Unified description of charge transfer mechanisms and vibronic dynamics in nanoscale junctions

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Abstract

We propose a general framework that unifies the description of counting statistics of transmitted (fermionic) charges as it is commonly used in the quantum transport community with the description of counting statistics of phonons (bosons). As a particular example, we study on the same footing the counting statistics of electrons transferred through a molecular junction and the corresponding population dynamics of the associated molecular vibrational mode. In the tunnel limit, non-perturbative results in the electron–phonon interaction are derived that unify complementary approaches based on rate equations or on the use of non-equilibrium Green functions.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The concept of counting statistics of transmitted charges as it was first defined and computed for non-interacting tunnel junctions by Levitov et al [1, 2] is based on an analogy between coherent electronic transport and quantum optics [3]. In both fields of research, the underlying electronic or photonic quantum field undergoes quantum fluctuations encoded in a fundamental quantity, namely the probability distribution $P(q)$ that $q$ charges are transferred through the junction or the stationary probability distribution $P(n)$ of detecting $n$ photons in the electromagnetic field, in a given amount of time.

This concept has proved to be a powerful one [4] by providing deep connections between the fields of molecular electronics [5] and quantum noise [6]. From a more fundamental point of view, the concept of counting statistics of transmitted charges drew the attention of the condensed matter community to the idea already present in quantum optics, that the quantum nature of transport mechanisms as well as the peculiar effects related to quantum mechanics are more generally encoded into correlation functions of the fields rather than into the mean value of a given observable.

Recently, ideas of measuring phonon shot noise have been reported in the literature [7], but interestingly, there is to our knowledge no work that considers both kinds of descriptions on the same footing. We thus assign the following goals to the present paper. The first is to provide such a general framework that unifies the description of counting statistics of transmitted (fermionic) charges as it is currently accepted in the field of quantum transport to the one of counting statistics of phonons (bosons) inherited from the quantum optics community. The next is to illustrate the fertility of such a framework by studying the concrete example of a quantum transport problem through an interacting nanoscale device. The corresponding issue is indeed relevant to the quantum transport community, where we can distinguish between two main approaches to derive the associated transport properties.

On the one hand, the study of single electron transistors has motivated theoretical investigations of sequential tunnelling of charges through local devices, in the presence of interactions with the electromagnetic environment [8] or with internal degrees of freedom (electron–electron or electron–phonon interactions). The corresponding theoretical framework based on rate equations with transition rates derived from the Fermi golden rule has been successfully applied in more recent works related to the problem of the Franck–Condon blockade [9] and observed experimentally in suspended carbon nanotubes [10]. In the presence of electron–phonon (e–ph) interactions, the obtained current versus voltage curves [11] exhibit characteristic patterns (satellite peaks at voltages of...
twice the phonon energy) due to the activation of tunnelling assisted by phonon emission, as well as a reduction of the low-bias conductance (Franck–Condon blockade). The underlying transport mechanism was shown to induce giant Fano factors for the fluctuations of the transmitted charges (current noise), when the vibrational population was driven far into the non-equilibrium regime [12]. The corresponding counting statistics of transmitted charges was derived for molecular junctions in [13, 14] and for nanoelectromechanical systems in [15].

On the other hand, the experimental works related to coherent transport through atomic chains [16] and molecular junctions [17] have driven a tremendous amount of theoretical work, based on the extensive use of the Keldysh non-equilibrium Green function formalism [18]. In both approaches based on model Hamiltonians [19–21] or on more sophisticated ab initio calculations [22–24], the conductance characteristics exhibit a jump at the inelastic threshold (vibrational) energy associated to the activation of tunnelling with the emission of a phonon, the sign of which is determined by the transmission coefficient of the junction. Such a feature is of great experimental interest in order to perform inelastic spectroscopy of the device [20] (spectroscopy of the vibrational modes, measurement of the e–ph coupling strength from the height of the jump of conductance). More recently, some theoretical works focused on the inelastic signatures of e–ph interactions on noise characteristics [25, 26] and on the full counting statistics of the transmitted charges in such a device as the result of a self-consistent competition of annihilation and creation channels [27–29]. The appearance of jumps in the derivative of the current noise versus voltage curves was shown to result from a competition mechanism between charge transfer through the junction and the dynamics of population of the local phonon mode. As an illustration, the full counting statistics (FCS) of transferred electrons and phonons are defined and computed exactly in the tunnel limit.

