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# Quantum transport, master equations, and exchange fluctuations

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We investigate to which extent a many-body Bloch-Redfield master-equation description of quantum transport is consistent with the exact generalized equilibrium conditions known as exchange fluctuation theorems. Thereby, we identify a class of master equations for which this is the case. Beyond this class, we find deviations which exhibit characteristic scaling laws as functions of the dot-lead tunneling, the interdot tunneling, and the temperature. These deviations are accompanied by an increase of lead energy fluctuations inherent in the Bloch-Redfield equation beyond a rotating-wave approximation. We illustrate our results with numerical data for a double quantum dot attached to four leads.

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## I. INTRODUCTION

Exchange fluctuation theorems are exact relations between probabilities for nonequilibrium transitions that start from a Gibbs state and reflect the time reversibility of the microscopic equations of motion [1,2]. Frequently they are expressed by the statistics of work performed at a system upon time-dependent parameter variation. A variant thereof concerns charge and heat exchange in quantum transport between leads [3–6] and can be verified experimentally [7–9]. Taylor expansion of these exchange fluctuation theorems at equilibrium provides relations between transport coefficients such as the Johnson-Nyquist relation [3,4,6].

Theoretical studies of quantum transport often rely on approximations such as perturbation theory in the tunneling between system and electron reservoirs to obtain a master-equation approach [10]. It has been demonstrated that a careless application of master equations may predict spurious currents at equilibrium [11] and thus may violate fluctuation theorems. The validity of exchange fluctuation theorems has been verified for master-equation descriptions of various specific situations [8,12–16]. Still the question arises whether any general statement for a whole class of master equations is possible.

A widely employed Markovian master equation for quantum systems weakly coupled to environmental degrees of freedom is provided by the Bloch-Redfield formalism [17]. Originally derived for dissipative quantum mechanics, it can be generalized straightforwardly to quantum transport, e.g., to coupled quantum dots in contact with electron reservoirs. Moreover, it is equivalent to various common master equations. In this work, we demonstrate that the Bloch-Redfield master equation is consistent with exchange fluctuation theorems only to some extent (it does not predict spurious equilibrium currents and maintains the Johnson-Nyquist relation), while it fully complies only after a rotating-wave approximation (RWA). Some previous results [12–15] emerge as limiting cases of our generic statements. Moreover, for the fluctuation theorem violation of the Bloch-Redfield equation, we predict a scaling behavior which we confirm by a numerical study.

## II. DOT-LEAD MODEL AND EXCHANGE FLUCTUATION THEOREM

We consider a transport setup of the type sketched in Fig. 1(a) and modeled by the Hamiltonian $H = H_S + V + \sum_\alpha H_\alpha$, where $H_S$ describes a central system, henceforth referred to as "quantum dots". Notably, in contrast to Refs. [1] and [18], our system Hamiltonian $H_S$ may contain Coulomb repulsion terms which in most quantum dots represent the largest energy scale. Thus, for the decomposition of the density operator, we will have to work in a many-body basis.

The other constituents of our system are leads modeled as free electrons with the Hamiltonian $H_\alpha = \sum_q \epsilon_{\alpha q} c_{\alpha q}^\dagger c_{\alpha q}$, where $c_{\alpha q}^\dagger$ creates an electron in mode $q$ of lead $\alpha$ with energy $\epsilon_{\alpha q}$. Initially the leads are in a Gibbs ensemble at a common temperature $T$, while the chemical potentials $\mu_\alpha$ are shifted from their equilibrium values $\mu_\alpha = 0$ by externally applied voltages. This implies the expectation values $\langle c_{\alpha q}^\dagger c_{\alpha' q'} \rangle = \delta_{\alpha\alpha'}\delta_{qq'} f(\epsilon_{\alpha q} - \mu_\alpha)$ with the Fermi function $f(x) = [\exp(\beta x) + 1]^{-1}$ and the inverse temperature $\beta = 1/k_B T$. Each lead $\alpha$ is tunnel coupled to one quantum dot $n_\alpha$ via a Hamiltonian $V_\alpha = \sum_q V_{\alpha q} c_{\alpha q}^\dagger c_{n_\alpha} + \text{H.c.}$, which is fully determined by the spectral density $\Gamma_\alpha(\epsilon) = 2\pi \sum_q |V_{\alpha q}|^2 \delta(\epsilon - \epsilon_{\alpha q})$. In our numerical calculations, we assume within a wide-band limit energy-independent couplings, $\Gamma_\alpha(\epsilon) \equiv \Gamma_\alpha$, while our analytical results are valid beyond.

For the computation of the stationary current and its low-frequency fluctuations, we employ the cumulant generating function [19] $Z(\boldsymbol{\chi}) = \lim_{t\to\infty} \frac{\partial}{\partial t} \ln\langle e^{i\boldsymbol{\chi}\cdot\boldsymbol{N}} \rangle$, which implicitly depends on the chemical potentials $\mu_\alpha$ [the vector components refer to the different leads, $(\boldsymbol{x})_\alpha \equiv x_\alpha$]. Its idea is to generate the lead electron number operator $N_\alpha$ via a derivative with respect to the counting variable $\chi_\alpha$, while the time derivative turns number cumulants into current cumulants. Taylor expansion of the generating function at $\boldsymbol{\chi} = \boldsymbol{\mu} = \boldsymbol{0}$ yields (particle) transport coefficients, i.e., derivatives of the current and its cumulants with respect to the applied voltages. In particular, $I_\alpha = (\partial Z/\partial i\chi_\alpha)|_{\boldsymbol{\chi}=\boldsymbol{\mu}=\boldsymbol{0}}$, the conductance $G_{\alpha,\beta} = -(\partial^2 Z/\partial i\chi_\alpha \partial\mu_\beta)|_{\boldsymbol{\chi}=\boldsymbol{\mu}=\boldsymbol{0}}$, while the zero-frequency

 

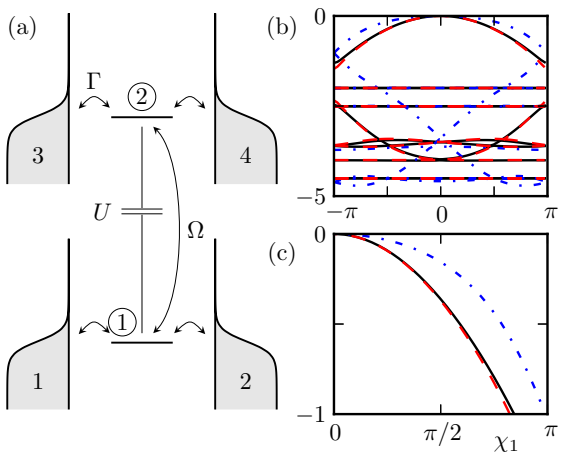


FIG. 1. (Color online) (a) Double quantum dot in contact with four leads, $\alpha = 1,\ldots,4$, used to exemplify our analytical results and the scaling of the deviations from the exact exchange fluctuation theorem (1). (b) Real part of the eigenvalues of the Liouvillians $\mathcal{L}_{\boldsymbol{\chi},0}$ (solid lines), $\mathcal{L}_{-\boldsymbol{\chi}-i\beta\boldsymbol{\mu},i\beta}$ (dashed lines, hidden by solid lines), and $\mathcal{L}_{-\boldsymbol{\chi}-i\beta\boldsymbol{\mu},0}$ (dash-dotted lines) [see Eq. (3)] as a function of the counting variable $\chi_1$ while all other $\chi_\alpha = 0$. The parameters are interdot tunneling $\Omega = 0.75\Gamma$, temperature $k_BT = 0.1\Gamma$, onsite energies $\epsilon_1 = 2\,\epsilon_2 = \Gamma$, and chemical potentials $\mu_1 = -\mu_2 = -\mu_3 = -\mu_4 = 0.25\,\Gamma$. (c) Enlargement of (b), revealing the slight difference between $\mathcal{L}_{\boldsymbol{\chi},0}$ and $\mathcal{L}_{-\boldsymbol{\chi}-i\beta\boldsymbol{\mu},i\beta}$.

