Finite-frequency counting statistics of electron transport: Markovian theory

D Marcos¹,³, C Emary², T Brandes² and R Aguado¹

¹ Departamento de Teoría y Simulación de Materiales, Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco 28049, Madrid, Spain
² Institut für Theoretische Physik, Hardenbergstrasse 36, TU Berlin, D-10623 Berlin, Germany
E-mail: david.marcos@icmm.csic.es

New Journal of Physics 12 (2010) 123009 (28pp)
Received 6 September 2010
Published 8 December 2010
Online at http://www.njp.org/
doi:10.1088/1367-2630/12/12/123009

Abstract. We present a theory of frequency-dependent counting statistics of electron transport through nanostructures within the framework of Markovian quantum master equations. Our method allows the calculation of finite-frequency current cumulants of arbitrary order, as we explicitly show for the second- and third-order cumulants. Our formulae generalize previous zero-frequency expressions in the literature and can be viewed as an extension of MacDonald’s formula beyond shot noise. When combined with an appropriate treatment of tunneling using, e.g., the Liouvillian perturbation theory in Laplace space, our method can deal with arbitrary bias voltages and frequencies, as we illustrate with the paradigmatic example of transport through a single resonant level model. We discuss various interesting limits, including the recovery of the fluctuation-dissipation theorem near linear response, as well as some drawbacks inherent to the Markovian description arising from the neglect of quantum fluctuations.
## 1. Introduction

Transport of electrons through nanoscopic conductors is a very powerful tool to learn about interactions and to characterize quantum systems [1]. Examples include the quantum Hall effect [2], weak localization [3] or universal conductance fluctuations [4]. Transport processes are governed by tunneling events, which are stochastic in nature. It is therefore natural to expect that the statistics of these tunneling events will be strongly influenced by interactions and quantum effects. Interestingly, these statistics, which can be analyzed by studying current fluctuations, contain a great deal of new information beyond that provided by dc transport [5, 6]. In particular, the second-order current correlation function (noise), can be used to determine the effective charge [7] and the statistics of the quasiparticles [8], and to reveal information on the transmission properties of the conductor [5]. Moreover, current correlations can be used to learn about entanglement [9, 10], quantum coherence [11] and the deep connection that exists with fluctuation theorems [12–14]. Further information can be gained from noise at high frequencies, which is valuable for extracting internal energy scales in systems such as quantum dots [15], spin-valves [16], Cooper pair boxes [17], diffusive wires [18] or chaotic cavities [19]. While most of the work on noise is theoretical (in particular at high frequencies), the field of noise and counting statistics is producing a great deal of experimental breakthroughs, including measurements of high-order cumulants [20–29]. Owing to this experimental progress, noise measurements at high frequencies, which until recently were scarce, are now possible [30–38].

A proper treatment of fluctuations in non-equilibrium transport is needed to address the problems listed above. While the list of theories available is too large to be given here, it is safe to say that they can be divided roughly into three families: the scattering approach [5, 39], the Keldysh Green’s functions method [40] and the various quantum master equation (QME) treatments [41] (for a recent overview of transport in this last context, see e.g. [42]).

### Acknowledgments

Appendix A. Derivation of frequency-dependent cumulants

Appendix B. Derivation of the self-energy

References

### Contents

1. **Introduction**  
2. **Theory**  
   2.1. Quantum master equation  
   2.2. Full counting statistics (FCS)  
   2.3. Finite-frequency full counting statistics  
   2.4. Finite-frequency cumulants  
   2.5. FCS of total and accumulated currents  
3. **Results**  
   3.1. Zero-frequency counting statistics  
   3.2. Finite-frequency counting statistics  
4. **Conclusions**  

References
A theory of counting statistics of electron transport was first formulated by Levitov and Lesovik [43] for non-interacting electrons using the scattering formalism, and later works enabled the treatment of interacting problems [44, 45]. QME approaches followed [46] and proved to be particularly useful for studying systems in the Coulomb blockade regime. Recent advances within this last scheme also involve studies of the counting statistics including non-Markovian dynamics [47]–[50].

In [51], we developed a method for calculating high-order current correlations at finite frequencies in the context of Markovian QMEs, and the aim of this paper is to significantly extend this work. We provide a detailed derivation of our multitime generating function, equation (27). We present a new approach for deriving finite-frequency cumulants from this expression, noting that only the stationary solution of the problem is required. We give analytical expressions for the second- and third-order current cumulants (noise and skewness, respectively). These results generalize previous zero-frequency expressions in the literature and recover the finite frequency shot noise expressions [52, 53] obtained using MacDonald’s formula [54]. Our method can thus be viewed as a generalization of this formula, as it allows us to obtain high-order spectra such as the frequency-dependent skewness (equation (35)). To illustrate the formalism we study the case of a single resonant level (SRL) model, and compare it with the exact solution and with the non-equilibrium version of the fluctuation-dissipation theorem (FDT), derived in various approaches, such as for tunnel junctions, or for the weak cotunneling regime in quantum dots [55]–[58].

The paper is organized as follows. In section 2 we present our formalism of finite-frequency cumulants in the context of Markovian QMEs. Subsections 2.1 and 2.2 are devoted to establishing the general framework of full counting statistics. In subsection 2.3, we derive a multitime cumulant generating function (CGF). Subsection 2.4 shows how to obtain finite-frequency cumulants of the current distribution. Here, exact equations for the frequency-dependent noise and skewness are given. We end this part with special emphasis on how to calculate the counting statistics of the ‘total’ and ‘accumulated’ currents (subsection 2.5). We explicitly show how both current correlations and charge correlations can be calculated. In section 3, we study the example of an SRL model, providing spectra for the frequency-dependent noise and skewness and a detailed comparison with the FDT, the finite-frequency version of the non-equilibrium FDT and the exact solution of the SRL model. First we focus on the zero-frequency case (subsection 3.1), where the general behavior of noise and skewness is presented as a function of different system parameters. In subsection 3.2 we extend this study to the finite-frequency case. Interestingly, we show that even though the theory does not contain quantum fluctuations, the Markovian limit is basically exact in transport configurations, level within the bias voltage window, as long as ℏω ≫ eV or ℏω ≪ eV. In intermediate situations, where ℏω ~ eV, or with the level outside the bias windows, the Markovian limit fails at finite frequencies due to its lack of quantum fluctuations. We also demonstrate that the noise spectra for particle currents and the ones for total currents significantly deviate from each other even for large asymmetric coupling to the leads, namely ΓR/ΓL ≠ 1. In section 4, we summarize our results. Most of the technical details and intermediate steps of the derivations in section 2 are discussed in detail in appendix A, where we also present a diagrammatic technique to arrive at the expressions for the cumulants shown in section 2.4. In appendix B, we describe how to calculate the kernel of the QME to lowest (sequential) order using perturbation theory in the Liouville space.
2. Theory

2.1. Quantum master equation

We are interested in phenomena that can be described by an equation of the type
\[ \dot{\rho}(t) = \mathcal{L}\rho(t), \]
where \( \mathcal{L} \) is the so-called Liouvillian, governing the evolution, and \( \rho \) is the density operator of the total system. Specifically, our theory will be useful for processes amenable to the counting of a classical stochastic variable \( n \), which can be, for example, the number of particles that have undergone a particular process in the system. We will focus in particular on transport systems, consisting of a central region, with a known set of many-body eigenstates \( \{|a\rangle\} \), and respective eigenenergies \( \{E_a\} \), attached to non-interacting electronic leads at different chemical potentials. This setup can be described by a Hamiltonian that takes the form \( \mathcal{H} = \mathcal{H}_S + \mathcal{H}_R + \mathcal{H}_T \), where \( \mathcal{H}_S \) and \( \mathcal{H}_R \) refer to the system and leads, respectively, and \( \mathcal{H}_T \) is the coupling between them. The different terms can be written as
\[ \mathcal{H}_S = \sum_a E_a |a\rangle\langle a|, \]
\[ \mathcal{H}_R = \sum_{\eta,\alpha} (\varepsilon_{\eta\alpha} + \mu_\alpha)c_{\eta\alpha}^+ c_{\eta\alpha}, \]
\[ \mathcal{H}_T = \sum_{\eta,\alpha,m} \mathcal{V}_{pam} c_{\eta\alpha}^+ d_m + \text{H.c.} \]

Here \( c_{\eta\alpha}^+ \) creates an electron with quantum numbers \( \eta \) in lead \( \alpha \), and \( d_m \) annihilates an electron from site \( m \) in the central region. \( \varepsilon_{\eta\alpha} \) are the eigenenergies of the electrons in the lead \( \alpha \), \( \mathcal{V}_{pam} \) is the coupling energy between a state in contact \( \alpha \) and the level \( m \) in the system, and \( \mu_\alpha \) is the chemical potential of lead \( \alpha \), which allows the system to be driven out of equilibrium.

Given the Hamiltonian, the full evolution can be written in terms of the Liouvillian by using the von Neumann equation
\[ \dot{\rho}(t) = -\frac{i}{\hbar} [\mathcal{H}, \rho(t)] \equiv \mathcal{L}\rho(t). \]

We are actually interested in the dynamics concerning the central system. We therefore trace out the reservoir degrees of freedom, arriving at an equation of motion for the reduced density operator, \( \rho_S(t) = \text{Tr}(\rho(t)) \), that, if we assume the dynamics of the reservoirs to be much faster than that of the central system, can be approximated as a Markovian master equation
\[ \dot{\rho}_S(t) = \mathcal{W}\rho_S(t), \]
where \( \mathcal{W} \) is a kernel driving the dynamics of the system. The charge flow through the conductor is governed by the stochastic hopping of electrons in and out of the central region. These processes are susceptible to classical counting and thus the reduced density operator can be unravelled into components \( \rho_S(n_\alpha, t) \), corresponding to having \( n_\alpha = \ldots, -1, 0, 1, \ldots \) extra electrons in lead \( \alpha \) [59, 60]. The kernel can also be split as \( \mathcal{W} = \mathcal{W}_0 + \sum_{\pm} \mathcal{W}_\pm^\alpha \), where \( \mathcal{W}_\pm^\alpha \) refers to the physical process in which one electron is created (+) or annihilated (−) at lead \( \alpha \),
and $\mathcal{W}_0$ corresponds to the part in which no tunneling processes take place in that lead. It can be shown that $\rho_S(n_\alpha, t)$ fulfills the equation (see e.g. [61]):

$$\dot{\rho}_S(n_\alpha, t) = \mathcal{W}_0 \rho_S(n_\alpha, t) + \mathcal{W}_\alpha^+ \rho_S(n_\alpha - 1, t) + \mathcal{W}_\alpha^- \rho_S(n_\alpha + 1, t),$$

valid provided that only single-particle tunneling processes occur. Although equation (7) focuses on the single counting at a particular lead $\alpha$, it can be generalized to account for tunneling processes of $k$ particles at the different system–reservoir junctions:

$$\rho_S(n_1, \ldots, n_M, t) = \mathcal{W}_0 \rho_S(n_1, \ldots, n_M, t) + \sum_{a, k, \pm} \mathcal{W}_{\alpha a k} \rho_S(n_1, \ldots, n_a \mp k, \ldots, n_M, t),$$

where $\mathcal{W}_0$ is the part in which the number of particles is not changed in the central region, $M$ the number of leads, and $k$ labels the process in which $k$ particles ‘jump’ at a time.