2. General framework

2.1. The model

In the following, we consider the simple model of a molecular junction (see figure 1) described by the Hamiltonian (in units $e = \hbar = k = 1$)

$$H = H_{\text{mol}} + \sum_{X=L,R} H_X + H_T. \quad (1)$$

In equation (1), the molecular system is encoded into the Hamiltonian $H_{\text{mol}} = (\omega_0 + \lambda \phi) \nu_0 + \omega_0 \nu_0^\dagger a^\dagger a$ that describes a single molecular (dot) level of energy $\omega_0$ interacting with a local phonon (vibrational) mode of energy $\omega_0$. The e–ph interaction is proportional to the electronic density operator $\nu_0 = d^\dagger d$ and to the vibronic position operator $\phi = a + a^\dagger$. It is characterized by the e–ph coupling strength $\lambda$. The second term in equation (1) is the Hamiltonian of non-interacting left (right) leads $H_{\text{L}}(R)$ both maintained under a symmetric potential drop $\mu_L = -\mu_R = V/2$. In such a system, charge might be transferred from the electrodes to the molecule by the tunnel Hamiltonian $H_T = (t_{\nu_0} \Psi^\dagger_L + t_{a^\dagger} \Psi^\dagger_R) d + \text{h.c.}$ that couples the dot level to the $X = L, R$ lead through the hopping term $t_{\nu_0}$. The typical energy scale corresponding to this charge transfer mechanism is given by the $X = L, R$ tunneling rate $\Gamma_X = |t_{\nu_0}|^2 / W$, where in the wide band approximation, the bandwidth $W = 1 / \pi \rho_0$ is inversely proportional to the flat density of states of the leads $\rho_0$.

Although simple, the model described by equation (1) exhibits a non-trivial phase diagram characterized by two competing energy scales [19], namely $\Gamma = \Gamma_L + \Gamma_R$ the total coupling strength to the leads and $\lambda^2 / \omega_0$ the e–ph coupling strength. In this paper, we concentrate on the regime of weak tunnelling for which $\Gamma \ll \lambda^2 / \omega_0$ is the smallest energy scale of the problem. In this regime, the e–ph interaction strongly normalizes electronic degrees of freedom and a non-perturbative approach in the e–ph coupling strength is needed.

We further perform a unitary Lang–Firsov (polaron) transformation [31] $U = e^{\theta_0 \nu_0 (a - a^\dagger)}$ in order to explicitly eliminate the e–ph interaction term from $H_{\text{mol}}$ by shifting the vibronic position operator $\phi$ ($g = \lambda / \omega_0$ is the dimensionless e–ph coupling strength). The obtained dual representation is then more adapted for perturbation calculations in leading orders of $\Gamma$, and the transformed Hamiltonian $\tilde{H} = U H U^\dagger$ now reads

$$\tilde{H} = \tilde{H}_{\text{mol}} + \sum_{X=L,R} \tilde{H}_X + \tilde{H}_T. \quad (2)$$

In equation (2), the Hamiltonian describing the molecular system $\tilde{H}_{\text{mol}} = \omega_0 \nu_0 + \omega_0 \nu_0^\dagger a^\dagger a$ does not couple any more
2. Counting statistics of electrons and phonons

The charge transfer mechanism in the molecular junction shown in figure 1 is a coherent, time dependent process involving tunneling of charges from the electrodes to the dot and energy exchange with the local phonon mode (emission and absorption of phonons). In the steady state, the electronic current (rate of charge transfer per unit of time) and the vibrational population are constant on average. However, both quantities might fluctuate in time. The most complete information about those fluctuations is encoded in the joint probability distribution $P(q, n)$, defined as the probability that $q$ charges are transferred through the junction and the number of phonons populating the mode has varied by an amount of $n$ quanta during the measuring time $t_0$ (this time is large enough to reach the stationary state). This quantity generalizes the notion of full counting statistics (FCS) of transmitted charges which is recovered by tracing out the vibrational degrees of freedom $P_\alpha(q) = \sum_{n=\infty} P(q, n)$. Similarly, one could obtain a phonon counting statistics by tracing out the electronic degrees of freedom $P_\alpha(n) = \sum_{q=\infty} P(q, n)$. In general, the joined distribution cannot be factorized due to the presence of e-ph correlations, i.e. $P(q, n) \neq P_\alpha(q)P_\alpha(n)$.

The aim of this paper is to provide a way of computing this joined distribution by treating electronic and vibronic fluctuations on the same footing. By analogy with the electronic case [1, 2, 32], we define the cumulant generating function (CGF) as the Fourier transform of the distribution $P(q, n)$, namely

$$S(\chi, \xi) = -\ln[(\sum_{n=\infty} \sum_{q=\infty} e^{i(\chi q + \xi n)} P(q, n))] = \sum_{n=\infty} \sum_{q=\infty} \frac{e^{i(\chi q + \xi n)}}{1 + e^{i(\chi q + \xi n)}}. \tag{3}$$

In equation (3), the tunnelling operator is obtained by

$$\tilde{H}_T = \left[\tilde{t}_{ld} \Psi^\dagger_l + \tilde{t}_{rd} \Psi^\dagger_r\right] dX + \text{h.c.}$$

The charge transfer mechanism in the molecular junction is not equivalent. As explained in appendix B, we chose the gauge preserving current conservation in the tunnel limit $\Gamma \rightarrow 0$.
3. Results in the tunnel regime

3.1. Electronic FCS

We derive from equation (4) an analytical expression for the electronic CGF in the tunnel regime, namely \( \delta S_{\text{el}}^{(1)}(\chi) = \delta S^{(1)}(\chi, \xi = 0) \)

\[
\delta S_{\text{el}}^{(1)}(\chi) = -\int_{L} \Gamma_{L \rightarrow R} (e^{i\chi} - 1) \Gamma_{R \rightarrow L} (e^{-i\chi} - 1). \tag{5}
\]