limit of the current correlation function $\langle I_\alpha, I_\beta\rangle_{\omega\to 0}$ reads [20] $S_{\alpha\beta} = (\partial^2/\partial i\chi_\alpha \partial i\chi_\beta) Z|_{\boldsymbol{\chi}=\mathbf{0}}$.

Using an exact formal solution of the dot-lead dynamics, one can demonstrate that the cumulant generating function obeys the exchange fluctuation theorem [6],

$$Z(\boldsymbol{\chi}) = Z(-\boldsymbol{\chi} - i\beta\boldsymbol{\mu}). \tag{1}$$

Its practical use is to derive relations between different transport coefficients. To first order, $I_\alpha = 0$, while to second order, one obtains, e.g., the Johnson-Nyquist relation $2k_BTG_{\alpha,\alpha} = S_{\alpha\alpha}$. For a proof of Eq. (1), one introduces a counting variable $\xi$ for the total lead energy [5,6,21,22] to obtain the relation $Z(\boldsymbol{\chi},\xi) = Z(-\boldsymbol{\chi} - i\beta\boldsymbol{\mu}, -\xi + i\beta)$. Then one argues that provided that the energy of the central system is negligible, the total lead energy is conserved and, thus, $Z$ is independent of $\xi$. In the following, we explore up to which extent a Bloch-Redfield theory for quantum transport complies with this exact statement.

## III. BLOCH-REDFIELD MASTER EQUATION

Within second-order perturbation theory for the dot-lead tunnel coupling $V$, we obtain for the reduced system density operator $\rho$, the Markovian master equation [17] (for ease of notation, we set $\hbar = 1 = e_0$ and consider particle currents)

$$\dot\rho = -i[H_S,\rho] - \frac{1}{2}\int_{-\infty}^{+\infty} d\tau\, \mathrm{tr}_{\mathrm{leads}}\left\{V,\left[\tilde V(-\tau),\rho\otimes\rho_{\boldsymbol{\mu}}^{\mathrm{leads}}\right]\right\}, \tag{2}$$

where $\rho_{\boldsymbol{\mu}}^{\mathrm{leads}} \propto \exp[-\beta\sum_\alpha(H_\alpha - \mu_\alpha N_\alpha)]$ and $\tilde V$ is the interaction picture version of the tunnel Hamiltonian with respect to $H_S + \sum_\alpha H_\alpha$. In order to achieve this form, we have symmetrized the time integral. This corresponds to neglecting principal parts, which can be justified by renormalization arguments.

In order to obtain the generating function within the Bloch-Redfield approach, $Z_{\mathrm{BR}}$, we multiply in Eq. (2) the density operator by $\exp(i\boldsymbol{\chi}\cdot\boldsymbol{N} + i\xi\sum_\alpha H_\alpha)$, which yields $\dot\rho_{\boldsymbol{\chi},\xi} = \mathcal{L}_{\boldsymbol{\chi},\xi}\rho_{\boldsymbol{\chi},\xi}$ with the generalized Liouvillian

$$\mathcal{L}_{\boldsymbol{\chi},\xi} = -i[H_S,\rho] - \mathcal{D} + \sum_\alpha\left[e^{-i\chi_\alpha}\mathcal{J}_\alpha^{\mathrm{in}}(\xi) + e^{i\chi_\alpha}\mathcal{J}_\alpha^{\mathrm{out}}(\xi)\right], \tag{3}$$

where $\mathcal{J}_\alpha^{\mathrm{in/out}}$ describe dot-lead tunneling, while $\mathcal{D}$ subsumes all other dissipative terms. For vanishing counting variables, $\mathcal{L}_{\mathbf{0},0} = \mathcal{L}$, which is the physical Liouvillian. Since $\mathrm{tr}\,\rho_{\boldsymbol{\chi},\xi}$ is the moment generating function for the leads electron number, the current cumulant generating function reads $Z_{\mathrm{BR}}(\boldsymbol{\chi},\xi) = \frac{\partial}{\partial t}\ln\mathrm{tr}\,\rho_{\boldsymbol{\chi},\xi}$. In the long-time limit, the right-hand side (rhs) of this expression becomes identical to the eigenvalue of $\mathcal{L}_{\boldsymbol{\chi},\xi}$ with the smallest real part, which reduces the computation of current cumulants to an eigenvalue problem [19].

We cope with the interaction picture operator in the master equation (2) by decomposing the density operator into the many-body eigenstates of the quantum dots, $\{|a\rangle\}$, where $H_S|a\rangle = E_a|a\rangle$. Since the counting variables appear only in combination with the jump terms $\mathcal{J}_\alpha^{\mathrm{in/out}}$, we restrict the discussion to these terms. Their eigenbasis representation reads

$$\begin{aligned}\left[\mathcal{J}_\alpha^{\mathrm{in}}(\xi)\right]_{ab,a'b'} = {}& \tfrac{1}{2}\langle a|c_{n_\alpha}^\dagger|a'\rangle\langle b'|c_{n_\alpha}|b\rangle \\ & \times\left\{F_\alpha^<(E_a - E_{a'})e^{-i(E_a-E_{a'})\xi}\right. \\ & \left. + F_\alpha^<(E_b - E_{b'})e^{-i(E_b-E_{b'})\xi}\right\},\end{aligned} \tag{4}$$

with the lesser and greater lead correlation function [23,24] $F_\alpha^<(t) = \sum_q|V_{\alpha q}|^2\langle c_{\alpha q}^\dagger(0)c_{\alpha q}(t)\rangle = F_\alpha^>(t - i\beta)e^{\beta\mu_\alpha}$. Their Fourier representation in the wide-band limit reads $F_\alpha^<(\epsilon) = \Gamma_\alpha f(\epsilon-\mu_\alpha) = \Gamma_\alpha - F_\alpha^>(\epsilon)$, while the corresponding tunneling-out operators $[\mathcal{J}_\alpha^{\mathrm{out}}(\xi)]_{ab,a'b'}$ follow from the replacement $\{c_n, F^<(\epsilon)\} \to \{c_n^\dagger, F^>(-\epsilon)\}$. Notice the dependence on energy differences of the many-body states, $E_a - E_{a'}$. Only for noninteracting systems does this difference become a single-particle energy.

