsilon_s)}}\{f_B(\epsilon_s)[1-f_A(\epsilon_s)]e^{i\lambda}$$
$$- f_A(\epsilon_s)[1-f_B(\epsilon_s)]e^{-i\lambda}\}. \tag{235}$$

Since $Z_s(\lambda) = \int_0^\lambda I(\lambda')$, we finally obtain

$$\mathcal{S}_s(\lambda) = -\frac{\Gamma}{2} + \sqrt{M(\lambda,\epsilon_s)}, \tag{236}$$

which coincides with the GF obtained from the GQME, Eq. (139).

3. The Levitov-Lesovik formula

Equation (217) with Eqs. (218)–(222) is the most general formula for the transport statistics at long times for a system of noninteracting electrons. It includes the effects of coherences between the various tunneling channels (system orbitals) available to an electron tunneling between the two leads. This is due to the nondiagonal structure of the self-energy in the Hilbert space of the system, Eqs. (219)–(222). Here we recover the Levitov-Lesovik formula (Levitov and Lesovik, 1993; Levitov *et al.*, 1996) for the counting statistics and again assume diagonal self-energies. As discussed in Sec. V.C.2, the cumulant GF in this case is simply the product of the GFs for each orbital. Thus all orbitals contribute independently to the electron transport.

Using self-energy expressions (226)–(229), the GF (231) can be expressed as

$$\mathcal{S}_s(\lambda) = \int \frac{d\omega}{2\pi} \ln\left[(\omega-\epsilon_s)^2 + \frac{\Gamma^2}{4} \right.$$
$$+ \Gamma^A\Gamma^B\{f_B(\omega)[f_A(\omega)-1](1-e^{i\lambda})$$
$$\left. + f_A(\omega)[f_B(\omega)-1](1-e^{-i\lambda})\} \right]. \tag{237}$$

Using Eq. (224), we can write for orbital s

$$|R_{ss}^{--}(\omega)|^{-2} = (\omega-\epsilon_s)^2 + \frac{\Gamma^2}{4}. \tag{238}$$

Substituting Eq. (238) into Eq. (237), we obtain

$$\mathcal{S}_s(\lambda) = -2\int \frac{d\omega}{2\pi} \ln|R_{ss}^{--}(\omega)|$$
$$+ \int \frac{d\omega}{2\pi} \ln(1 + \mathcal{T}(\omega)\{f_B(\omega)[f_A(\omega)-1](1-e^{i\lambda})$$
$$+ f_A(\omega)[f_B(\omega)-1](1-e^{-i\lambda})\}), \tag{239}$$

where $\mathcal{T}(\omega) = \Gamma^A\Gamma^B|R_{ss}^{--}(\omega)|^2$ is the transmission coefficient for the tunneling region. The first term on the right-hand side of Eq. (239) can be ignored since it does not contribute to the average current or its fluctuations (independent on λ). Therefore

$$\mathcal{S}_s(\lambda) = \int \frac{d\omega}{2\pi} \ln(1 + \mathcal{T}(\omega)\{f_B(\omega)[f_A(\omega)-1](1-e^{i\lambda})$$
$$+ f_A(\omega)[f_B(\omega)-1](1-e^{-i\lambda})\}) \tag{240}$$

which is the Levitov-Lesovik formula (Levitov and Lesovik, 1993; Levitov *et al.*, 1996; Levitov and Reznikov, 2004). This formula has been recently generalized to a multiterminal model for a noninteracting tight-binding model (Schönhammer, 2007). Equation (240) is valid to all orders of the coupling. The only approximation required to obtain the Levitov-Lesovik expression (240) is to ignore the coherence effects between different orbitals in the tunneling junction. Note that if $T(\omega)$ is small, we can expand the logarithm in Eq. (240). This is equivalent to making a perturbation in the coupling $\hat{V}$. The leading order in the expansion gives Eq. (197) with Eq. (162).

Since $f_A(\omega)[1-f_B(\omega)] = e^{\beta eV} f_B(\omega)[1-f_A(\omega)]$, it is straightforward to see that the GF (240) satisfy $\mathcal{S}(\lambda) = \mathcal{S}(-\lambda - i\beta eV)$ and the FT (141) follows.

Taking the derivative with respect to λ of the GF (240) at $\lambda = 0$, the average current is

$$I = \int \frac{d\omega}{2\pi} \mathcal{T}(\omega)[f_B(\omega) - f_A(\omega)], \tag{241}$$

which is the Landauer-Buttiker expression for the average current through a tunneling junction with transmission coefficient $T(\omega)$ (Blanter and Büttiker, 2000).

VI. NONLINEAR COEFFICIENTS

As we have seen, the FT implies a specific symmetry of the GF which depends on the nonequilibrium constraints imposed on the system. For weak constraints, i.e., close to equilibrium, this symmetry can be used to

derive fluctuation-dissipation relation as well as Onsager symmetry relations (Gallavotti, 1996a, 1996b; Lebowitz and Spohn, 1999; Andrieus and Gaspard, 2004). A systematic expansion of the GF in the nonequilibrium constrains allows one to derive similar fundamental relations further away from equilibrium. This has been done for stochastic systems (Andrieux and Gaspard, 2007a), for counting statistics (Tobiska and Nazarov, 2005; Förster and Büttiker, 2008; Saito and Utsumi, 2008; Utsumi and Saito, 2009), and for the work FT (Andrieux and Gaspard, 2008). FTs therefore provide a systematic approach for studying generalized fluctuation-dissipation relations such as those considered by Chou *et al.* (1985), Stratonovich (1992), and Wang and Heinz (2002).

A. Single nonequilibrium constraint

We assume that a FT of the form $p(k, \mathcal{A}) = e^{\mathcal{A}k} p(-k, \mathcal{A})$ holds in a system maintained in a nonequilibrium steady state by a single nonequilibrium constraint $\mathcal{A}$, where $p(k, \mathcal{A})$ is the probability distribution that a net amount of energy or matter k crossed the system during a given time. The cumulant GF defined as

$$\mathcal{Z}(\lambda, \mathcal{A}) = \ln\left(\sum_k e^{i\lambda k} p(k, \mathcal{A})\right), \tag{242}$$

then possesses the symmetry

$$\mathcal{Z}(\lambda, \mathcal{A}) = \mathcal{Z}(i\mathcal{A} - \lambda, \mathcal{A}). \tag{243}$$

Taking the derivative with respect to $\mathcal{A}$ of both sides and using Eq. (242), we find that in the $\mathcal{A} \to 0$ limit

$$\frac{\partial}{\partial \mathcal{A}}[\mathcal{Z}(\lambda, 0) - \mathcal{Z}(-\lambda, 0)] = -i\frac{\partial}{\partial \lambda}\mathcal{Z}(\lambda, 0). \tag{244}$$

The cumulant GF is expressed in terms of cumulants as

$$\mathcal{Z}(\lambda, \mathcal{A}) = \sum_{m=1}^{\infty} \frac{(i\lambda)^m}{m!} K_m(\mathcal{A}). \tag{245}$$

Using Eq. (245) in Eq. (244), we find at each order in λ that

$$[1 - (-1)^m]\frac{\partial}{\partial \mathcal{A}}K_m(0) = K_{m+1}(0). \tag{246}$$

Equation (246) implies that at equilibrium odd cumulants are zero and event cumulants are related to the derivative with respect to the nonequilibrium constraints of the nonequilibrium odd cumulants when approaching equilibrium,

$$K_{2m-1}(0) = 0, \tag{247}$$

$$K_{2m}(0) = 2\frac{\partial}{\partial \mathcal{A}}K_{2m-1}(0). \tag{248}$$

Below we show that this leads to the well-known fluctuation-dissipation relations.

We next consider the second derivative with respect to $\mathcal{A}$ of both sides of Eq. (243). Using Eqs. (243) and (246) and after some algebra, we find in the $\mathcal{A} \to 0$ limit that

$$\frac{\partial^2}{\partial \mathcal{A}^2}[\mathcal{Z}(\lambda, 0) - \mathcal{Z}(-\lambda, 0)] = -i\frac{\partial^2}{\partial \lambda \partial \mathcal{A}}[\mathcal{Z}(\lambda, 0) + \mathcal{Z}(-\lambda, 0)]. \tag{249}$$

Using Eq. (245), we find at each order in λ that

$$[1 - (-1)^m]\frac{\partial^2}{\partial \mathcal{A}^2}K_m(0) = [1 + (-1)^{m+1}]\frac{\partial}{\partial \mathcal{A}}K_{m+1}(0). \tag{250}$$

This relation is only useful for odd m and implies

$$\frac{\partial^2}{\partial \mathcal{A}^2}K_{2m-1}(0) = \frac{\partial}{\partial \mathcal{A}}K_{2m}(0). \tag{251}$$

This procedure can be continued for higher derivative of $\mathcal{Z}(i\mathcal{A} - \lambda, \mathcal{A})$ with respect to $\mathcal{A}$.

We can always expand the average process in term of the nonequilibrium constrain as

$$K_1(\mathcal{A}) = K_1(0) + L^{(1)}\mathcal{A} + L^{(2)}\mathcal{A}^2 + \mathcal{O}(\mathcal{A}^3). \tag{252}$$

$L^{(1)}$ is the Onsager coefficient. Using Eqs. (247), (248), and (251) for $m=1$, we find that $K_1(0) = 0$ and

$$L^{(1)} = \frac{\partial}{\partial \mathcal{A}}K_1(0) = \frac{K_2(0)}{2}, \tag{253}$$

$$L^{(2)} = \frac{1}{2}\frac{\partial^2}{\partial \mathcal{A}^2}K_1(0) = \frac{1}{2}\frac{\partial}{\partial \mathcal{A}}K_2(0). \tag{254}$$

Equation (253) is a fluctuation-dissipation relation. As an illustration, we consider a biased quantum junction such as in Sec. IV.B.1. k represents the number of electron crossing the junction and the nonequilibrium constraint is given by $\mathcal{A} = \beta eV$, where V is the potential bias across the junction. In this case, close to equilibrium $\langle I \rangle = \beta e^2 V L^{(1)}$ is the average electrical current through the junction and $e^2 K_2(0)$ is the Fourier transform of the equilibrium current correlation functions at zero frequency. Equation (253) indicates that the resistance of the junction, which characterize the dissipation, is related to the current fluctuation at equilibrium by $R = \partial_V \langle I \rangle = \beta e^2 L^{(1)} = \beta e^2 K_2(0)/2$.

