Current noise in molecular junctions: effects of the electron-phonon interaction

Federica Haupt,1,† Tomáš Novotný,2,‡ and Wolfgang Belzig1,‡

1Fachbereich Physik, Universität Konstanz, D-78457 Konstanz, Germany
2Department of Condensed Matter Physics, Faculty of Mathematics and Physics, Charles University in Prague, Ke Karlovu 5, CZ-121 16 Praha 2, Czech Republic

(Dated: October 27, 2010)

We study inelastic effects on the electronic current noise in molecular junctions, due to the coupling between transport electrons and vibrational degrees of freedom. Using a full counting statistics approach based on the generalized Keldysh Green’s function technique, we calculate in an unified manner both the mean current and the zero-frequency current noise. For multilevel junctions with weak electron-phonon coupling, we give analytical formulas for the lowest order inelastic corrections to the noise in terms of universal temperature- and voltage-dependent functions and junction-dependent prefactors, which can be evaluated microscopically, e.g. with ab-initio methodologies. We identify distinct terms corresponding to the mean-field contribution to noise and to the vertex corrections, and we show that the latter contribute substantially to the inelastic noise. Finally, we illustrate our results by a simple model of two electronic levels which are mutually coupled by the electron-phonon interaction and show that the inelastic noise spectroscopy is a sensitive diagnostic tool.

PACS numbers: 72.70.+m, 72.10.Di, 85.65.+h, 73.63.-b

I. INTRODUCTION

Recent progress in experimental techniques, such as break junctions and scanning tunneling microscopy, allows to electrically contact single molecules, to create and manipulate atomic wires, and to investigate the electronic transport properties of these nanoscopic objects.3–12 Contrary to larger devices, atomic-scale ones usually retain their microscopic features, which are then observable in the transport spectroscopy. Apart from the purely electronic contributions, other degrees of freedom such as vibrational modes or local spins can be addressed and revealed by point-contact spectroscopy3 (PCS) or by inelastic electron tunneling spectroscopy (IETS).4 These techniques have been extensively used in the recent past to reveal inelastic features in the non-linear conductance due to vibrations5–15 or local spin excitations16–18 triggering an intense theoretical activity. So far most studies focused on the current-voltage characteristics, and present day PCS/IETS theories19–31, often based on ab-initio calculations, allow to make detailed predictions for the conductance that compare favorably with experimental results.

Electronic current (shot) noise32,33 is another quantity of fundamental interest in transport, representing the second cumulant of the current distribution within the full counting statistics methodology.34,35 Although the measurement of higher order cumulants is experimentally challenging, shot noise in atomic contacts and molecular junctions has been already measured in the small voltage (elastic) regime36–38 and there are ongoing experimental efforts to address the inelastic noise signal as well.39 These progresses made the investigation of effects due to electron-phonon (e-ph) interaction on the current noise an appealing task from the theoretical point of view, with the ultimate goal of allowing for prediction for the noise in molecular junctions as reliable as those now available for the non-linear conductance.

Since the noise is technically represented by a two-particle non-equilibrium correlation function, its direct evaluation poses a significant challenge compared to the mean current. For molecular junctions weakly coupled to leads, noise calculations based on one-level models have been put forward within the rate equation approach.39–40 In the opposite limit, pioneering works based on the non-equilibrium Green’s functions formalism41–42 adopted a mean-field-like approximation for the noise, thus neglecting the contributions due to the vertex corrections. A very convenient tool to overcome these limitations is the full counting statistics,43,44 since it allows to address the noise and other current cumulants, while taking consistently into account all contributions due to e-ph coupling up to a given order in perturbation theory. Simultaneously with other two groups45–47 we exploited such an approach to analyze the transport properties of a simple model for molecular junctions consisting of a single resonant level symmetrically coupled to metallic leads and weakly interacting with a single phonon mode.48 Despite its simplicity, this model can be applied to the experimentally relevant case of junctions formed by a single hydrogen/deuterium molecule between platinum leads,7 and in this case we predicted a significant inelastic contribution to the current noise.49

In this paper we go beyond such a simple model and we extend our theory for inelastic noise to more complex molecular junctions and to atomic wires. In fact, we consider the case of a junction formed by multiple electronic levels with asymmetric coupling to leads, and derive analytical formulas for the corrections to current and noise due to weak electron-phonon coupling. We express our result in terms of universal temperature- and voltage-dependent functions and junction-dependent prefactors.
These expressions, when supplemented with \textit{ab-initio} calculations to estimate microscopically the prefactors characterizing a given junction, can serve as a basis to make realistic predictions for the current noise in a relevant class of molecular and atomic-size junctions. In this respect, our work can be viewed as a direct extension of the corresponding lowest order expansion scheme developed for the non-linear conductance.\textsuperscript{18,22} In addition, we identify the contributions to noise due to the vertex corrections and show that, even in limit of weak \textit{e-ph} coupling, they need to be taken into account in order to obtain accurate results and to comply with the fluctuation-dissipation theorem.

The paper is organized as follows. After a brief description of the model of a multi-level junction coupled to leads and weakly interacting with a number of vibronic modes (phonons) in Sec. II, we introduce the methodology of the noise calculation via extended Keldysh Green’s functions in Sec. III. In Sec. IV we consider the case of no interactions and recover the standard results for the elastic current and noise. Our original contribution is presented in Secs. V and VI, where we discuss the corrections to the current and noise due to the Hartree and dissipation theorem. Finally, we conclude and give an outlook of open issues and possible extensions of the present work.

II. MODEL

The system we consider can be schematically represented as a central device region (representing the molecule or the atomic-wire) which is tunnel-coupled to non-interacting metallic leads

\[ \hat{H} = \hat{H}_C + \hat{H}_{L,R} + \hat{H}_T. \]

Neglecting for simplicity the spin degree of freedom\textsuperscript{47} the central region can be described by the following Hamiltonian

\[ \hat{H}_C = \hat{H}_d + \hat{H}_{ph} + \hat{H}_{e-ph} \]  \hspace{0.5cm} \text{(2a)}

\[ \hat{H}_d = \sum_{i,j} h_{ij} \hat{d}_i^\dagger \hat{d}_j \]  \hspace{0.5cm} \text{(2b)}

\[ \hat{H}_{ph} = \sum_{\ell} \hbar \omega_{\ell} \hat{b}_\ell^\dagger \hat{b}_\ell \]  \hspace{0.5cm} \text{(2c)}

\[ \hat{H}_{e-ph} = \sum_{\ell} \sum_{i,j} M_{ij}^\ell \hat{d}_i^\dagger \hat{b}_\ell (\hat{b}_\ell^\dagger + \hat{b}_\ell), \]  \hspace{0.5cm} \text{(2d)}

where \( \hat{d}_i \) (\( \hat{d}_i^\dagger \)) and \( \hat{b}_\ell \) (\( \hat{b}_\ell^\dagger \)) are the electron and phonon annihilation (creation) operators, respectively; \( \hat{H}_d \) is the single-particle effective Hamiltonian of the electrons moving in a static arrangement of atomic nuclei, \( \hat{H}_{ph} \) is the Hamiltonian of free uncoupled phonons, \( \hat{H}_{e-ph} \) is the \textit{e-ph} coupling within the harmonic approximation, and \( M_{ij}^\ell \) is the \textit{e-ph} coupling matrix for the \( \ell \)-th phonon mode. Here, boldface notation stands for matrices in the system electronic space. The leads and tunneling Hamiltonians are given by

\[ \hat{H}_{L,R} = \sum_{k,\alpha=L,R} \epsilon_{\alpha,k} \hat{c}_{\alpha,k}^\dagger \hat{c}_{\alpha,k}, \]  \hspace{0.5cm} \text{(3)}

\[ \hat{H}_T = \sum_{k,\alpha=L,R} \sum_i (V_{ij} \epsilon_{\alpha,k} \hat{c}_{\alpha,k}^\dagger \hat{d}_i + \text{h.c.}). \]  \hspace{0.5cm} \text{(4)}