Unfortunately, solving equation (8) in $n$-space requires truncation to a certain $n$ and diagonalization of a tridiagonal matrix. It is therefore more convenient to solve it taking its Fourier transform. Multiplying (8) by $e^{i n_1 \chi_1} \cdots e^{i n_M \chi_M}$ and summing over $n_1, \ldots, n_M$, we obtain

$$\dot{\rho}_S(\chi, t) = \mathcal{W}(\chi) \rho_S(\chi, t).$$

Here the counting field $\chi$ refers implicitly to all counting fields, and we have defined $\rho_S(\chi, t) = \sum_{n_1, \ldots, n_M} e^{i n_1 \chi_1} \cdots e^{i n_M \chi_M} \rho_S(n_1, \ldots, n_M, t)$ and $\mathcal{W}(\chi) = \mathcal{W}_0 + \sum_{a, \pm} \mathcal{W}_{\alpha a}^\pm e^{\mp i \chi a}$. For a time-independent kernel, the solution to equation (9) is

$$\rho_S(\chi, t) = \Omega(\chi, t-t_0) \rho_S(\chi, t_0),$$

with the time-evolution operator $\Omega(\chi, t-t_0) := e^{\mathcal{W}(\chi)(t-t_0)}$.

### 2.2. Full counting statistics (FCS)

Importantly, knowledge of the system’s density operator resolved in $n$ allows us to obtain the FCS of the system, that is, the probability distribution $P(n_1, \ldots, n_M, t)$ of the number of electrons transmitted through the system–reservoir junctions. This is accomplished by noting that

$$P(n_1, \ldots, n_M, t) = \text{Tr} \{ \rho_S(n_1, \ldots, n_M, t) \}. $$

Transforming the probability distribution to the $\chi$-space, we have the moment generating function (MGF)

$$G(\chi, t) = \sum_n P(n, t) e^{i n \chi},$$

where now $n$ refers implicitly to $n_1, \ldots, n_M$. Using equation (10), one has

$$G(\chi, t) = \text{Tr} \{ \Omega(\chi, t-t_0) \rho_S(t_0) \} ,$$

an equation that was already derived by Bagrets and Nazarov [46]. The $N$th derivative of the MGF with respect to $\chi$ gives the $N$th moment of the distribution of the number of particles that have gone in or out a particular lead $\alpha$:

$$\langle n_\alpha^N(t) \rangle = \left. \frac{\partial^N G(\chi, t)}{\partial (i \chi)^N} \right|_{\chi \rightarrow 0} .$$

When equation (13) is used, averages with respect to the stationary state are established by taking $\rho_S(t_0) = \rho_S^{\text{stat}}$ (defined by $\mathcal{W}^{\text{stat}} = 0$). This means that counting will start at a time $t_0$ at
which the system has reached its steady state and therefore the fluctuations we study are around this state.

The moments of the current distribution can be calculated as

\[ \langle I^{N}_{\alpha}(t) \rangle = \frac{d}{dt} \langle n^{N}_{\alpha}(t) \rangle. \] (15)

This relation is important as it relates the stochastic variable \( n \) to the current of particles flowing through the system. Even though the current studied here is a classical variable, it contains quantum effects present in the system. In the formalism, these are inherited from the Liouvillian operator in equation (1). Generally, we are interested in the cumulants, rather than the moments, of the current distribution. These can be obtained from the derivatives of the CGF, defined by

\[ \mathcal{F}(\chi, t) := \ln G(\chi, t), \]

Therefore we have

\[ \langle I^{N}_{\alpha} \rangle_{c} = \frac{d}{dt} \frac{\partial^{N} \mathcal{F}(\chi, t)}{\partial (i \chi_{\alpha})^{N}} \bigg|_{\chi \rightarrow 0, t \rightarrow \infty}, \] (16)

where \( \langle \cdots \rangle_{c} \) denotes cumulant average [62] and the limit \( t \rightarrow \infty \) ensures that the average is performed in the stationary state. Also, note that the probability distribution itself can be obtained by inverse Fourier transform of the MGF.

From the \( \chi \)-independent kernel of the reduced QME (6), the \( \chi \) dependence leading to equation (9) can be actually introduced in a simpler way than resolving the density operator in \( n \) and taking the Fourier transform. As we describe in appendix B, it is enough to include counting fields in the appropriate tunneling terms of the kernel [63], and this procedure is fully equivalent to solving a generalized von Neumann equation

\[ \dot{\rho}(\chi, t) = -\frac{i}{\hbar} (\mathcal{H}^{+}(t) \rho(\chi, t) - \rho(\chi, t) \mathcal{H}^{-}(t)), \] (17)

in which the time evolution in the forward (+) and backward (−) Keldysh parts of the real-time axis is governed by different Hamiltonians [55], specifically \( \mathcal{H}_{\chi}^{\pm} = \sum_{\eta, \alpha, m} V_{\eta \alpha m} e^{\pm i \chi / 2} c_{\eta \alpha}^\dagger d_m + \text{H.c.} \). Tracing out the reservoir degrees of freedom in equation (17), one can get equation (9) and proceed to obtain the FCS of the system.

2.3. Finite-frequency full counting statistics

In this paper, we want to study correlations at finite frequencies, for which the scheme presented above has to be generalized. To this end, one needs to consider a joint probability distribution, \( P(n_1, t_1, \ldots, n_N, t_N) \), defined as the probability that \( n_1 \) electrons have undergone a particular process after a time \( t_1 \), \( n_2 \) electrons after a time \( t_2 \) and so on. Here, we focus for simplicity on a particular lead, and denote \( n \) as the number of particles transferred to (from) it, with associated counting field \( \chi \) (−\( \chi \)). It is straightforward to include processes at different leads.

The connection between this joint probability and the density operator (analogue to equation (11)) is not straightforward. To connect them we first need to specify a prescription for

---

4 In the following, all the averages will be taken with respect to this steady state. An average in the Liouville space will be therefore written as \( \langle A \rangle = \langle 0 | A | 0 \rangle \), where \( | 0 \rangle \) is the normalized stationary system density matrix (written as a vector), and \( t_\dagger \equiv \langle 0 | \) is the transposed trace vector that sums over the population degrees of freedom.

5 Throughout the paper we will use \( e \) (electron charge) = \( k \) (Boltzmann’s constant) = \( \hbar \) (Planck’s constant/\( 2\pi \)) = 1.

6 These ideas were already present in the early literature on finite-frequency shot noise in single-electron transistors in the context of classical Master equations.
the symmetrization of the cumulants and the probability distribution. This prescription actually depends on the detection scheme [64]–[66]. Here, we assume that ‘classical’ detection is carried out, so the detector is incapable of distinguishing emission from absorption. This means that the results we will present correspond to the fully symmetrized version of the power spectrum

\[ S^{(N)}(\omega_1, \ldots, \omega_N) := \int_{-\infty}^{\infty} dt_1 \ldots dt_N e^{-i\omega_1 t_1} \ldots e^{-i\omega_N t_N} T_S \langle I(t_1) \ldots I(t_N) \rangle, \]  

where \( T_S \) is the symmetrization operator that sums over all possible time (or frequency) switchings; that is, we have, for example, \( T_S \langle I(t_1) I(t_2) \rangle = \langle I(t_1) I(t_2) \rangle + \langle I(t_2) I(t_1) \rangle \).

The spectrum (18) can be derived from a \( N \)-time (symmetrized) CGF \( \mathcal{F}^{(N)} \), defined by

\[ e^{-\mathcal{F}^{(N)}[\chi, t]} = \mathcal{G}^{(N)}[\chi, t] := \sum_{n_1, \ldots, n_N} e^{i\omega_1 t_1 + \cdots + i\omega_N t_N} P^{(N)}[n, t], \]

where \( \chi := (\chi_1, \ldots, \chi_N)_T, \ t := (t_1, \ldots, t_N)_T \) and \( n := (n_1, \ldots, n_N)_T \); \( P^{(N)} \) refers to the symmetrized joint probability, \( \mathcal{G}^{(N)} \) to the multitime MGF and the subscript \( T \) to the transpose of a column vector. That is, we have

\[ S^{(N)}(\omega_1, \ldots, \omega_N) = \int_{-\infty}^{\infty} dt_1 \ldots dt_N e^{-i\omega_1 t_1} \ldots e^{-i\omega_N t_N} \partial_{\chi_1} \ldots \partial_{\chi_N} \mathcal{F}^{(N)}[\chi, t] \bigg|_{\chi = 0}. \]  

Using the property of the Fourier transform of a derivative, we obtain

\[ S^{(N)}(\omega_1, \ldots, \omega_N) = (i\omega_1) \ldots (i\omega_N) \int_{-\infty}^{\infty} dt_1 \ldots dt_N e^{-i\omega_1 t_1} \ldots e^{-i\omega_N t_N} \partial_{\chi_1} \ldots \partial_{\chi_N} \mathcal{F}^{(N)}[\chi, t] \bigg|_{\chi = 0}. \]  

Both the probability \( P^{(N)}[n, t] \) and the CGF \( \mathcal{F}^{(N)}[\chi, t] \) can be calculated from the density operator and the kernel \( W \) if we use the Markovian approximation in the coupling with the central system–reservoir coupling. Within that limit we have the evolution local in time given by (10) and also the factorization property

\[ P^>(n_1, t_1, \ldots, n_N, t_N) = P(n_1, t_1) P(n_2, t_2|n_1, t_1) \ldots P(n_N, t_N|n_{N-1}, t_{N-1}), \]  

where the symbol ‘\( > \)’ constraints the times to \( t_k > t_{k-1} \). Note that as we are considering the totally symmetric correlation function, we need to consider \( P^{(N)}[n, t] = T P^>(n_1, t_1, \ldots, n_N, t_N) \), where \( T \) is the time-ordering operator [51]. \( P(n, t|n', t') \) is the conditional probability of counting \( n \) electrons after time \( t \) provided that we counted \( n' \) electrons after time \( t' \), and can be computed as

\[ P(n, t|n', t') = \frac{\text{Tr}\{\Omega(n - n', t - t') \rho_S(n', t')\}}{\text{Tr}\{\rho_S(n', t')\}}, \]  

where the normalization in the denominator accounts for the collapse of the state due to the measurement, as given by von Neumann’s projection postulate [67]. \( \Omega(n, t) \) is the propagator in \( n \)-space, that is,

\[ \rho_S(n, t) = \sum_{n'} \Omega(n - n', t - t') \rho_S(n', t'), \]  

and can be extracted from equation (8) or by inverse Fourier transform of the propagator in \( \chi \)-space:

\[ \Omega(n, t) = \int \frac{d\chi}{2\pi} e^{-in\chi} \Omega(\chi, t). \]
An expression for the joint probability distribution in terms of propagators can be then derived using (21) together with (22) and (23). Alternatively, it can be obtained using the Chapman–Kolmogorov property for Markovian evolutions, from which we have

\[ P(n_N; t_N) = \text{Tr} \sum_{n_1, \ldots, n_{N-1}} \Omega(n_N - n_{N-1}; t_N - t_{N-1}) \times \Omega(n_{N-1} - n_{N-2}; t_{N-1} - t_{N-2}) \ldots \Omega(n_1; t_1) \rho_S(t_0). \]  