B. Multiple nonequilibrium constraints

When multiple nonequilibrium constrains are applied to the system, the FT can be used to find important symmetries of the response coefficients (Andrieux and Gaspard, 2004, 2007a). In case of N nonequilibrium constraints, the cumulant GF is given by

$$\mathcal{Z}(\{\lambda_\gamma\}, \{\mathcal{A}_\gamma\}) = \ln\left(\sum_{\{k_\gamma\}} e^{i\bar{\lambda}\cdot\bar{k}} p(\{k_\gamma\}, \{\mathcal{A}_\gamma\})\right), \tag{255}$$

where $\bar{\lambda}\cdot\bar{k} = \sum_{\gamma=1}^{N}k_\gamma\lambda_\gamma$. We assume that it satisfies the FT symmetry

$$\mathcal{Z}(\{\lambda_\gamma\},\{\mathcal{A}_\gamma\}) = \mathcal{Z}(\{i\mathcal{A}_\gamma - \lambda_\gamma\},\{\mathcal{A}_\gamma\}). \qquad (256)$$

Proceeding as in Sec. VI.A, we find that Eq. (244) generalizes to

$$\frac{\partial}{\partial\mathcal{A}_\beta}[\mathcal{Z}(\{\lambda_\gamma\},\{0\}) - \mathcal{Z}(\{-\lambda_\gamma\},\{0\})] = -i\frac{\partial}{\partial\lambda_\beta}\mathcal{Z}(\{\lambda_\gamma\},\{0\}). \qquad (257)$$

The cumulant GF can be expressed as

$$\mathcal{Z}(\{\lambda_\gamma\},\{\mathcal{A}_\gamma\}) = \sum_{\{m_\gamma\}=1}^{\infty}\left(\prod_{\gamma=1}^{N}\frac{(i\lambda_\gamma)^{m_\gamma}}{m_\gamma!}\right)K_{\{m_\gamma\}}(\{\mathcal{A}_\gamma\}), \quad (258)$$

where the cumulants are given by

$$K_{\{m_\gamma\}}(\{\mathcal{A}_\gamma\}) = \left(\prod_{j=1}^{\gamma}(-i)^{m_j}\frac{\partial^{m_j}}{\partial\lambda_j^{m_j}}\right)\mathcal{Z}(\{0\},\{\mathcal{A}_\gamma\}). \qquad (259)$$

The generalization of Eq. (246) is found using Eq. (258) in Eq. (257) so that at a given order in the λ's

$$\left(1 - \prod_{\gamma=1}^{N}(-1)^{m_\gamma}\right)\frac{\partial K_{\{m_\gamma\}}(\{0\})}{\partial\mathcal{A}_\beta} = K_{\{m_\gamma+\delta_{\gamma\beta}\}}(\{0\}). \qquad (260)$$

If we choose $\{m_\gamma\} = \{\delta_{\gamma\alpha}\}$, we obtain

$$\frac{\partial K_{\{\delta_{\gamma\alpha}\}}(\{0\})}{\partial\mathcal{A}_\beta} = K_{\{\delta_{\gamma\alpha}+\delta_{\gamma\beta}\}}(\{0\}). \qquad (261)$$

Close to equilibrium, the average processes can be expanded in term of the nonequilibrium constraints as

$$K_{\{\delta_{\gamma\alpha}\}}(\{\mathcal{A}_\gamma\}) = \sum_\gamma L_{\alpha\gamma}\mathcal{A}_\gamma + \sum_{\gamma,\gamma'} L_{\alpha\gamma\gamma'}\mathcal{A}_\gamma\mathcal{A}_{\gamma'} + \cdots. \qquad (262)$$

Since the Onsager linear response coefficients are given by

$$L_{\alpha\beta} = \frac{\partial K_{\{\delta_{\gamma\alpha}\}}(\{0\})}{\partial\mathcal{A}_\beta}, \qquad (263)$$

using Eq. (261) we find the Onsager reciprocity relation

$$L_{\alpha\beta} = L_{\beta\alpha}. \qquad (264)$$

The generalization of Eq. (250) to multiple nonequilibrium constraints is given by

$$\frac{\partial^2}{\partial\mathcal{A}_\alpha\partial\mathcal{A}_\beta}[\mathcal{Z}(\{\lambda_\gamma\},\{0\}) - \mathcal{Z}(\{-\lambda_\gamma\},\{0\})]$$
$$= -i\left[\frac{\partial^2}{\partial\lambda_\alpha\partial\mathcal{A}_\beta}\mathcal{Z}(\{\lambda_\gamma\},\{0\})\right.$$
$$\left. + \frac{\partial^2}{\partial\lambda_\beta\partial\mathcal{A}_\alpha}\mathcal{Z}(\{-\lambda_\gamma\},\{0\})\right]. \qquad (265)$$

This implies that

$$\left(1 - \prod_{\gamma=1}^{N}(-1)^{m_\gamma}\right)\frac{\partial^2 K_{\{m_\gamma\}}(\{0\})}{\partial\mathcal{A}_\alpha\partial\mathcal{A}_\beta}$$
$$= -i\left[\frac{\partial K_{\{m_\gamma+\delta_{\gamma\beta}\}}(\{0\})}{\partial\mathcal{A}_\alpha}\right.$$
$$\left. + \left(1 - \prod_{\gamma=1}^{N}(-1)^{m_\gamma+\delta_{\gamma\beta}}\right)\frac{\partial K_{\{m_\gamma+\delta_{\gamma\alpha}\}}(\{0\})}{\partial\mathcal{A}_\beta}\right]. \qquad (266)$$

For $\{m_\gamma\} = \{\delta_{\gamma\theta}\}$, we obtain

$$L_{\theta\alpha\beta} = \frac{\partial^2 K_{\{\delta_{\gamma\theta}\}}(\{0\})}{\partial\mathcal{A}_\alpha\partial\mathcal{A}_\beta} - i\left(\frac{\partial K_{\{\delta_{\gamma\theta}+\delta_{\gamma\beta}\}}(\{0\})}{\partial\mathcal{A}_\alpha}\right.$$
$$\left. + \frac{\partial K_{\{\delta_{\gamma\theta}+\delta_{\gamma\alpha}\}}(\{0\})}{\partial\mathcal{A}_\beta}\right), \qquad (267)$$

which implies the expected symmetry $L_{\theta\alpha\beta} = L_{\theta\beta\alpha}$.

VII. CONCLUSIONS AND PERSPECTIVES

The approach to quantum statistics adopted in this review is based on a two-point projective measurement. This, together with considerations about the symmetry between the forward and the time-reversed quantum dynamics, allow us to recover from a simple and unified perspective all previously derived fluctuation theorems (FTs) for quantum systems (transient as well as steady-state FTs). This was the object of Secs. II and III.

A generalized quantum master equation (GQME) is presented in Sec. IV for a quantum system weakly coupled to reservoirs. The equation describes the evolution of the generating function (GF) associated with the system density matrix conditional to the outcome from a two-point measurement (of energy or number of particles) on the reservoir. When summed over all possible outcomes, the quantum master equation (QME) for the system reduced density matrix is recovered. This formalism has been applied to various model systems and used to directly demonstrate the validity of steady-state FTs.

The GQME formalism circumvents the unraveling of the QME, used to calculate the quantum statistics of particles or energy, and originally developed in quantum optics (Wiseman and Milburn, 1993a, 1993b; Plenio and Knight, 1998; Brun, 2000, 2002; Gardiner and Zoller, 2000; Breuer and Petruccione, 2002). Since the unraveling of a QME is not unique, a continuous time measurement on the reservoir is assumed in order to connect the resulting quantum trajectories to measurable quantities. This procedure is only possible for Markovian QME which preserve complete positivity [in the rotating wave approximation (RWA)]. In this regime, the GQME formalism predicts the same statistics as the unraveling formalism. This equivalence between the two types of measurements in the weak coupling limit was first found by De Roeck (2007) and Derezinski et al. (2008) and results from the fact that the reservoirs are assumed to always remain described by the same canonical or grand canonical equilibrium density matrix (Esposito and Gas-

pard, 2003, 2007) and are therefore not affected by the measurement. The net number of particles or the net amount of energy transferred during a given time interval is then the same if the reservoir is continuously monitored or only measured twice at the beginning and at the end. The unraveling of non-Markovian QME has been an active field of research this last decade (Strunz, 1996; Diósi *et al.*, 1998; Gaspard and Nagaoka, 1999a; Strunz *et al.*, 1999), but the connection between the resulting quantum trajectories and measurable quantities is not straightforward (Gambetta and Wiseman, 2002, 2003; Warszawski and Wiseman, 2003a, 2003b; Breuer, 2004; Diósi, 2008). In the GQME formalism, the connection to measurable quantities in the non-Markovian regime is unambiguous. Exploring non-Markovian effects on the particle or energy statistics could be an important future application.

In order to go beyond the approximations used in the GQME formalism (i.e., initially factorized density matrix, weak coupling), we presented an alternative approach based on superoperator nonequilibrium Green's functions (SNGF) in Sec. V. This Liouville space formalism provides a powerful tool for calculating the particle statistics in many-body quantum systems. Using this formalism, we showed that initial coherences in the basis of the measured observable do not affect the steady-state counting statistics and the FT. This is to be expected since at steady state, the long-time limit destroys the information about the initial condition. Using a noninteracting electron model we showed for both direct and indirect (transport) tunneling between two reservoirs. However, for transient FTs such as the Crooks relation, the assumption that the system density matrix is initially diagonal in the basis of the measured observable seems unavoidable for the FT to be satisfied. We applied the SNGF formalism to compute the counting statistics in some simple models and discussed the limit in which the statistics predicted by the QME is recovered. The Levitov-Lesovik formula for electron tunneling between two reservoirs, which goes beyond the weak coupling limit of the QME, was also recovered. We discussed the approximations required to recover the Levitov-Lesovik expression from a more general result expressed in terms of the SNGF for the tunneling region. In particular, we showed that when several energy channels are available to tunneling electrons, the Levitov-Lesovik approach does not capture the quantum coherence between different channels. This amounts to ignoring the off-diagonal elements of the self-energy in the eigenbasis of the system.