Its Fourier transform provides a bidirectional Poissonian distribution for the electronic FCS \( P_{\text{el}}(q) \) with corresponding left to right (right to left) rates \( \Gamma_{L \rightarrow R} (\Gamma_{R \rightarrow L}) \). Those coefficients are evaluated within the scope of an approximation derived in appendix B, which is, by construction, current conserving and consistent with the non-interacting limit \( g \rightarrow 0 \). We obtain in the case of symmetric coupling to the leads \( \Gamma_{L} = \Gamma_{R} = \Gamma/2 \)

\[
\begin{align*}
\Gamma_{L \rightarrow R} &= \frac{1}{4} \left\{ f_{L} \Gamma_{Rb} + (1 - f_{L}) \Gamma_{Lc} \right\}(\tilde{\omega}_{0}) \\
\Gamma_{R \rightarrow L} &= \frac{1}{4} \left\{ f_{R} \Gamma_{Lb} + (1 - f_{R}) \Gamma_{Rc} \right\}(\tilde{\omega}_{0}).
\end{align*} \tag{6}
\]

In equations (6) and (7), the electronic and hole rates for multi-phonon processes in the lead \( X = L, R \) are, respectively, defined as \( \Gamma_{X}(\omega) = \Gamma e^{\xi^{2}} \sum_{n=0}^{+\infty} \frac{\omega^{n}}{n!} \int_{X}(\omega + n\omega_{0}) \) and \( \Gamma_{b}(\omega) = \Gamma e^{\xi^{2}} \sum_{n=0}^{+\infty} \frac{\omega^{n}}{n!} \int_{b}(\omega - n\omega_{0}) \). It is interesting to notice that the left to right and right to left rates of the Poissonian distribution exhibit a non-analytical behaviour in the e–ph coupling strength \( g \) at low temperature, i.e., a non-perturbative calculation in \( g \) is necessary to derive the correct results in the tunnel limit \( \Gamma \rightarrow 0 \). Compared to the existing results in the literature [12–14], the expression for the CGF derived in equation (5) does not contain interaction-induced corrections to the Poissonian distribution. Such corrections were shown to arise from an avalanche (electron bunching) mechanism for the dynamics of the transferred electrons [13] which is not accounted for in the lowest order expansion presented in equation (4). Such terms will emerge from a non-perturbative evaluation of the CGF (‘all order in \( \Gamma \)’ dressing of the dot Green function), which is out of the scope of the present paper 2.

3.1.1. Electronic current.

The first cumulant \( \langle q \rangle^{(1)} = \Gamma_{L \rightarrow R}^{(1)} - \Gamma_{R \rightarrow L}^{(1)} \) corresponds to the mean current \( I(V) \) that flows across the junction. We show in figure 3 typical \( I(V) \) curves obtained by varying the dot position and the e–ph coupling strength. For the case \( \tilde{\omega}_{0} = 0 \), the \( I(V) \) characteristics exhibit an inelastic threshold at \( V = \pm 2\omega_{0} \) corresponding to the activation of inelastic tunnelling, i.e., an electron on the dot may tunnel to the leads by emitting a phonon. Additional inelastic channels open when increasing \( \lambda \) for voltages multiple of \( V = \pm n\omega_{0} \), and correspond to the onset of multiple phonon emission. It is interesting to notice that those inelastic patterns are simply explained by the Pauli principle that forbids

Such a resummation of the most divergent diagrams in the linked cluster expansion might be difficult to achieve, because Wick’s theorem is not valid when dealing with the Hamiltonian of equation (2). Any approximation based on a Dyson-like equation is thus not strictly justified and the approximation made (compared to the unknown exact result) appears to be difficult to control.

\[\frac{\omega_{0}}{\Gamma} \ll 1, \quad \omega_{0} \ll \omega_{e}\]

\[\frac{\omega_{0}}{\Gamma} \ll 1, \quad \omega_{0} \ll \omega_{e}\]

3.1.2. Electronic current noise.

A similar behaviour (the presence of inelastic thresholds) is observed for the case of the second cumulant \( \langle q^{2} \rangle^{(1)} = \Gamma_{L \rightarrow R}^{(1)} + \Gamma_{R \rightarrow L}^{(1)} \), that corresponds to the current-noise characteristics \( S(V) \) in figure 4. In the case of low voltages \( 0 \leq \omega_{0}, V \ll \omega_{0} \), the noise is given by

\[
\langle q^{2} \rangle^{(1)} \approx \int_{L} \frac{\Gamma_{L} e^{\xi^{2}}}{2} \{ f_{L}(1 - f_{R}) + f_{R}(1 - f_{L}) \}(\tilde{\omega}_{0}). \tag{9}
\]

