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# Electron-phonon interaction and full counting statistics in molecular junctions

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The full counting statistics of a molecular level weakly interacting with a local phonon mode is derived. We find an analytic formula that gives the behavior of arbitrary irreducible moments of the distribution upon phonon excitation. The underlying competition between quasielastic and inelastic processes results in the formation of domains in parameter space characterized by a given sign in the jump of the irreducible moments. In the limit of perfect transmission, the corresponding distribution is distorted from Gaussian statistics for electrons to Poissonian transfer of holes above the inelastic threshold.

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It is now well established that the current noise generated by electronic nanodevices contains valuable information on microscopic transport processes not available from measurements of the current-voltage characteristics.[1] A full characterization of the transport properties of a device requires not only the knowledge of current-current correlations but rather the full counting statistics (FCS) has to be determined.[2] This amounts to determine the whole probability distribution $P_{t_0}(q)$ that a given charge $q$ is transmitted through the device during a certain measurement time $t_0$.

Studies of FCS have been mainly restricted to noninteracting systems. Notable examples of such studies are single channel conductors[3] or double quantum dot systems.[4] The case of FCS in the presence of electron-electron interactions in the coherent transport regime has been much less analyzed.[5] In particular, the Kondo regime in quantum dots has been addressed in Ref. 6.

On the other hand, molecular electronics is becoming a field of intense research activity.[7] In this case the coupling to vibrational modes plays an important role and provides an additional source for electronic correlations, which may affect the counting statistics.[8] The case of atomic chains suspended between metallic electrodes provides another test system to analyze the effects of electron-phonon (e-ph) coupling in transport properties.[9] At low temperatures (quantum regime) the onset of phonon emission processes is signaled by abrupt jumps in the system differential conductance.[10,11] When certain conditions are met, the behavior of the conductance jumps is entirely controlled by the transmission probability, evolving from a drop in conductance at high transmission to an increase at low transmission. These predictions were quantitatively confirmed in recent experiments.[12] A natural question, which arises, concerns the behavior of noise and, more generally, the FCS for energies corresponding to the excitation of vibrational modes. Although some works have been devoted to the analysis of noise in the presence of e-ph coupling,[13] none of them tackled the problem of the determination of the FCS in the presence of e-ph interaction.

The aim of this work is to study how the FCS of a molecular junction is modified by the coupling to a vibrational mode. On the basis of a simple model, we derive a compact analytical expression encoding the FCS for the experimentally relevant regime of weak e-ph interactions and strong coupling to the leads, which corresponds to the conditions of Ref. 12. This expression allows analysis of the change of arbitrary irreducible moments of the distribution $P_{t_0}(q)$ upon phonon excitation, as well as giving a picture of the underlying interplay between quasielastic and inelastic processes.

The starting point of our derivation is the following model Hamiltonian:

$$H = \sum_{\mu} H_{\mu} + \epsilon_d \sum_{\sigma} d_{\sigma}^{\dagger} d_{\sigma} + \omega_0 a^{\dagger} a + V + V_{e\text{-}ph},$$

$$V = \sum_{\mu,k,\sigma} t_{\mu d} \psi_{\mu k \sigma}^{\dagger} d_{\sigma} + \text{H.c.}; \quad V_{e\text{-}ph} = \lambda (a + a^{\dagger}) \sum_{\sigma} d_{\sigma}^{\dagger} d_{\sigma} \quad (1)$$

where a single molecular level of energy $\epsilon_d$ is coupled to the left (right) electrode by a hopping element $t_{Ld}(t_{Rd})$ and interacts with a local phonon mode of energy $\omega_0$ with e-ph coupling constant $\lambda$. The indexes $(\mu,k,\sigma)$ label the state of the $\mu = L,R$ uncoupled electrode, characterized by wave vector $k$ and spin $\sigma$. We further define the cumulant generating function (CGF) $S(\chi) = -\sum_{n=1}^{+\infty} \frac{(i\chi)^n}{n!} \langle q^n \rangle_c$ as the functional generating the irreducible moments of the distribution $\langle q^n \rangle_c$. The connection of this definition to the former Hamiltonian is given by[3]