Transient FTs, valid for arbitrary time, were presented in Sec. III.B. The work FT derived for an isolated driven system in Sec. III.B.1 is always valid since, besides an initial canonical density matrix, no assumptions have been made. The work FT for open driven system derived in Sec. III.B.2 assumes an initially factorized canonical density matrix between the system and the reservoir and a definition of work which is only consistent for a weak system-reservoir interaction. The transient FT for direct heat and matter transfer between two finite

systems and derived in Sec. III.B.3 assumes that the systems are each initially at equilibrium and weakly interacting. The steady-state FTs, only valid for long time, presented in Sec. III.C and derived more systematically in Sec. IV assume a weak system-reservoir coupling and the RWA. However, the FT has been recently shown numerically to hold for QME without RWA (Welack *et al.*, 2008) and the Levitov-Lesovik formula presented in Sec. V.C.3 is obtained nonperturbatively and satisfies the FT. FTs seem therefore to characterize universal features of nonequilibrium fluctuations in quantum as well as in classical systems.

We now discuss some future perspectives.

We mentioned in the Introduction and in Sec. II that an alternative approach to counting statistics, where the GF used is an influence functional following from a path integral description of the system-detector interaction, has been developed during the last decade. It is only in a semiclassical limit that the two-point measurement approach predicts the same statistics as this approach. Determining the region in which to apply both prescriptions is an open problem that could lead to a better understanding of quantum measurements.

Various numerical methods have been developed for using the Jarzynski relation to efficiently calculate equilibrium free energies of classical systems (Lechner *et al.*, 2006; Lechner and Dellago, 2007; Vaikuntanathan and Jarzynski, 2008). Extending these methods to quantum systems will be of future interest.

Finally, we note that in this review we have focused on systems maintained in a steady-state distribution by a single nonequilibrium constraint. Investigating systems subjected to multiple nonequilibrium constraints could reveal interesting features.

ACKNOWLEDGMENTS

APPENDIX A: TIME-REVERSED EVOLUTION

Here we explain why Eq. (34) corresponds to the time-reversed expression of the two-point probability (4) and discuss how to physically implement a time-reversed evolution. The effect of a static magnetic field is also discussed.

In order to implement the time-reversal operation in quantum mechanics, it is necessary to introduce the antilinear operator Θ ($\Theta i = -i\Theta$), which satisfies $\Theta^2 = 1$ (i.e., $\Theta^{-1} = \Theta$) (Wigner, 1960; Merzbacher, 1970). An arbitrary observable $\hat{A}$ can be even or odd with respect to the time-reversal operation, i.e.,

$$\Theta \hat{A} \Theta = \epsilon_A \hat{A}, \tag{A1}$$

where $\epsilon_A = \pm 1$. For example, the position operator $\hat{R}$ is even ($\epsilon_R = 1$) while the momentum $\hat{P}$ or angular momentum $\hat{L}$ is odd ($\epsilon_{P,L} = -1$). It can be verified that the Heisenberg commutation relations are preserved under the time-reversal operation. When acting on a time-dependent Hamiltonian $\hat{H}(t;B)$ that depends on a static magnetic field B, we obtain

$$\Theta \hat{H}(t;B) \Theta = \hat{H}(t;-B). \tag{A2}$$

If a forward evolution operator [as in Eq. (2) but with a static magnetic field] evolves according to

$$\frac{d}{dt} \hat{U}(t,0;B) = -\frac{i}{\hbar} \hat{H}(t;B) \hat{U}(t,0;B), \tag{A3}$$

with the initial condition $\hat{U}(0,0;B) = \hat{1}$, then the time-reversed evolution operator is defined by (Andrieux and Gaspard, 2008)

$$\hat{U}_{\mathrm{tr}}(t,0;-B) \equiv \Theta \hat{U}(T-t,0;B) \hat{U}^\dagger(T,0;B) \Theta$$
$$= \Theta \hat{U}(T-t,T;B) \Theta \tag{A4}$$

and its evolution is given by

$$\frac{d}{dt} \hat{U}_{\mathrm{tr}}(t,0;-B) = -\frac{i}{\hbar} \hat{H}(T-t;-B) \hat{U}_{\mathrm{tr}}(t,0;-B), \tag{A5}$$

with the initial condition $\hat{U}_{\mathrm{tr}}(0,0;B) = \hat{1}$. This can be verified using the change of variable $t \to T-t$ in Eq. (A3), multiplying the resulting equation by Θ from the left and by $\hat{U}^\dagger(T,0;B)\Theta$ from the right, and then using Eqs. (A2) and (A4)

From now on we choose $t = T$ (the time at which the time reversal operation is performed is t), and define

$$\hat{\rho}(t) \equiv \hat{U}(t,0;B) \hat{\rho}_0 \hat{U}^\dagger(t,0;B), \tag{A6}$$

$$\Theta \hat{\rho}^{\mathrm{tr}}(t) \Theta \equiv \hat{U}_{\mathrm{tr}}(t,0;-B) \Theta \hat{\rho}_0^{\mathrm{tr}} \Theta \hat{U}_{\mathrm{tr}}^\dagger(t,0;-B). \tag{A7}$$

We note that by multiplying Eq. (A7) by Θ from the left and from the right, we obtain

$$\hat{\rho}^{\mathrm{tr}}(t) = \hat{U}^\dagger(t,0;B) \hat{\rho}_0^{\mathrm{tr}} \hat{U}(t,0;B). \tag{A8}$$

We verify that if $\hat{\rho}_0^{\mathrm{tr}} = \hat{\rho}(t)$, then $\hat{\rho}^{\mathrm{tr}}(t) = \hat{\rho}_0$. This means that, as for classical systems, if a system initially described by $\hat{\rho}_0$ evolves according to the forward evolution between 0 and t, then the time-reversal operation is applied and the resulting density matrix is evolved according to the backward evolution during a time t and finally the time-reversal operation is again applied, the resulting density matrix is the initial condition $\hat{\rho}_0$. It follows from this discussion that if the two-point probability (4) (with a static magnetic field B) is defined as

$$P[a_t, a_0] \equiv \mathrm{Tr}\{\hat{P}_{a_t} \hat{U}(t,0;B) \hat{P}_{a_0} \hat{\rho}_0 \hat{P}_{a_0} \hat{U}^\dagger(t,0;B) \hat{P}_{a_t}\}, \tag{A9}$$

the time-reversed expression of this two-point probability must to be defined as

$$P^{\mathrm{tr}}[a_0, a_t] \equiv \mathrm{Tr}\{\hat{P}_{a_0} \hat{U}_{\mathrm{tr}}(t,0;-B)$$
$$\times \hat{P}_{a_t} \Theta \hat{\rho}_0^{\mathrm{tr}} \Theta \hat{P}_{a_t} \hat{U}_{\mathrm{tr}}^\dagger(t,0;-B) \hat{P}_{a_0}\}. \tag{A10}$$

We note that we could have included the final time-reversal operation in the definition, but it has no effect anyway due to the trace invariance. By inserting Θ^2 in between all the operators in Eq. (A10), and using Eq. (A4) with $T = t$, we find that

$$P^{\mathrm{tr}}[a_0, a_t] \equiv \mathrm{Tr}\{\hat{P}_{a_0} \hat{U}^\dagger(t,0;B) \hat{P}_{a_t} \hat{\rho}_0^{\mathrm{tr}} \hat{P}_{a_t} \hat{U}(t,0;B) \hat{P}_{a_0}\}, \tag{A11}$$

which is identical to the definition used in Eq. (34). It is convenient to use Eq. (A11) as a starting point because it allows one to avoid discussing the presence of a static magnetic field. However, it is important to keep in mind that the physical evolution corresponding to the time-reversed dynamics associated to a forward dynamics with an Hamiltonian $\hat{H}(t;B)$ is an evolution with an Hamiltonian where the driving protocol is time reversed, where the sign of the static magnetic field is changed $\hat{H}(T-t;-B)$, and where the initial condition is $\Theta \hat{\rho}_0^{\mathrm{tr}} \Theta$.

APPENDIX B: FLUCTUATION THEOREM FOR COARSE-GRAINED DYNAMICS

Here we show that using a coarse graining of the initial density matrices, R defined in Sec. III.A becomes a measurable quantity and $\langle R \rangle$ a difference of Gibbs–von Neumann entropy. We follow closely the work of Callens *et al.* (2004) and Yacobs and Maes (2005).