In the appropriate low-\( \Gamma \) limit, equation (9) coincides with the scattering result for shot noise [6] when \( g \rightarrow 0 \).
and plain curves are obtained, respectively, with the dot position 
the source of the difficulty originates from the low-
In equation (10), 
plot are 
/\Gamma_1 
from the initial vibrational state 
/\Gamma_1 
| 
P 
the probability 
3.2. Population dynamics of the phonon mode
3.2.1. Derivation of the master equation for the phonons.
The computation of the phonon stationary distribution, namely the probability \( P_{\text{ph}}(n) \) of having \( n \) phonons populating the mode in steady state, is more difficult to achieve than the corresponding calculation of the electronic FCS. The source of the difficulty originates from the low-\( \Gamma \) expansion of equation (4) that does not take into account phonon emission and absorption on the same footing, i.e. equation (4) provides multi-phonon emission processes at this order in the \( \Gamma \)-expansion but lacks the higher-order absorption processes that are necessary to reach a steady state.

We adopt in the following a self-consistent treatment that cures the problem by including in equation (4) any excited state \( |m\rangle \) of the local vibrational mode. More generally, we define \( T_{\text{ph}}^{(n)}(t) \) as the probability of transition from the initial vibrational state \( |m\rangle \) to the final state \( |m+n\rangle \) during the measuring time \( t \), after tracing out the electronic degrees of freedom. This quantity is computed from the generalized vibrational CGF, namely \( \delta S^{(1)}_{\text{ph},m}(\xi) = \delta S^{(1)}_{\text{ph}}(\chi = 0, \xi) \), that includes the contribution of vibronic Green functions \( P^{(n)}_{\text{ph}}(t) = \langle \text{Tr}(X(t)X^\dagger(0)) \rangle_m \) averaged over the excited phonon state \( m \) quanta in the phonon mode. A detailed derivation of the generalized vibronic Green functions and phonon CGF is proposed in appendices A and C, respectively.

In the absence of any external damping mechanism for the phonons (non-equilibrated phonons), the dynamics of the phonon population is self-determined for each time interval \( t_0 \) by the electronic tunnelling mechanism as

\[
P_{\text{ph}}(t_0; n) = \sum_{m=0}^{+\infty} T_{\text{ph}}^{(n)}(n-m) P_{\text{ph}}(0; m).
\] (10)

In equation (10), \( P_{\text{ph}}(t_0; n) \) is the probability of having \( n \) phonons populating the local vibrational mode at time \( t_0 \). The stationary distribution of the phonons is obtained in the long time limit as the fixed point of equation (10). In the tunnel limit \( \Gamma \rightarrow 0 \), the transition rate \( T_{\text{ph}}^{(n)}(n) \) is expanded in the leading order of \( \Gamma \) as

\[
T_{\text{ph}}^{(n)}(n) \approx \delta_{n,0} + t_0 \Gamma_{\text{ph}}^{(n)}(n) + o(t^2, \Gamma^2)
\] (11)

\[
\Gamma_{\text{ph}}^{(n)}(m) = - \int_{-\pi}^{\pi} \frac{d\xi}{2\pi} \frac{1}{\Gamma_1} \delta S^{(1)}_{\text{ph},m}(\xi) e^{-in\xi}.
\] (12)

In equation (11), \( \Gamma_{\text{ph}}^{(n)}(n) \) is a transition rate per unit of time corresponding to the multi-phonon process \( |m\rangle \rightarrow |m+n\rangle \). It is formally related to the Fourier transform of the phonon CGF \( S_{\text{ph}}^{(n)}(n) \) (see equation (12)). It is interesting to notice that the matrix \( \Gamma_{\text{ph},m,m} = \Gamma_{\text{ph}}^{(m)}(n-m) \) might be evaluated analytically (see appendix C) and has the property of conserving the normalization of the phonon distribution, i.e. for each index \( m \) we have the following relation amongst matrix elements \( \sum_{m=0}^{+\infty} \Gamma_{\text{ph},m,m} = 0 \). Equations (12) and (13) are an important result of this paper. They are the constitutive relations that connect the formulation of transport based on perturbation theory in Keldysh space (usually used in the coherent transport regime) to the one based on the master equation in the tunnel limit. Including equation (11) in equation (10), we derive from our formalism the standard quantum master equation for the dynamics of the phonon population

\[
P_{\text{ph}}(t; n) = \sum_{m=0}^{+\infty} \Gamma_{\text{ph},m,m} P_{\text{ph}}(t; m)
\] (13)

\[
- \sum_{m=0}^{+\infty} \Gamma_{\text{ph},m,n} P_{\text{ph}}(t; n).
\]