The states in the leads are occupied according to the Fermi distributions \( f_\alpha(\varepsilon) = f(\varepsilon - \mu_\alpha) \), with \( f(\varepsilon) = (1 + e^{\beta \varepsilon})^{-1} \), \( \beta = 1/k_B T \) the inverse temperature, and \( \mu_\alpha \) the chemical potential of lead-\( \alpha \). The applied bias voltage is \( eV = \mu_L - \mu_R \).

III. METHODS

A. The generalized Keldysh Green’s function technique

To calculate the average current and the zero-frequency noise in the stationary regime, we employ the generalized non-equilibrium Keldysh Green’s function technique.\textsuperscript{42} In this approach, one is interested in finding the cumulant generating function \( \mathcal{S}(\lambda) \), which in the case of charge transport is defined as

\[ e^{-\mathcal{S}(\lambda)} = \sum_N e^{iN\lambda} P_{t_0}(N) \]  \hspace{0.5cm} \text{(5)}

where \( P_{t_0}(N) \) is the probability for \( N \) charges to be transferred through the system during the measuring time \( t_0 \) and \( \lambda \) is a continuous parameter known as counting field. Given \( \mathcal{S}(\lambda) \), the cumulants \( \langle \delta N^k \rangle \) of the charge transfer distribution can be straightforwardly calculated according to the prescription

\[ \langle \delta N^k \rangle = - \left. \frac{\partial^k}{\partial (\lambda)^k} \mathcal{S}(\lambda) \right|_{\lambda=0}. \]  \hspace{0.5cm} \text{(6)}

The applied bias voltage is \( eV = \mu_L - \mu_R \).
Under the assumption that the measuring time $t_0$ is much longer than any correlation time of the system ($t_0 \to \infty$), the first two cumulants of $P_N(N)$ are directly proportional to the average current through the system $I$ and to the zero-frequency current noise $S$,

$$I = e \frac{\langle \delta N \rangle}{t_0}, \quad S = e^2 \frac{\langle \delta N^2 \rangle}{t_0},$$

(7)

which are the quantities we are primarily interested in.

The key idea for calculating the cumulant generating function for transport through a quantum system is to modify the Hamiltonian by introducing a time-dependent counting field $\lambda(t)$ and to relate $S(\lambda)$ to the Keldysh Green’s function of the system in the presence of $\lambda(t)$, i.e. to $G_{ij}^{\tau}(t, t') = -i \hbar^{-1}(\mathcal{T} \delta_i \delta_j(t)(t')_\lambda)$, where the evolution is due to the modified Hamiltonian $\hat{H}_T$. One way to accomplish this is to add a time-dependent phase $\lambda(t)/2$ to the tunneling matrix elements $V_{L,k}$,

$$\hat{H}_T \to \hat{H}_T^\lambda = \sum_{k,j} V_{L,k}^j e^{-i\lambda(t)/2} e_k \delta_j + V_{R,K}^j e_k \delta_j + h.c.$$ and $\text{Tr}_K$ stands for the trace over the electronic degrees of freedom and the Keldysh space, i.e. $\text{Tr}_K \{ \mathcal{O} \} = \text{Tr} \{ \mathcal{O}^{--} + \mathcal{O}^{++} \}$, with $\mathcal{T} \{ \cdots \}$ being the trace in the system electronic space. The check sign $\check{}$ indicates matrices in the Keldysh space and the superscripts $-/+ \leftrightarrow$ correspond to the forward/backward branch of the Keldysh contour. Note that in Eq. (11) we have used the following sign convention for the elements of the Keldysh-matrix for the self-energy $\Sigma$

$$\check{\Sigma} = \begin{pmatrix} \Sigma^{--} & \Sigma^{-+} \\ \Sigma^{+-} & \Sigma^{++} \end{pmatrix}. \quad (11)$$

Finally, $\Gamma_{ij}^\alpha(\varepsilon) = 2\pi \sum_k V_{\alpha,k}^i V_{\alpha,k}^j \delta(\varepsilon - \varepsilon_{k,\alpha})$ is the level broadening due to the coupling to the lead $\alpha$.

According to Eq. (8), the problem of evaluating current and noise (as well as any higher order cumulant of the charge transfer distribution) is reduced to the calculation of the system single-particle Green’s function $G_\lambda$. The latter can be obtained from the solution of the Dyson equation

$$G_\lambda(\varepsilon) = g_\lambda(\varepsilon) + g_\lambda(\varepsilon) \check{\Sigma}_\text{eph}(\varepsilon) G_\lambda(\varepsilon), \quad (12)$$

where $\check{\Sigma}_\text{eph}$ is the self-energy solely due to the e-ph coupling, and $g_\lambda$ is the free Green’s function of the system in the presence of the leads and of the counting field but without the e-ph interaction $g_\lambda = (\mathcal{E} 1 - \mathcal{H}_d)^{-1}$, with

$$g_\lambda(\varepsilon) = \begin{pmatrix} \mathcal{E} - \mathcal{H}_d & 0 \\ 0 & -\mathcal{E} + \mathcal{H}_d \end{pmatrix}^{-1}. \quad (13)$$

with $\lambda(t) = \lambda \theta(t) \theta(t_0 - t)$ on the forward branch of the Keldysh contour and $\lambda(t) = -\lambda \theta(t) \theta(t_0 - t)$ on the backward one, where $\theta(x)$ is the Heaviside step-function.

Here we extend the result derived by Gogolin and Komnik for the Anderson model to the case in which the central region has several electronic states. Generalizing the derivation of Ref. [49] to a multilevel system, we obtain the following expression for the derivative of the cumulant generating function

$$\frac{\partial S(\lambda)}{\partial \lambda} = t_0 \int \frac{d\varepsilon}{2\pi \hbar} \text{Tr}_K \{ \check{\Sigma}_T'(\varepsilon) \check{G}_\lambda(\varepsilon) \}, \quad (8)$$

where $\check{G}_\lambda$ represents the Keldysh-Green’s function of the system in Keldysh space

$$\check{G}_\lambda(\varepsilon) = \begin{pmatrix} G^{++}_{\lambda}(\varepsilon) & G^{+-}_{\lambda}(\varepsilon) \\ G^{-+}_{\lambda}(\varepsilon) & G^{--}_{\lambda}(\varepsilon) \end{pmatrix}, \quad (9)$$

$$\check{\Sigma}_T' \equiv \partial \check{\Sigma}_T / \partial \lambda, \text{ with } \check{\Sigma}_T \text{ the self-energy due to the modified tunneling Hamiltonian } \hat{H}_T^\lambda.$$

and the Green’s function of the isolated dot. It is important to notice that $\check{\Sigma}_\text{eph}$, depending on the Green’s function of the system, is itself a function of the counting field $\lambda$ (see Sec. III.C).