We define

$$R[a_t, a_0] \equiv \ln \frac{P[a_t, a_0]}{P^{\mathrm{tr}}[a_0, a_t]} \equiv -R^{\mathrm{tr}}[a_0, a_t], \tag{B1}$$

and

$$p(R) \equiv \sum_{a_t, a_0} P[a_t, a_0] \delta(R - R[a_t, a_0]),$$

$$p^{\mathrm{tr}}(R) \equiv \sum_{a_t, a_0} P^{\mathrm{tr}}[a_0, a_t] \delta(R - R^{\mathrm{tr}}[a_0, a_t]). \tag{B2}$$

Note that Eq. (B1), in contrast to Eq. (50), is expressed exclusively in terms of measurable quantities [eigenvalues of $A(t)$]. An integral FT follows

$$\langle e^{-R} \rangle \equiv \sum_{a_t, a_0} P[a_t, a_0] e^{-R[a_t, a_0]} = 1, \tag{B3}$$

which implies $\langle R \rangle \geq 0$, as well as a detailed FT

$$\frac{p(R)}{p^{tr}(-R)} = e^R. \tag{B4}$$

The coarse graining of a density matrix $\hat{\rho}$ within its non-measured part is given by

$$\tilde{\rho} = \sum_a \frac{p_a}{d_a} \hat{P}_a, \tag{B5}$$

where $p_a = \text{Tr}\,\hat{\rho}\hat{P}_a$ is the probability to measures a and d_a is the number of states with the value a. When, such a procedure is applied to $\hat{\rho}_0^{tr}$ and $\hat{\rho}_0$ (see De Roeck and Maes, 2006), $\langle R \rangle$ can be related to an entropy change. In this case

$$P[a_t, a_0] = \text{Tr}\{\hat{U}^\dagger(t,0)\hat{P}_{a_t}\hat{U}(t,0)\hat{P}_{a_0}\}\frac{p_{a_0}}{d_{a_0}},$$

$$P^{tr}[a_0, a_t] = \text{Tr}\{\hat{U}^\dagger(t,0)\hat{P}_{a_t}\hat{U}(t,0)\hat{P}_{a_0}\}\frac{p_{a_t}^{tr}}{d_{a_t}}. \tag{B6}$$

Therefore, using Eq. (B6) in Eq. (B1), we obtain

$$R[a_t, a_0] = s_{a_t}^{tr} - s_{a_0}, \tag{B7}$$

where

$$s_{a_t}^{tr} \equiv -\ln\frac{p_{a_t}^{tr}}{d_{a_t}}, \quad s_{a_0} \equiv -\ln\frac{p_{a_0}}{d_{a_0}}. \tag{B8}$$

The average of R is given by

$$\langle R \rangle = \sum_{a_t, a_0} R[a_t, a_0]P[a_t, a_0] = S^{tr} - S, \tag{B9}$$

where

$$S^{tr} \equiv \sum_{a_t} s_{a_t}^{tr} p_{a_t}^{tr}, \quad S \equiv \sum_{a_0} s_{a_0} p_{a_0} \tag{B10}$$

are the Gibbs–von Neumann entropies associated to the coarse-grained density matrix $\hat{\rho}_0^{tr}$ and $\hat{\rho}_0$. Indeed, if the coarse-grained density matrix $\tilde{\rho}$ is used in the expression for the Gibbs–von Neumann entropy $S = \text{Tr}\,\tilde{\rho}\ln\tilde{\rho}$, we obtain $S = \sum_a s_a p_a$.

APPENDIX C: LARGE DEVIATION AND FLUCTUATION THEOREM

Here we describe large deviation theory and show that a symmetry of the long-time limit of the cumulant GF such as Eq. (140) or (158) translates into a steady-state FT for the probabilities.

We consider a probability distribution $p(t,k)$, where k is a counting variable associated to a continuous time random walk (we assume that the waiting time distributions have a finite first and second moment). For fixed time, the central limit theorem is only valid up to a given accuracy in a central region of the probability distribution, whose width does not converge uniformly with time. Large deviation goes beyond the central limit theorem and allows one to describe the behavior of the

tail of the distribution (Sornette, 2006; Touchette, 2009). It relies on the assumption that the probability $\tilde{p}(t,\xi)$ that $\xi = k/t$ takes a value in the interval $[\xi, \xi + d\xi]$ behaves as

$$\tilde{p}(t,\xi) = C(\xi,t)e^{R(\xi)t}, \tag{C1}$$

where the large deviation function (LDF) is defined by

$$R(\xi) \equiv \lim_{t \to \infty} \frac{1}{t}\ln\tilde{p}(t,\xi) \tag{C2}$$

and

$$\lim_{t \to \infty} \frac{1}{t}\ln C(\xi,t) = 0. \tag{C3}$$

We show that the LDF is determined by the long-time limit of the cumulant GF given by

$$\mathcal{S}(\lambda) \equiv \lim_{t \to \infty} \frac{1}{t}\ln G(t,\lambda), \tag{C4}$$

where the moment GF is defined as

$$G(t,\lambda) \equiv \sum_k p(t,k)e^{-\lambda k}. \tag{C5}$$

Note that for convenience we have absorbed a factor $-i$ in the definition of λ compared to the standard definition of the moment GF used in the main text. The GF can be rewritten in terms of $\tilde{p}(t,\xi)$ as

$$G(t,\lambda) = \int d\xi\,\tilde{p}(t,\xi)e^{-\lambda\xi t}. \tag{C6}$$

We can then rewrite Eq, (C6) as

$$G(t,\lambda) = \int d\xi\,C(\xi,t)e^{[R(\xi)-\lambda\xi]t}. \tag{C7}$$

At long times, the main contribution to this integral comes from the value of ξ, ξ^*, which maximizes the argument of the exponential. ξ^* is therefore the value of ξ such that $\lambda = dR/d\xi|_{\xi = \xi^*}$. At long times, using steepest descent integration, Eq. (C7) becomes

$$G(t,\lambda) \approx e^{[R(\xi^*)-\lambda\xi^*]t}\int d\xi\,C(\xi,t)$$
$$\times e^{-(1/2)|[d^2R(\xi)/d\xi^2]|_{\xi=\xi^*}|(\xi-\xi^*)^2 t}$$
$$\approx e^{[R(\xi^*)-\lambda\xi^*]t}C(\xi^*,t)\left(\left|\frac{d^2R(\xi)}{d\xi^2}\right|_{\xi=\xi^*}\frac{t}{2\pi}\right)^{-1/2}. \tag{C8}$$

We assumed $R(\xi)$ concave to have a maximum. Substituting Eq. (C8) into Eq. (C4) gives

$$\mathcal{S}(\lambda) = R(\xi) - \lambda\xi, \tag{C9}$$

where

$$\lambda = \frac{dR(\xi)}{d\xi}. \tag{C10}$$

This shows that $S(\lambda)$ is the inverse Legendre transform of the LDF. By taking the derivative of Eq. (C9) with respect to λ, we get

$$\frac{dS(\lambda)}{d\lambda} = \frac{dR(\xi)}{d\xi}\frac{d\xi}{d\lambda} - \lambda\frac{d\xi}{d\lambda} - \xi, \tag{C11}$$

which using Eq. (C10) leads to

$$\xi = -\frac{dS(\lambda)}{d\lambda}. \tag{C12}$$

This shows that the LDF is given by the Legendre transform of $S(\lambda)$

$$R(\xi) = S(\lambda) + \lambda\xi. \tag{C13}$$

By taking the derivative of Eq. (C12) with respect to λ and using the derivative of Eq. (C10) with respect to ξ, we can confirm that $R(\xi)$ is concave because $S(\lambda)$ is convex.

We now assume that the cumulant GF satisfies the symmetry

$$S(\lambda) = S(A - \lambda). \tag{C14}$$

We note that the symmetry (C14) with the standard definition of the moment GF is given by $S(\lambda) = S(iA - \lambda)$. Using the symmetry (C14), Eq. (C13) implies that $R(-\xi) = S(A - \lambda) - (A - \lambda)\xi$ so that

$$R(\xi) - R(-\xi) = A\xi. \tag{C15}$$

Using Eq. (C1), we obtain

$$\ln\frac{\tilde{p}(t,\xi)}{\tilde{p}(t,-\xi)} = A\xi t + \ln\frac{C(\xi,t)}{C(-\xi,t)}. \tag{C16}$$

Using Eq. (C3), this gives the steady-state FT

$$\lim_{t\to\infty}\frac{1}{t}\ln\frac{p(t,k)}{p(t,-k)} = A\xi, \tag{C17}$$

which is often written as

$$\frac{p(t,k)}{p(t,-k)} \stackrel{t\to\infty}{=} e^{Ak}. \tag{C18}$$

Equations (141) and (149) are of this form.

APPENDIX D: DERIVATION OF THE GENERALIZED QUANTUM MASTER EQUATION

Equation (106) satisfies the equation of motion

$$\dot{\hat{\rho}}(\lambda,t) = \check{L}_\lambda\hat{\rho}(\lambda,t)$$

$$= -\frac{i}{\hbar}[\hat{H}_\lambda\hat{\rho}(\lambda,t) - \hat{\rho}(\lambda,t)\hat{H}_{-\lambda}]$$

$$= (\check{L}_0 + v\check{L}'_\lambda)\hat{\rho}(\lambda,t)$$

$$= -\frac{i}{\hbar}[\hat{H}_0,\hat{\rho}(\lambda,t)] - v\frac{i}{\hbar}[\hat{V}_\lambda\hat{\rho}(\lambda,t) - \hat{\rho}(\lambda,t)\hat{V}_{-\lambda}], \tag{D1}$$

where we multiplied $\hat{V}$ by a scalar v to keep track of the order in the perturbation expansion below. Superoperators are denoted by a breve (see Appendix F). In the interaction representation where

$$\hat{\rho}_I(\lambda,t) = e^{-\check{L}_0 t}\hat{\rho}(\lambda,t) = e^{(i/\hbar)\hat{H}_0 t}\hat{\rho}(\lambda,t)e^{-(i/\hbar)\hat{H}_0 t}, \tag{D2}$$

$$\check{L}'_\lambda(t) = e^{-\check{L}_0 t}\check{L}'_\lambda e^{\check{L}_0 t}, \tag{D3}$$

Eq. (D1) takes the simple form

$$\dot{\hat{\rho}}_I(\lambda,t) = v\check{L}'_\lambda(t)\hat{\rho}_I(\lambda,t). \tag{D4}$$

By integrating Eq. (D4) and truncating it to order v^2, we get the perturbative expansion

$$\hat{\rho}_I(\lambda,t) = \check{W}(\lambda,t)\hat{\rho}(0) = e^{-\check{L}_0 t}e^{\check{L}_\lambda t}\hat{\rho}(0)$$

$$= [\check{W}_0(\lambda,t) + v\check{W}_1(\lambda,t) + v^2\check{W}_2(\lambda,t)$$

$$+ \mathcal{O}(v^3)]\hat{\rho}(0), \tag{D5}$$

where

$$\check{W}_0(\lambda,t) = \check{1},$$

$$\check{W}_1(\lambda,t) = \int_0^t dT\check{L}'_\lambda(T),$$

$$\check{W}_2(\lambda,t) = \int_0^t dT\int_0^T d\tau\check{L}'_\lambda(T)\check{L}'_\lambda(T-\tau). \tag{D6}$$