A rather important feature of the Bloch-Redfield master equation (2) is that in the absence of any bias voltage, i.e., for all $\mu_\alpha = \mu_0$, its stationary solution is the grand canonical state of the central system, $\rho_{\mathrm{eq}} \propto \exp[-\beta(H_S - \mu_0 N)]$. While within the RWA discussed below, this is quite obvious, the proof for the full master equation is more involved and can be found at the end of Appendix B. Moreover, our master equation is generally not of Lindblad form [25,26] so that it may violate the positivity of the reduced density operator. Studies of specific systems, however, indicate that generally this occurs only far from equilibrium and during a short transient stage at which the reduced dynamics is non-Markovian [27]. Therefore, we do not expect any problem of this kind as long as we stay close to the thermal state $\rho_{\mathrm{eq}}$. Let us also emphasize that there are cases such as a double quantum dot with small interdot tunneling and vanishing interaction in which a RWA leads

to significant deviations from the exact scattering solution, while a treatment beyond RWA yields the exact stationary current [28]. Thus it is essential to keep the non-RWA terms.

A first glance of the results derived below is provided by the spectra of $\mathcal{L}_{\boldsymbol{\chi},\xi}$, $\mathcal{L}_{-\boldsymbol{\chi}-i\beta\boldsymbol{\mu},-\xi+i\beta}$, and $\mathcal{L}_{-\boldsymbol{\chi}-i\beta\boldsymbol{\mu},\xi}$ at $\xi = 0$ [Figs. 1(b) and 1(c)]. One notices that the former and the latter clearly disagree, which demonstrates that for $Z_{\mathrm{BR}}$, it is not sufficient to consider only the number counting variable $\boldsymbol{\chi}$. Thus, $Z_{\mathrm{BR}}$ does not fulfill Eq. (1), i.e., the full Bloch-Redfield equation violates the exchange fluctuation theorem. When also the energy counting variable is substituted as $\xi \to -\xi + i\beta$, the difference between the spectra becomes significantly smaller, which indicates that the fluctuation theorem violation relates to the total lead energy.

### A. RWA master equation for many-body states

If, after an irrelevant transient stage, the density operator becomes practically diagonal in the energy basis, one may employ the RWA ansatz $\rho_{ab} = P_a\delta_{ab}$, where the populations $P_a$ obey $\dot{P}_a = \sum_{a'} w_{a\leftarrow a'} P_{a'}$. The transition rates $w_{a\leftarrow a'}$ consist of the tunnel-in contributions for each lead,

$$\begin{aligned} w^{\alpha,\mathrm{in}}_{a\leftarrow a'}(\boldsymbol{\chi},\xi) &= \left[\mathcal{J}^{\mathrm{in}}_{\alpha}\right]_{aa,a'a'} \\ &= |\langle a|c^{\dagger}_{n_\alpha}|a'\rangle|^2 e^{i\chi_\alpha} e^{-i(E_a-E_{a'})\xi} F^{<}_{\alpha}(E_a - E_{a'}), \end{aligned} \tag{5}$$

and the corresponding $w^{\alpha,\mathrm{out}}_{a\leftarrow a'}$. Adding both contributions and using the Kubo-Martin-Schwinger relation [23,24] $F^{<}_{\alpha}(\epsilon)e^{\beta(\epsilon-\mu_\alpha)} = F^{>}_{\alpha}(\epsilon)$, we find

$$w_{a'\leftarrow a}(\boldsymbol{\chi},\xi) = w_{a\leftarrow a'}(-\boldsymbol{\chi} - i\beta\boldsymbol{\mu}, -\xi + i\beta), \tag{6}$$

i.e., the substitution $\boldsymbol{\chi},\xi \to -\boldsymbol{\chi} - i\beta\boldsymbol{\mu}, -\xi + i\beta$ corresponds to the transposition of the RWA Liouvillian. Moreover, the $\xi$ dependence can be removed via the similarity transformation $w \to S^{-1}wS$ with $S_{a,a'} = \delta_{aa'}e^{iE_a\xi}$. Since both the transposition and the transformation with $S$ leave the spectrum unchanged, we can draw two conclusions for the generating function being the lowest eigenvalue: First, $Z_{\mathrm{RWA}}$ is $\xi$ independent, which implies that the lead energy is conserved in the long-time limit. Second, $Z_{\mathrm{RWA}}(\boldsymbol{\chi})$ fulfills Eq. (1).

The validity of the exchange fluctuation theorem relates to the local detailed balance condition [8,14–16] for the incoherent transitions between the states $|a\rangle$ and $|a'\rangle$ manifest in Eq. (6). Notice that the full Bloch-Redfield master equation contains coherent quantum oscillations and, thus, is beyond a description with transition rates.

### B. RWA class of master equations

The above statement about the Bloch-Redfield master equation in RWA can be applied also to master equations that are seemingly not of that form. Moreover, the cases of vanishing Coulomb interaction and of infinitely strong repulsion emerge as single-particle limits of our statements. In that sense, we can identify a whole "RWA class" of master equations for which Eq. (1) holds.

A most relevant case is a master equation for capacitively coupled but electrically isolated quantum dots, each modeled as single level. Owing to the lack of coherent tunneling, the Hamiltonian of this system is diagonal in the onsite basis, while no quantum coherence emerges. Thus, off-diagonal density-matrix elements vanish exactly, so that the resulting master equation in a localized basis assumes the form of the RWA limit of the Bloch-Redfield equation. Recently, the validity of the exchange fluctuation theorem has been exemplified for various particular situations of this kind [12–16]. They represent special cases of our generic statement.

Moreover, there are limits in which our many-body master equation becomes, in fact, a single-particle equation. This is naturally the case for very strong interdot Coulomb repulsion, such that, at most, one electron can enter the system. Then only eigenstates with one electron play a role and the energy differences in the jump operator (4) become single-particle energies. In the opposite limit of noninteracting electrons, the many-body states $|a\rangle$ are Slater determinants of single-particle states, while all $E_a$ are sums of single-particle energies, a case that has been considered, e.g., in Ref. [1]. Again only the single-particle energies appear in the decomposition of $\mathcal{J}$. We emphasize that genuine many-body effects or correlation effects typically emerge for intermediate interaction and, thus, are beyond those limits.

## IV. EXCHANGE FLUCTUATION THEOREM VIOLATION

### A. Charge fluctuations

Having seen that the full Bloch-Redfield equation violates the fluctuation theorem, we turn to a quantitative analysis of the deviations. To this end, we introduce as a measure the $(m+n)$th-order Taylor coefficients of the difference between the terms appearing in Eq. (1),

$$R^{\alpha_1\cdots\alpha_m}_{\beta_1\cdots\beta_n} = \frac{(-i)^m\partial^{m+n}}{\partial\chi_{\alpha_1}\cdots\partial\mu_{\beta_n}}\{Z_{\mathrm{BR}}(\boldsymbol{\chi}) - Z_{\mathrm{BR}}(-\boldsymbol{\chi} - i\beta\boldsymbol{\mu})\}|_{\boldsymbol{\chi}=\boldsymbol{\mu}=\mathbf{0}}, \tag{7}$$

which are constructed such that they vanish if the exchange fluctuation theorem (1) is fulfilled. Notice that $Z_{\mathrm{BR}}$ possesses also an implicit $\boldsymbol{\mu}$ dependence, so that generally the contribution of the first term does not vanish. Since, the rhs of Eq. (7) consists of derivatives of current cumulants evaluated at equilibrium $\boldsymbol{\mu} = \mathbf{0}$, the fact that $R^{\beta_1\cdots\beta_n}_{\alpha_1\cdots\alpha_m}$ must vanish provides a relation between transport coefficients [6]. For example, the mentioned Johnson-Nyquist relation is of second order and reads $R^{\alpha}_{\alpha} = 0 = \beta S_{\alpha\alpha} - 2G_{\alpha,\alpha}$. This rather important relation represents an interesting special case of Eq. (7) because it is fulfilled also by the full Bloch-Redfield equation beyond RWA, as we prove in Appendix B.