(25)

As we also have \( P(n_N; t_N) = \sum_{n_1, \ldots, n_{N-1}} P^\rightarrow(n_1, t_1, \ldots, n_N, t_N) \), recalling that \( \rho_S(t_0) = \rho_S^{\text{stat}} \), we find

\[ P^{(N)}[n, t] = T \left( \prod_{k=1}^{N} \Omega(\nu_{N-k}, \tau_{N-k}) \right), \]  

(26)

where \( \nu_k := n_{k+1} - n_k \), \( \tau_k := t_{k+1} - t_k \) and \( (\bullet) := \text{Tr} \{ \bullet \rho_S^{\text{stat}} \} \). Transforming expression (26) to the \( \chi \)-space, we find the CGF

\[ \mathcal{F}^{(N)}[\chi, t] = \ln T \left( \prod_{k=1}^{N} \Omega(\tilde{\chi}_k, \tau_{N-k}) \right), \]  

(27)

where \( \tilde{\chi}_k := \sum_{i=N+1-k}^{N} \chi_i \). The structure in equation (27) is encountered in many branches of physics, such as statistical physics and field theory, where connected correlation functions are obtained by taking derivatives of the logarithm of the corresponding generating functional (the partition function, the \( S \)-matrix, etc). Note, in particular, the analogy with the partition function presented in [62].

2.4. Finite-frequency cumulants

Equation (27) permits us to obtain frequency-dependent current cumulants to arbitrary order. This was used in [51] to study the second and third cumulants in single and double quantum dot models. Explicit derivatives of (27) and the eigen-decomposition of the kernel were used then to that end. In this subsection, we show that only the stationary solution of the problem (solution to an algebraic equation) is needed for computing the finite-frequency current cumulants. We give analytical expressions (valid within the Markovian approximation) for the noise (second cumulant) and skewness (third cumulant) of the distribution of charge flowing through a conductor.

Let us decompose the Fourier transform in equation (18) into a set of Laplace transforms (defined as \( f(z) := \int_0^\infty dt \, e^{-zt} f(t) \)), and the cumulant averages in terms of moments (cf for example equation (2.8) of [62]). Doing so, we find\(^7\)

\[ S^{(1)\rightarrow}(z_1) = S^{(1)\rightarrow}_m(z_1), \]  

(28)

\[ S^{(2)\rightarrow}(z_1, z_2) = S^{(2)\rightarrow}_m(z_1, z_2) - \left( \frac{-1}{z_1} \right) \left( \frac{-1}{z_2} \right) \langle I \rangle^2, \]  

(29)

\^7 Note that equations (28)–(30) can also be derived if the derivatives of the CGF are decomposed in terms of derivatives of MGFs. For example, for \( N = 3 \) we have \( \mathcal{F}^{(3)} = g_1^{(3)} - g_1^{(3)} g_2^{(3)} - g_1^{(3)} g_1^{(2)} + 2g_1^{(3)} g_2^{(3)} g_3^{(3)} + 2g_1^{(3)} g_2^{(3)} g_3^{(3)} \), with \( f_i := \partial_{\chi_i} f \big|_{\chi_i = 0} \), \( f_{ij} := \partial_{\chi_i} \partial_{\chi_j} f \big|_{\chi_i, \chi_j = 0} \), and \( f_{ijk} := \partial_{\chi_i} \partial_{\chi_j} \partial_{\chi_k} f \big|_{\chi_i, \chi_j, \chi_k = 0} \).
\[
S^{(3)}(z_1, z_2, z_3) = S_{m}^{(3)}(z_1, z_2, z_3) - \left( \frac{-1}{z_1} \right) \langle I \rangle S_{m}^{(2)}(z_2, z_3) - \left( \frac{-1}{z_2} \right) \langle I \rangle S_{m}^{(2)}(z_1, z_3)
- \left( \frac{-1}{z_3} \right) \langle I \rangle S_{m}^{(2)}(z_1, z_2) + 2 \left( \frac{-1}{z_1} \right) \left( \frac{-1}{z_2} \right) \left( \frac{-1}{z_3} \right) \langle I \rangle^3.
\]

The notation \(\langle \cdot \rangle\) denotes the unsymmetrized correlated function corresponding to the time ordering \(t_N > \cdots > t_2 > t_1\). Symmetrization in the frequency space implies adding the part corresponding to negative \(z\) and summing over all the possible switchings of frequencies. The subscript \(m\) means moment. This can be obtained as

\[
S_{m}^{(N)}(z_1, \ldots, z_N) = z_1 \cdots z_N \partial_{\chi_1} \cdots \partial_{\chi_N} G^{(N)}[\chi, z] \bigg|_{\chi = 0},
\]

with \(z \equiv (z_1, \ldots, z_N)_{\mathcal{T}}\) and

\[
G^{(N)}[\chi, z] = \left( \prod_{k=1}^{N} \Omega(\tilde{\chi}_k, \tilde{z}_k) \right)^{\infty},
\]

and \(\Omega(\chi, z) \equiv [z - \mathcal{W}(\chi)]^{-1}\).

The advantage of having moment averages is that we can use a diagrammatic technique (see appendix A) to easily obtain the correlation functions. Symmetrizing \(S^{(N)}[z]\) and evaluating it at \(z = i\omega\) (where \(\omega \equiv (\omega_1, \ldots, \omega_N)_{\mathcal{T}}\), we find that \(S^{(N)}[\omega]\) is proportional to \(\delta(\omega_1 + \cdots + \omega_N)\), as required by time-translational invariance. Defining the jump superoperators \(J^{(1)}_{\chi} := [\mathcal{W}(\chi) - \mathcal{W}(\chi = 0)]\) and their derivatives \(J^{(n)}_{\chi} \equiv \partial_{\chi} J_{\chi} |_{\chi = 0}\), we arrive at the following expressions for the current, noise and skewness of the current distribution (cf appendix A for details):

\[
i I_{\text{stat}} = \langle J^{(1)}_{0} \rangle, \tag{33}
\]

\[
i^2 S^{(2)}(\omega) = \langle J^{(2)}_{0} \rangle + \langle J^{(1)}_{0} \Omega_0(i\omega) J^{(1)}_{0} \rangle + \langle J^{(1)}_{0} \Omega_0(-i\omega) J^{(1)}_{0} \rangle, \tag{34}
\]

\[
i^3 S^{(3)}(\omega, \omega') = \langle J^{(3)}_{0} \rangle + \langle J^{(2)}_{0} \Omega_0(i\omega) J^{(1)}_{0} \rangle + \langle J^{(2)}_{0} \Omega_0(-i\omega) J^{(1)}_{0} \rangle + \langle J^{(1)}_{0} \Omega_0(i\omega - i\omega') J^{(1)}_{0} \rangle + \langle J^{(1)}_{0} \Omega_0(-i\omega - i\omega') J^{(1)}_{0} \rangle
+ \langle J^{(1)}_{0} \Omega_0(i\omega') J^{(1)}_{0} \rangle + \langle J^{(1)}_{0} \Omega_0(-i\omega') J^{(1)}_{0} \rangle + \langle J^{(1)}_{0} \Omega_0(i\omega - i\omega') J^{(1)}_{0} \rangle + \langle J^{(1)}_{0} \Omega_0(-i\omega - i\omega') J^{(1)}_{0} \rangle,
\tag{35}
\]

where \(\Omega_0(\omega) := [z - \mathcal{W}(\chi = 0)]^{-1}\). These equations generalize the zero-frequency results found in [61] (cf their equations (7) and (8)) to finite frequencies (see appendix A for the zero-frequency limit of (33)–(35)). Results for higher-order cumulants can be similarly obtained.

In the frequency domain, the prescription \(\langle \cdot \rangle\) can be taken similarly, that is, \(z_N > \cdots > z_2 > z_1\), and finally symmetrize the result.

\[\text{New Journal of Physics 12 (2010) 123009 (http://www.njp.org/)}\]
The relation between cumulants and moments can be formally expressed more generally at the level of the generating function. To do this, one should follow the derivation by Kubo [62], making use of the property \(<\exp(\sum_i n_i \chi_i)\> = \exp\{\langle\exp(\sum_i n_i \chi_i)\> - 1\}\) in our context, arriving at a similar result to (7.25) of [62]. This allows for the calculation of frequency-dependent cumulants of the current distribution up to any order, reproducing in particular the results presented above. If a diagrammatic expansion in Liouvillian space is used [68]–[70], cumulant averages become particularly useful since one can then keep only connected diagrams as those contributing to the average, in a similar way to how this is done in quantum field theory.

2.5. FCS of total and accumulated currents

At finite frequencies, to have a theory consistent with current conservation it is essential to include the so-called displacement currents [5]. This point is of vital importance to reproduce correctly the noise spectra measured experimentally. Although our discussion has focused, by construction, on particle currents so far, we show here how to include the effect of displacement currents in our formalism.

Let us illustrate this point by considering a quantum well with two terminals (L and R) in contact with Fermi leads at different chemical potentials. There will be then a net current flowing through both terminals, but also, charge can ‘accumulate’ in the well for some time. Therefore charge conservation can be expressed as

\[ \dot{Q}(t) = I_L - I_R \equiv I_{\text{accum}}, \]

with \( Q \) being the charge in the well and \( I_L, I_R \) referring to the currents through the left and right contacts, respectively. \( \dot{Q} \) represents the displacement current, \( I_{\text{dis}} \), which can be partitioned as \( I_{\text{dis}} = (\alpha + \beta)I_{\text{dis}} = I_{\text{dis}}^R + I_{\text{dis}}^L \), where \( \alpha \) and \( \beta \) describe how the displacement current is divided between the right and left reservoirs (obviously \( \alpha + \beta = 1 \)). This partitioning allows us to write the current conservation as \( I_L - I_{\text{dis}}^L = (I_R + I_{\text{dis}}^R) = 0 \). Equivalently, \( I_{\text{tot}} = I_L - I_{\text{dis}}^L = I_R + I_{\text{dis}}^R = \alpha I_L + \beta I_R \), which is the so-called Ramo–Shockley theorem. In the simplest wide-band limit, the partition coefficients can be written in terms of tunnel rates only as \( \alpha := \Gamma_R/(\Gamma_L + \Gamma_R) \) and \( \beta := \Gamma_L/(\Gamma_L + \Gamma_R) \) [71] \(^9\), and this will be the partitioning we will use throughout the paper.