$$e^{-S(\chi)} = \left\langle T_c \exp\left\{ -i \int_c V_{\chi(t)}(t) dt \right\} \right\rangle, \quad (2)$$

where $V_{\chi(t)}$ denotes $V$ with the substitution in the left hopping element $t_{Ld}$ by $t_{Ld} e^{-i\chi(t)/2}$ and $T_c$ means time ordering on the Keldysh contour going forward from time 0 to time $t_0$ and backward from time $t_0$ to time 0. The counting field $\chi(t)$ equals to $\pm\chi$ on the forward (backward) branch of the Keldysh contour and accounts for a virtual measurement of the charge being transmitted.[2] As shown in Ref. 14, it is convenient to work with the generalized current $I(\chi) = s \frac{i}{t_0} \frac{\partial}{\partial \chi} S(\chi)$ that can be expressed in terms of the Keldysh Green functions of the interacting molecular level $G_{dd}^{\alpha\beta}(t,t') = -i \langle T_c d(t_\alpha) d^{\dagger}(t'_\beta) \rangle$ and of the uncoupled lead $g_{LL}^{\alpha\beta}$ (with indexes $\alpha, \beta = \pm$),

 

$$I(\chi) = \frac{s}{2\pi} W\Gamma_L \int d\omega \{e^{i\chi} G_{dd}^{-+}(\omega) g_{LL}^{+-}(\omega) - e^{-i\chi} G_{dd}^{+-}(\omega) g_{LL}^{-+}(\omega)\}. \tag{3}$$

In the former expression, $s=2$ stands for spin degeneracy and $\Gamma_L = t_{Ld}^2/W$ is the coupling to the left contact expressed in units of the inverse of density of states $W=1/\pi\rho_L$ (supposed to be constant).

At second order in perturbation due to e-ph interaction, the dot Green's function can be written $\hat{G}_{dd} \approx \hat{G}_{dd}^{(0)} + \hat{G}_{dd}^{(0)} \hat{\Sigma}_{dd}^{e\text{-}ph} \hat{G}_{dd}^{(0)}$, and the problem of finding the CGF is thus equivalent to the one of computing e-ph self-energy in Keldysh space $\hat{\Sigma}_{dd}^{e\text{-}ph}$ in the presence of the counting field. We retain two diagrams for the former. The first one is a Hartree-like diagram [Fig. 1(a)], which is diagonal in Keldysh space, frequency independent, of order $\lambda^2/\omega_0$, and does not exhibit any jump at the inelastic threshold ($V=\omega_0$). The second diagram is the exchange diagram [Fig. 1(b)] that is responsible for the behavior of transport properties at the inelastic threshold. The corresponding bubble expansion of $S(\chi)$ is shown on Fig. 1(c) for the unperturbed CGF, Fig. 1(d) for the Hartree term and Fig. 1(e) for the exchange term. Taking into account the Keldysh indexes, one obtains a natural decomposition of $I(\chi)$ as $I_0(\chi) + I_{in}(\chi) + I_{el}(\chi)$, where $I_{in}(\chi)$ is an inelastic contribution, which arises from the nondiagonal elements of the e-ph self-energy ($\Sigma_{dd}^{+-}$ and $\Sigma_{dd}^{-+}$) and $I_{el}(\chi)$ from the diagonal ones ($\Sigma_{dd}^{++}$ and $\Sigma_{dd}^{--}$).[15] This decomposition is equivalent to the one in Ref. 16.