Before entering numerical calculations, we like to conjecture the scaling behavior of the deviations (7) as a function of (i) the incoherent tunnel rates $\Gamma$ and (ii) the coherent tunnel coupling $\Omega$. In each case, we depart from a limit in which the fluctuation theorem (1) is fulfilled, so that all $R$ indeed vanish. Concerning (i), we recall that the master equation (2) is based on a perturbation theory in the dot-lead coupling which cannot capture the Lorentzian broadening of the quantum dot resonance denominator $\propto (\epsilon^2 + \Gamma^2)^{-1}$. Thus, corrections to the exact equilibrium density matrix should be of the order of $\Gamma^2$. Moreover, since all transport coefficients inherit a prefactor $\Gamma$ from the jump operators [see Eq. (4)],

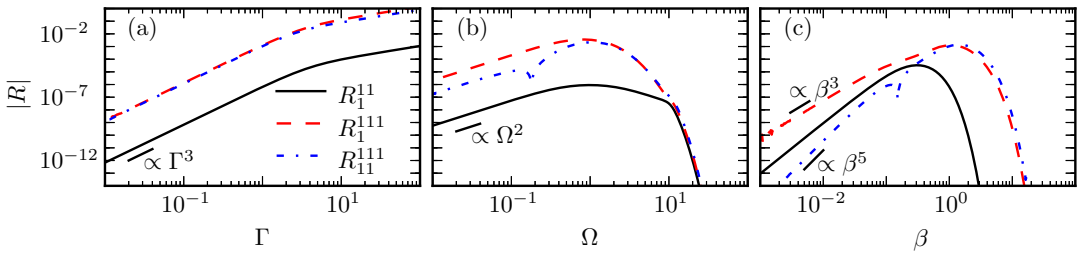


FIG. 2. (Color online) Violation of the exchange fluctuation theorem by the Redfield master equation beyond RWA for the double quantum dot sketched in Fig. 1(a) as a function of (a) the dot-lead coupling $\Gamma$, (b) the interdot tunneling $\Omega$, and (c) the inverse temperature $\beta = 1/k_B T$ for the parameters $\Gamma = 0.5\,\Omega = k_B T$ and $\epsilon_\alpha = \mu_\alpha = 0$. The scaling behavior verifies the conjecture (8) for the selected generalized Casimir-Onsager relations $R_1^{11} = 0$ (solid line), $R_1^{111} = 0$ (dashed line), and $R_{11}^{111} = 0$ (dash-dotted line).

we expect $R \propto \Gamma^3$. For case (ii), we notice that for $\Omega = 0$, no coherent tunneling is present and the full Bloch-Redfield falls into the RWA class identified above, so that the fluctuation theorem holds exactly. Since expectation values typically depend only on even powers of tunnel matrix elements, we anticipate deviations of the order of $\Omega^2$. Assuming that the deviations from $R = 0$ depend on the smaller of both parameters, we can conjecture the generic behavior

$$R \propto \begin{cases} \Gamma^3 & \text{for} \quad \Gamma \ll \Omega, \\ \Omega^2 & \text{for} \quad \Omega \ll \Gamma. \end{cases} \tag{8}$$

For the verification of this hypothesis for systems such as the one sketched in Fig. 1, we have to derive a numerical method for the computation of transport coefficients to high orders. For this purpose, we generalize an iteration scheme for the computation of current cumulants [29] to the computation of their derivatives with respect to the chemical potentials $\mu_\alpha$ and the presence of an energy counting variable $\xi$. The method is based on the fact that the transport coefficients are Taylor coefficients of the generating function in the variables $\chi_\alpha$, $\xi$, and $\mu_\alpha$, which can be computed iteratively by Rayleigh-Schrödinger perturbation theory; see Appendix A.

Figures 2(a) and 2(b) depict the scaling behavior of three different deviations as functions of $\Gamma$ and $\Omega$, which confirms the conjecture (8). In some particular cases, we found that $R$ vanishes even faster with small $\Gamma$ or $\Omega$ which means that Eq. (8) is a rather conservative estimate. For particular $R$'s (e.g., for $R_1^1$ as discussed above) or particular systems, the scaling may even be more favorable. As an example, we present, in Appendix C, results for the quadruple quantum dot.

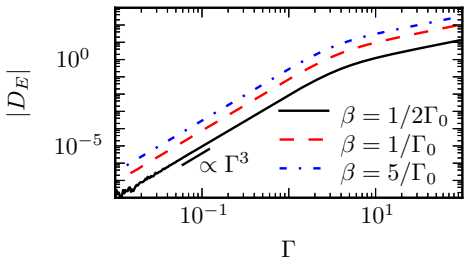


FIG. 3. (Color online) Fluctuations of the total lead energy manifest in the energy diffusion constant $D_E = \lim_{t\to\infty} \langle \Delta E^2_{\text{leads}} \rangle / t$ as a function of the dot-lead tunnel rate $\Gamma$ and various temperatures. The chemical potentials at the upper quantum dot are $\mu_1 = -\mu_2 = 3\,\Gamma$, while all other parameters are as in Fig. 2(a).

As a function of the temperature $k_B T = 1/\beta$, the deviations behave even more interestingly because they vanish in both the high-temperature and the low-temperature limit [see Fig. 2(c)]. For the high-temperature limit $\beta \to 0$, this is expected since the substitution $\xi \to -\xi + i\beta$, by and large, cures the fluctuation theorem violation, while being irrelevant for $\beta = 0$. Quantitatively, we find the scaling $R \propto \beta^3$ or even higher powers. For the experimentally rather relevant low-temperature limit $\beta \to \infty$, we find that the deviations turn rather rapidly to zero, but do not follow a power law. Once $k_B T \lesssim \Gamma/10, \Omega/10$, all deviations from $R = 0$ are already many orders smaller than the individual terms of $R$.

### B. Energy fluctuations

In the exact treatment, the total energy is conserved while the central system can only ingest a finite amount. Therefore, cumulants of the lead energy cannot grow indefinitely, so that the energy current cumulants must vanish [6]. For the RWA master equation, they vanish as well owing to the $\xi$ independence of the generating function; see discussion after Eq. (5). Beyond RWA, this need not be the case because the full Bloch-Redfield equation allows electrons to lose coherence while residing on the central system. Such coherence loss can cause transitions between states with different energy, e.g., between bonding and antibonding states. Therefore, the variance of the total lead energy might grow diffusively, as is confirmed by the results shown in Fig. 3. The scaling with the dot-lead rate is $\propto \Gamma^3$, i.e., equal to that of the generic deviations from $R = 0$. For the usual dot-lead models, this seems to be a consequence of the approximations underlying the Bloch-Redfield equation.