Experimentally, one can measure correlations of the current through the device by transport measurements [20, 21] or indirectly by studying the current through a charge sensor, such as a quantum point contact [22]–[24], which reveals whether the well is ‘charged’ or ‘uncharged’. The second method gives the statistics of the transport current only for very large bias voltages (unidirectional counting) but, in general, the time-dependent transport current and the charge statistics are different. Moreover, when the device itself is used as a detector, the difference between transport fluctuations and charge fluctuations leads to profound physical consequences. Unlike the inelastic backaction induced by current fluctuations of the detector [65], the one induced by charge fluctuations is the fundamental Heisenberg backaction associated with the measurement [73]. Both transport and charge fluctuations can be accounted for in our formalism by considering counting fields

\[ \chi_{\text{tot}} := \chi_L + \chi_R, \]

\(^9\) In this paper, we mean ‘total’ cumulant when a subscript is omitted.

\(^{10}\) In a Coulomb blockade model, the partition coefficients read \( \alpha = C_R/(C_L + C_R) \) and \( \beta = C_L/(C_L + C_R) \), where \( C_L, C_R \) are the capacitances of each barrier and we have neglected capacitive effects from the gate. See for instance [72].
\[ \chi_{\text{accum}} := \beta \chi_L - \alpha \chi_R, \]  

(38)

which lead to the respective jump operators

\[ \mathcal{J}_{X,L}^{(n)} \equiv \alpha^n \mathcal{J}_{X,L} + \beta^n \mathcal{J}_{X,R}, \]

\[ \mathcal{J}_{X,R}^{(n)} \equiv \mathcal{J}_{X,L}^{(n)} + (-1)^n \mathcal{J}_{X,R}^{(n)}, \]

(39)

(40)

where \( \mathcal{J}_{X,L} \) and \( \mathcal{J}_{X,R} \) refer to the two independent tunneling processes occurring at each barrier.

The ‘total’ cumulant through a two-terminal device can then be calculated performing derivatives of the CGGF with respect to \( \chi_{\text{tot}} \) defined in (37). This leads to expressions (33)–(35) with \( \mathcal{J}_0^{(n)} \) substituted by \( \mathcal{J}_{0,\text{tot}}^{(n)} \) everywhere. Also, the spectrum of charge fluctuations

\[ S_Q^{(N)}(\omega_1, \ldots, \omega_N) := \int_{-\infty}^{\infty} dt_1 \ldots dt_N e^{-i\omega_1 t_1} \ldots e^{-i\omega_N t_N} T_S(\mathcal{Q}(t_1) \ldots \mathcal{Q}(t_N)) \]

(41)

follows from

\[ S_Q^{(N)}(\omega) = \frac{\delta(i\omega_1 + \cdots + i\omega_N)}{(i\omega_1) \ldots (i\omega_N)} S_{\text{accum}}^{(N)}[\omega], \]

(42)

with \( S_{\text{accum}}^{(N)}[\omega] \) obtained from equations (33)–(35) upon the change \( \mathcal{J}_0 \rightarrow \mathcal{J}_{0,\text{accum}} \). For example, \( S_Q^{(2)}(\omega) = (1/\omega^2) S_{\text{accum}}^{(2)}(\omega) \). Note that for a capacitive conductor, due to the relation between charge and voltage, this charge noise is proportional to the voltage noise. Finally, the ‘left’ and ‘right’ cumulants can be computed with \( \mathcal{J}_0 \rightarrow \mathcal{J}_{0,L} \) and \( \mathcal{J}_0 \rightarrow \mathcal{J}_{0,R} \), respectively, in (33)–(35).

3. Results

To illustrate our method, we analyze the transport statistics of the prototypical example of spinless electrons passing through a SRL model. The system consists of a two-terminal conductor with a discrete energy level in the central region, and is described by the Hamiltonian

\[ \mathcal{H} = \varepsilon |1\rangle \langle 1| + \sum_{k, a \in L, R} (\varepsilon_{ka} + \mu_a) c^\dagger_{ka} c_{ka} + \sum_{k, a \in L, R} \mathcal{V}_{ka} c^\dagger_{ka} |0\rangle \langle 1| + \text{H.c.}, \]

(43)

where \( k \) is the momentum and \(|0\rangle\) and \(|1\rangle\) are the only two possible states (referring to empty and occupied level) due to Coulomb blockade, with respective energies 0 and \( \varepsilon \).

In the infinite bias limit (voltage \( V \) much larger than the other energy scales, excepting the bandwidth of the Fermi leads), the Hamiltonian (43) leads to the kernel

\[ \mathcal{W}(\chi) = \begin{pmatrix} -\Gamma_L & \Gamma_R e^{i\chi_R} \\ \Gamma_R e^{-i\chi_L} & -\Gamma_R \end{pmatrix} \]

(44)

expressed in the basis \(|0\rangle, |1\rangle\), and where \( \Gamma_a \equiv \Gamma_a(E) := 2 \pi \sum_k |\mathcal{V}_{ka}|^2 \delta(E - \varepsilon_{ka}) \) are the rates accounting for the system–reservoir coupling. Using (33)–(35), the simplicity of the model allows us to derive analytical results in this limit; for example, the current gives

\[ I_{\text{stat}} = \Gamma_L \Gamma_R/\Gamma, \]

where \( \Gamma := \Gamma_L + \Gamma_R \), and the ‘total’ noise expressed in terms of the Fano factor

\[ F^{(2)}(\omega) = \frac{\Gamma_L^2 + \Gamma_R^2 + (1 - 2\alpha\beta)\omega^2}{\Gamma^2 + \omega^2}. \]

(45)

New Journal of Physics 12 (2010) 123009 (http://www.njp.org/)
At finite bias voltages, the kernel in equation (44) is no longer valid. Among the various choices to calculate $\mathcal{W}(\chi)$ in this case, we use Schoeller’s approach [68]–[70] (cf appendix B), which allows us to calculate the Markovian kernel to the desired order (sequential tunneling in our case) without further uncontrolled approximations (such as the secular approximation). It is important to mention that the frequency-dependent shot noise of the SRL model can be solved exactly [74] and therefore one does not need to use the above approximations. However, to the best of our knowledge, a finite-frequency study for this model beyond shot noise is yet lacking. Here, we use the exact solution as a benchmark of the Markovian approximation in order to identify the regions of validity of our theory. This benchmark is important because most of the papers in the literature discussing shot noise in the context of QMEs make use of the Markovian approximation.

Another important check for the theory is to reproduce the FDT in the appropriate regimes. Near linear response, that is, for applied voltages $V$ much smaller than the temperature $T$, the low-frequency noise spectrum should follow the Johnson–Nyquist relation $S^{(2)} = 2kT G$ [75, 76], where $G$ is the dc conductance. This equilibrium FDT was later extended by Callen and Welton to include quantum fluctuations [77], relevant when the measured frequencies are larger than the temperature. The FDT takes then the form $S^{(2)}(\omega) = \hbar \omega \coth(\frac{\hbar \omega}{2kT}) G(\omega)$, where $G(\omega)$ is the ac conductance. This expression can be equivalently written in terms of the Bose–Einstein distribution $N_{BE}(\omega) \equiv 1/[\exp(\hbar \omega/kT) - 1]$, since $\coth(\frac{\hbar \omega}{2kT}) = 2N_{BE}(\omega) + 1 = N_{BE}(\omega) - N_{BE}(-\omega)$, and it becomes clear that the symmetrized noise, which we are considering here, contains both absorption and emission. Out of equilibrium, a fluctuation–dissipation relation can also be found for some particular cases, such as tunnel junctions [56, 57], or for quantum dots in the weak cotunneling regime [58]. For a two-terminal conductor driven out of equilibrium, the symmetrized noise spectrum takes the general form [5, 32, 78, 79]

$$S^{(2)}(\omega) = \hbar \omega \coth\left(\frac{\hbar \omega}{2kT}\right) \sum_n D_n^2 + \left[ \frac{(\hbar \omega + eV)}{2} \coth\left(\frac{\hbar \omega + eV}{2kT}\right) \right] \sum_n D_n (1 - D_n),$$

where $D_n$ is the transmission coefficient of the conduction channel $n$, and again we have ignored the spin of the electrons. This expression has various interesting limits. First, in the tunneling regime ($D_n \ll 1$), it gives the non-equilibrium fluctuation–dissipation theorem (NEFDT) as reported in [56, 57] for tunnel junctions:

$$S^{(2)}(\omega) = \frac{1}{2} \sum_{p=\pm} I_{stat}(eV + p\hbar \omega) \coth\left(\frac{eV + p\hbar \omega}{2kT}\right).$$

an expression that is also exact for quantum dots in the weak cotunneling regime [58], and whose zero-frequency limit $S^{(2)} = I_{stat} \coth(\frac{eV}{2kT})$ has been derived in the context of counting statistics [55]. For low voltages, $eV \ll kT$, equation (46) recovers the Callen and Welton equilibrium relation, and if also $\hbar \omega \ll kT$, it gives the Johnson–Nyquist FDT (thermal noise regime). Finally, if $eV \gg kT$, $\hbar \omega$ (shot noise regime), we find that $S^{(2)} = \zeta \Gamma$, where the coefficient $\zeta \equiv \sum_n D_n (1 - D_n)/\sum_n D_n$ is the Fano-factor.

11 For a non-symmetrized version of the noise spectrum through a two-terminal conductor cf, for example, [65].
Figure 1. Zero-frequency noise $S^{(2)}(\omega = 0)$ at finite voltage for the SRL model as a function of temperature. For comparison we also show the FDT, NEFDT and the exact solution. In the main figure, the level is within the bias window $\varepsilon = 0$. The inset shows a regime with the level outside the bias window $\varepsilon/eV = 5$. The rest of the parameters: $\Gamma_L/eV = \Gamma_R/eV = 0.1$. In the main figure, all the quantities coincide when $kT \geq eV$, as expected. In the inset, all fluctuations are thermal and therefore all quantities coincide in the whole range of temperatures. Typical physical units are $T \sim 10–100$ mK, $V \sim 10–100$ µV and $\Gamma \sim 10–100$ MHz.