3.2.2. Results for the phonon stationary distribution. As an example, we compute the phonon stationary distribution \( P_{\text{ph}}(n) = \lim_{t \rightarrow +\infty} P_{\text{ph}}(t; n) \) obtained as the zero eigenvector of the \( [\Gamma_{\text{ph}}] \) matrix (see equation (13)). For voltages below the inelastic threshold \( V = 0.5\omega_0 \) for the black curve of figure 5), phonon emission is forbidden by the Pauli principle and the phonon mode is not populated whatever the strength of \( e-\text{ph} \) coupling. In this case, the distribution \( P_{\text{ph}}(n) \) is a peak at \( n = 0 \) given by the Bose equilibrium distribution. For voltages above the inelastic threshold, a pumping mechanism appears: the onset of phonon emission strongly drives the population of the vibrational mode out of equilibrium. For weak \( e-\text{ph} \) coupling \( \lambda = 0.3\omega_0 \) and \( V = 2.5\omega_0 \) (see the blue (dark grey) curves on figure 5), it gets closer to the equilibrium distribution (the tail is shorter). The corresponding non-monotonic behaviour of \( P_{\text{ph}}(n) \) with \( \lambda \) results from the competition between the emission–absorption mechanism given by equation (13) and the selection rules imposed by the transition matrix \( [\Gamma_{\text{ph}}] \) (when \( \lambda \) increases, the de-excitation of highly excited states toward the ground state is more likely to happen [19]).
describe off-resonant transport in the deep Franck–Condon blockade [9] or to derive results valid in the limit of large present work is to investigate the role of higher-order terms in Green functions techniques (in the coherent regime).

A framework that unifies previous studies based on rate equations processes [34, 35] are expected to be important in order to transmission (resonant tunnelling) [36, 37]. Following the recent work of Maier et al [38], such an issue could be investigated by using a self-consistent scheme to compute the FCS in the strong coupling regime. More generally, the nature of transport properties and mechanisms in the polaron crossover regime is an important, unsolved problem [39] that deserves future investigations following the lines drawn in the present paper.

A.1. Electronic Green functions

In this part, we compute the non-interacting electronic Green functions of the dot and of the X = L, R leads, namely \( \hat{g}_{dd}(\omega) \) and \( \hat{g}_{XX}(\omega) \).

We suppose that the leads are maintained in equilibrium and characterized by a flat density of states \( \rho_0 \) and a chemical potential \( \mu_{L(R)} = (+,-)V/2 \). The corresponding free Green functions are given by

\[
\hat{g}_{XX}(\omega) = \frac{i}{W} \left[ \frac{2f_X - 1}{2 - f_X - 1} \right](\omega)
\]

where \( f_X(\omega) \) is the Fermi distribution of the lead \( X = L, R \) and \( W = 1/\pi \rho_0 \) its bandwidth.

The free (non-interacting) dot Green function is determined in the case of symmetric contacts to the leads \( \Gamma_L = \Gamma_R = \Gamma/2 \) as

\[
g_{dd}^{\alpha\alpha}(\omega) = \frac{\alpha(\omega - \omega_0) + i\Gamma(f_L + f_R - 1)}{\Delta_{\chi}}(\omega)
\]

\[
g_{dd}^{+\alpha\alpha}(\omega) = \frac{\Gamma(1 - f_L + f_R)}{\Delta_{\chi}}(\omega)
\]

\[
g_{dd}^{-\alpha\alpha}(\omega) = -i\Gamma\left(1 - f_L + f_R\right)(\omega)
\]

where the Keldysh determinant is given by

\[
\Delta_{\chi}(\omega) = (\omega - \omega_0)^2 + \Gamma^2 + \Gamma^2 \left(\left(1 - f_L\right)\left(1 - f_R\right) - \left(1 - f_L\right)f_R(1 - f_L)\right)(\omega).
\]

The mean population of the dot \( \langle n_d \rangle \) is obtained after integration of the non-diagonal component of the dot Green function \( g_{dd}^{+\alpha\alpha}(\omega) \) expressed at zero counting field

\[
\langle n_d \rangle = \int \frac{d\omega}{2\pi} \frac{\Gamma}{(\omega - \omega_0)^2 + \Gamma^2} \left(f_L(\omega) + f_R(\omega)\right).
\]

In the atomic limit \( \Gamma \to 0 \), far from resonance \( |\omega_0| \gg \Gamma \), the Lorentzian integrand of equation (19) is approximated by a delta function and we obtain for the voltage dependent mean population of the dot

\[
\lim_{\Gamma \to 0} \langle n_d \rangle = \frac{1}{2} \left(f_L(\omega_0) + f_R(\omega_0)\right).
\]

Similarly, the atomic limit of the non-interacting Green function is obtained as

\[
g_{dd}^{\alpha\alpha}(\omega) = \alpha \left\{ \frac{1 - \langle n_d \rangle}{\omega - \omega_0 + i\eta} + \frac{\langle n_d \rangle}{\omega - \omega_0 - i\eta} \right\}
\]

\[
g_{dd}^{+\alpha\alpha}(\omega) = i2\pi(\langle n_d \rangle)\delta(\omega - \omega_0)
\]

\[
g_{dd}^{-\alpha\alpha}(\omega) = -i2\pi(1 - \langle n_d \rangle)\delta(\omega - \omega_0).
\]

A.2. Phononic Green functions

We have developed a theoretical framework that unifies previous studies based on rate equations processes [34, 35] are expected to be important in order to transmission (resonant tunnelling) [36, 37]. Following the recent work of Maier et al [38], such an issue could be investigated by using a self-consistent scheme to compute the FCS in the strong coupling regime. More generally, the nature of transport properties and mechanisms in the polaron crossover regime is an important, unsolved problem [39] that deserves future investigations following the lines drawn in the present paper.