The inverse of $\check{W}(t)$ reads

$$\check{W}^{-1}(\lambda,t) = \check{W}_0(\lambda,t) - v\check{W}_1(\lambda,t) + v^2[\check{W}_1^2(\lambda,t)$$

$$- \check{W}_2(\lambda,t)] + \mathcal{O}(v^3). \tag{D7}$$

Indeed, one can check that $\check{W}(\lambda,t)\check{W}^{-1}(\lambda,t) = \check{1} + \mathcal{O}(v^3)$. For later use, we also note that

$$\dot{\check{W}}(\lambda,t)\check{A}\check{W}^{-1}(\lambda,t) = v\dot{\check{W}}_1(\lambda,t)\check{A} + v^2[\dot{\check{W}}_2(\lambda,t)\check{A}$$

$$- \dot{\check{W}}_1(\lambda,t)\check{A}\check{W}_1(\lambda,t)] + \mathcal{O}(v^3). \tag{D8}$$

We define the projection superoperator (acting in reservoir space)

$$\check{P} = \sum_r |\rho_R^{\text{eq}}\rangle\rangle\langle\langle rr|, \tag{D9}$$

where $\hat{\rho}_R^{\text{eq}}$ is the equilibrium density matrix of the reservoir. We used the Liouville space notation (see Appendix F). $\check{P}$ satisfies the usual properties of projection superoperators $\check{P} + \check{Q} = \check{1}$, $\check{P}^2 = \check{P}$, $\check{Q}^2 = \check{Q}$, and $\check{P}\check{Q} = \check{Q}\check{P} = 0$. When acting on the density matrix $\hat{\rho}(t)$, the projection operator is given by

$$\check{P}|\rho(\lambda,t)\rangle\rangle = |\rho_S(\lambda,t)\rangle\rangle \otimes |\rho_R^{\mathrm{eq}}\rangle\rangle. \tag{D10}$$

We now let $\check{P}$ and $\check{Q}$ act on the density matrix of the total system in the interaction picture (D5) and find

$$\check{P}|\rho_I(\lambda,t)\rangle\rangle = \check{P}\check{W}(t)(\check{P}+\check{Q})|\rho_I(0)\rangle\rangle, \tag{D11}$$

$$\check{Q}|\rho_I(\lambda,t)\rangle\rangle = \check{Q}\check{W}(t)(\check{P}+\check{Q})|\rho_I(0)\rangle\rangle. \tag{D12}$$

Hereafter, we consider initial conditions such that $\check{Q}|\rho(0)\rangle\rangle = 0$. This means that the reservoir part of the initial condition is diagonal in the reservoir eigenbasis and is thus invariant under the evolution when $v=0$. Taking the time derivative of Eqs. (D11) and (D12) and using $|\rho_I(0)\rangle\rangle = \check{W}^{-1}(\lambda,t)|\rho_I(\lambda,t)\rangle\rangle$, we obtain

$$\check{P}|\dot{\rho}_I(\lambda,t)\rangle\rangle = \check{P}\dot{\check{W}}(\lambda,t)\check{P}\check{W}^{-1}(\lambda,t)\check{P}|\rho_I(\lambda,t)\rangle\rangle$$
$$+ \check{P}\dot{\check{W}}(\lambda,t)\check{P}\check{W}^{-1}(\lambda,t)\check{Q}|\rho_I(\lambda,t)\rangle\rangle, \tag{D13}$$

$$\check{Q}|\dot{\rho}_I(\lambda,t)\rangle\rangle = \check{Q}\dot{\check{W}}(\lambda,t)\check{P}\check{W}^{-1}(\lambda,t)\check{P}|\rho_I(\lambda,t)\rangle\rangle$$
$$+ \check{Q}\dot{\check{W}}(\lambda,t)\check{P}\check{W}^{-1}(\lambda,t)\check{Q}|\rho_I(\lambda,t)\rangle\rangle. \tag{D14}$$

So far these equations are exact. If we restrict ourselves to second-order perturbation theory in v, we can obtain the result that the $\check{P}$ projected density matrix evolution is decoupled from the $\check{Q}$ projected part. Indeed, with the help of Eq. (D8), we obtain

$$\check{P}\dot{\check{W}}(\lambda,t)\check{P}\check{W}^{-1}(\lambda,t)\check{Q} = v\check{P}\dot{\check{W}}_1(\lambda,t)\check{P}\check{Q}$$
$$+ v^2\check{P}\dot{\check{W}}_2(\lambda,t)\check{P}\check{Q}$$
$$- v^2\check{P}\dot{\check{W}}_1(\lambda,t)\check{P}\check{W}_1(\lambda,t)\check{Q}$$
$$+ \mathcal{O}(v^3). \tag{D15}$$

The first two terms of the right-hand side are zero because $\check{P}\check{Q}=0$ and the third one also because

$$\check{P}\dot{\check{W}}_1(\lambda,t)\check{P} = \sum_{r,r'}|\rho_R^{\mathrm{eq}}\rangle\rangle\langle\langle rr|\check{L}_I'(\lambda,t)|\rho_R^{\mathrm{eq}}\rangle\rangle\langle\langle r'r'| \tag{D16}$$

vanishes since $\hat{\rho}_R^{\mathrm{eq}}$ commutes with $\hat{H}_R$.

Having shown that the relevant projected density matrix evolves in an autonomous way, we now evaluate the generator of its evolution using second-order perturbation theory. Again using Eq. (D8), we find that

$$\check{P}\dot{\check{W}}(\lambda,t)\check{P}\check{W}^{-1}(\lambda,t)\check{P} = v\check{P}\dot{\check{W}}_1(\lambda,t)\check{P} + v^2\check{P}\dot{\check{W}}_2(\lambda,t)\check{P}$$
$$- v^2\check{P}\dot{\check{W}}_1(\lambda,t)\check{P}\check{W}_1(\lambda,t)\check{P}$$
$$+ \mathcal{O}(v^3). \tag{D17}$$

The only term of right-hand side which is not zero is the second one [see Eq. (D16)], whereupon we get

$$\check{P}|\dot{\rho}_I(\lambda,t)\rangle\rangle = v^2\check{P}\int_0^t d\tau \check{L}_\lambda'(t)\check{L}_\lambda'(t-\tau)\check{P}|\rho_I(\lambda,t)\rangle\rangle$$
$$+ \mathcal{O}(v^3). \tag{D18}$$

Now leaving the interaction representation and using the fact that $\check{P}e^{-\check{L}_0 t} = e^{-\check{L}_S t}\check{P}$, we obtain

$$\check{P}|\dot{\rho}(\lambda,t)\rangle\rangle = \check{L}_S\check{P}|\rho(\lambda,t)\rangle\rangle$$
$$+ v^2 e^{\check{L}_S t}\check{P}\int_0^t d\tau \check{L}_\lambda'(t)\check{L}_\lambda'(t-\tau)$$
$$\times e^{-\check{L}_S t}\check{P}|\rho(\lambda,t)\rangle\rangle. \tag{D19}$$

By taking the trace of Eq. (D19) we obtain

$$\dot{\hat{\rho}}_S(\lambda,t) = \check{L}_S\hat{\rho}_S(\lambda,t) + v^2\sum_r \int_0^t d\tau\, e^{\check{L}_S t}\langle\langle rr|\check{L}_\lambda'(t)\check{L}_\lambda'(t-\tau)$$
$$\times|\rho_R^{eq}\rangle\rangle e^{-\check{L}_S t}\hat{\rho}_S(\lambda,t). \tag{D20}$$

Explicit evaluation leads to Eq. (I10).

APPENDIX E: BIDIRECTIONAL POISSON STATISTICS

The GF of Sec. IV.B.4 corresponds to a bidirectional Poisson process. We give here some basic properties of this process.

The GF of the probability distribution $p(k)$ can be expanded in terms of moments $\langle k^n \rangle$ as

$$G(\lambda) = \sum_k e^{i\lambda k}p(k) = \sum_{n=1}^\infty \langle k^n\rangle \frac{(i\lambda)^n}{n!}. \tag{E1}$$

The Poisson distribution and its GF are given by

$$p(k) = \frac{\mu^k e^{-\mu}}{k!}, \quad G(\lambda) = \exp\{\mu(e^{i\lambda}-1)\}. \tag{E2}$$

Note that $\mu = \langle k \rangle$. If $k = k_1 - k_2$ where $p(k_1,k_2) = p_1(k_1)p_1(k_2)$ and $p_1(k)$ and $p_2(k)$ are Poissonian, we obtain

$$G(\lambda) = G_1(\lambda_1 = \lambda)G_2(\lambda_2 = -\lambda)$$
$$= \exp\{\mu_1(e^{i\lambda}-1) + \mu_2(e^{-i\lambda}-1)\}. \tag{E3}$$

If the average of the positive process is related to the average of the negative one by $\mu_1 = \mu_2\exp(-A)$, we find that the GF displays the FT symmetry $G(\lambda) = G(A-\lambda)$. By inverting Eq. (E3), we obtain

$$p(k) = e^{-(\mu_1+\mu_2)}e^{Ak/2}I_k\left(-\frac{\mu_1-\mu_2}{\sinh(A/2)}\right), \tag{E4}$$

where I_k is the modified Bessel function of order k.