In this section, we show the solution given by our theory for the SRL model, as well as how it recovers the FDT and NEFDT in the appropriate limits. By contrasting these results with the exact solution, we will be able to show that the Markovian approximation does not contain quantum fluctuations, thereby needing a non-Markovian approach to capture the physics of quantum noise [50]. It is therefore interesting to see to what extent the four results coincide, and in what regimes our Markovian approach is valid and recovers the proper physics. We will see that when $kT \gg eV$, $\hbar\omega$ the theory captures well both the exact solution and the FDT and NEFDT. Also, in transport configurations, with the level within the bias window, the Markovian approximation agrees well with the exact solution, reproducing in particular previous studies with $eV \gg kT$ [15]–[17], [80]. However, in a situation with level outside the bias window, the Markovian approach presented here does not capture quantum noise physics, an effect that we observe at high frequencies ($\hbar\omega \gtrsim kT, eV$). Although in this situation transport due to cotunneling processes becomes more relevant, the difference is due to the Markovian assumption as can be seen using a non-Markovian extension of the theory [50]. We also study the finite-frequency skewness of the current distribution as given by equation (35). This shows to be insensitive to thermal fluctuations near equilibrium, therefore revealing the ‘shot’ contribution in a situation in which thermal fluctuations dominate in the noise spectrum ($kT \gg eV, \hbar\omega$).
3.1. Zero-frequency counting statistics

Let us start by showing the zero-frequency noise spectra corresponding to the SRL model. Although this limit has already been studied in detail, a full comparison between our theory and the exact solution will help us to understand the finite-frequency case. Particularly important is the linear response regime, in which studies of this model are scarce. As mentioned before, in this regime the noise should exhibit thermal fluctuations in order to fulfill a fluctuation–dissipation relation, while the skewness, on the other hand, should go to zero as the voltage $V$ goes to zero [55]. Figure 1 shows how our calculation captures correctly the FDT, $S^{(2)} = 2kTG$, in the proximity of linear response, $kT \gtrsim eV$. For comparison, we also plot the zero-frequency limit of the NEFDT in equation (47), namely $S^{(2)} = I_{\text{stat}} \coth(eV/2kT)$ [55]. In the opposite regime, $kT \lesssim eV$, the Markovian approximation is larger than the exact solution, a discrepancy that can be understood as originating from the lack of cotunneling contributions in our calculation [70]. As expected, below $kT/eV \sim 1$ the FDT is not fulfilled. We can also see that the NEFDT, exact for tunnel junctions, for a two-terminal device performs quite badly when $kT \lesssim eV$, but correctly in the opposite limit. This failure of the NEFDT at low temperatures disappears when the level is outside the bias window. This is a low-current regime and thus a tunneling limit. The inset of figure 1 shows this situation, where all fluctuations are thermal and the four curves coincide in the whole range of temperatures. At finite frequencies we expect a
quantum noise step in the spectrum at frequencies $\hbar \omega \sim \varepsilon$, an effect that will be studied in the next subsection.

The behavior of the zero-frequency noise spectrum close to equilibrium with respect to $\varepsilon$ is shown in figure 2(a). Here we see how the FDT is fulfilled by our theory and the good agreement with the exact solution. We also plot the zero-frequency skewness, which although of small magnitude in the same scale, is non-zero in a situation where the noise spectrum is completely dominated by thermal fluctuations. This insensitivity of the skewness to temperature allows us to extract intrinsic correlation effects in near-equilibrium conditions. In figure 2(b), we show the same quantities as a function of voltage. Interestingly, the Markovian result coincides with the exact solution in the whole range of voltages. The FDT, however, starts to disagree with these for voltages $eV/\varepsilon \gtrsim 0.2$. As anticipated, the skewness vanishes as the voltage goes to zero. In figure 3(a), we plot noise and skewness as a function of $\varepsilon$ for increasing voltages. As the bias increases, the skewness (dashed lines) shows peaks evolving into plateaus at values of $\varepsilon$ corresponding to the chemical potentials of the reservoirs. This effect, which is due to non-equilibrium fluctuations, is completely masked in the noise (solid lines) even at the highest voltages due to thermal fluctuations. This is clearly seen in figure 3(b), where we show the same

**Figure 3.** (a) Increasing noise (black full lines going up) and skewness (red dashed lines going up) as a function of $\varepsilon$ for increasing voltages $eV/\hbar \Gamma_R = 1, 10, 20, 40, 60, 80, 100, 120$ (parameters $kT/\hbar \Gamma_R = 20$, $\Gamma_L/\Gamma_R = 1$). (b) Excess noise $S^{(2)}(V) - S^{(2)}(V = 0)$ and skewness versus $\varepsilon$ for increasing voltages.
Figure 4. Noise, FDT and NEFDT as a function of temperature for $\omega/eV = 10$. In the main figure the level is within the bias window $\varepsilon = 0$. The inset shows a regime with the level outside the bias window $\varepsilon/eV = 5$. The rest of the parameters: $h\Gamma_L/eV = h\Gamma_R/eV = 0.1$. In the main figure all quantities coincide when $kT \geq eV + \hbar\omega$. In the inset all fluctuations are thermal and, therefore, the shot noise and FDT coincide in the whole range of temperatures. When $kT \leq eV + \hbar\omega$, the NEFDT is above due to quantum fluctuations. The exact solution contains also corrections due to cotunneling processes, which are dominating in this regime.

comparison after subtracting thermal fluctuations from the noise value (excess noise defined as $S^{(2)}(V) - S^{(2)}(V = 0)$). Here, it is clear that at low detuning, $\varepsilon \lesssim eV/2$ (position of the peaks in the figure), and when $kT \gtrsim eV$, the skewness can reveal the ‘shot’ contribution, while this is masked by thermal fluctuations in the noise spectrum.

3.2. Finite-frequency counting statistics

To study the case of finite frequencies, we use our formulae (33)–(35) applied to the SRL model. In a situation with the level within the bias window, we find similar behavior to figure 1. However, now the NEFDT—equation (47)—is fulfilled for temperatures $kT \gtrsim eV + \hbar\omega$. This is shown in figure 4. Remarkably, at finite frequencies the Markovian approximation is basically exact in this direct transport regime. In the high-bias regime, $eV \gg \hbar\omega$, $kT$ we also find that the Markovian approximation agrees perfectly with the exact result (not shown), in accordance with previous studies [15]–[17], [80]. When the level lies outside the voltage window, the situation changes drastically (see the inset of figure 4). Here the Markovian approximation is no longer appropriate when $kT \lesssim eV + \hbar\omega$. Both the exact result and the NEFDT contain quantum fluctuations, while the Markovian calculation only captures the thermal contribution (and therefore fulfills the FDT). The exact solution presents a small structure at temperatures of the order of $\varepsilon$. This cannot be resolved with the NEFDT. As expected, when $kT \gtrsim eV + \hbar\omega$, all curves coincide.
Figure 5. $S^{(2)}$ near linear response ($eV/kT = 0.0005$) as a function of frequency. For comparison we also show the NEFDT (equation (47)) and the exact solution. $S^{(2)}(\omega)$ is flat for the whole range of frequencies, and coincides with the equilibrium FDT as expected. The NEFDT, however, disagrees with these two, showing also quantum fluctuations, which are absent in the Markovian noise spectrum. The quantum noise steps shown by the NEFDT are, however, at $\hbar\omega = 2\varepsilon$, in contrast to the exact solution, which shows steps at $\hbar\omega = \varepsilon$. This is due to the fact that the NEFDT works well for tunnel junctions, but does not capture partition noise. This becomes clear also from the saturation value at large frequencies, as described in the text. The rest of the parameters: $h\Gamma_L/kT = h\Gamma_R/kT = 0.05$. The inset compares the exact solution with the Markovian approximation for a different regime, namely $eV/kT = 25$. We see that while the Markovian limit is flat for all frequencies, the exact solution presents a dip at $\hbar\omega = \pm|\varepsilon \pm eV/2|$. The rest of the parameters: $\varepsilon = 0$, $h\Gamma_L/kT = h\Gamma_R/kT = 0.25$.

The general trends explained so far become more evident in figure 5, where we plot the noise and FDT near linear response as a function of frequency. Here the Markovian noise is always flat and equals $S^{(2)} = 2kT G$, whereas the NEFDT and exact solution lie above and show quantum noise steps. Let us start by considering the case $\varepsilon = 0$. In the whole range of frequencies, the Markovian approximation is basically exact in this situation of direct transport. The NEFDT shows the correct zero-frequency limit, since then the fluctuations are purely thermal. At high frequencies, however, the NEFDT converges to the Poisson value of a single barrier with tunneling rate $\tilde{\Gamma}/2$, where $\tilde{\Gamma} := (\Gamma_L + \Gamma_R)/2$ (cf $S^{(2)}_L$ in the plot). This is in agreement with the validity of equation (47) for a tunnel junction and in contrast with the exact solution, which contains partitioning, and therefore its $\omega \to \infty$ limit is $\tilde{\Gamma}/4$. In the case where the energy lies outside the bias window ($\varepsilon/kT = 5$ in the figure), transport is possible because of the finite temperature as well as due to quantum fluctuations. The Markovian noise only contains the former and is flat with frequency, while the exact result contains both and shows a quantum noise step centered at $\hbar\omega/kT = \varepsilon/kT = 5$. Although in this regime cotunneling contributions are important, the difference lies in the Markovian approximation, as can be seen using a non-Markovian extension of our theory [50]. The NEFDT shows in this situation a quantum noise step centered at $\hbar\omega = 2\varepsilon$. This discrepancy with respect to the exact solution can be understood.
Figure 6. (a) $S^2(\omega)$ and (b) $S^3(\omega, -\omega)$ for $eV / h \Gamma_R = 50$, $kT / h \Gamma_R = 20$ and $\varepsilon = 0$. The spectra for particle currents and for total currents significantly deviate from each other even for large asymmetry. The insets correspond to noise and skewness through the left barrier for $\Gamma_L / \Gamma_R = 10$.

in terms of the tunneling approximation leading to equation (47), which presents a step located at an effective chemical potential $2\varepsilon$. Again, the high-frequency limit coincides with that of $S^2_L$. The intermediate regime where $\hbar \omega \sim eV$ is studied in the inset. Here, we set $eV / kT = 25$ and observe flat behavior for the Markovian solution, whereas the exact solution presents a dip at $\hbar \omega = \pm |\varepsilon \pm eV/2|$ (coinciding with the position of the chemical potentials with respect to the energy level). This clearly illustrates how the Markovian approximation captures well the physics in the linear response regime and a direct transport configuration, but when the frequency is comparable to the applied bias, it fails to capture the quantum noise.