Anisotropic effective medium model

In this part, we compute the non-interacting electronic Green functions of the dot and of the X = L, R leads, namely \( \hat{g}_{dd}(\omega) \) and \( \hat{g}_{XX}(\omega) \).

We suppose that the leads are maintained in equilibrium and characterized by a flat density of states \( \rho_0 \) and a chemical potential \( \mu_{L(R)} = (+,-)V/2 \). The corresponding free Green functions are given by

\[
\hat{g}_{XX}(\omega) = \frac{i}{W} \left[ \frac{2f_X - 1}{2 - f_X - 1} \right](\omega)
\]

where \( f_X(\omega) \) is the Fermi distribution of the lead \( X = L, R \) and \( W = 1/\pi \rho_0 \) its bandwidth.

The free (non-interacting) dot Green function is determined in the case of symmetric contacts to the leads \( \Gamma_L = \Gamma_R = \Gamma/2 \) as

\[
g_{dd}^{\alpha\alpha}(\omega) = \frac{\alpha(\omega - \omega_0) + i\Gamma(f_L + f_R - 1)}{\Delta_{\chi}}(\omega)
\]

\[
g_{dd}^{+\alpha\alpha}(\omega) = \frac{\Gamma(1 - f_L + f_R)}{\Delta_{\chi}}(\omega)
\]

\[
g_{dd}^{-\alpha\alpha}(\omega) = -i\Gamma\left(1 - f_L + f_R\right)(\omega)
\]

where the Keldysh determinant is given by

\[
\Delta_{\chi}(\omega) = (\omega - \omega_0)^2 + \Gamma^2 + \Gamma^2 \left(\left(1 - f_L\right)\left(1 - f_R\right) - \left(1 - f_L\right)f_R(1 - f_L)\right)(\omega).
\]

The mean population of the dot \( \langle n_d \rangle \) is obtained after integration of the non-diagonal component of the dot Green function \( g_{dd}^{+\alpha\alpha}(\omega) \) expressed at zero counting field

\[
\langle n_d \rangle = \int \frac{d\omega}{2\pi} \frac{\Gamma}{(\omega - \omega_0)^2 + \Gamma^2} \left(f_L(\omega) + f_R(\omega)\right).
\]

In the atomic limit \( \Gamma \to 0 \), far from resonance \( |\omega_0| \gg \Gamma \), the Lorentzian integrand of equation (19) is approximated by a delta function and we obtain for the voltage dependent mean population of the dot

\[
\lim_{\Gamma \to 0} \langle n_d \rangle = \frac{1}{2} \left(f_L(\omega_0) + f_R(\omega_0)\right).
\]

Similarly, the atomic limit of the non-interacting Green function is obtained as

\[
g_{dd}^{\alpha\alpha}(\omega) = \alpha \left\{ \frac{1 - \langle n_d \rangle}{\omega - \omega_0 + i\eta} + \frac{\langle n_d \rangle}{\omega - \omega_0 - i\eta} \right\}
\]

\[
g_{dd}^{+\alpha\alpha}(\omega) = i2\pi(\langle n_d \rangle)\delta(\omega - \omega_0)
\]

\[
g_{dd}^{-\alpha\alpha}(\omega) = -i2\pi(1 - \langle n_d \rangle)\delta(\omega - \omega_0).
\]
A.2. Vibronic Green functions

The free vibronic Green function \( \mathcal{P}_{\xi=0}(t) = \langle T_{\xi} X(t) X^{\dagger}(0) \rangle_0 \) is evaluated by performing the average over the phonon ground state \((m = 0 \text{ quanta in the vibrational mode})\). Using the Glauber equality \([3]\) \( e^{tD} = e^{tE} e^{t\frac{1}{2}[C,D]} \) which is valid for any operators \((C, D)\) that commute with their commutator, we obtain similarly to \([40]\)

\[
\mathcal{P}_{\xi=0}^{\text{eq}}(\omega) = e^{-\omega} \sum_{n=0}^{\infty} \frac{1}{n!} \, \frac{1}{\omega - \alpha n \omega_0 + i \eta} \left( \frac{1}{\omega - \alpha n \omega_0 - i \eta} \right)
\]

\[
(24)
\]

where the correlators \( C \) to multiple phonon emission. Only when considering an equation (4)), the only possible processes available correspond to be understood as well in the appropriate low-\(G\) and low-transmission limit stated above.