Finally, we remark in passing that for $\lambda \neq 0$ it is $g_\lambda^{--} + g_\lambda^{++} \neq g_\lambda^{+-} + g_\lambda^{-+}$, i.e. in the presence of the counting field $\lambda$, the four Keldysh Green’s functions are all independent.

B. Current and Noise

Although Eq. (8) gives access to all cumulants of the charge transfer distribution through the system, in this work we will focus only on the study of the average current $I$ and the zero frequency noise $S$, which are the quantities most easily accessible from the experimental point of view.

The average current is directly obtained from Eq. (8) by setting $\lambda = 0$

$$I = e \int \frac{d\varepsilon}{2\pi \hbar} \text{Tr}_K \{ \check{\Sigma}_T'(\varepsilon) \check{G}_\lambda(\varepsilon) \}_{\lambda = 0}, \quad (14)$$

while the noise is given by

$$S = e^2 \int \frac{d\varepsilon}{2\pi \hbar} \text{Tr}_K \{ \check{\Sigma}_T' \check{\Sigma}_T' \check{G}_\lambda + \check{\Sigma}_T' \check{G}_\lambda \check{\Sigma}_T' \check{G}_\lambda \}_{\lambda = 0} + e^2 \int \frac{d\varepsilon}{2\pi \hbar} \text{Tr}_K \{ \check{\Sigma}_T' \check{G}_\lambda \check{\Sigma}_\text{eph} \check{G}_\lambda \}_{\lambda = 0}, \quad (15)$$
where, we have used the identity \( \partial_\lambda \mathcal{O} = -\bar{\mathcal{O}}(\partial_\lambda \mathcal{O}^{-1})\bar{\mathcal{O}} \) together with the Dyson equation \( \mathcal{G}_\lambda^{-1} = \mathcal{G}_\text{el}^{-1} - \mathcal{G}_\lambda \mathcal{G}_\text{el} \mathcal{G}_\lambda \). It turns out that the first term of Eq. (15) corresponds exactly to Eq. (30) of Ref. [50], which gives the expression for the noise within a mean-field approximation (see Appendix A). For this reason, we identify

\[
S^{(\text{mf})} = e^2 \int \frac{d\varepsilon}{2\pi \hbar} \text{Tr}_K \left\{ \Sigma_T^{\nu} \mathcal{G}_\lambda + \Sigma_T^{\nu} \mathcal{G}_\lambda \Sigma_T^{\nu} \mathcal{G}_\lambda \right\}_{\lambda=0}^{-1}
\]

as the mean-field contribution to noise. The remaining term constitutes the vertex correction

\[
S^{(\text{vc})} = e^2 \int \frac{d\varepsilon}{2\pi \hbar} \text{Tr}_K \left\{ \Sigma_T^{\nu} \mathcal{G}_\lambda + \Sigma_T^{\nu} \mathcal{G}_\lambda \Sigma_T^{\nu} \mathcal{G}_\lambda \right\}_{\lambda=0}
\]

As we will discuss in detail in the following, the vertex correction \( S^{(\text{vc})} \) can give a significant contribution to the total noise, comparable to the mean-field part and thus, contrary to what was done in some pioneering works,\textsuperscript{41,42} it cannot be omitted even in the limit of weak interaction. Moreover, neglecting \( S^{(\text{vc})} \) generally leads to violation of the fluctuation-dissipation theorem, see Appendix B.

C. Weak electron-phonon coupling

In order to make use of Eqs. (14), (15), we need to determine the full Green’s function \( \mathcal{G}_\lambda \). Being interested in the experimentally relevant limit of weak electron-phonon coupling, we truncate the Dyson equation at the lowest (second) order in the \( \mathcal{e} \)-\( \mathcal{p} \) coupling

\[
\mathcal{G}_\lambda \approx \mathcal{g}_\lambda + \mathcal{g}_\lambda \Sigma_{\text{el}}^{(2)} \mathcal{g}_\lambda,
\]

where \( \Sigma_{\text{el}}^{(2)} = \Sigma_H + \Sigma_F \) is the Hartree-Fock self-energy, depicted diagrammatically in Fig. 1 with

\[
\Sigma_{\text{el}}^{(2)}(\nu, \nu) = \delta_{\nu\bar{\nu}} \sum_{\ell=1}^{N_\ell} \sum_{\ell'} \int \frac{d\varepsilon}{2\pi} \mathcal{d}_\ell^{\nu,\nu}(\varepsilon - \varepsilon') \mathcal{M}_\ell \mathcal{g}_\lambda^{\nu,\nu}(\varepsilon') \mathcal{M}_{\ell'},
\]

and \( \eta, \bar{\eta} = \pm \). Above, \( \mathcal{d}_\ell^{\nu,\nu}(\varepsilon) \) represent the free thermalized phonon Green’s functions of the \( \ell \)-th phonon mode

\[
\mathcal{d}_{\ell}^{\pm}(\varepsilon) = \sum_{s=\pm} \left[ -i\pi(2N_\ell + 1)\delta(\varepsilon + s\hbar\omega_\ell) \mp \frac{s}{\varepsilon + s\hbar\omega_\ell} \right] d_{\ell}^{\pm}(\varepsilon) = -2\pi i[(N_\ell + 1)\delta(\varepsilon \pm \hbar\omega_\ell) + N_\ell \delta(\varepsilon \mp \hbar\omega_\ell)]
\]

with \( N_\ell \equiv (e^{\beta\hbar\omega_\ell} - 1)^{-1} \) the thermal expectation value of the mode occupation. The proper inclusion of possible heating effects on noise, involving non-equilibrium phonon occupation and its potential back-action on the electronic transport, is beyond the scope of this publication; some of the involved issues are discussed in the concluding Sec. VII.

In Eq. (19) we introduced the generalized electronic density \( \mathcal{n}_\lambda^{\nu} \) on the two branches of the Keldysh contour \((\nu = \pm)\) in the presence of the counting field

\[
\mathcal{n}_\lambda^{\nu} = \frac{1}{2\pi \hbar} \lim_{t \to t'+0^+} -i \int \frac{d\varepsilon}{2\pi} e^{-i\varepsilon(t-t')/\hbar} \mathcal{g}_\lambda^{\nu}(\varepsilon).
\]

Note that, on the two branches of the Keldysh contour, the electronic density \( \mathcal{n}_\lambda^{\nu} \) is given by different limits \( t \to t' \) of the corresponding Green’s functions \( \mathcal{g}_\lambda^{\nu}(t-t') \). As a consequence, even if \( \lambda(t) = \pm \) on the forward/backward branch, \( \mathcal{n}_\lambda^{\nu} \neq \mathcal{n}_{\lambda^\mp} \) for any finite value of \( \lambda \). On the other hand, at \( \lambda = 0 \) one gets

\[
\mathcal{n}_\lambda^{\nu=0} = \mathcal{n}_{\lambda=0} = \mathcal{n}_e = -i \int \frac{d\varepsilon}{2\pi \hbar} \mathcal{g}_\lambda^{\nu=0}(\varepsilon),
\]

where \( \mathcal{n}_e \) is the electronic density in the noninteracting case.