The unperturbed current $I_0(\chi)$ corresponds to resonant tunneling across the molecular junction in absence of e-ph interaction and is given by

$$I_0(\chi) = \frac{s}{2\pi} \int \frac{d\omega}{\Delta_\chi} \{e^{i\chi} f_L(1-f_R) - e^{-i\chi} f_R(1-f_L)\},$$

$$\Delta_\chi(\omega) = \frac{1}{T} + (e^{i\chi}-1) f_L(1-f_R) + (e^{-i\chi}-1) f_R(1-f_L), \tag{4}$$

where $f_{L(R)}$ is the Fermi distribution of the left (right) lead, $T(\omega) = 4\Gamma_L\Gamma_R/[\Gamma^2 + (\omega-\epsilon_d)^2]$ the zero bias transmission coefficient and $\Gamma = \Gamma_L + \Gamma_R$ the total coupling to the leads. The corresponding CGF coincides with the one derived by Levitov *et al.*[3] Effects of e-ph interaction are included in the two remaining terms. The inelastic contribution $I_{in}(\chi)$ can be written as

$$\begin{aligned} I_{in}(\chi) = -\frac{s}{2\pi} \frac{2i}{\Gamma^2 T(\epsilon_d)} \int \frac{d\omega}{\Delta_\chi} \Bigg\{ & \Gamma_L [e^{i\chi} f_L \Sigma_{dd}^{-+} + e^{-i\chi}(1-f_L)\Sigma_{dd}^{+-}] \\ & + \frac{i}{\Delta_\chi} \frac{\partial \Delta_\chi}{\partial \chi} [(e^{i\chi}\Gamma_L f_L + \Gamma_R f_R)\Sigma_{dd}^{-+} \\ & - (e^{-i\chi}\Gamma_L(1-f_L) + \Gamma_R(1-f_R))\Sigma_{dd}^{+-}] \Bigg\}. \end{aligned} \tag{5}$$

This corresponds to tunneling processes with absorption (emission) of a phonon. During such a process, the final energy of the scattered electrons increases (decreases) by an amount $\omega_0$ and the mean number of phonons decreases (increases) by one unit. The last term $I_{el}(\chi)$ accounts for elastic processes during which the energy of the scattered electrons is conserved and is given by

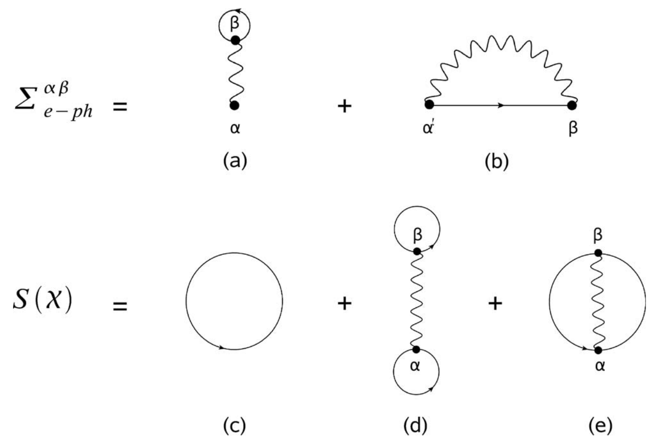


FIG. 1. Upper figure: second-order electron-phonon self energy in Keldysh space ($\alpha, \beta = \pm$). (a) Hartree term. (b) Exchange term. lower figure: corresponding bubble expansion of the CGF $S(\chi)$. (c) Unperturbed term. (d) Hartree term. (e) Exchange term.

$$\begin{aligned} I_{el}(\chi) = -\frac{s}{2\pi} \frac{i}{\Gamma^2 T(\epsilon_d)} \int \frac{d\omega}{\Delta_\chi^2} \frac{\partial \Delta_\chi}{\partial \chi} \{ & (\omega - \omega_d)[\Sigma_{dd}^{++} - \Sigma_{dd}^{--}] \\ & + i[\Gamma_L(2f_L-1) + \Gamma_R(2f_R-1)][\Sigma_{dd}^{++} + \Sigma_{dd}^{--}]\}. \end{aligned} \tag{6}$$

The term involving $\Sigma_{dd}^{++} - \Sigma_{dd}^{--}$ corresponds to a renormalization of the transmission factor that gives logarithmic corrections, whereas the term involving $\Sigma_{dd}^{++} + \Sigma_{dd}^{--}$ corresponds to quasielastic tunneling with emission reabsorption of a phonon (hence the phonon population is unchanged) together with a virtual leaking of the propagating electrons into the leads.