More generally, we define the \( \xi \)-dependent free vibronic Green function as \( \mathcal{P}_{\xi}^{(m)}(t) = \langle T_{\xi} X(t) X^{\dagger}(0) \rangle_{m,}\) where the mean value is performed over an excited phonon state \((m \neq 0 \text{ quanta in the mode})\). We obtain in general

\[
\mathcal{P}_{\xi}^{(m,a)}(t) = \theta(t) \mathcal{C}_{a,m}^{\pm}(t) + \theta(-t) \mathcal{C}_{a,m}^{-}(t)
\]

\[
(26)
\]

where the correlators \( C_{1,0}^{\pm}(t) = \langle m \mid X_{\xi}^{\pm}(t) X_{\xi}^{\dagger}(0) \rangle m \) and \( C_{-1,0}^{\pm}(t) = \langle m \mid X_{\xi}^{\pm}(0) X_{\xi}^{\dagger}(t) \rangle m \) are given in the Fourier representation by

\[
C_{\pm 1,0}^{\pm}(\omega) = \frac{2 \pi e^{-\frac{\omega}{2}}}{\omega} \sum_{m} \sum_{p_1=0}^{m} \sum_{p_2=0}^{m} \sum_{p_3=0}^{m} \sum_{p_4=0}^{m} \frac{\sin^{2}(p_1 + p_2)}{p_1! p_2!} C_{m}^{\pm} C_{p_1}^{\pm} C_{p_2}^{\pm} C_{p_4}^{\pm} (-1)^{p_3} \delta[\omega \mp (p_1 + p_2 - p_3) \omega_0].
\]

(28)

It is interesting to notice that only the non-diagonal components of the phonon propagator are explicitly dependent on the phonon counting field. If the phonon states are restricted to the \( m = 0 \) ground state (like in the low-\(G\) result of equation (4)), the only possible processes available correspond to multiple phonon emission. Only when considering an excited phonon state \((m \geq 1)\) are absorption processes allowed.

Appendix B. Rates of the Poisson distribution

B.1. The non-interacting case

Using our formalism and the expression of the dot Green functions (see equations (15)–(17)), the electronic CGF of the resonant level in the non-interacting case \((g = 0)\) might be determined in all orders of \(G\). This provides the Levitov–Lesovik result \([1, 2, 32]\) for the free electronic CGF \( S_{d\xi}^{(0)}(\omega)\), and the associated binomial FCS of transmitted electrons

\[
S_{d\xi}^{(0)}(\chi) = -i \int \frac{d \omega}{2 \pi} \ln \left[ 1 + T(\omega)(e^{i \chi} - 1) f_L (1 - f_R) + (e^{-i \chi} - 1) f_R (1 - f_L) \right] (\omega). \tag{29}
\]

Equation (29) is associated with resonant tunnelling of electrons and holes through the dot, characterized by a transmission factor

\[
T(\omega) = \frac{\Gamma^2}{(\omega - \omega_d)^2 + \Gamma^2}. \tag{30}
\]

The limit of low-\(G\) and off-resonant situation \(|\omega_d| \gg \Gamma\) corresponds to an approximate transmission factor \(T(\omega) \approx \pi \Gamma \delta(\omega - \omega_d)\). The corresponding expansion of the electronic CGF in the lowest order of \(G\) provides the Poissonian result \( S_{d\xi}^{(0)}(\omega) \approx -i \int \frac{d \omega}{2 \pi} \left[ f_L (e^{i \chi} - 1) + f_R (e^{-i \chi} - 1) \right] \) with rates expressed as

\[
\Gamma_{L,\xi}^{(0)} \approx \frac{\Gamma}{2} f_L (\omega_d) [1 - f_R (\omega_d)] \tag{31}
\]

\[
\Gamma_{R,\xi}^{(0)} \approx \frac{\Gamma}{2} f_R (\omega_d) [1 - f_L (\omega_d)]. \tag{32}
\]

In the following, the results for the interacting case have to be understood as well in the appropriate low-\(G\) and low-transmission limit stated above.

B.2. Interacting case: choice of the gauge

When evaluating the lowest order in the \(G\)-expansion of the electronic CGF, one is not ensured (if no self-consistency is achieved) that current conservation is fulfilled, namely that the obtained cumulants versus voltage curves have a well defined symmetry under the transformation \(V \rightarrow - V\), nor that the obtained CGF coincides with the non-interacting result of equations (31) and (32) when \( g \rightarrow 0 \).

We use this constraint of both charge conservation and recovering the non-interacting Levitov–Lesovik result to select the proper gauge in implementing the electronic counting field in the Hamiltonian. Clearly, the choice of a gauge that incorporates the electronic counting field in the left electrode only \( h_d \rightarrow \frac{h_d e^{-i \chi(1/2)}}{2} \) breaks the symmetry between the left and right electrodes when expanding the CGF to the lowest order in \( G\), i.e. this choice of gauge is not current conserving. The symmetry between both electrodes (and hence current conservation) is restored by introducing the electronic counting field symmetrically in both leads, namely \( h_{L,Rd} \rightarrow \frac{h_{L,Rd} e^{i \chi(1/2)}}{2} \). In the following, we make this choice of a symmetric gauge that is, by construction, current conserving.