We now proceed to discuss the finite-frequency noise and skewness spectra of the total—and particle–current distribution. In the previous discussion, the Markovian noise was always flat as a function of frequency, something that is well known for symmetric systems ($\Gamma_L = \Gamma_R$) —see for instance [5]. In the case $\Gamma_L \neq \Gamma_R$, a proper partitioning of displacement currents (see the discussion in subsection 2.5) becomes essential as we will show next, and the way this is done significantly affects the spectrum. Figure 6(a) shows $S^2(\omega)$ in a transport configuration, $eV / h \Gamma_R = 50$ and $\varepsilon = 0$. As in the results shown previously, the total noise, spectrum is flat for a symmetric configuration. Interestingly, this flat behavior persists even when the system is made asymmetric ($\Gamma_L \neq \Gamma_R$). This is due to the current-partitioning model assumed here: $I_{\text{tot}} = \alpha I_L + \beta I_R$ with $\alpha = \Gamma_R / \Gamma$ and $\beta = \Gamma_L / \Gamma$. The noise spectrum corresponding to particle currents displays information about the rates; in contrast to the total noise, it shows a dip with half-width $2\Gamma$. In figure 6(b), we show the skewness along the representative direction.
our' = −ω. Interestingly, the skewness corresponding to the total current starts to develop a dip that shows the asymmetry of the system. The particle-current skewness presents similar behavior to the noise counterpart. However, for \((3 - \sqrt{5})/2 \leq \Gamma_L / \Gamma_R \leq (3 + \sqrt{5})/2\) it develops a minimum whose position depends on the value of the rates. In the asymmetric case, \(\Gamma_L \neq \Gamma_R\), the particle-current noise and skewness can even present different lineshapes. This can be seen contrasting the insets of figures 6(a) and (b). In the linear response regime, the curves for the noise look similar (not shown). The skewness, in contrast, goes to zero in magnitude and shows a structure that depends on temperature and that changes from a dip to a peak as \(\varepsilon\) is increased from zero to a finite value. In summary, we see that the spectra for total and particle currents differ significantly from each other even for large asymmetry. This means that the assumption of calculating noise spectra using particle currents only, used commonly in the literature, is flawed. Here we have assumed the current partitioning given by \(\alpha = \Gamma_R / \Gamma, \beta = \Gamma_L / \Gamma\). If the more simplistic partitioning \(\alpha = \beta = 1/2\) is assumed, the results for the total cumulants in the asymmetric case change drastically (not shown). In particular, the noise is then no longer flat but has a dip structure, and the skewness shows a peak around zero frequency.

4. Conclusions

In conclusion, we have developed a theory of frequency-dependent counting statistics of electron transport through nanostructures within the framework of Markovian quantum master equations. We have illustrated our method with calculations of noise and skewness in a single resonant level model at finite bias voltages and frequencies. By comparing with both the exact solution and the finite-frequency version of the NEFDT, equation (47), we have identified the regimes of validity of our Markovian theory at finite frequencies. In particular, we have shown that the Markovian limit is basically exact in transport configurations (level within the bias voltage window), as long as \(\hbar \omega \gg eV\) or \(\hbar \omega \ll eV\). In intermediate situations where \(\hbar \omega \sim eV\), or with the level outside the bias window, the Markovian limit fails at finite frequencies due to the lack of quantum fluctuations [50].

We have also discussed how the noise spectra for particle currents and for total currents significantly deviate from each other, even for large asymmetries \(\Gamma_R / \Gamma_L \neq 1\). This demonstrates that calculating spectra using particle currents only leads to incorrect results in general. Our method allows the calculation of finite-frequency current cumulants of arbitrary order, as we have explicitly shown for the second and third order cumulants, equations (34) and (35). These formulae generalize previous zero-frequency expressions and can be viewed as an extension of MacDonald's formula beyond shot noise. Recently, this has been extended to study the time-averaged shot noise spectrum in the presence of periodic ac fields [81, 82]. Interesting extensions of our study along these lines would allow us to study frequency-dependent high-order cumulants in nanostructures driven by time-dependent fields or, even more challenging, in systems showing non-trivial nonlinear dynamics such as self-sustained oscillations without external time-dependent driving [83].


12 Even without time-dependent driving, interacting nanostructures attached to biased leads may reach a dynamical state characterized by self-sustained current oscillations instead of evolving to a steady state.
we make use of this energy conservation inherited from the time-translational symmetry of
switchings. In this step we take into account that
the result. This means adding the expressions corresponding to all the possible frequency
change to 'physical' frequencies
\( \omega \). We have

\[ \chi_{m}(z) = \sum_{j} z^{j} \frac{\partial_{j} \Omega(\chi, z)}{\partial_{j} \Omega(\chi, z)} \]

where

\[ \chi_{m}(z) = \sum_{j} z^{j} \frac{\partial_{j} \Omega(\chi, z)}{\partial_{j} \Omega(\chi, z)} \]

and add the 'lesser' part (\( \eta \)) and 'greater' part (\( \eta \)) parts. Finally,
we find

\[ \lim_{\eta \to 0} \left( \frac{1}{i \omega + \eta} + \frac{1}{-i \omega + \eta} \right) = \lim_{\eta \to 0} \frac{2 \eta}{\omega^{2} + \eta^{2}} = 2 \pi \delta(\omega), \]

where \( \eta \to 0 \) is a small parameter coming from the 'greater' (\( > \)) or 'lesser' (\( < \)) parts. Finally, we make use of this energy conservation inherited from the time-translational symmetry of

\[ \text{Appendix A. Derivation of frequency-dependent cumulants} \]

Expressions (33)–(35) follow from derivatives of MGFs. Performing derivatives of (32), we find

\[ \langle I(z)^{n} \rangle = \frac{\partial^{n} \langle \Omega(\chi, z) \rangle_{0}}{\partial^{n} \Omega(\chi, z)} = z^{-n} \langle J_{n}^{(1)} \rangle, \]  

\[ S_{m}^{(2)}(z_{1}, z_{2}) = \langle z_{1} z_{2} \frac{\partial_{1} \partial_{2} \Omega(\chi_{2}, z_{2}) \Omega(\chi_{12}, z_{12})}{\partial_{1} \partial_{2} \Omega(\chi_{2}, z_{2}) \Omega(\chi_{12}, z_{12})} \rangle_{0} \]

\[ = \left( z_{1} z_{2} \right) \frac{\partial_{12} \Omega(\chi_{12}, z_{12})}{\partial_{12} \Omega(\chi_{12}, z_{12})} + z_{12} \frac{\partial_{1} \partial_{2} \Omega(\chi_{12}, z_{12})}{\partial_{1} \partial_{2} \Omega(\chi_{12}, z_{12})} \]

\[ = \left( z_{1} z_{2} \right) \frac{\partial_{12} \Omega(\chi_{12}, z_{12})}{\partial_{12} \Omega(\chi_{12}, z_{12})} + z_{12} \frac{\partial_{1} \partial_{2} \Omega(\chi_{12}, z_{12})}{\partial_{1} \partial_{2} \Omega(\chi_{12}, z_{12})} \]

\[ = \left( z_{1} z_{2} \right) \frac{\partial_{12} \Omega(\chi_{12}, z_{12})}{\partial_{12} \Omega(\chi_{12}, z_{12})} + z_{12} \frac{\partial_{1} \partial_{2} \Omega(\chi_{12}, z_{12})}{\partial_{1} \partial_{2} \Omega(\chi_{12}, z_{12})} \]

\[ = \left( z_{1} z_{2} \right) \frac{\partial_{12} \Omega(\chi_{12}, z_{12})}{\partial_{12} \Omega(\chi_{12}, z_{12})} + z_{12} \frac{\partial_{1} \partial_{2} \Omega(\chi_{12}, z_{12})}{\partial_{1} \partial_{2} \Omega(\chi_{12}, z_{12})} \]

\[ = \left( z_{1} z_{2} \right) \frac{\partial_{12} \Omega(\chi_{12}, z_{12})}{\partial_{12} \Omega(\chi_{12}, z_{12})} + z_{12} \frac{\partial_{1} \partial_{2} \Omega(\chi_{12}, z_{12})}{\partial_{1} \partial_{2} \Omega(\chi_{12}, z_{12})} \]

\[ = \left( z_{1} z_{2} \right) \frac{\partial_{12} \Omega(\chi_{12}, z_{12})}{\partial_{12} \Omega(\chi_{12}, z_{12})} + z_{12} \frac{\partial_{1} \partial_{2} \Omega(\chi_{12}, z_{12})}{\partial_{1} \partial_{2} \Omega(\chi_{12}, z_{12})} \]

where \( z_{ij} := z_{i} + z_{j}, z_{ijk} := z_{i} + z_{j} + z_{k} \). Next we use

\[ \Omega_{0}(z_{2})\Omega_{0}(z_{1} + z_{2}) = \frac{1}{z_{1}} \left[ \Omega_{0}(z_{2}) - \Omega_{0}(z_{1} + z_{2}) \right], \]

and add the 'lesser' part (\( \eta \)) corresponding to negative Laplace frequencies. At this point we change to 'physical' frequencies \( \omega := \omega_{2} + \cdots + \omega_{N}, \omega := \omega_{3} + \cdots + \omega_{N}, \) etc, and symmetrize the result. This means adding the expressions corresponding to all the possible frequency switchings. In this step we take into account that

\[ \lim_{\eta \to 0} \left( \frac{1}{i \omega + \eta} + \frac{1}{-i \omega + \eta} \right) = \lim_{\eta \to 0} \frac{2 \eta}{\omega^{2} + \eta^{2}} = 2 \pi \delta(\omega), \]

where \( \eta \to 0 \) is a small parameter coming from the 'greater' (\( > \)) or 'lesser' (\( < \)) parts. Finally, we make use of this energy conservation inherited from the time-translational symmetry of

**Acknowledgments**

We thank C Flindt for stimulating discussions, for his help in recovering the proper zero-
frequency limit of our theory and for a careful reading of the manuscript. We also thank
A Braggio, M Böttiker, T Novotný, M Wegewijs, S Kohler, J L F Barbón, M García
Pérez, B Wünsch and P Zedler for discussions. This work was supported by MEC-Spain
(grant no. FIS2009-08744) and Acción Integrada Spain–Germany grant no. HA2007-0086.
DM acknowledges funding from grant no. FPU AP2005-0720.
the cumulants. We then arrive at equations (33)–(35) used in the main text. Importantly, after frequency symmetrization one can realize that the first three cumulant formulae are equal to their moment counterparts.

A.1. Diagrams

Interestingly, the results (A.1)–(A.3) given above can be derived following a diagrammatic technique, similarly to how this is done with Feynman diagrams in the expansion of the partition function or the S-matrix. Similarly, we write the CGF in terms of a series expansion, either in the time domain or in the frequency space. To that end we expand each of the \( \chi \)-dependent propagators in the CGF as a Dyson series:

\[
\Omega(\chi, z) = \frac{1}{z - W(\chi)} = \Omega_0(z) \sum_{n=0}^{\infty} [J_\chi \Omega_0(z)]^n.
\]  

(A.6)

This suggests the use of diagrams of the form given in figure A.1(a). In the frequency domain\(^\text{13}\), these rules are

- For each bare propagator \( \Omega_0(\tilde{z}_i) \) in the expansion, we associate a line with a superscript \( \tilde{k} = \sum_{i=N+1-k}^{N} i \), where \( N \) is the order of the cumulant we want to obtain.
- For each jump operator \( J_\chi \) in the expansion, we associate an encircled cross with superscript \( \tilde{k} \).

The formula for the generating function to a given order can therefore be written diagrammatically. For example, to second order we have

\[
G(\chi, z) = T_S \text{Tr}\{(\Omega_0(\tilde{z}_1, \tilde{z}_2) + \Omega_0(z_2)) \rho_{\text{stat}}^{\tilde{k}} + \cdots) \\
\times (\Omega_0(z_1 + z_2) + J_\chi \Omega_0(z_1 + z_2)]^n \rho_{\text{stat}}^{\tilde{k}} \}.
\]  

(A.7)

We can then multiply the different terms using diagrams as described above. The multiplication of propagators implies joining them together. The result can be simplified using (A.4), and needs to be multiplied by \( z_1 z_2 \) (case \( N = 2 \)), coming from the Fourier transform of the time derivatives in the frequency domain. We finally need to take the average in the stationary state and symmetrize the result as dictated by \( T_S \).