APPENDIX F: LIOUVILLE SPACE AND SUPEROPERATOR ALGEBRA

In Liouville space, a $N \times N$ Hilbert space operators $\hat{\rho}$ is mapped into a N^2 vector $|\rho\rangle\rangle$ and a superoperator $\check{A}$ (linear map) acting on an operator $\hat{\rho}$ becomes a N^2

$\times N^2$ matrix acting on the vector $|\rho\rangle\rangle$: $\check{A}\hat{\rho} \leftrightarrow \check{A}|\rho\rangle\rangle$ (Fano, 1963; B.-Reuven, 1975; Zwanzig, 2001; Harbola and Mukamel, 2006, 2008). We recall some basic definitions

scalar product: $\langle\langle A|B\rangle\rangle \equiv \mathrm{Tr}\,\hat{A}^\dagger\hat{B}$, (F1)

identity: $\check{1} \equiv \sum_{n,n'} |nn'\rangle\rangle\langle\langle nn'|$, (F2)

$|nn'\rangle\rangle \leftrightarrow |n\rangle\langle n'|, \quad \langle\langle nn'| \leftrightarrow |n'\rangle\langle n|$. (F3)

Useful consequences of these definitions are

$\langle\langle nn'|\bar{n}\bar{n}'\rangle\rangle = \delta_{n\bar{n}}\delta_{n'\bar{n}'}$, (F4)

$\langle\langle nn'|A\rangle\rangle = \langle n|A|n'\rangle$, (F5)

$\langle\langle 1|A\rangle\rangle = \mathrm{Tr}\,\hat{A}$. (F6)

We define left and right Liouville space operators as

$\check{A}_L|X\rangle\rangle \leftrightarrow \hat{A}\hat{X}, \quad \check{A}_R|X\rangle\rangle \leftrightarrow \hat{X}\hat{A}$. (F7)

We also define

$\check{A}_+ \equiv \frac{1}{\sqrt{2}}(\check{A}_L + \check{A}_R), \quad \check{A}_- \equiv \frac{1}{\sqrt{2}}(\check{A}_L - \check{A}_R)$. (F8)

This linear transformation is symmetric. The inverse transformation can be obtained by simply interchanging $+$ and $-$ with L and R, respectively. Thus most of the expressions in the following are symmetric and the indices used to represent superoperators can take both $+$, $-$ and L, R values without any other change. The advantage of the $+$, $-$ representation is that a single operation A_- in Liouville space represents the commutation with A in Hilbert space. Thus all the intertwined commutations, which appear in perturbation expansions in Hilbert space, transform to a compact notation that is more easy to interpret in terms of the double-sided Feynmann diagrams (Mukamel, 1995). Similarly a single operation of A_+ in Liouville space corresponds to an anticommutator in Hilbert space:

$\check{A}_-|X\rangle\rangle \leftrightarrow \frac{1}{\sqrt{2}}(\hat{A}\hat{X} - \hat{X}\hat{A})$, (F9)

$\check{A}_+|X\rangle\rangle \leftrightarrow \frac{1}{\sqrt{2}}(\hat{A}\hat{X} + \hat{X}\hat{A})$. (F10)

For any product of operators in Hilbert space, we can define corresponding superoperators in Liouville space using the following identities:

$(\hat{A}_i\hat{A}_j\cdots\hat{A}_k)_L = \check{A}_{iL}\check{A}_{jL}\cdots\check{A}_{kL}$,

$(\hat{A}_i\hat{A}_j\cdots\hat{A}_k)_R = \check{A}_{kR}\cdots\check{A}_{jR}\check{A}_{iR}$. (F11)

Applying this one immediately obtains

$(\hat{A}_i\hat{A}_j)_- = \frac{1}{2\sqrt{2}}[[\check{A}_{i+},\check{A}_{j+}] + [\check{A}_{i-},\check{A}_{j-}] + \{\check{A}_{i+},\check{A}_{j-}\}$

$+ \{\check{A}_{i-},\check{A}_{j+}\}]$, (F12)

$(\hat{A}_i\hat{A}_j)_+ = \frac{1}{2\sqrt{2}}[\{\check{A}_{i+},\check{A}_{j+}\} + \{\check{A}_{i-},\check{A}_{j-}\} + [\check{A}_{i+},\check{A}_{j-}]$

$+ [\check{A}_{i-},\check{A}_{j+}]]$. (F13)

Equations (F11)–(F13) are useful for recasting functions of Hilbert space operators, such as the Hamiltonian, in terms of the superoperators in Liouville space.

Another useful quantity in Liouville space is the time ordering operator $\check{T}$; when acting on a product of superoperators (each at different times), it rearranges them in increasing order of time from right to left:

$$\check{T}\check{A}_{i\alpha}(t)\check{A}_{j\beta}(t') = \begin{cases} \check{A}_{j\beta}(t')\check{A}_{i\alpha}(t), & t < t' \\ \check{A}_{i\alpha}(t)\check{A}_{j\beta}(t'), & t' < t, \end{cases}$$ (F14)

where $\alpha,\beta = L,R,+,-$. Note that, unlike the Hilbert space where we have two time ordering operators describing the evolution in opposite (forward and backward) directions, a Liouville space operator $\check{T}$ always acts to its right and therefore all processes are given in terms of forward time alone. This makes it easier to give physical interpretation to various algebraic expressions commonly obtained in perturbation expansions, which can be converted readily in terms of different Liouville space diagrams.

We finally note that using Eqs. (F6) and (F7) we obtain for $\alpha = L,R$

$\langle\langle I|\check{A}_\alpha|\rho\rangle\rangle = \langle\hat{A}\rangle = \mathrm{Tr}\{\hat{A}\hat{\rho}\}$, (F15)

and using Eqs. (F7), (F8), and (F15), we obtain

$\langle\langle I|\check{A}_-|\rho\rangle\rangle = 0, \quad \langle\langle I|\check{A}_+|\rho\rangle\rangle = \sqrt{2}\langle\hat{A}\rangle$. (F16)

APPENDIX G: PROBABILITY DISTRIBUTION FOR ELECTRON TRANSFERS

In the model considered in Sec. V.A, we consider electron transfer between system A and B. We measure the number of electron in system A at time 0 and t. The number operator for system A is defined as $\hat{N} = \Sigma_{i\in A}\hat{c}_i^\dagger\hat{c}_i$, where $\hat{c}^\dagger$ ($\hat{c}$) are creation (annihilation) operators. Only the coupling $\hat{V}$ can induce electron transfer: $[\hat{H}_A + \hat{H}_B, \hat{N}] = 0$.

The total density matrix follows a unitary dynamics in Liouville space,

$|\rho(t)\rangle\rangle = \check{U}(t,0)|\rho(0)\rangle\rangle = \check{U}_L(t,0)\check{U}_R^\dagger(t,0)|\rho(0)\rangle\rangle$, (G1)

where

$$\check{U}(t,0) = \exp\{-i\sqrt{2}\check{H}_-t\}, \tag{G2}$$

with $\check{H}_-$ the superoperator corresponding to the total Hamiltonian, $\sqrt{2}\check{H}_- = \check{H}_L - \check{H}_R$, and

$$\check{U}_\alpha(t,0) = \exp\{-i\sqrt{2}\check{H}_\alpha t\}, \quad \alpha = L, R. \tag{G3}$$

By measuring the number of electrons in A, when the system right before the measurement is described by $|\rho(0)\rangle\rangle$, we obtain the outcome n with a probability $\langle\langle I|\check{P}_n|\rho(0)\rangle\rangle$ and the density matrix of the system after the measurement becomes $\check{P}_n|\rho(0)\rangle\rangle$, where the projection operator in Liouville space is defined as

$$\check{P}_n = \delta_K(n - \check{N}_L)\delta_K(n - \check{N}_R)$$
$$= \int_0^{2\pi} \frac{d\lambda d\lambda'}{(2\pi)^2} e^{-i\lambda(n-\check{N}_L)} e^{-i\lambda'(n-\check{N}_R)}. \tag{G4}$$

δ_K is the Kronecker delta and $\check{N}_\alpha$ are the left and right superoperators corresponding to the number operator in A. We have $\check{P}_n\check{P}_{n'} = \delta_K(n-n')\check{P}_n$ and

$$\exp\{i\lambda\check{N}_\alpha\}\check{P}_n = \exp\{i\lambda n\}\check{P}_n. \tag{G5}$$

The net number of electrons k transferred between A and B during time t is a fluctuating quantity. The probability for measuring k electrons during this time interval is given by

$$p(k,t) = \sum_n \langle\langle I|\check{P}_{n-k}\check{U}(t,0)\check{P}_n|\rho(0)\rangle\rangle. \tag{G6}$$

Substituting Eqs. (G1) and (G4) into Eq. (G6) and using Eq. (G5) with the fact that left and right superoperators commute, we obtain

$$p(k,t) = \int_0^{2\pi} \frac{d\lambda_1 d\lambda_2}{(2\pi)^2} e^{i(\lambda_1+\lambda_2)k}$$
$$\times \langle\langle I|e^{i\lambda_1\check{N}_L}\check{U}_L(t,0)e^{-i\lambda_1\check{N}_L}$$
$$\times e^{i\lambda_2\check{N}_R}\check{U}_R^\dagger(t,0)e^{-i\lambda_2\check{N}_R}|\rho(0)\rangle\rangle. \tag{G7}$$

Making the change of variables, $\lambda_1 = -\Lambda - \lambda/2$ and $\lambda_2 = \Lambda - \lambda/2$, we obtain

$$p(k,t) = \int_0^{2\pi} \frac{d\lambda}{2\pi} e^{-i\lambda k} G(\lambda,t), \tag{G8}$$

where the GF is given by

$$G(\lambda,t) = \int_0^{2\pi} \frac{d\Lambda}{2\pi} G(\lambda,\Lambda,t), \tag{G9}$$

and

$$G(\lambda,\Lambda,t) = \langle\langle I|e^{-i(\Lambda+\lambda_X/2)\check{N}_L}\check{U}_L(t,0)e^{i(\Lambda+\lambda_X/2)\check{N}_L}$$
$$\times e^{i(\Lambda-\lambda_X/2)\check{N}_R}\check{U}_R^\dagger(t,0)e^{-i(\Lambda-\lambda_X/2)\check{N}_R}|\rho(0)\rangle\rangle. \tag{G10}$$

Equation (G9) is identical to the trace of $\hat{\rho}(\lambda,t)$ defined in Eq. (25).