## V. CONCLUSIONS

By studying exchange fluctuation theorems for quantum transport, we have identified a class of master equations for which these theorems hold exactly. Equations of this class are characterized by an equivalence to a RWA master equation in a many-body basis, for which we proved the validity of the fluctuation theorem. The many-body aspect is rather crucial for the direct application to coupled quantum dots given that Coulomb interaction represents the largest energy scale in these systems. Interestingly, various previous studies [12–15] represent special cases of our more generic statements.

Despite that the RWA version of the Bloch-Redfield master equation obeys the fluctuation theorem (1) exactly and, thus, possesses a desirable formal property, it is not necessarily the preferential choice because coherences may be of the same order as the populations so that neglecting coherences may lead to even qualitatively wrong predictions [28]. Going beyond RWA, we quantified the degree of fluctuation theorem violation of the full Bloch-Redfield master equation, in particular its scaling behavior as a function of the coherent and the incoherent tunneling. Most important for the application of the Bloch-Redfield master equation to real experiments is the fact that at low temperatures, the discrepancies become rather tiny.

Even though our investigation already provides a general proof for the consistency of a whole class of master equations with exchange fluctuation theorems, two further generalizations seem desirable. On the one hand, one should consider also spin effects, which requires a refined treatment of time-reversal symmetry [16]. On the other hand, one may include quantum dissipation for which, in the absence of electron reservoirs, similar conclusions about the compliance of master equations with fluctuation theorems can be drawn [30], while for the combination of transport and dissipation, the fluctuation theorem holds at least to some extent [31].

## ACKNOWLEDGMENTS

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## APPENDIX A: ITERATIVE COMPUTATION OF TRANSPORT COEFFICIENTS

In order to compute transport coefficients, we adapt the method developed in Ref. [29] for the computation of current cumulants. It is based on two facts: First, for a master equation, the zero-frequency current cumulant generating function is given by the eigenvalue of the generalized Liouvillian $\mathcal{L}_\chi$ with the smallest real value, where $\chi$ is the counting variable [19]. Second, the cumulants are the Taylor coefficients appearing in the expansion of the generating function $Z(\chi)$. Since Rayleigh-Schrödinger perturbation theory [32] provides a series expansion of eigenvalues, it can be used to iteratively compute cumulants [29].

In our case, we have to generalize this method in two respects. On the one hand, we like to also compute energy exchange cumulants which requires additional counting variables $\xi_\alpha$ for each lead $\alpha$. On the other hand, we are interested in the transport coefficients, i.e., in a series expansion in the chemical potentials of the leads, $\mu_\alpha$, around their equilibrium value $\mu_0$ which we set to zero for ease of notation. While the formal aspects of the iteration scheme are the same as in its original version, the required series expansion of the Liouvillian in the variables $\boldsymbol{\chi}$, $\boldsymbol{\xi}$, and $\boldsymbol{\mu}$ is no longer that of a simple exponential.

Following the idea of Ref. [29], we start by writing the generalized Liouvillian (3) as a series in all these variables,

$$\mathcal{L}_{\boldsymbol{\chi},\boldsymbol{\xi},\boldsymbol{\mu}} = \mathcal{L} + \sum_\alpha \sum_{k,k',k''=0}^{\infty} \frac{i^{k+k'}}{k!\,k'!\,k''!} \mathcal{W}^\alpha_{k,k',k''} \chi_\alpha^k \xi_\alpha^{k'} \mu_\alpha^{k''}, \tag{A1}$$

with the Taylor coefficients $\mathcal{W}^\alpha_{0,0,0} = 0$ and $\mathcal{W}^\alpha_{k,k',k''} = \mathcal{W}^{\alpha,\mathrm{in}}_{k,k',k''} + \mathcal{W}^{\alpha,\mathrm{out}}_{k,k',k''}$, while for $k'' > 0$,

$$\mathcal{W}^{\alpha,\mathrm{out}}_{k,k',k''} = \partial_{i\chi_\alpha}^k \partial_{i\xi_\alpha}^{k'} \partial_{\mu_\alpha}^{k''} \mathcal{L}^{\mathrm{out}}_{\boldsymbol{\chi},\boldsymbol{\xi},\boldsymbol{\mu}}\big|_{\boldsymbol{\chi},\boldsymbol{\xi},\boldsymbol{\mu}=\mathbf{0}} = \int d\tau\; \partial_{i\xi_\alpha}^{k'} \partial_{\mu_\alpha}^{k''} F^>_\alpha(\tau - \xi_\alpha)\Big|_{\boldsymbol{\xi},\boldsymbol{\mu}=\mathbf{0}} \begin{cases} J^{\mathrm{out}}_{n_\alpha}(\tau) - D^{\mathrm{out}}_{n_\alpha}(\tau) & \text{for} \quad k = k' = 0 \\ J^{\mathrm{out}}_{n_\alpha}(\tau) & \text{else,} \end{cases} \tag{A2}$$

with the superoperators

$$J^{\mathrm{out}}_{n_\alpha}(\tau)\rho = \tfrac{1}{2}\{\tilde{c}_{n_\alpha}(-\tau)\rho c^\dagger_{n_\alpha} + c_{n_\alpha}\rho\tilde{c}^\dagger_{n_\alpha}(\tau)\}, \tag{A3}$$

$$D^{\mathrm{out}}_{n_\alpha}(\tau)\rho = \tfrac{1}{2}\{c^\dagger_{n_\alpha}\tilde{c}_{n_\alpha}(-\tau)\rho + \rho\tilde{c}^\dagger_{n_\alpha}(\tau)c_{n_\alpha}\}. \tag{A4}$$

The latter appear in the integrals that provide the jump operators and the dissipator, respectively, of the Liouvillian. $\mathcal{W}^{\alpha,\mathrm{in}}_{k,k',k''}$ follows from the substitution $\{c_n, F^>(t)\} \to \{c^\dagger_n, F^<(-t)\}$ and multiplication by a factor $(-1)^k$. Notice that no cross terms between different leads occur. Furthermore, we separate the Liouvillian into $\mathcal{L}\rho = -i[H_S,\,\rho] + \mathcal{L}^{\mathrm{in}}\rho + \mathcal{L}^{\mathrm{out}}\rho$ where $H_S$ refers to the system Hamiltonian, while $\mathcal{L}^{\mathrm{in}}$ and $\mathcal{L}^{\mathrm{out}}$ are the terms in the master equation (2) that contain the lead correlation functions $F^<$ and $F^>$, respectively.