Plugging Eqs. (19), (20) into Eq. (18), we can rewrite Eqs. (14), (15) as \( I = I_{\text{el}} + I_{\text{ph}} \) and \( S = S_{\text{el}} + S_{\text{ph}} \), where

\[
I_{\text{el}} = ie \int \frac{d\varepsilon}{2\pi \hbar} \text{Tr}_K \left\{ \Sigma_T^{\nu} \mathcal{g}_\lambda \right\}_{\lambda=0},
\]

\[
S_{\text{el}} = e^2 \int \frac{d\varepsilon}{2\pi \hbar} \text{Tr}_K \left\{ \Sigma_T^{\nu} \mathcal{g}_\lambda + \Sigma_T^{\nu} \mathcal{g}_\lambda \Sigma_T^{\nu} \mathcal{g}_\lambda \right\}_{\lambda=0},
\]

are the elastic current and noise, and

\[
I_{\text{ph}} = I_F + I_H, \quad S_{\text{ph}} = S_F + S_H
\]

give the respective corrections due to electron-phonon coupling, with

\[
I_{H(F)} = ie \int \frac{d\varepsilon}{2\pi \hbar} \text{Tr}_K \left\{ \Sigma_T^{\nu} \mathcal{g}_\lambda \Sigma_{H(F)} \mathcal{g}_\lambda \right\}_{\lambda=0},
\]

\[
S_{H(F)} = e^2 \int \frac{d\varepsilon}{2\pi \hbar} \text{Tr}_K \left\{ \Sigma_T^{\nu} \mathcal{g}_\lambda \Sigma_{H(F)} \mathcal{g}_\lambda + 2 \Sigma_T^{\nu} \mathcal{g}_\lambda \Sigma_T^{\nu} \mathcal{g}_\lambda \right\}_{\lambda=0},
\]

is the mean-field contribution and

\[
S_{\text{vc}}^{(\text{H})} = e^2 \int \frac{d\varepsilon}{2\pi \hbar} \text{Tr}_K \left\{ \Sigma_T^{\nu} \mathcal{g}_\lambda \Sigma_{H(F)} \mathcal{g}_\lambda \right\}_{\lambda=0}.
\]

the vertex correction. The previous equations can be schematically expressed by the diagrams of Fig. 2.
The box represents purposes in the considered weak coupling limit. Counting field \( O \) charge conservation can only occur in the next order, i.e. between the device and the leads. Potential violations of charge conservation in that order. This implies that both mean current and the noise as functions of the applied bias voltage and other system parameters. It should be noted however, that approximation (ii) potentially leads to problems for integrals over infinite range and, in this case, it might be necessary to lift it. Specifically, this happens in the calculation of the electron density entering the Hartree term, see Appendix [B] and in the evaluation of the real parts of the retarded/advanced Fock self-energy via Kramers-Kronig relations, see Appendix [C].

**IV. ELASTIC CURRENT AND NOISE**

For sake of completeness, before discussing the corrections to \( I \) and \( S \) due to the e-ph coupling, we consider briefly the results for the elastic current and noise.

In the eWBL approximation, the elastic current is simply proportional to the voltage

\[
I_{el} = \frac{e^2}{h} \text{Tr}(T) e V,
\]

(27)

with \( T = \Gamma_L g^* \Gamma_R g^a \), while the noise is given by

\[
S_{el} = \frac{e^2}{h} \left[ \frac{2}{\beta} \text{Tr}(T^2) + \text{Tr}(T(1 - T))U(eV) \right],
\]

(28)

where we have introduced the function \( U(x) = x \coth(\beta x/2) \).

The eigenvalues of the matrix \( T \) give the “PIN-code” of transmission eigen-channels of the molecule connected to leads (without e-ph interaction), and Eqs. (27), (28) are indeed equivalent to the standard results for current and noise in a non-interacting system derived within the scattering theory. However, \( T \) is not equal to the matrix product \( tt^\dagger \) of the transmission amplitudes \( t \) of the scattering theory (it cannot be as \( T \) is in general non-hermitian, for example). The two matrices are related though by a similarity (non-unitary) transformation, which among others ensures \( \text{Tr}(T) = \text{Tr}(tt^\dagger) \). With this caveat in mind, for sake of simplicity we will nevertheless call \( T \) the transmission matrix in the rest of this paper. The construction of the scattering eigenstates within the NGF formalism is described in detail in Ref. [53].

We now turn our attention to the corrections to the current and noise induced by the e-ph interaction. In order to make the discussion as clear as possible, we will consider the contributions coming from the Hartree and the Fock diagrams separately.
FIG. 3. Diagrammatic representations of $S_{H}^{(mf)}$ and $S_{H}^{(vc)}$. Here, plain and wiggly lines stand for the electronic and phononic Green’s functions, respectively. The single cross stands for $\Sigma_{\alpha}^{0}$ and the doubled one for $\Sigma_{\alpha}^{\prime}$. Finally, the dot represents the e-ph constant M.

V. CORRECTIONS DUE TO THE HARTREE DIAGRAM

A. Current

We start by considering the contributions to the current $I_{H}$ coming from the Hartree diagram. After integrating Eq. (25) in the eWBL approximation we obtain

$$I_{H} = \frac{e}{\hbar} \text{Tr}\{T_{H}^{(qel)}\} eV,$$

(29)

with

$$T_{H}^{(qel)} = -\frac{2i\Gamma_{L}(g^{r}M_{A}R + h.c.}{\hbar\omega_{0}}$$

(30)

with $n_{e}$ the noninteracting electron density [ Eq. (22)] and $A_{\alpha} = g^{r}\Gamma_{L}g^{a}$. The correction $I_{H}$ is therefore a smooth function of the voltage with no features at the phonon emission threshold. For this reason $I_{H}$ has been often discarded in previous works on the effects of e-ph interaction on the current.17-20,23,26,42,54

It should be noticed, however, that $I_{H}$ is generally non-linear in $eV$, since $n_{e}$ can be a (smooth) function of the applied bias voltage. Such a dependence is nevertheless rather weak in the eWBL (see Appendix B), and in such a case it is possible to interpret Eq. (29) as a quasi-elastic correction to an effective transmission matrix $T = T + T_{H}^{(qel)}$, i.e. because of the e-ph coupling, the current is not proportional to the bare transmission coefficient Tr{T} but rather to Tr{T}.