The density matrix right before the first measurement ($t=0$) can be constructed by switching the interaction V adiabatically from the remote past, $t \to -\infty$. This gives

$$G(\lambda,\Lambda,t) = \langle\langle I|\check{U}_0(t,0)\check{U}_I(\gamma(t),t,-\infty)|\rho(-\infty)\rangle\rangle, \tag{G11}$$

where

$$\check{U}_I(\gamma(t),t,-\infty) = \exp_+\left\{-i\int_{-\infty}^t d\tau\sqrt{2}\check{V}_-(\gamma(\tau),\tau)\right\},$$

$$\check{U}_0(t,0) = \theta(t)\exp\{-i\sqrt{2}(H_0-t)\}. \tag{G12}$$

We define

$$\sqrt{2}\check{V}_-(\gamma(\tau),\tau) = \check{V}_L(\gamma_L(\tau),\tau) - \check{V}_R(\gamma_R(\tau),\tau), \tag{G13}$$

where

$$\check{V}_L(\gamma_L(\tau),\tau) = e^{-i\gamma_L(\tau)\check{N}_L}[\check{V}_L(\tau)]e^{i\gamma_L(\tau)\check{N}_L},$$

$$\check{V}_R(\gamma_R(\tau),\tau) = e^{i\gamma_R(\tau)\check{N}_R}[\check{V}_R(\tau)]e^{-i\gamma_R(\tau)\check{N}_R}, \tag{G14}$$

with $\check{V}_\alpha = \check{J}_\alpha + \check{J}_\alpha^\dagger$ and

$$\gamma_L(t) = \theta(t)(\Lambda + \lambda/2),$$

$$\gamma_R(t) = \theta(t)(\Lambda - \lambda/2). \tag{G15}$$

The time dependence of the operators in Eq. (G12) is in the interaction picture with respect to $\hat{H}_0$.

$$\check{V}_\alpha(t) = e^{i\sqrt{2}\check{H}_0-t}\check{V}_\alpha e^{-i\sqrt{2}\check{H}_0-t}. \tag{G16}$$

Equation (G11) is the GF used in Eq. (173).

APPENDIX H: PATH-INTEGRAL EVALUATION OF THE GENERATING FUNCTION FOR FERMION TRANSPORT

The fermion coherent states $|\psi\rangle$ are defined through the eigenvalue equation for the Fermi destruction operators $\hat{c}_x|\psi_i\rangle = \psi_{xi}|\psi\rangle$ and $\langle\psi_i|\hat{c}_x^\dagger = \langle\psi|\bar{\psi}_{xi}$, where ψ and $\bar{\psi}$ are independent Grassmann variables (see Appendix I), which satisfy anticommutation relations similar to the Fermi operators (Negele and Orland, 1998).

It is convenient to introduce coherent states in Liouville space corresponding to the superoperator $\check{c}_{x\alpha}$, $x = a, b, s$, as

$$\check{c}_{xL}|\psi\rangle\rangle = \psi_{xL}|\psi\rangle\rangle,$$

$$\check{c}_{xR}^\dagger|\psi\rangle\rangle = \psi_{xR}|\psi\rangle\rangle. \tag{H1}$$

The state $|\psi\rangle\rangle$ can be expressed in terms of the vacuum state

$$|\psi\rangle\rangle = \exp\left[\sum_x \left(-\psi_{xL}\check{c}^\dagger_{xL} - \psi_{xR}\check{c}_{xR}\right)\right]|0\rangle\rangle \tag{H2}$$

and

$$\langle\langle\psi| = \langle\langle 0|\exp\left[\sum_x \left(\bar{\psi}_{xL}\check{c}_{xL} - \bar{\psi}_{xR}\check{c}^\dagger_{xR}\right)\right]. \tag{H3}$$

Note that $\check{c}^\dagger_R$ is not the Hermitian conjugate of $\check{c}_R$ (Harbola and Mukamel, 2008). Grassmann variables ψ_α and $\bar{\psi}_\beta$ anticommute between themselves and with the creation and annihilation operators. Note that, unlike usual fermion case, we now have four generators for the Grassmann algebra, two corresponding to each index α. Using Eqs. (H1)–(H3) it can be shown that

$$\langle\langle\psi'|\check{c}^\dagger_L\check{c}_R|\psi\rangle\rangle = \bar{\psi}'_R\bar{\psi}'_L\langle\langle\psi'|\psi\rangle\rangle, \tag{H4}$$

$$\langle\langle\psi'|\check{c}^\dagger_R\check{c}_L|\psi\rangle\rangle = \psi_R\psi_L\langle\langle\psi'|\psi\rangle\rangle, \tag{H5}$$

$$\langle\langle\psi'|\check{c}^\dagger_L\check{c}_L|\psi\rangle\rangle = \bar{\psi}'_L\psi_L\langle\langle\psi'|\psi\rangle\rangle, \tag{H6}$$

$$\langle\langle\psi'|\check{c}_R\check{c}^\dagger_R|\psi\rangle\rangle = \psi_R\bar{\psi}'_R\langle\langle\psi'|\psi\rangle\rangle. \tag{H7}$$

These matrix elements will be useful in the path-integral formulation below. The scalar product of two coherent states is

$$\langle\langle\psi'|\psi\rangle\rangle = \exp\left(\sum_\alpha \bar{\psi}'_\alpha\psi_\alpha\right). \tag{H8}$$

Grassmann variables satisfy the closure relation

$$1 = \int \mathcal{D}(\bar{\psi}\psi)\exp\left(-\sum_\alpha \bar{\psi}_{ix\alpha}\psi_{ix\alpha}\right)|\psi_i\rangle\rangle\langle\langle\psi_i|, \tag{H9}$$

where $\mathcal{D}(\bar{\psi}\psi) = \Pi_{i,x,\alpha}(d\bar{\psi}_{ix\alpha})(d\psi_{ix\alpha})$.

We next switch to $+$, $-$ notation (Harbola and Mukamel, 2006), represented by the index $\nu = +, -$. The superoperators $\check{H}_{0-}$ and $\check{\mathcal{V}}_-(\gamma)$ are

$$\sqrt{2}\check{H}_{0-} = \sum_{x\nu} \epsilon_x(\check{c}^\dagger_{x+}\check{c}_{x+} - \check{c}_{x-}\check{c}^\dagger_{x-}),$$

$$\sqrt{2}\check{\mathcal{V}}_-(\gamma(t),t) = \sum_{x\neq x'} \sum_{\nu\nu'} J^{\nu\nu'}_{xx'}(\gamma(t))\check{c}^\dagger_{x\nu}(t)\check{c}_{x\nu'}(t), \tag{H10}$$

where $J^{\nu\nu'}_{xx'}(\gamma)(=J^{\nu\nu'\dagger}_{x'x})$ is 2×2 matrices for $\nu, \nu' = +, -$ with elements

$$J^{++}_{xx'}(\gamma) = J^{--}_{xx'}(\gamma) = J_{xx'}(e^{i\gamma_L} + e^{i\gamma_R})/2,$$

$$J^{+-}_{xx'}(\gamma) = J^{-+}_{xx'}(\gamma) = J_{xx'}(e^{i\gamma_L} - e^{i\gamma_R})/2, \tag{H11}$$

while for $x, x' = b, s, J^{++}_{xx'}(\gamma) = J^{--}_{xx'}(\gamma) = J_{xx'}$ and $J^{+-}_{xx'}(\gamma) = J^{-+}_{xx'}(\gamma) = 0$.

We encounter the matrix element of an exponential operator of the type

$$\langle\langle\psi'|e^{\sqrt{2}\check{H}_{0-}}|\psi\rangle\rangle = \langle\langle\psi'|e^{\check{H}_{0L}-\check{H}_{0R}}|\psi\rangle\rangle$$

$$= \langle\langle\psi'|e^{\sum_x \epsilon_x(\check{c}^\dagger_{xL}\check{c}_{xL}-\check{c}_{xR}\check{c}^\dagger_{xR})}|\psi\rangle\rangle$$

$$= e^{\sum_x \epsilon_x(\bar{\psi}'_{xL}\psi_{xL}+\bar{\psi}'_{xR}\psi_{xR})}\langle\langle\psi'|\psi\rangle\rangle,$$

where in going from second to the third line we used Eqs. (H6) and (H7). We now make the linear transformation from L/R variables to the $+/-$ variables. In Hilbert space this corresponds to the Keldysh rotation (Kamenev, 2002). Using this transformation we can write above matrix element as

$$\langle\langle\psi'|e^{\sqrt{2}\check{H}_{0-}}|\psi\rangle\rangle = \exp\left(\sum_{x\nu\nu'} \epsilon^{\nu\nu'}_x\bar{\psi}'_{x\nu}\psi_{x\nu'}\right)\langle\langle\psi'|\psi\rangle\rangle, \tag{H12}$$

where $\epsilon^{++}_x = \epsilon^{--}_x = \epsilon_x$ and $\epsilon^{+-}_x = \epsilon^{-+}_x = 0$. This matrix element (H12) can also be obtained directly by formally defining the Grassmann variables corresponding to $+, -$ operators, $\check{c}_{x\nu}$ and $\check{c}^\dagger_{x\nu}$, by $\psi_{x\nu}$ and $\bar{\psi}_{x\nu}$, respectively, and using Eq. (H10). We use the $+/-$ formulation in the remainder of the section. The advantage of using this notation is that we directly work with the retarded and advanced functions which are naturally linked to the observables (when $\lambda = 0$).

We can express the trace in Eq. (G11) in terms of the coherent states basis,

$$G(\lambda, \Lambda, t) = \int \mathcal{D}(\bar{\psi}\psi)$$
$$\times e^{-\bar{\psi}\psi}\langle\langle\psi|\check{U}_0(t,0)\check{U}_I(\gamma(t),t,-\infty)|\rho(-\infty)\rangle\rangle. \tag{H13}$$

We next divide the time from 0 to t in Eq. (H13) into N equal segments of length δt and introduce the closure relation (H9) after each time interval. We then obtain

$$G(\lambda, \Lambda, t) = \int \mathcal{D}(\bar{\psi}\psi)\langle\langle\psi_0|\rho(-\infty)\rangle\rangle$$
$$\times \langle\langle\psi_1|\check{U}_I(\gamma(t),t,-\infty)|\psi_0\rangle\rangle$$
$$\times \prod_{i=2}^N \langle\langle\psi_i|\check{U}_0(\delta t_i)|\psi_{i-1}\rangle\rangle. \tag{H14}$$

Here the index i on ψ_i carries time index so that ψ_{i+1} is at δt time ahead of ψ_i.