The derivatives with respect to the heat counting variables $\xi_\alpha$ and the chemical potentials $\mu_\alpha$ act upon the lead correlation functions as

$$\frac{\partial^{k'}}{\partial(i\xi_\alpha)^{k'}} \frac{\partial^{k''}}{\partial\mu_\alpha^{k''}} F^>_\alpha(\tau - \xi_\alpha)\Big|_{\boldsymbol{\xi}=\boldsymbol{\mu}=\mathbf{0}} = \frac{\Gamma_\alpha}{2\pi} \int d\tau\; e^{-iE\tau} E^{k'} \frac{\partial^{k''}}{\partial\mu_\alpha^{k''}} [1 - f(E - \mu_\alpha)]\Big|_{\boldsymbol{\mu}=\mathbf{0}}, \tag{A5}$$

where we have restricted ourselves to the wide-band limit, $F^>_\alpha(\epsilon) = \Gamma_\alpha[1 - f(\epsilon - \mu_\alpha)]$, with the Fermi function $f(E - \mu) = \{\exp[\beta(E - \mu)] + 1\}^{-1}$. Its derivatives at equilibrium chemical potential can be expressed as a series,

$$\frac{\partial^{k''}}{\partial\mu^{k''}} f(E - \mu)\Big|_{\mu=0} = (-\beta)^{k''} \sum_{m=0}^{k''} (-1)^m m!\; S_{k'',m} \times [1 - f(E)]^m f(E), \tag{A6}$$

with $S_{k'',m}$ the Stirling numbers of the second kind [33]. To derive this formula, we start with the expression $\partial_x^n (e^x + 1)^{-1}$

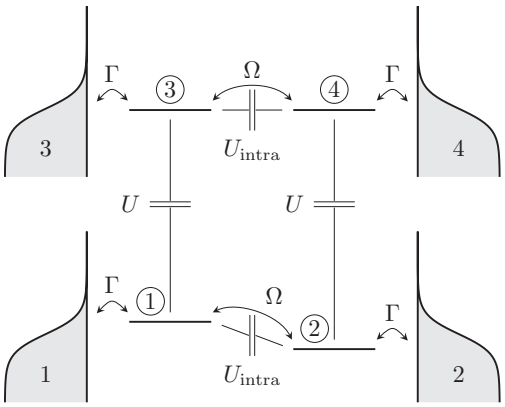


FIG. 4. Quadruple quantum dot in contact with four leads, $\alpha = 1,\ldots,4$. The system can be considered as two coupled transport channels, each formed by a double quantum dot and interacting capacitively with the other.

and employ Faà di Bruno's formula [34] for the derivative of nested functions. Exploiting a relation between Stirling numbers and partial Bell polynomials, $B_{n,k}(e^x,\ldots,e^x) = e^{kx}S_{n,k}$, yields

$$\frac{\partial^n}{\partial x^n}\frac{1}{e^x+1} = \sum_{k=0}^{n}(-1)^k k!\; S_{n,k}\frac{e^{kx}}{(e^x+1)^{k+1}}, \qquad \text{(A7)}$$

by which we immediately obtain the $n$th derivative of the Fermi function with respect to the chemical potential and, hence, the Taylor series (A6).

Finally, we end up with the eigenvalue problem $\mathcal{L}_{\boldsymbol{x}}\phi(\boldsymbol{x}) = \lambda(\boldsymbol{x})\phi(\boldsymbol{x})$, with $\boldsymbol{x} = \{\chi_1,\xi_1,\mu_1,\chi_2,\xi_2,\mu_2,\ldots\}$, which is equivalent to the one of Ref. [29] but with the additional perturbations $\boldsymbol{\xi}$ and $\boldsymbol{\mu}$. We are interested in the Taylor coefficients of the eigenvalue with the smallest real part,

$$\lambda(\boldsymbol{x}) = \sum_{\boldsymbol{n}}\frac{\lambda_{\boldsymbol{n}}}{\boldsymbol{n}!}(i\chi_1)^{n_1}(i\xi_1)^{n_2}\mu_1^{n_3}(i\chi_2)^{n_4}(i\xi_2)^{n_5}\mu_2^{n_6}\cdots, \qquad \text{(A8)}$$

where the factorial of the multi-index is defined as $\boldsymbol{n}! = n_1!\,n_2!\,n_3!\ldots$. Despite that the coefficients of $\mathcal{L}_{\boldsymbol{x}}$ now look more involved, the iteration scheme derived there can be adapted to the multiterminal case and the dependence on $\boldsymbol{\xi}$ and $\boldsymbol{\mu}$ straightforwardly, with the result that the transport coefficients $\lambda_{\boldsymbol{n}}$ follow from the recursion

$$\lambda_{\boldsymbol{n}} = \sum_{\boldsymbol{m}\neq\boldsymbol{0}}\binom{\boldsymbol{n}}{\boldsymbol{m}}\mathrm{tr}(\mathcal{W}_{\boldsymbol{m}}\phi_{\boldsymbol{n}-\boldsymbol{m}}), \qquad \text{(A9)}$$

$$\phi_{\boldsymbol{n}} = (\mathcal{Q}\mathcal{L}\mathcal{Q})^{-1}\sum_{\boldsymbol{m}\neq\boldsymbol{0}}\binom{\boldsymbol{n}}{\boldsymbol{m}}(\kappa_{\boldsymbol{m}}-\mathcal{W}_{\boldsymbol{m}})\phi_{\boldsymbol{n}-\boldsymbol{m}}, \qquad \text{(A10)}$$

with the initial condition $\lambda_{\boldsymbol{0}} = 0$ and $\phi_{\boldsymbol{0}} = \rho_{\rm eq}$. The superoperator $\mathcal{Q} = (\mathbb{1} - \rho_{\rm eq}\,\mathrm{tr})$ denotes the projector to the Liouville subspace orthogonal to the equilibrium density operator.

## APPENDIX B: JOHNSON-NYQUIST RELATION AND EQUILIBRIUM SOLUTION

Even though the Bloch-Redfield master equation beyond RWA does not fulfill the fluctuation theorem exactly, the resulting conductance $G_{\alpha,\alpha} = -\partial I_\alpha/\partial\mu_\alpha|_{\boldsymbol{\mu}=\boldsymbol{0}}$ and the zero-frequency noise $S_{\alpha\alpha} = \partial^2 Z/\partial\chi_\alpha^2|_{\boldsymbol{\chi}=\boldsymbol{\xi}=\boldsymbol{0}}$ at equilibrium nevertheless obey the Johnson-Nyquist relation $2G_{\alpha,\alpha} = \beta S_{\alpha\alpha}$. For a proof, we perform the iteration described above up to second order which yields the expressions

$$S_{\alpha\alpha} = \langle\mathcal{W}^\alpha_{2,0,0}\rangle + 2\langle\mathcal{W}^\alpha_{1,0,0}\mathcal{R}\mathcal{W}^\alpha_{1,0,0}\rangle, \qquad \text{(B1)}$$

$$G_{\alpha,\alpha} = -\langle\mathcal{W}^\alpha_{1,0,1}\rangle - \langle\mathcal{W}^\alpha_{1,0,0}\mathcal{R}\mathcal{W}^\alpha_{0,0,1}\rangle - \langle\mathcal{W}^\alpha_{0,0,1}\mathcal{R}\mathcal{W}^\alpha_{1,0,0}\rangle, \qquad \text{(B2)}$$

where the angular brackets denote the expectation value with respect to the grand canonical density operator of the central system, $\rho_{\rm eq} \propto e^{-\beta(H_S-\mu_0 N)}$. Notice that $\rho_{\rm eq}$ is the equilibrium solution of the Bloch-Redfield master equation (2), i.e., $\mathcal{L}\rho_{\rm eq} = 0$ if all lead chemical potentials are equal, $\mu_\alpha = \mu_0$; see remark at the end of this section. Here, $\mathcal{R} = -(\mathcal{Q}\mathcal{L}\mathcal{Q})^{-1}$ denotes the pseudoresolvent of the Liouvillian at zero frequency (i.e., $-\mathcal{R}$ is the pseudoinverse) with $\mathcal{Q} = (\mathbb{1} - \rho_{\rm eq}\,\mathrm{tr})$.