The former compact formulas can be used to implement a numerical computation of the FCS.[15] Of particular interest is the behavior of $I(\chi)$ at inelastic threshold, which is encoded in the jump of the generalized conductance $\Delta G(\chi) = \frac{\partial}{\partial V} I(\chi)|_{\omega_0^+} - \frac{\partial}{\partial V} I(\chi)|_{\omega_0^-}$. At zero temperature (assuming phonon population $f_B = 0$), we find an analytical formula for $\Delta G(\chi)$,

$$\Delta G(\chi) = \Delta G_{in}(\chi) + \Delta G_{el}(\chi),$$

$$\Delta G_{in}(\chi) = \frac{s}{2\pi} \lambda_{e\text{-}ph}^2 \frac{e^{i\chi}}{T(\epsilon_d)} \left\{ \frac{1}{\Delta_{\chi;+}\Delta_{\chi;-}} - e^{i\chi} L_1 \right\},$$

$$\begin{aligned} \Delta G_{el}(\chi) = \frac{s}{2\pi} \lambda_{e\text{-}ph}^2 \frac{e^{i\chi}}{T(\epsilon_d)} \Bigg\{ & \frac{\left(\frac{\omega_0}{2}\right)^2 - \epsilon_d^2}{4\Gamma_L\Gamma_R} [L_2 + L_3 - L_1] \\ & - \frac{\alpha - 1}{4\alpha} [(\alpha-1)L_1 + (\alpha+1)(L_3 - L_2)] \Bigg\}, \end{aligned} \tag{7}$$

where we have introduced the dimensionless e-ph coupling $\lambda_{e\text{-}ph}^2 = \lambda^2/\Gamma^2$ and the parameter $\alpha = \Gamma_L/\Gamma_R$ measuring the asymmetry in the coupling to the leads. The following notation is adopted $\Delta_{\chi;\pm} \equiv \Delta_\chi(\pm\frac{\omega_0}{2})$, $T_\pm \equiv T(\pm\frac{\omega_0}{2})$, $L_1$