With the diagrammatic approach we realize that the diagrams contributing to the final result can be arranged in tables (see figures A.1(b)–(d)). These reproduce the results given in

\(^{13} \) If we work in the time domain, it is enough to label the propagating lines with the corresponding times at the beginning and the end of each line (see figure A.1(a)).
Figure A.1. Diagrammatics to obtain the frequency-dependent cumulants. (a) Building pieces for the diagrammatic technique. A line is associated with a bare propagator, a cross with a jump operator, and a circle with the time dependence of $\mathcal{J}$ (term $(e^{ix} - 1)$ in the single-particle unidirectional tunneling case). Derivatives with respect to counting fields eliminate circles correspondingly. Diagrams can be simplified using rules like (A.8). (b) Diagrams for the noise. Reading this table we find the expression $2\Omega_0(\tilde{z}_1)\Omega_0(\tilde{z}_2)\mathcal{J}^{(1)}_0\Omega_0(\tilde{z}_2)\mathcal{J}^{(1)}_0\Omega_0(\tilde{z}_2)\mathcal{J}^{(1)}_0\Omega_0(\tilde{z}_2) + \Omega_0(\tilde{z}_1)\Omega_0(\tilde{z}_2)\mathcal{J}^{(1)}_0\Omega_0(\tilde{z}_2) + \Omega_0(\tilde{z}_1)\Omega_0(\tilde{z}_2)\mathcal{J}^{(1)}_0\Omega_0(\tilde{z}_2)$. (c) Diagrams for the second-order cross correlation $S^{(2)}_{LR}$. Reading this table, we find the expression $\Omega_0(\tilde{z}_1)\mathcal{J}^{(1)}_0\Omega_0(\tilde{z}_1)\Omega_0(\tilde{z}_2)\mathcal{J}^{(1)}_0\Omega_0(\tilde{z}_2) + \Omega_0(\tilde{z}_1)\Omega_0(\tilde{z}_2)\mathcal{J}^{(1)}_0\Omega_0(\tilde{z}_2) + \Omega_0(\tilde{z}_1)\Omega_0(\tilde{z}_2)\mathcal{J}^{(1)}_0\Omega_0(\tilde{z}_2) + \Omega_0(\tilde{z}_1)\Omega_0(\tilde{z}_2)\mathcal{J}^{(1)}_0\Omega_0(\tilde{z}_2)$. (d) Diagrams to derive the frequency-dependent skewness formula.
To arrive at an expression for the cumulant of order \( N \), write a table with \( N \) time (frequency) intervals and corresponding superscripts \( k \). The propagation of time will be taken from right to left.

Write all the possible diagrams having \( N \) crosses (jumps) distributed in the different intervals, with the constraint that the maximum number of crosses in each is set by the corresponding index \( k \). Diagrams with \( n \) jumps occurring at the same time have to be included as well. These crosses are enclosed together with a box, and contribute with the jump operator \( \mathcal{J}_0^{(n)} := \partial^n \mathcal{J} \big|_{\lambda=0} \).

Taking into account that jumps occurring in the same interval are indistinguishable and that each cross can be associated with one of the possible counting fields \( \chi_1, \ldots, \chi_k \) present in that interval, write the multiplicity of each diagram on the right.

Write the mathematical expression corresponding to each diagram (see figure A.1(a)) and sum the different terms evaluated at \( z = i \omega \).

Take the average in the stationary state and multiply by \( (-i)^N \). The resulting expression corresponds to the unsymmetrized (‘greater’, \( > \) moment of the number of particles.

Multiply by \( (i \omega_1) \ldots (i \omega_N) \). This gives the unsymmetrized moment of the current distribution.

Add the ‘lesser’ (\( < \)) part, that is, the expression corresponding to negative frequency.

Finally, symmetrize the result, adding all the possible switchings of frequencies. This gives the symmetrized moment of the current distribution. The result can be simplified using (A.4) and (A.5).

As mentioned above, explicit derivation gives the same result for the expressions of cumulants of the current distribution as those derived for the moments up to \( N = 3 \). To higher orders it is unknown for us if this property still holds or not. Expressions for the cross correlations, e.g. \( \mathcal{S}_{LR}^{(2)} := \langle I(t_1)I(t_2) \rangle \), between two (or more) stochastic processes, e.g. L and R, can also be derived with this technique. To this end we simply need to label each of the jumps occurring at L or R accordingly (see figure A.1(c)), having two types of jump operators, \( \mathcal{J}_L \) and \( \mathcal{J}_R \). Also, expressions for the total current \( (\alpha I_L + \beta I_R) \) or accumulated current \( (I_L - I_R) \) can be derived using the jump operators (39) and (40) in the diagrams.

A.2. Equivalent form

We can write down an equivalent form to expressions (33)–(56). This will allow us to obtain an analytical expression for their zero-frequency limit, which is not well defined in the form given above. To this end we make use of the projectors \( P := [0]\langle 0| \) and \( Q := \mathbb{1} - P \), where \( P \) projects onto the subspace spanned by the stationary state \([0]\rangle \equiv \rho_\text{stat}^{14} \); and we define the pseudo-inverse \( R_0(z) := Q \Omega_0(z) \), such that \( \Omega_0(z) = R_0(z) + P/z \). Making this change in (A.1)–(A.3) and symmetrizing the expression (including positive and negative frequencies), we obtain

\[
\begin{align}
\langle I(z) \rangle &= \delta(z) \langle \mathcal{J}_0^{(1)} \rangle, \\
i^2 \mathcal{S}^{(2)}(z_1, z_2) &= \delta(z_1 + z_2) \langle \mathcal{J}_0^{(2)} + \mathcal{J}_0^{(1)} R_0(z_1) + \mathcal{J}_0^{(1)} R_0(z_2) + \mathcal{J}_0^{(1)} \rangle.
\end{align}
\]

\( ^{14} \)The state \( \langle 0| \) denotes the left eigenvector of the Liouvillian. The tilde indicates that it is not the adjoint to \( |0\rangle \), since the Liouvillian is not Hermitian.

New Journal of Physics 12 (2010) 123009 (http://www.njp.org/)
\[ i^3 S^{(3)}(z_1, z_2, z_3) = \delta(z_1 + z_2 + z_3) \langle J_0^{(3)} \rangle + J^{(1)}_0 [R_0(z_1) + R_0(z_2) + R_0(z_3)] J^{(2)}_0 \]
\[ + J^{(2)}_0 [R_0(z_{12}) + R_0(z_{23}) + R_0(z_{13})] J^{(1)}_0 + J^{(1)}_0 [R_0(z_1 J^{(1)}_0 R_0(z_1) + R_0(z_{12}) + R_0(z_{13})] J^{(1)}_0 \]
\[ + J^{(1)}_0 R_0(z_2) J^{(1)}_0 [R_0(z_{12}) + R_0(z_{23})] J^{(1)}_0 + J^{(1)}_0 R_0(z_3) J^{(1)}_0 [R_0(z_{13}) + R_0(z_{23})] J^{(1)}_0 \]
\[ + z_1^{-1} \langle J^{(1)}_0 \rangle J^{(1)}_0 [R_0(z_{12}) - R_0(z_2) + R_0(z_{13}) - R_0(z_3)] J^{(1)}_0 \]
\[ + z_2^{-1} \langle J^{(1)}_0 \rangle J^{(1)}_0 [R_0(z_{12}) - R_0(z_1) + R_0(z_{23}) - R_0(z_3)] J^{(1)}_0 \]
\[ + z_3^{-1} \langle J^{(1)}_0 \rangle J^{(1)}_0 [R_0(z_{13}) - R_0(z_1) + R_0(z_{23}) - R_0(z_2)] J^{(1)}_0 \]. \tag{A.11} \]

Now we make use of the delta function to write \( z_2 = -z_1 \) in the noise expression and \( z_3 = -z_1 - z_2 \) in the skewness result. Performing the change of variables \( z_1 \rightarrow -i\omega, z_2 \rightarrow i\omega \) in the noise and \( z_1 \rightarrow -i\omega, z_2 \rightarrow i\omega - i\omega', z_3 \rightarrow i\omega' \) in the skewness, we obtain

\[ i L_{\text{stat}} = \langle J^{(1)}_0 \rangle, \tag{A.12} \]

\[ i^2 S^{(2)}(\omega) = \langle J^{(2)}_0 \rangle + J^{(1)}_0 R_0(i\omega) J^{(1)}_0 + J^{(1)}_0 R_0(-i\omega') J^{(1)}_0, \tag{A.13} \]

\[ i^3 S^{(3)}(\omega, \omega') = \langle J^{(3)}_0 \rangle + J^{(1)}_0 [R_0(-i\omega) + R_0(i\omega - i\omega') + R_0(i\omega')] J^{(2)}_0 \]
\[ + J^{(2)}_0 [R_0(-i\omega') + R_0(i\omega') + R_0(i\omega - i\omega')] J^{(1)}_0 \]
\[ + J^{(1)}_0 R_0(-i\omega) J^{(1)}_0 [R_0(-i\omega') + R_0(i\omega' - i\omega')] J^{(1)}_0 \]
\[ + J^{(1)}_0 R_0(i\omega - i\omega') J^{(1)}_0 [R_0(-i\omega') + R_0(i\omega')] J^{(1)}_0 \]
\[ + J^{(1)}_0 R_0(i\omega') J^{(1)}_0 [R_0(i\omega' - i\omega) + R_0(i\omega)] J^{(1)}_0 \]
\[ + (-i\omega)^{-1} \langle J^{(1)}_0 \rangle J^{(1)}_0 [R_0(-i\omega') - R_0(i\omega - i\omega') + R_0(i\omega' - i\omega) - R_0(i\omega') J^{(1)}_0 \]
\[ + (i\omega - i\omega')^{-1} \langle J^{(1)}_0 \rangle J^{(1)}_0 [R_0(-i\omega') - R_0(-i\omega) + R_0(i\omega') - R_0(i\omega')] J^{(1)}_0 \]
\[ + (i\omega')^{-1} \langle J^{(1)}_0 \rangle J^{(1)}_0 [R_0(i\omega' - i\omega) - R_0(-i\omega) + R_0(i\omega) - R_0(i\omega - i\omega')] J^{(1)}_0 \]. \tag{A.14} \]

The limit \( \omega \rightarrow 0 \) of these expressions is well defined, and they can therefore be used to check that the proper result is recovered in that limit.