B. Noise

The mean-field contributions and the vertex correction to noise due to the Hartree diagram can be schematically represented by the diagrams in Fig. 3 which are the result of inserting the Hartree self-energy from Fig. 1 into appropriate diagrams in Fig. 2. In the usual eWBL, $S_{H}^{(mf)}$ takes the simple form

$$\frac{S_{H}^{(mf)}}{e^{2}/h} = \text{Tr}\{(1 - 2T)T_{H}^{(qel)}\} U(eV) + 4\beta \text{Tr}\{TT_{H}^{(qel)}\}.$$  

(31)

Analogously to the current $I_{H}$, this contribution has a simple interpretation in terms of the renormalization of the transmission matrix introduced above $T \rightarrow \tilde{T} = T + T_{H}^{(qel)}$. This can be seen easily, as Eq. (31) corresponds exactly to the contribution of order $M^{2}$ to the elastic shot-noise of a system with transmission matrix $\tilde{T}$:

$$\frac{2e}{\beta} \text{Tr}\{T^{2}\} + \text{Tr}\{(1 - \tilde{T})U(eV) + 4\beta \text{Tr}\{\tilde{T}T_{H}^{(qel)}\} + \mathcal{O}(M^{4}),$$

(32)

where $S_{el}$ is given in Eq. (28).

Making use of the cyclic invariance of the trace, the vertex correction $S_{H}^{(vc)}$ can be rewritten as

$$\frac{S_{H}^{(vc)}}{e^{2}/h} = \frac{2i}{\hbar\omega_{0}} \left[\left(\text{Tr}\{Mn_{+}^{\prime}\}\right)^{2} - \left(\text{Tr}\{Mn_{+}^{\prime}\}\right)^{2}\right],$$

(33)

where we have used the fact that $n_{+}^{\prime} = -n_{+}$, with $n_{+}^{\prime} = (\partial n_{+}^{0}/\partial \lambda)_{\lambda=0}$. Performing the integrals over energy in the usual eWBL approximation one obtains

$$\text{Re} \left[\text{Tr}\{Mn_{+}^{\prime}\}\right] = -\frac{1}{2} \text{Tr}\{\Gamma_{L}A_{R}Mg^{a} + h.c.\} eV,$$

$$\text{Im} \left[\text{Tr}\{Mn_{+}^{\prime}\}\right] = -\frac{i}{2} \text{Tr}\{\Gamma_{L}g^{r}_{R}M_{A}R - h.c.\} eV$$

$$-\frac{i}{2} \text{Tr}\{\Gamma_{L}g^{r}_{R}M_{A}R - h.c.\} U(eV) + \frac{1}{4} \text{Tr}\{\Gamma_{L}(A_{L}M_{A}R - A_{R}M_{A}R + h.c.)\} \times \left(\frac{2}{\beta} - U(eV)\right)$$

with $g^{r}_{R} = \text{Re} g^{r}$. Contrary to $S_{H}^{(mf)}$, Eq. (32) has no simple interpretation in terms of an effective transmission coefficient and it represents a distinctive contribution to noise coming from the Hartree term. From the physical point of view, it stems from the coupling of occupations of the electronic levels with the current fluctuations.29,30

We note, however, that $\text{Im} [\text{Tr}\{Mn_{+}^{\prime}\}] = 0$ in the case of a system with a single electronic level symmetrically coupled to leads. Therefore in this particular case the correction to noise induced by the Hartree term is given by $S_{H}^{(mf)}$ alone.

VI. CORRECTIONS DUE TO THE FOCK DIAGRAM

A. Current

We now turn our attention to the corrections to current induced by the Fock diagram. Integrating Eq. (25) in the
usual eWBL approximation, we obtain

\[
\frac{I_F}{e/\hbar} = \text{Tr}\{T_F^{(qel)}\} eV + \text{Tr}\{T_F^{(inel)}\} g(eV)
+ 2N_0 \text{Tr}\{T_F^{(qel)} + T_F^{(inel)}\} eV + \text{Tr}\{T_F^{(asym)}\} h(eV)
\]

(33)

where

\[
T_F^{(qel)} = \Gamma_L (g^* M g \Gamma R + h.c.)
\quad (34a)
\]

\[
T_F^{(inel)} = \Gamma_L g^* \left[ M A_R M I_R - \frac{i}{2}(M A_M T_R - h.c.) \right] g^a
\quad (34b)
\]

\[
T_F^{(asym)} = \Gamma_L g^* \left[ M (A_L - A_R) \Gamma R + h.c. \right] g^a
\quad (34c)
\]

with \( A \equiv A_L + A_R = \imath (g^r - g^a) \) the spectral density. All the involved quantities depend only on the properties of the system at the Fermi level and can be determined by ab-initio calculations.\(^{18-20,23}\)

The voltage dependence of \( I_F \) is carried by the functions

\[
g(eV) = \frac{1}{2} \left[ U(eV - \hbar \omega_0) - U(eV + \hbar \omega_0) + 2eV \right],
\quad (35)
\]

and

\[
h(eV) = \frac{1}{2} \int \text{d}\varepsilon \left[ \{ n_F(\varepsilon) - n_F(\varepsilon + eV) \}
\right.
\times \left. \mathcal{H}_c \{ \{ n_F(\varepsilon' - \hbar \omega_0) - n_F(\varepsilon' + \hbar \omega_0) \}\} (\varepsilon), \quad (36)
\]

where \( \mathcal{H}_c \{ f(\varepsilon')\} (\varepsilon) = (1/\pi) \Pi \int \text{d}\varepsilon' f(\varepsilon')/(\varepsilon' - \varepsilon) \) is the Hilbert transform. Eq. (33) is in agreement with the result of Viljas et al.\(^{12}\) while a term \( (1 + 2N_0)\text{Tr}\{T_F^{(qel)}\} eV \) is missing in Refs.\(^{18,20}\). Such a discrepancy is further discussed in Appendix D.\(^{18}\)

The functions \( g(eV) \) and \( h(eV) \) give contributions to \( dI/dV \) which are even/odd in bias, respectively (see Fig. 4). The term proportional to \( h(eV) \) vanishes in the case of symmetric coupling to the leads, and it is typically much smaller than the contribution proportional to \( g(eV) \), even for asymmetric junctions.\(^{23,26}\) Moreover, experimentally measured conductance curves are usually very weakly asymmetric under reversal of \( V \) and at present it is unclear if the asymmetry is caused by phonons or by other effects.

At low temperature \( (k_B T < \hbar \omega_0, N_0 \approx 0) \), the main contribution to \( I_F \) is therefore given by the first two terms of Eq. (33) alone. The first of these terms, linear in \( eV \), is a quasi-elastic correction that, similarly to \( I_H \), contributes to an effective transmission matrix \( \tilde{T} = T + T_F^{(qel)} \). The second one has instead a threshold behavior at the phonon emission energy, as seen in Fig. 4 and it is responsible for the jump in the conductance observed in IETS and PCS experiments.

The sign of the conductance step at the phonon emission threshold (positive or negative) depends on the coefficient \( \text{Tr}\{T_F^{(inel)}\} \), and it has been discussed in detail in Refs.\(^{18,20}\). As a rule of thumb, in the case of a molecular junction with low (high) bare transmission \( \text{Tr}\{T\} \), inelastic e-ph scattering results in an increase (decrease) of the conductance above the phonon emission threshold.