We proceed by showing that in Eq. (B2), the first two terms obey the relations $2\langle\mathcal{W}^\alpha_{1,0,1}\rangle = -\beta\langle\mathcal{W}^\alpha_{2,0,0}\rangle$ and $\mathcal{W}^\alpha_{0,0,1}\rho_{\rm eq} = -\beta\mathcal{W}^\alpha_{1,0,0}\rho_{\rm eq}$, respectively, while the last term vanishes, $\mathrm{tr}\,\mathcal{W}^\alpha_{0,0,1} = 0$. The latter relation follows from the fact that the trace condition of the Liouvillian is independent of the lead chemical potential, so that the corresponding Taylor expansion vanishes to all orders.

The proof for the other two relations is more involved. It is based on the Kubo-Martin-Schwinger relation for the lead correlation functions [23,24],

$$F^>_\alpha(t) = e^{-\beta\mu_\alpha}\,F^<_\alpha(t+i\beta), \qquad \text{(B3)}$$

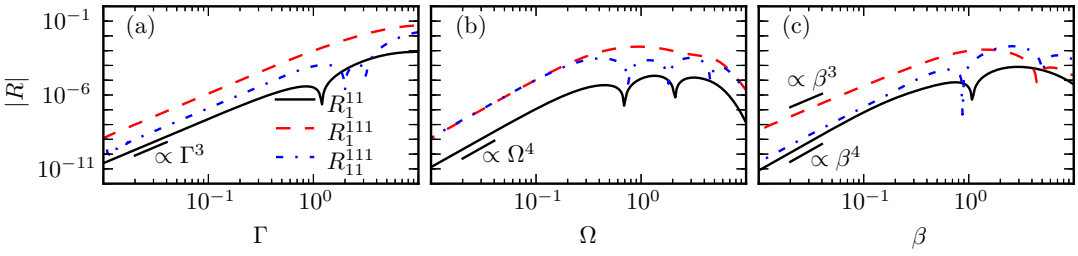


FIG. 5. (Color online) Deviation of the exchange fluctuation theorem for the quadruple quantum dot as a function of (a) the dot-lead coupling Γ, (b) the interdot tunneling Ω, and (c) the inverse temperature $\beta = 1/k_BT$ for the parameters $\Gamma = 0.5\,\Omega = k_BT = 10\epsilon_1 = -10\epsilon_2$ and $\mu_\alpha = 0$. The selected generalized Casimir-Onsager relations are those of Fig. 2, i.e., $R_1^{11} = 0$ (solid line), $R_1^{111} = 0$ (dashed line), and $R_{11}^{111} = 0$ (dash-dotted line).

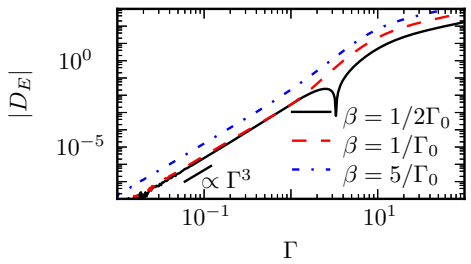


FIG. 6. (Color online) Diffusion constant $D_E = \lim_{t\to\infty} \langle \Delta E^2_{\text{leads}} \rangle / t$ of the total lead energy for the setup sketched in Fig. 4 as a function of the dot-lead tunnel rate $\Gamma \equiv \Gamma_\alpha$ and various temperatures. The chemical potential of leads 1 and 2 reads $\mu_1 = -\mu_2 = 3\,\Gamma$, while all other parameters are as in Fig. 5(a).

and a related detailed balance relation for the interaction picture operators,

$$\tilde{c}_{n_\alpha}(t) e^{-\beta(H_S-\mu_0 N)} = e^{\beta\mu_0} e^{-\beta(H_S-\mu_0 N)} \tilde{c}_{n_\alpha}(t - i\beta). \tag{B4}$$

The latter holds for fermionic annihilation operators in the interaction picture with respect to $H_S$, i.e., for any $\tilde{c}_{n_\alpha}(t) = e^{iH_S t} c_{n_\alpha} e^{-iH_S t}$ of the system, owing to the commutator $[N, c_{n_\alpha}] = -c_{n_\alpha}$. From this relation follow detailed balance relations for the jump operators,

$$D^{\text{in}}_{n_\alpha}(t)\rho_{\text{eq}} = e^{-\beta\mu_0} J^{\text{out}}_{n_\alpha}(-t - i\beta)\rho_{\text{eq}}, \tag{B5}$$

$$D^{\text{out}}_{n_\alpha}(t)\rho_{\text{eq}} = e^{\beta\mu_0} J^{\text{in}}_{n_\alpha}(-t - i\beta)\rho_{\text{eq}}, \tag{B6}$$

which we use to transform the superoperators appearing in $S_{\alpha\alpha}$.

We start with the tunnel-out contribution of the first term of Eq. (B2),

$$\text{tr}\, \mathcal{W}^{\alpha,\text{out}}_{1,0,1}\rho_{\text{eq}} = \text{tr} \int d\tau\, \frac{\partial}{\partial\mu_\alpha} F^{>}_\alpha(\tau) J^{\text{out}}_{n_\alpha}(\tau)\Big|_{\mu_\alpha=\mu_0} \rho_{\text{eq}}, \tag{B7}$$

insert Eqs. (B3), (B5), and (B6), and substitute the integration variable $\tau \to -\tau - i\beta$. Again we use that $\mathcal{W}^{\alpha,\text{out}}_{0,0,1}$ is trace free and obtain

$$\langle \mathcal{W}^{\alpha,\text{out}}_{1,0,1} \rangle = -\beta \langle \mathcal{W}^{\alpha,\text{in}}_{2,0,0} \rangle - \langle \mathcal{W}^{\alpha,\text{in}}_{1,0,1} \rangle. \tag{B8}$$

This relation, together with the corresponding expression for the tunnel-in term, $\langle \mathcal{W}^{\alpha,\text{in}}_{1,0,1} \rangle = -\beta \langle \mathcal{W}^{\alpha,\text{out}}_{2,0,0} \rangle - \langle \mathcal{W}^{\alpha,\text{out}}_{1,0,1} \rangle$, yields $\langle \mathcal{W}^{\alpha}_{1,0,1} \rangle = -(\beta/2) \langle \mathcal{W}^{\alpha}_{2,0,0} \rangle$, which links the first term of Eq. (B1) to the first term of Eq. (B2).