A.3. Zero-frequency limit

As mentioned, expressions (A.12)–(A.14) are well behaved when \( \omega \rightarrow 0 \). The zero-frequency noise comes straightforwardly from (A.13) setting \( \omega = 0 \). For the skewness, this limit requires nevertheless noting that

\[ \lim_{\omega \rightarrow 0} [R_0(i\omega) - R_0(-i\omega)] = 2i \omega \partial_\omega R_0(i\omega) |_{\omega = 0}. \tag{A.15} \]
So the zero-frequency skewness can be written as
\[
i \Sigma^{(2)}(0, 0) = \langle \mathcal{J}_0^{(3)} + 3 \mathcal{J}_0^{(1)} R_0(0) \mathcal{J}_0^{(2)} + 3 \mathcal{J}_0^{(2)} R_0(0) \mathcal{J}_0^{(1)} \rangle
\]
\[+ 6 \mathcal{J}_0^{(1)} R_0(0) \mathcal{J}_0^{(1)} R_0(0) \mathcal{J}_0^{(1)} \rangle + 6 \langle \mathcal{J}_0^{(1)} \rangle \langle \mathcal{J}_0^{(1)} \partial_w R_0(0) \mathcal{J}_0^{(1)} \rangle.
\] (A.16)

Now, since \( \partial_w R_0(0) = R(0) R(0) \), we have
\[
i \Sigma^{(3)}(0, 0) = \langle \mathcal{J}_0^{(3)} + 3 \mathcal{J}_0^{(1)} R_0(0) \mathcal{J}_0^{(2)} + 3 \mathcal{J}_0^{(2)} R_0(0) \mathcal{J}_0^{(1)} \rangle
\]
\[+ 6 \mathcal{J}_0^{(1)} R_0(0) \mathcal{J}_0^{(1)} R_0(0) \mathcal{J}_0^{(1)} \rangle + 6 \langle \mathcal{J}_0^{(1)} \rangle \langle \mathcal{J}_0^{(1)} R_0(0) R_0(0) \mathcal{J}_0^{(1)} \rangle,
\] (A.17)

which is the zero-frequency limit found in [61].

**Appendix B. Derivation of the self-energy**

To calculate the kernel of equation (17), we follow the perturbative treatment by Schoeller and co-workers [68, 69]. Let \( \mathcal{L}_S \), \( \mathcal{L}_R \) and \( \mathcal{L}_T \) be the corresponding Liouvillians to (2)–(4). The last can be written in the form
\[
\mathcal{L}_T = -i \sum_{\eta, \alpha, m, \xi, p} V_{\eta \alpha m} G_{m}^{\xi p} J_{\eta \alpha}^{\xi p}(\chi),
\] (B.1)

where \( \xi = + (-) \) refers to the creation (annihilation) of particles in the leads, and \( G_{m}^{\xi p} \) and \( J_{\eta \alpha}^{\xi p}(\chi) \) are system and reservoir superoperators, respectively, that act on an operator \( A \) as
\[
G_{m}^{\xi p} A = \begin{cases} g_{m}^{\xi} A & \text{if } p = +, \\ -A g_{m}^{\xi} & \text{if } p = -, \end{cases}
\] (B.2)

\[
J_{\eta \alpha}^{\xi p}(\chi) A = \begin{cases} j_{\eta \alpha}^{\xi} (\chi) A & \text{if } p = +, \\ -A j_{\eta \alpha}^{\xi} (\chi) & \text{if } p = -, \end{cases}
\] (B.3)

where \( g_{m}^{\xi} \) and \( j_{\eta \alpha}^{\xi} \) are defined as
\[
g_{m}^{+} = \sum_{a a'} \langle a | d_{m} | a' \rangle | a \rangle \langle a' |,
\] (B.4)

\[
j_{\eta \alpha}^{+} (\chi) = e^{i \chi / \hbar \kappa_{\alpha}} / 2,
\] (B.5)

and \( g_{m}^{-} = (g_{m}^{+})^{\dagger}, \ j_{\eta \alpha}^{-} (\chi) = (j_{\eta \alpha}^{+} (\chi))^{\dagger} \). The index \( s_{\alpha} = \pm 1 \) is taken according to the sign convention for the current flow in lead \( \alpha \).

With this notation, the self-energy to order \( |\chi|^{2} \) reads [68]–[70]
\[
\Sigma^{(2)}(z, \chi) \rho_{S}(t_{0}) = \sum_{\eta, \alpha} \text{Tr}_{R} \left\{ V_{\eta \alpha m}^{\xi p} J_{\eta \alpha}^{\xi p}(\chi) \frac{-1}{z - \mathcal{L}_{S} - \mathcal{L}_{R}} V_{\eta' \alpha' m'}^{\xi' p'} J_{\eta' \alpha'}^{\xi' p'}(\chi) \rho(t_{0}) \right\}
\]
\[= \frac{1}{2\pi} \sum_{\eta, \alpha} \int_{-D}^{D} \frac{G_{m}^{\xi p}(\epsilon, \chi) G_{m}^{\xi p'}(\epsilon + i \lambda_{\alpha} - i \epsilon) | a \rangle \langle a | G_{m'}^{\xi p'}}{\epsilon_{D}^{\xi p} / kT} d\epsilon \rho_{S}(t_{0})
\]
\[= \sum_{\eta, \alpha} \left[ \frac{1}{2} \text{Tr}_{a m}^{\xi p}(\epsilon, \chi) G_{m}^{\xi p}| a \rangle \langle a | G_{m'}^{\xi p'}
\]
\[\times \left\{ \frac{1}{2} f (p(\lambda_{\alpha} + \xi \mu_{\alpha} - i \epsilon)) + \frac{ip}{2\pi} \phi (p(\lambda_{\alpha} + \xi \mu_{\alpha} - i \epsilon)) \right\} \rho_{S}(t_{0}),
\] (B.6)
where the summations run over all scripts, and $D$ is a high-energy cutoff set by the bandwidth of the Fermi leads—larger than the rest of the energy scales in the problem. In this expression, we have introduced a complete set of eigenstates of the system Liouvillian, $L_S |a\rangle = i\lambda_a |a\rangle$, and the definitions $f(x) := (e^{x/kT} + 1)^{-1}$ and

$$\Gamma_{a,m}^{\xi p'}(\epsilon, \chi) := \Gamma_{a,m}^{\xi}(\epsilon)e^{i\chi_\xi((p'-p)/2)}\lambda_a,$$

$$\phi(x) := \text{Re} \Psi\left(\frac{1}{2} + i\frac{x}{2\pi kT}\right) - \ln \frac{D}{2\pi kT},$$

being $\Gamma_{a,m}^{\xi}(\epsilon) \equiv \frac{2\pi}{\hbar} \sum_q V_{a,m} V_{a,m} \delta(\epsilon - \epsilon_{qa})$ (which we take to be independent of the energy $\Gamma_{a,m}^{\xi}(\epsilon) \approx \Gamma_{a,m}^{\xi}$), and $\Psi$ the digamma function. The self-energy (B.6) is important as it permits us to explore correctly the low bias limit ($eV \ll kT$) to sequential tunneling order. This self-energy is non-Markovian as the Markovian approximation has not been made up to this point. This can be made (together with the secular approximation) taking the limit $z \to 0$ of (B.6), and it is what has been used throughout the text.

References

[1] Kouwenhoven L P, Marcus C M, McEuen P L, Tarucha S, Westervelt R M and Wingreen N S 1997 Mesoscopic Electron Transport (NATO ASI Series E) (Dordrecht: Kluwer)

[2] Klitzing K V 1980 Phys. Rev. Lett. 45 494

[3] Anderson P W 1958 Phys. Rev. 109 1492

[4] Altshuler B L 1985 Pis'ma Zh. Eksp. Teor. Fiz. 41 530

[5] Blanter Y M and Büttiker M 2000 Phys. Rep. 336 1

[6] Nazarov Y V 2003 Quantum Noise in Mesoscopic Systems (NATO Science Series vol 97) (Dordrecht: Kluwer)

[7] Kane C L and Fisher M P A 1994 Phys. Rev. Lett. 72 724

[8] Henny M et al 1999 Science 284 296

[9] Beenakker C W J 2006 Proc. Int. School Phys. E Fermi vol 162 (Amsterdam: IOS Press)

[10] Klich I and Levitov L 2009 Phys. Rev. Lett. 102 100502

[11] Kiesslich G, Schöll E, Brandes T, Hohls F and Haug R J 2007 Phys. Rev. Lett. 99 206602

[12] Esposito M, Harbola U and Mukamel S 2009 Rev. Mod. Phys. 81 1665

[13] Saito K and Utsumi Y 1998 Phys. Rev. B 57 115429

[14] Förster H and Büttiker M 2008 Phys. Rev. Lett. 101 136805

[15] Aguado R and Brandes T 2004 Phys. Rev. Lett. 92 206601

[16] Braun M, König J and Martinek J 2006 Phys. Rev. B 74 075328

[17] Choi M S, Plastina F and Fazio R 2003 Phys. Rev. B 67 045105

[18] Nagaev K E 1998 Phys. Rev. B 58 4622

[19] Nagaev K E, Pilgram S and Büttiker M 2004 Phys. Rev. Lett. 92 176804

[20] Reulet B, Senzier J and Prober D E 2003 Phys. Rev. Lett. 91 196601

[21] Bomze Y, Gershon G, Shovkun D, Levitov L S and Reznikov M 2005 Phys. Rev. Lett. 95 176601

[22] Lu W, Ji Z, Pfeiffer L, West K W and Rimberg A J 2003 Nature 423 422

[23] Gustavsson S et al 2006 Phys. Rev. Lett. 96 076605

[24] Fujisawa T et al 2006 Science 312 1634
[67] Korotkov A N 2001 Phys. Rev. B 63 115403
[68] Schoeller H 2009 Eur. Phys. J. 168 179
[69] Leijnse M and Wegewijs M R 2008 Phys. Rev. B 78 235424
[70] Emary C 2009 Phys. Rev. B 80 235306
[71] Wang B, Wang J and Guo H 1999 Phys. Rev. Lett. 82 398
[72] Bruder C and Schoeller H 1994 Phys. Rev. Lett. 72 1076
[73] Young C E and Clerk A A 2010 Phys. Rev. Lett. 104 186803
[74] Averin D V 1993 J. Appl. Phys. 73 2593
[75] Johnson J B 1928 Phys. Rev. 32 97
[76] Nyquist H 1928 Phys. Rev. 32 110
[77] Callen H B and Welton T A 1951 Phys. Rev. 83 34
[78] Yang S E 1992 Solid State Commun. 81 375
[79] Büttiker M 1992 Phys. Rev. B 45 3807
[80] Gurvitz S A and Prager Y S 1996 Phys. Rev. B 53 15932
[81] Clerk A A and Girvin S M 2004 Phys. Rev. B 70 121303
[82] Wu B H and Timm C 2010 Phys. Rev. B 81 075309
[83] Sánchez D, Moscoso M, Bonilla L L, Platero G and Aguado R 1999 Phys. Rev. B 60 4489
   Kurth S, Stefanucci G, Khosravi E, Verdozzi C and Gross E K U 2010 Phys. Rev. Lett. 104 236801