In the case of a system with a single electronic level symmetrically coupled to the leads via \( \Gamma_L = \Gamma_R = \Gamma \), \( T_F^{(inel)} \) reduces to \( T_F^{(inel)} = (M^2 T^2 / \Gamma^2)(1 - 2T) \), where \( T = T^2 |g|^2 |^2 \) is the transmission coefficient. In this case, the crossover from an increase to a decrease in the conductance is predicted to occur at \( T = 1/2.18,20 \). This behavior has been explored and confirmed experimentally in Ref.\(^{18}\).

B. Noise

We finally address the corrections to noise due to the Fock diagram \( S_F^{(mf)} + S_F^{(vc)} \), which are schematically represented by the diagrams in Fig. 4.

After lengthy but straightforward calculations, integration over energy in the usual eWBL approximation leads to analytic results for \( S_F^{(mf/vc)} \) as functions of the applied bias voltage. The final expressions are, however, rather cumbersome and, for simplicity, we consider here only the limit of zero temperature \( T = 0 \). The complete expressions for \( S_F^{(mf/vc)} \) at finite temperature are given in the supplementary material,\(^{57}\) while the limit \( eV \to 0 \) is discussed in Appendix D in relation to the fluctuation-dissipation theorem.

In the limit of zero temperature, we obtain

\[
\frac{S_F^{(mf)}}{e^2/\hbar} = \text{Tr}\{(1 - 2T)T_F^{(qel)}\} eV
+ \text{Tr}\{(1 - 2T)T_F^{(inel)}\} (|eV| - \hbar \omega_0) \theta(|eV| - \hbar \omega_0)
+ \text{Tr}\{K_F^{(mf)}\} \text{sign}(eV) \hbar \langle eV \rangle \bigg|_{T=0},
\quad (37)
\]

FIG. 4. Upper panel: Plots of the dependencies of the functions \( g(eV) \) and \( h(eV) \) on the applied bias voltage (Eqs. (35) and (36), respectively). Lower panel: Same as above, but for the derivatives \( \partial g/\partial V \) and \( \partial h/\partial V \). In both panels \( k_B T = \hbar \omega_0/30 \).
As in Fig. 3, plain and wiggly lines stand for the electronic and phononic Green's functions, respectively. The single cross stands for $\Sigma_F'$ and the doubled one for $\Sigma_F''$. Finally, the dot represents the e-ph coupling constant $M$.

and

$$S_F^{(vc)} = \frac{\partial S_F}{\partial V} = -\frac{1}{2} \left[ \mathcal{Q}_F^{(inel)} \right] V \frac{\partial V}{\partial \omega} + \frac{1}{2} \left[ \mathcal{Q}_F^{(inel)} \right] \frac{\partial \omega}{\partial V} \left|_{T=0} \right.$$ 

where $T_F^{(inel/inel)}$ are given in Eqs. (34a), (34b),

$$\mathcal{Q}_F^{(inel)} = -g^s r g^r L \left[ M A_R \Gamma_L A_R M + M A_R \Gamma_L g^s + h.c. \right].$$

and

$$K_1^{(mf)} = (1 - 2 T) \Gamma_L \left[ A_R M (A_L - A_R) M g^s + h.c. \right].$$

Finally,

$$h(eV) \left|_{T=0} = \frac{\hbar \omega_0}{2} \sum_{s=\pm 1} f \left( \frac{eV}{\hbar \omega_0} + s \right) \ln \left( \frac{eV}{\hbar \omega_0} + s \right) \right.$$ 

is the zero temperature limit of Eq. (39). The corrections to noise $S_F^{(mf/vc)}$ can then be divided into a symmetric term, which is even in bias, and an antisymmetric one, which contains the Hilbert transform $h(eV) \left|_{T=0} \right.$ and yields an odd contribution. We notice that, while $h(eV) \left|_{T=0} \right.$ is a continuous function, its derivative shows logarithmic divergencies at $eV = \pm \hbar \omega_0$. These zero-temperature divergencies are, however, an artifact of treating the phonons as non-interacting modes, and they are regularized either by finite temperature or if any broadening of the phonon spectrum is taken into account. This issue, however, goes beyond the scope of this work.

At zero temperature, the symmetric contribution to $S_F$ is a piece-wise linear function of $eV$. At low voltages, $|eV| < \hbar \omega_0$, it is given by the first term of Eq. (37) alone. Following the same reasoning as for Eq. (31), this linear contribution can be directly interpreted in terms of the renormalization of the transmission $T \rightarrow \tilde{T} = T + T_F^{(inel)}$, consistently with the sub-threshold correction to the current. Above the phonon emission threshold, $|eV| > \hbar \omega_0$, inelastic processes come into play and their contribution to the noise is given both by the second term of Eq. (37) and by the vertex correction Eq. (38). It is important to notice that these two contributions are in general of the same order (see below the Sec. IV.C for a demonstrative example), so that the latter cannot be discarded.

Experimentally, $\frac{\partial S}{\partial eV}$ is often measured directly by a lock-in technique. Such a quantity shows at the phonon emission threshold a sharp and distinguishable jump on top of a featureless background due to the elastic and quasi-elastic contributions. Therefore, we define here the inelastic noise signal as the difference of the plateau values of the noise derivative just above and below the jump

$$\Delta S' = \frac{\partial S}{\partial eV} \left|_{eV=\hbar \omega_0 + \epsilon} - \frac{\partial S}{\partial eV} \left|_{eV=\hbar \omega_0 - \epsilon} \right.$$ 

with $\epsilon \sim 5$ accounting for the finite jump width at finite temperatures. At low enough temperatures, terms proportional to $h(eV)$ give a very small contribution to the inelastic noise signal due to the symmetric shape of $\delta V/\hbar$ around $|eV| = \hbar \omega_0$ (for details see Appendix E) and we can then approximate

$$\Delta S' \approx \frac{\epsilon^2}{h} \left( (1 - 2 T) \mathcal{Q}_F^{(inel)} + \mathcal{Q}_F^{(inel)} \right),$$

i.e. at low temperatures $\Delta S'$ carries the structural information about the junction given by the terms with the threshold behavior at the phonon emission energy.

C. Independent electronic levels

We now consider a toy model for molecular junctions, in which we assume the electronic levels to be mutually coupled only via the e-ph interaction. In this case, the relevant matrices in the system electronic space are given by

$$[\Gamma_{L(R)}]_{ij} = \delta_{ij} \Gamma_{i,L(R)}; \quad [g^s]_{ij} = \frac{\delta_{ij}}{\Delta_i + i(\Gamma_{i,L} + \Gamma_{i,R})/2},$$

and $[M]_{ij} = M_{ij}$, where $i, j = 1, \ldots, N$, and $N$ is the number of electronic levels involved in the transport. Under the further assumption that each channel is symmetrically coupled to the leads ($\Gamma_L = \Gamma_R = \Gamma$), the prefactors $\text{Tr} \left\{ K_1^{(mf/vc)} \right\}$ vanish identically and Eqs. (37), (38) can be rewritten in a particularly suggestive form in terms of the transmission probabilities $T_i = \Gamma_i^2 / (\Delta_i^2 + \Gamma_i^2)$ of the individual levels.
where we have introduced the dimensionless coupling constants $\gamma_{ij} = |M_{ij}|^2 T_i T_j / (\Gamma_i \Gamma_j)$. For $N = 1$, Eqs. (44a) and (44b) reduce directly to the result of Refs. 44–46. The voltage dependence of $S_F^{(mf)}$ and $S_F^{(vc)}$ is presented in Fig. 6 for the case of a systems with only two levels. We notice that $S_F^{(vc)} < 0$ (see also Eq. 44b), meaning that the vertex corrections correspond to processes that lead to a suppression of the noise through the system. Moreover, Fig. 6 evidences that the contributions to the noise due to the vertex corrections can be of the same order of magnitude as the mean-field ones, and that they generally need to be taken into account in order to make accurate predictions for the phonon-assisted current noise.