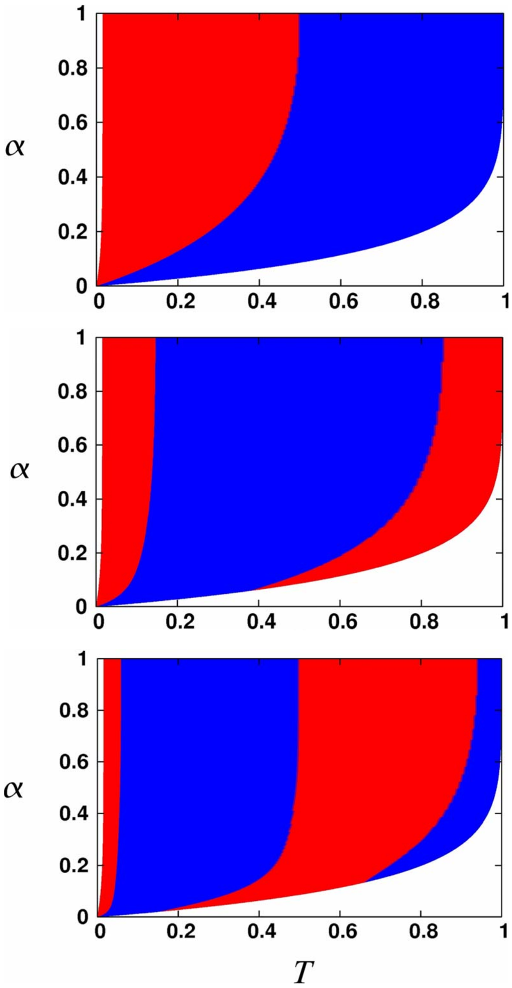


FIG. 2. (Color online) Sign of the jump in the derivative with respect to voltage of the order $n$ cumulant at phonon energy $\Delta F_n$. Parameter space is $\{\alpha, T(0)\}$, and phonon energy is $\omega_0=10^{-2}\Gamma$. From up to down: $\Delta F_1$ (jump in the conductance), $\Delta F_2$ (jump in the noise), and $\Delta F_3$ (jump in the third moment). The blue (red) color encodes a negative (positive) jump.

$=1/\Delta_{\chi;+}\Delta_{\chi;-}\{1/\Delta_{\chi;+}+1/\Delta_{\chi;-}\}$, and $L_{2(3)}=T_{\mp}/\Delta^2_{\chi;\pm}$.

This formula is the main result of the Rapid Communication. We emphasize that it encodes the full energy dependence of the model, i.e., it is not restricted to wide band approximation, and allows to explore the behavior of the derivative with respect to voltage of the order $n$ cumulant $F_n=\frac{1}{t_0 T(0)\lambda^2_{e\text{-}ph}}\frac{\partial}{\partial V}\langle q^n\rangle_c$, which exhibits a jump at phonon energy given by

$$\Delta F_n = \left.\frac{1}{i^{n-1}\lambda^2_{e\text{-}ph}}\frac{\partial^{n-1}}{\partial\chi^{n-1}}\frac{\Delta G(\chi)}{T(0)}\right|_{\chi=0}. \qquad (8)$$

We show in Fig. 2 the phase diagrams derived for the first three $F_n$ factors, when exploring parameter space $\{\alpha, T(0)\}$ by modulating $\alpha=\Gamma_L/\Gamma_R$ and shifting the molecular level $\epsilon_d$. The first $F_1$ factor exhibits a jump at phonon energy $\Delta F_1$ (jump in the conductance), easily expressed as

$$\Delta F_{1;in} = \frac{s}{2\pi}\frac{T_+T_-}{T(0)T(\epsilon_d)}\{1-(T_+ + T_-)\}, \qquad (9)$$

$$\Delta F_{1;el} = -\frac{s}{2\pi}\frac{T_+T_-}{T(0)T(\epsilon_d)}\frac{\alpha-1}{2\alpha}\{\alpha T_- - T_+\}. \qquad (10)$$

The sign of $\Delta F_1$ (represented on upper panel of Fig. 2) has been studied in Refs. 10–12. We find two regions of the parameter space corresponding to a negative jump (in blue) and a positive one (in red). If $\omega_0 \ll \Gamma$ (which is the case for Fig. 2 where $\omega_0=10^{-2}\Gamma$), the contribution due to inelastic processes $\Delta F_{1;in}$ is positive when $T(0)\leq 1/2$, due to the opening of an inelastic channel and negative when $T(0)\geq 1/2$, due to enhanced inelastic backscattering (the correction to this strong coupling behavior is of second order in $\omega_0/\Gamma$). On the other hand, the contribution of quasielastic processes to the jump $\Delta F_{1;el}$ (of first order in $\omega_0/\Gamma$) is always negative due to elastic backscattering. Interestingly, $\Delta F_{1;el}$ is proportional to $\alpha-1$ and exactly zero when the contact is symmetric ($\alpha=1$). We emphasize that quasielastic processes contribute to the jump because of virtual propagation into the electrodes during the emission-reabsorption process that is Pauli blocked when $V\leq\omega_0$ (no available final scattering states). In the limit $\alpha\to 0$, both quasielastic and inelastic processes are of the same order of magnitude and fully compete. The case of the second factor $F_2$ (middle panel of Fig. 2) corresponds to the jump in the noise at phonon energy $\Delta F_2$,