Following the same path for the second term, we find

$$\begin{aligned} \mathcal{W}^{\alpha,\text{out}}_{0,0,1}\rho_{\text{eq}} &= \int d\tau\, \partial_{\mu_\alpha} F^{>}_\alpha(\tau) \big[ J^{\text{out}}_{n_\alpha}(\tau) - D^{\text{out}}_{n_\alpha}(\tau) \big]\big|_{\mu_\alpha=\mu_0} \rho_{\text{eq}} \\ &= \big[ \mathcal{W}^{\alpha}_{1,0,1} - \beta \mathcal{W}^{\alpha,\text{in}}_{1,0,0} \big] \rho_{\text{eq}}, \end{aligned} \tag{B9}$$

as well as $\mathcal{W}^{\alpha,\text{in}}_{0,0,1}\rho_{\text{eq}} = (-\mathcal{W}^{\alpha}_{1,0,1} - \beta \mathcal{W}^{\alpha,\text{out}}_{1,0,0})\rho_{\text{eq}}$. Thus, also the second terms in Eqs. (B1) and (B2) differ only by a factor $\beta/2$, which completes our proof that the conductivity and the zero-frequency noise computed with the full Bloch-Redfield master equation (2) obey the Johnson-Nyquist relation $S_{\alpha\alpha} = 2k_B T G_{\alpha,\alpha}$.

Finally, let us remark that Eqs. (B3), (B5), and (B6) can be used to demonstrate that the grand canonical state of the central system, $\rho_{\text{eq}} \propto \exp[-\beta(H_S - \mu_0 N)]$, represents the equilibrium solution of the Bloch-Redfield master equation (2) both within RWA and beyond. Thus, $\mathcal{L}\rho_{\text{eq}} = 0$ and $\mathcal{L}_{\text{RWA}}\rho_{\text{eq}} = 0$, provided that no bias voltages are applied so that all lead chemical potentials are equal. As a further consequence, for both master equations, the current vanishes at equilibrium as expected.

## APPENDIX C: NUMERICAL RESULTS FOR A QUADRUPLE QUANTUM DOT

As a special system for which the deviations from the fluctuation theorem scale even more favorably than the behavior given by Eq. (7), we present numerical results for a quadruple quantum dot coupled to four leads, as is sketched in Fig. 4. The deviation from $R = 0$ as a function of the dot-lead coupling $\Gamma$ and the inverse temperature $\beta = 1/k_B T$ [Figs. 5(a) and 5(c)] is the generic one, i.e., $R \propto \Gamma^3$, while $R$ vanishes in the high-temperature limit $\propto \beta^3$ or faster. In the low-temperature limit $\beta \to \infty$, the deviations decay rapidly without following any power law. Also the variance of the lead energy behaves generically, as can be appreciated in Fig. 6. The main difference from the generic behavior is found as a function of the coherent interdot tunneling $\Omega$: We observe a decay $R \propto \Omega^4$, i.e., faster than the generic $\propto \Omega^2$ discussed in the main text.


[1] M. Esposito, U. Harbola, and S. Mukamel, Rev. Mod. Phys. **81**, 1665 (2009).
[2] M. Campisi, P. Hänggi, and P. Talkner, Rev. Mod. Phys. **83**, 771 (2011).
[3] J. Tobiska and Y. V. Nazarov, Phys. Rev. B **72**, 235328 (2005).
[4] D. Andrieux and P. Gaspard, J. Stat. Mech. (2006) P01011.
[5] K. Saito and A. Dhar, Phys. Rev. Lett. **99**, 180601 (2007).
[6] K. Saito and Y. Utsumi, Phys. Rev. B **78**, 115429 (2008).
[7] S. Nakamura, Y. Yamauchi, M. Hashisaka, K. Chida, K. Kobayashi, T. Ono, R. Leturcq, K. Ensslin, K. Saito, Y. Utsumi, and A. C. Gossard, Phys. Rev. Lett. **104**, 080602 (2010).
[8] Y. Utsumi, D. S. Golubev, M. Marthaler, K. Saito, T. Fujisawa, and G. Schön, Phys. Rev. B **81**, 125331 (2010).
[9] O.-P. Saira, Y. Yoon, T. Tanttu, M. Möttönen, D. V. Averin, and J. P. Pekola, Phys. Rev. Lett. **109**, 180601 (2012).
[10] S. A. Gurvitz and Ya. S. Prager, Phys. Rev. B **53**, 15932 (1996).
[11] T. Novotný, Europhys. Lett. **59**, 648 (2002).
[12] R. Sánchez, R. López, D. Sánchez, and M. Büttiker, Phys. Rev. Lett. **104**, 076801 (2010).
[13] G. Bulnes Cuetara, M. Esposito, and P. Gaspard, Phys. Rev. B **84**, 165114 (2011).
[14] D. S. Golubev, Y. Utsumi, M. Marthaler, and G. Schön, Phys. Rev. B **84**, 075323 (2011).
[15] G. Bulnes Cuetara, M. Esposito, G. Schaller, and P. Gaspard, Phys. Rev. B **88**, 115134 (2013).

[16] R. López, J. S. Lim, and D. Sánchez, Phys. Rev. Lett. **108**, 246603 (2012).
[17] A. G. Redfield, IBM J. Res. Develop. **1**, 19 (1957).
[18] M. Esposito, U. Harbola, and S. Mukamel, Phys. Rev. B **75**, 155316 (2007).
[19] D. A. Bagrets and Yu. V. Nazarov, Phys. Rev. B **67**, 085316 (2003).
[20] Ya. M. Blanter and M. Büttiker, Phys. Rep. **336**, 1 (2000).
[21] J. Ren, P. Hänggi, and B. Li, Phys. Rev. Lett. **104**, 170601 (2010).
[22] L. Nicolin and D. Segal, J. Chem. Phys. **135**, 164106 (2011).
[23] R. Kubo, J. Phys. Soc. Jpn. **12**, 570 (1957).
[24] P. C. Martin and J. Schwinger, Phys. Rev. **115**, 1342 (1959).
[25] G. Lindblad, Commun. Math. Phys. **48**, 119 (1976).
[26] V. Gorini, A. Kossakowski, and E. C. G. Sudarshan, J. Math. Phys. **17**, 821 (1976).
[27] P. Pechukas, Phys. Rev. Lett. **73**, 1060 (1994).
[28] F. J. Kaiser, M. Strass, S. Kohler, and P. Hänggi, Chem. Phys. **322**, 193 (2006).
[29] C. Flindt, T. Novotný, A. Braggio, M. Sassetti, and A.-P. Jauho, Phys. Rev. Lett. **100**, 150601 (2008).
[30] J. Thingna, J.-S. Wang, and P. Hänggi, J. Chem. Phys. **136**, 194110 (2012).
[31] T. Krause, G. Schaller, and T. Brandes, Phys. Rev. B **84**, 195113 (2011).
[32] J. J. Sakurai, *Modern Quantum Mechanics*, 2nd ed. (Addison-Wesley, Reading, 1995).
[33] I. M. Gradshteyn and I. S. Ryzhik, *Table of Integrals, Series, and Products*, 5th ed. (Academic, San Diego, 1994).
[34] W. P. Johnson, Am. Math. Monthly **109**, 217 (2002).