In terms of the transmission coefficients of the different channels, the inelastic noise signal $\Delta S'$ is given by

$$\Delta S' = \frac{e^2}{h} \sum_{i=1}^{N} \left\{ \gamma_{ii}(1 - T_i)(1 - 2T_i) + \sum_{j>i} \gamma_{ij} [T_i(1 - 2T_i) + T_j(1 - 2T_j)] \sqrt{\frac{(1 - T_i)(1 - T_j)}{T_i T_j}} \right\}$$

$$+ ([eV] - h\omega_0) \theta([eV] - h\omega_0) \sum_{i=1}^{N} \left\{ \gamma_{ii}(1 - 2T_i)^2 + 2 \sum_{j>i} \gamma_{ij} (1 - 2T_i(1 - T_i) - 2T_j(1 - T_j)) \right\},$$

(44a)

$$(44b)$$

In conclusion, in this work we have studied the corrections due to weak electron-phonon coupling to the average current and the zero-frequency noise in a molecular junction. To address both quantities in a compact and efficient way, we employed the generalized Keldysh Green’s functions technique. Importantly, for the noise we were able to identify distinct terms representing the mean-field contribution and the vertex corrections, respectively. We included in our calculations both the contributions due to the Hartree and to the Fock diagrams and, under the assumption that the densities of states of the system and of the leads depend weakly on energy (eWBL), we derived analytic expressions for $I_H(F)$ and $S_H(F)$ as functions of the bias voltage at arbitrary temperature. These expressions can serve as a basis for ab-initio calculations to make realistic predictions for the current noise in an experimentally significant class of molecular junctions. Finally, we considered a toy model for molecular junctions to elucidate the sensitivity of the inelastic phonon signal to the parameters characterizing the junction.

Throughout this paper we have assumed the phonon mode to be at equilibrium with an external thermal bath, i.e. we have taken the occupation $N_0$ to be fixed according to the Bose-Einstein distribution $N_0 = (e^{\beta h\omega_0} - 1)^{-1}$. Such an approximation is strictly consistent with the
lowest-order perturbation theory in the e-ph coupling when we implicitly assume strong thermalization of the phonon mode. However, it turns out in practice that often heating effects cannot be disregarded and they influence in turn the non-linear conductance.\textsuperscript{17,19,23,39}

From the theoretical point of view, the problem of non-equilibrium phonon heating can be addressed by extending the system Hamiltonian to include the coupling of the molecular phonon to other degrees of freedom (typically bulk phonons in the leads). The value of the corresponding coupling constants can ultimately be obtained from \textit{ab-initio} calculations, which allow to assess the influence of the environment from a microscopical description.\textsuperscript{60}

In the case of zero counting field $\lambda = 0$, the non-equilibrium phonon occupation for weak e-ph coupling can be equivalently obtained either by a full non-equilibrium calculation evaluating the phonon Green’s function\textsuperscript{19,39,61,62} or by solving a master equation describing the heating of the device\textsuperscript{17,23,39} which can be viewed as a kinetic-equation-like approximation to the full non-equilibrium Green’s functions studies. Knowing the non-equilibrium phonon occupation allows to take consistently into account the effects of phonon heating in the non-linear conductance. In our pilot study\textsuperscript{48} we used such an ingredient also to phenomenologically include heating effects in the noise through a single level\textsuperscript{63}.

However, for a fully microscopical calculation of the noise, the situation is considerably more complicated because at finite counting field $\lambda \neq 0$, heating effects \textit{cannot} be expressed solely in terms of the non-equilibrium occupation of the phonon mode. In fact, to include phonon-heating effects in the generalized Keldysh GF technique one has to solve the Dyson equation for the phonon Keldysh Green’s function $D_\lambda = \tilde{d} + \tilde{d} \Pi_\lambda D_\lambda$, with the polarization operator $\Pi_\lambda$ being given in the lowest order by the electron-hole bubble,\textsuperscript{19,39,64} see Fig. 8. Note that $\Pi_\lambda$ is explicitly $\lambda$-dependent via the electronic Green’s functions and so is consequently also the dressed phonon Green’s function $D_\lambda$. At $\lambda \neq 0$ the four Keldysh components of $D_\lambda$ are all independent and therefore, even in the kinetic limit (phonon line-width neglected), it is not possible to express the effect of heating just in terms of a single non-equilibrium occupation. It is important to notice that substituting $D_\lambda$ for the free phonon Green’s function in the expressions for the e-ph self-energies $\Sigma_H(F)$ generates extra (additive) contributions to the vertex corrections $S_H^{(ve)}$ and $S_F^{(ve)}$. These contributions, which are related to the influence of phonon fluctuations on the electronic transport ("feedback"), are not included in our previous phenomenological treatment of heating effects on noise,\textsuperscript{56} and they could possibly account for the discrepancy between our result and an unpublished one by Jouravlev and coworkers\textsuperscript{65} which predicts the noise to grow with voltage above the phonon emission threshold as $S_{\text{eph}}^{(\text{Ref. 65})} \sim V^4$, in contrast to the quadratic behavior of Ref. 46, $S_{\text{eph}}^{(\text{Ref. 46})} \sim V^2$. The idea that phonon heating effects could be responsible for a nonlinear voltage dependence of $\partial S_{\text{eph}} / \partial V$ is further corroborated by a recent work by Urban \textit{et al.}\textsuperscript{66} which, however, predicts $S_{\text{eph}}^{(\text{Ref. 64})} \sim V^3$. An independent calculation is therefore required to settle this issue. Careful inclusion of phonon heating effects into the noise calculations then certainly represents a relevant extension of our studies, furthermore urged by the relevance of heating in several IETS and PCS experiments.

Very recently, a lot of interest has been paid to the study of current-induced excitations of local spin degrees of freedom in spin-dependent IETS set-ups.\textsuperscript{14,15,66,70} Several of these calculations\textsuperscript{66,68,69} rely on a perturbative approach analogous to the lowest order expansion of Ref. 48, also used in this paper. So far, those studies have dealt exclusively with the non-linear conductance and the study of current noise in those spin systems would be a most natural next step. Our method can be straightforwardly extended in this direction, as long as the occupation of spin states is described in a phenomenological way via the master equation\textsuperscript{64} (or just by thermal distribution). However, possible further extensions to account for fluctuations of a non-equilibrated spin remain, even conceptually, an open question, because of the anharmonic nature of the free spin. Furthermore, the applicability of the lowest order expansion itself for the description of the spin-dependent IETS experiments seems to be currently under debate and renormalized perturbation theories might be necessary for a proper description of observed phenomena. Addressing these problems in the noise context constitutes an interesting future research direction.