We then evaluate the electronic CGF from equation (4), using equations (24) and (25) for the free phonon propagator

\[
\delta S_{d\xi}^{(1)}(\chi) \approx \int \frac{d \omega}{2 \pi} \left[ \frac{1}{\Gamma} e^{-i \chi} \sum_{m=0}^{\infty} \frac{\sin^{2m}(\omega)}{n! \omega_0} \sum_{n=0}^{\infty} \frac{1}{\omega - \alpha n \omega_0 + i \eta} \left( \frac{1}{\omega - \alpha n \omega_0 - i \eta} \right) \right] \left[ \frac{1}{\Gamma} e^{i \chi} \sum_{m=0}^{\infty} \frac{\sin^{2m}(\omega)}{n! \omega_0} \sum_{n=0}^{\infty} \frac{1}{\omega - \alpha n \omega_0 + i \eta} \left( \frac{1}{\omega - \alpha n \omega_0 - i \eta} \right) \right]. \tag{33}
\]

In equation (33), the free dot Green function \( \hat{g}_{d\xi}(\omega) \) has to be evaluated. However, by implementing naïvely the bare dot Green function given in the atomic limit by equations (21)–(23), the obtained CGF although current conserving does not reproduce the limiting case of the Levitov–Lesovik formula when \( g \rightarrow 0 \). This is related to the fact that the non-equilibrium state of the dot level subsystem is ill defined in
the atomic limit $\Gamma \rightarrow 0$, i.e. one has to artificially include the presence of electrodes maintained under a constant voltage bias as an external boundary term (for instance, as a voltage dependent population of the dot in the expression of the bare dot Green function in equations (21)–(23)). We have found the following procedure to overcome this difficulty and safely compute the electronic CGF in such a way that the non-interacting limit of the rates as given by equation (31) and (32) is recovered. We first use the expression of the free dot Green function in all orders of $\Gamma$ as written in equation (15)–(17) and obtain for the CGF

$$
\delta S^{(1)}_{\text{el}}(\chi) = -\frac{\hbar}{2} \int \frac{d\omega}{2\pi} \Delta_{\chi} f_{L} A_{Lh} + (1 - f_{L}) A_{Le}
\quad + f_{R} A_{Rh} + (1 - f_{R}) A_{Re} + e^{i\chi} [f_{L} A_{Rh} + (1 - f_{L}) A_{Re}]
\quad + e^{-i\chi} [f_{R} A_{Lh} + (1 - f_{R}) A_{Le}]\omega.
$$

We finally evaluate the Keldysh determinant $\Delta_{\chi}(\omega)$ at zero electronic counting field $\chi = 0$ and go to the limit $\Gamma \rightarrow 0$. We obtain equation (5)–(7) for the electronic CGF and its corresponding rates.

**Appendix C. Transition rates for the phonons**

In this appendix, we derive analytical expressions for the generalized phonon CGF $\delta S^{(1)}_{\text{ph},n}(\xi)$ and for the corresponding multi-phonon transition rates per unit of time $\Gamma^{(m)}_{\text{ph}}(n)$. We first write equation (4) in terms of the generalized phonon Green functions defined in appendix A

$$
\delta S^{(1)}_{\text{ph},n}(\xi) \approx -\frac{\hbar}{2} W e^{-x^2} \sum_{p_{1}=0}^{\infty} \sum_{p_{2}=0}^{\infty} \sum_{p_{3}=0}^{\infty} g_{1}^{2}(p_{1}+p_{2}) C_{p_{1}}^{m} C_{p_{2}}^{m} (1-p_{3}) \times
\quad \left[\frac{\omega_{2}(p_{1}+p_{2}-p_{3})}{\omega_{1}}\right] \int \frac{d\omega_{3}}{2\pi} \left[\delta_{\omega_{1,\omega_{3}}} - A_{\omega_{1},\omega_{3}} \right] f_{\omega_{3}}(\omega_{1})
\quad \times \left[\Gamma_{L,\omega_{1} \omega_{2}} + \Gamma_{R,\omega_{1} \omega_{3}} \right] (\delta_{1,\alpha} - \omega_{1} - \omega_{2} - \omega_{3}),
\quad (35)
$$

Putting the evaluation of the leads and the dot Green functions as given by equation (14) and equations (21)–(23), we obtain, after Fourier transforming equation (35), the following expression for the transition rates

$$
\Gamma^{(m)}_{\text{ph}}(n) = e^{-x^2} \sum_{p_{1}=0}^{\infty} \sum_{p_{2}=0}^{\infty} \sum_{p_{3}=0}^{\infty} g_{1}^{2}(p_{1}+p_{2}) C_{p_{1}}^{m} C_{p_{2}}^{m} (1-p_{3}) \times
\quad \left\{\delta_{n,1}(1 - f_{L}) + \Gamma_{R}(1 - f_{R})\omega_{1} \right\} + (1 - \delta_{n,1}) \Gamma_{L,1}\quad \times
\quad \left[\delta_{n,p_{1}+p_{2}-1} - \delta_{n,0}\right],
\quad (36)
$$

where $\omega_{1,\alpha} = \omega_{1} \pm (p_{1} + p_{2} - p_{3})\omega_{0}$. The constraints on summations due to the last term in equation (36) imply that the transition rates are conserving the phonon probability, namely that $\sum_{n=0}^{\infty} \Gamma_{\text{ph},n,m} = 0$.

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