$\check{U}_I$ can be formally evaluated by dividing the time interval from the initial time $-t_0$ (at the end we can put $t_0 \to \infty$) to t in N' number of equal time steps. We then obtain

$$\langle\langle\psi_1|\check{U}_I(\gamma(t),t,t_0)|\psi_0\rangle\rangle = \langle\langle\psi_1|e^{-i\sum_i^{N'}\sqrt{2}\check{\mathcal{V}}_-(\gamma(t_i),t_i)\delta t_i}|\psi_0\rangle\rangle. \tag{H15}$$

Here $\delta t > 0$ is small enough so that only the linear order term contributes. The exponential can then be factorized into products of exponentials. By inserting the identity between exponentials, we obtain (repeated indices are summed over)

$$\langle\langle\psi_{i+1}|e^{-i\sqrt{2}\breve{\mathcal{V}}_-(i\gamma(t_i),t_i)\overline{\delta t}_i}|\psi_i\rangle\rangle$$

$$\approx e^{-iV_{xx'}^{\nu\nu'}(\gamma(t_i))\bar{\psi}_{ix\nu}\psi_{ix'\nu'}\delta t_i}\langle\langle\psi_{i+1}|\psi_i\rangle\rangle. \tag{H16}$$

The second matrix element of the evolution operator $\breve{U}_0(t)$ between two coherent states is

$$\langle\langle\psi_{i+1}|\breve{U}_0(\delta t_i)|\psi_i\rangle\rangle \approx e^{-i\epsilon_x^{\nu\nu'}\bar{\psi}_{ix\nu}\psi_{ix\nu}\delta t_i}\langle\langle\psi_{i+1}|\psi_i\rangle\rangle. \tag{H17}$$

Using Eqs. (H16) and (H17) in Eq. (H13), we obtain for the GF

$$G(\lambda,\Lambda,t) = \int \mathcal{D}[\bar{\psi}\psi]\langle\langle\psi_0|\rho(-\infty)\rangle\rangle$$

$$\times \prod_{i=1}^{M=N+N'} \exp\left\{i\bar{\psi}_{ix\nu}\left(i\frac{\psi_{ix\nu}-\psi_{i-1x\nu}}{\delta t_i}\right.\right.$$

$$\left.\left.- \epsilon_x\psi_{ix\nu}\right)\delta t_i\right\}$$

$$\times\exp\{-i\bar{\psi}_{ix\nu}V_{xx'}^{\nu\nu'}(\gamma(t_i))\psi_{ix'\nu'}\delta t_i\}. \tag{H18}$$

Here $\gamma(t_i)=0$ for $i<M-N$.

Setting $M\to\infty$, $t_0\to\infty$, and $\delta t_i\to 0$, we obtain

$$G(\lambda,\Lambda,t) = \int \mathcal{D}[\bar{\psi}\psi]e^{iS(\bar{\psi},\psi)}, \tag{H19}$$

where in the continuous time notation $\mathcal{D}[\bar{\psi}\psi] \equiv \Pi_\tau d\bar{\psi}(\tau)d\psi(\tau)$ and the action $S(\bar{\psi},\psi)$ is defined as

$$S(\bar{\psi},\psi) = \int d\tau[\bar{\psi}_{x\nu}(\tau)g_{xx'}^{\nu\nu'-1}(\tau)\psi_{x'\nu'}(\tau)$$

$$- \bar{\psi}_{x\nu}(\tau)V_{xx'}^{\nu\nu'}(\gamma(\tau))\psi_{x'\nu'}(\tau)]. \tag{H20}$$

$g_{xx'}^{\nu\nu'}$ is a 2×2 matrix corresponding to $\nu,\nu'=+,-$ which satisfies

$$\left(i\frac{\partial}{\partial t}-\epsilon_x\right)g_{xx'}^{\nu\nu'}(t,t') = \delta(t-t')\delta_{x,x'}\delta_{\nu\nu'}. \tag{H21}$$

Using the integral identity for independent Grassmann variables $\bar{\eta}$, η, $\bar{\kappa}$, and κ,

$$\int \mathcal{D}(\bar{\eta},\eta)e^{-\bar{\eta}_i A_{ij}\eta_j}e^{\bar{\kappa}_i\eta_i+\bar{\eta}_i\kappa_i} = \mathrm{Det}[A]e^{\bar{\kappa}_i[A]_{ij}^{-1}\kappa_j}, \tag{H22}$$

we can trace out the leads' degrees of freedom to obtain

$$G(\lambda,\Lambda,t) = \int \mathcal{D}[\bar{\psi}\psi]e^{iS(\bar{\psi}\psi)}, \tag{H23}$$

with

$$S(\bar{\psi}\psi) = \int d\tau d\tau' \bar{\psi}_{s\nu}(\tau)[g_{ss'}^{\nu\nu'-1}(\tau,\tau')$$

$$- \Sigma_{ss'}^{\nu\nu'}(\tau,\tau',\gamma)]\psi_{s'\nu'}(\tau'). \tag{H24}$$

The self-energy $\Sigma(\gamma)$ is

$$\Sigma_{ss'}^{\nu\nu'}(t,t',\gamma) = \sum_{xx'\in A,B}\sum_{\nu_1\nu_2} V_{sx}^{\nu\nu_1}(\gamma(t))g_{xx'}^{\nu_1\nu_2}(t,t')$$

$$\times V_{x's'}^{\nu_2,\nu'}(\gamma(t')), \tag{H25}$$

where repeated arguments are summed over and $g_{xx'}$ are the Greens functions for the noninteracting leads. The counting parameter appears in the self-energy only through coupling terms $V_{xs}^{\nu\nu'}(\gamma)$. Finally, using Eq. (H22) we can perform the Gaussian integral in Eq. (H23) to obtain

$$G(\lambda,\Lambda,t) = \exp[\mathcal{Z}(\lambda,\Lambda,t)], \tag{H26}$$

where

$$\mathcal{Z}(\lambda,\Lambda,t) = \int_{-\infty}^t d\tau \ln \mathrm{Det}[g^{-1}(\tau=0) - \Sigma(\tau,\tau,\gamma(\tau))]. \tag{H27}$$

Here $g(\tau,\tau')$ and $\Sigma(\tau,\tau',\gamma(\tau))$ are matrices in $+,-$ superoperator indices and defined in the system space. This result for the GF was used in Eq. (209).

APPENDIX I: GRASSMANN ALGEBRA

Here we review some properties of the Grassmann algebra used in Appendix H. Fermion coherent states $|\eta\rangle$ are defined in terms of the vacuum state $|0\rangle$ (Negele and Orland, 1998)

$$|\eta\rangle = e^{c^\dagger\eta}|0\rangle = |0\rangle + c^\dagger\eta|0\rangle, \tag{I1}$$

$$\langle\eta| = \langle 0|e^{\eta^*c} = \langle 0| + \langle 0|\eta^*c, \tag{I2}$$

where η and η^* are two independent complex numbers. We consider a single degree of freedom. This can be generalized easily for several degrees of freedom for which, $|\eta\rangle = \exp(\Sigma_i\hat{c}_i^\dagger\eta_i)|0\rangle$.

Since coherent states are the eigenstates of the annihilation operator $c|\eta\rangle=\eta|\eta\rangle$ from Eq. (I1) we have

$$(\eta)^2 = (\eta^*)^2 = 0, \tag{I3}$$

which is a consequence of $c^2=(c^*)^2=0$. Also since c, $c^\dagger$ anticommute, it can be shown from the eigenvalue equations

$$\eta\eta^* + \eta^*\eta = 0. \tag{I4}$$

The independent variables η and η^* which satisfy Eqs. (I1) and (I3) are called Grassmann variables. Thus elements of the Grassmann algebra can be second-order polynomials at the most

$$f(\eta,\eta^*) = A + B\eta + C\eta^* + D\eta\eta^*, \tag{I5}$$

and the complex conjugate of a product of two elements is equal to the product of the conjugates written in the reverse order.

Using Eqs. (I1) and (I3), we can write the overlap between the two coherent states as

$$\langle \eta | \eta \rangle = 1 + \eta^* \eta = e^{\eta^* \eta}. \tag{I6}$$

Integration of the Grassmann variables is defined by

$$\int d\eta = \int d\eta^* = 0, \tag{I7}$$

$$\int d\eta \, \eta = \int d\eta^* \eta^* = 1. \tag{I8}$$

The differential elements $d\eta$ and $d\eta^*$ anticommute with each other. Using Eqs. (I1) and (I6)–(I8) it is straightforward to show that

$$\int d\eta \, d\eta^* e^{\eta^* \eta} | \eta \rangle \langle \eta | = 1, \tag{I9}$$

which is the closure relation for coherent states.

Differentials of the Grassmann variables are defined as

$$\frac{\partial}{\partial \eta} f(\eta, \eta^*) = B + D\eta^*, \quad \frac{\partial}{\partial \eta^*} f(\eta, \eta^*) = C - D\eta. \tag{I10}$$

This implies that

$$\frac{\partial}{\partial \eta} \frac{\partial}{\partial \eta^*} = - \frac{\partial}{\partial \eta^*} \frac{\partial}{\partial \eta}. \tag{I11}$$

Taking integral of $f(\eta, \eta^*)$ with respect to η or η^* and comparing with Eqs. (I11), we obtain the operator identities

$$\int d\eta = \frac{\partial}{\partial \eta}, \quad \int d\eta^* = \frac{\partial}{\partial \eta^*}. \tag{I12}$$

Using Eqs. (I7), (I8), and (I12), it is straightforward to see that for any $N \times N$ matrix A,

$$\int \mathcal{D}(\eta^* \eta) \exp\left(\sum_{ij} \eta_i^* A_{ij} \eta_j \right) = \text{Det}[A], \tag{I13}$$

where $\mathcal{D}(\eta^* \eta) = \Pi_i d\eta_i^* d\eta_i$.

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