$$\Delta F_{2;in} = \frac{s}{2\pi}\frac{T_+T_-}{T(0)T(\epsilon_d)}\{1-3(T_+ + T_-)+2(T_+^2+T_-^2+T_+T_-)\}, \qquad (11)$$

$$\Delta F_{2;el} = \frac{s}{2\pi}\frac{T_+T_-}{T(0)T(\epsilon_d)}\left\{\frac{T_+T_-}{2\Gamma_L\Gamma_R}\left[\left(\frac{\omega_0}{2}\right)^2-\epsilon_d^2\right] - \frac{\alpha-1}{2\alpha}[\alpha T_-(1-2T_- - T_+) - T_+(1-2T_+ - T_-)]\right\}. \qquad (12)$$

We find three regions of parameter space. For $\omega_0\ll\Gamma$, and in the limiting case of a symmetric junction ($\alpha=1$), the resulting total jump in the noise $\Delta F_2=\Delta F_{2;in}+\Delta F_{2;el}$ is positive when $T(0)\leq 1/2-1/2\sqrt{2}$ or $T(0)\geq 1/2+1/2\sqrt{2}$ and negative otherwise. This change in sign can be understood by the following qualitative arguments. In the regime where $T(0)$ goes to 0 or 1, shot noise goes to zero due to Pauli principle, and activated e-ph interactions open an inelastic channel (positive contribution to noise). In the intermediate regime where $T(0)\approx\frac{1}{2}$, shot noise is maximal and activated e-ph interactions result in a negative contribution to noise. The same type of diagram is shown for the jump in the third moment $\Delta F_3$ (jump in the skewness) on lower panel of Fig. 2, where the competition between quasielastic and inelastic processes results in the partition of parameter space in four regions.

The behavior of an arbitrary $\Delta F_n$ and the whole FCS can be determined in the limit $T\to 1$, where we obtain the following analytic approximation of the CGF (Ref. 17):

$$S(\chi)\approx -i\bar{q}_0\chi - \bar{q}_1(e^{-i\chi}-1), \qquad (13)$$

where $\bar{q}_0 = t_0 V/2\pi$ and $\bar{q}_1 = t_0/2\pi\lambda^2_{e\text{-}ph}/T(\epsilon_d)(V-\omega_0)\theta(V-\omega_0)$. Below the inelastic threshold ($V<\omega_0$), the distribution $P_{t_0}(q)$ is Gaussian (a delta peak at zero temperature) due to perfect transfer of mean charge $\bar{q}_0$, whereas above that threshold ($V \geq \omega_0$), $P_{t_0}(q)$ is distorted to a Poisson distribution for holes due to the activation of spontaneous phonon emission (rare event for weak e-ph coupling).

In conclusion, we have derived a compact formula for computing the FCS of a molecular level weakly interacting with a local phonon mode. The competition between quasielastic and inelastic processes results in the partition of the parameter space $\{\alpha, T(0)\}$ into $n+1$ domains characterized by a given sign in the jump of the generalized cumulant of order $n$ at phonon energy $\Delta F_n$. In the limit of perfect transmission, $P_{t_0}(q)$ evolves from a Gaussian distribution for electrons to Poissonian distribution for holes, under activation of e-ph interaction. Of immediate experimental interest is the change of sign in the jump of noise. For temperatures in the range of $T=4-17$ K, and typical energy of the phonon mode $\omega_0 \approx 50$ meV, the ratio $T/\omega_0 \approx 10^{-2}-4.10^{-2}$ is very small, and the jump is not smeared by thermal effects. The amplitude of the jump being of order a few percent, we expect that the change in sign could be tested experimentally along the lines of Ref. 12. At this point we would also like to mention that we recently became aware of two closely related papers.[18]

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