**FIG. 7.** (Color online) Contour plots of $\Delta S'$ at zero temperature as a function of $T_1$ and $T_2$ for different values of the e-ph coupling matrix elements $M_{ij}$. a) $M_{11} \neq 0$ and $M_{22} = M_{12} = 0$; b) $M_{11} \neq 0, M_{22} = 0.1 M_{11}$ and $M_{12} = 0$; c) $M_{11} \neq 0, M_{22} = M_{11}$ and $M_{12} = 0$; d) $M_{12} \neq 0$ and $M_{11} = M_{22} = 0$. In all panels, $\Gamma_1 = \Gamma_2 = \Gamma$. 
Finally, the calculation of arbitrary cumulants based on the generalized Keldysh GF technique can be implemented numerically\cite{54,64} to address the cases of structured tunneling density of states and/or stronger e-ph coupling, which go beyond our analytical treatment. On the other hand, for the case of weak coupling addressed in this work, such numerical methods will face convergence/efficiency problems due to very sharp phonon line-shapes and unnecessary self-consistency loops. In this respect, when complemented by \textit{ab-initio} calculations for the transport coefficients $\text{Tr}\{T\}, \text{Tr}\{T_{H}^{(m)}\}, \ldots$, our approach is designed to be a very efficient alternative to the full numerics in the limit of weak coupling and slowly varying electronic density of states. It uses the realistic static calculations of the electronic Green’s functions, phonon modes, and their coupling as input parameters and yields reliable results for the dynamical effects in the electronic noise.

\section*{Acknowledgments}

We thank D. Bagrets, A.-P. Jauho, D. F. Urban, and J. M. van Ruitenbeek for useful discussions, Yu. V. Nazarov for providing us with Ref. \textsuperscript{65} and A. Braggio for invaluable help with \texttt{Mathematica}. We acknowledge the financial support by DFG via SFB 767 (F. H. and W. B.), by the Czech Science Foundation via the grant 202/07/J051 and the Ministry of Education of the Czech Republic via the research plan MSM 0021620834 (T. N.).

\appendix

\section*{Appendix A: Mean-field contribution to noise}

Using the invariance of the trace under cyclic permutations, Eq. (10) can be recast in the following form

\begin{equation}
S^{(nt)} = \int \frac{d\varepsilon}{\sqrt{2\pi}} \left[ i\text{Tr}\{f_L G^> - (1 - f_L) G^< \} + \Gamma_L G^> \Gamma_L G^< + \Gamma_L (G^r - G^a) T_L (f_L G^> - (1 - f_L) (G^a T_L G^r) \right.
\end{equation}

\begin{equation}
\left. - (1 - f_L) G^<) - f_L (1 - f_L) (G^a T_L G^r T_L + G^r T_L G^a T_L) \right],
\end{equation}

with $G^\pm = G_{\lambda=0}^\pm$, $G^r = G_{\lambda=0}^{r-} - G_{\lambda=0}^{r+}$ and $G^a = [G^r]^\dagger$. Such an expression corresponds exactly\cite{54,64} to Eq. (30) of Ref.\textsuperscript{50}. We stress that their result was obtained by truncating the $S$-matrix expansion by breaking two-particle Green’s functions into products of one-particle Green’s functions, see Refs.\textsuperscript{50,52} or Sec. 13.8 for further details. This procedure holds in a mean-field theory, but it misses the contributions given by the vertex correction. For this reason we identified Eq. (10) with the \textit{mean-field contribution to noise}.

It can be furthermore shown that Eq. (A1) is equivalent to Eq. (10) of Ref.\textsuperscript{11} and to the zero-frequency limit of Eq. (9) of Ref.\textsuperscript{51} which therefore represent again \textit{solely} the mean-field contribution to the noise. We stress however that, as we will discuss in Appendix\textsuperscript{14} approximating the noise with the mean-field contribution generally leads to violation of the fluctuation-dissipation theorem.

\section*{Appendix B: Electronic density}

The electronic density in the system is given by

\begin{equation}
n_e = -i \int \frac{d\varepsilon}{2\pi} g_{\lambda=0}(\varepsilon),
\end{equation}

where $g_{\lambda=0} = g^\dagger \Sigma^+ g^i |_{\lambda=0}$ is the lesser Green’s function without the electron-phonon coupling. It should be noticed that the integrand of Eq. (B1) does \textit{not} have a finite support and therefore in this case integration over energy cannot be carried out in the eWBL approximation. Instead, the energy dependence of $g^{(a)}$ has to be taken into account while calculating the integral, and only subsequently one is allowed to consider the limits $\Gamma \gg eV, \hbar \omega_0, k_B T$ or $|\varepsilon_{res} - E_F| \gg \Gamma, eV, \hbar \omega_0, k_B T$ corresponding to the eWBL.

As an example we consider here the case of a system with a single electronic level symmetrically coupled to unstructured leads with constant $\Gamma_L = \Gamma_R \equiv \Gamma$. In this case

\begin{equation}
n_e = -i \int \frac{d\varepsilon}{2\pi} \Gamma [f_L(\varepsilon) + f_R(\varepsilon)] - \frac{1}{4\pi} (\varepsilon - \varepsilon_0)^2 + \frac{1}{2\Gamma}.
\end{equation}

Assuming zero temperature and symmetric voltage drop at the barriers $\mu_L = -\mu_R = eV/2$ one gets

\begin{equation}
n_e = \frac{1}{2} + \frac{1}{2\pi} \left[ \arctan \left( \frac{eV - 2\varepsilon_0}{2\Gamma} \right) \right] - \frac{1}{4\pi} (\varepsilon_0)^2 + \frac{1}{2\Gamma} \varepsilon_0 + \frac{1}{4\pi (\varepsilon_0^2 + \varepsilon_0^2)} (eV)^2 + O((eV)^3),
\end{equation}

which shows that in the eWBL $n_e$ depends very weakly on the applied bias voltage.

\section*{Appendix C: Explicit form of the Fock self-energy at zero counting field}

At $\lambda = 0$, the Keldysh components of $\Sigma_F$ satisfy the identity $(\Sigma_F^+ - \Sigma_F^-)|_{\lambda=0} = (\Sigma_F^+ + \Sigma_F^-)|_{\lambda=0}$. In this
case, it is meaningful to introduce the retarded and advanced self-energies by $\Sigma_F^{\text{R}} = (\Sigma_F^{-} - \Sigma_F^{+})_{\lambda=0}$ and $\Sigma_F^{\text{A}} = [\Sigma_F^{+}]^\dagger$. For definiteness, we also introduce the notation $\Sigma_F^{\text{R}}_{\lambda=0}$ for the lesser and greater components at zero counting field. The latter can be easily calculated from Eq. [29] giving

$$
\Sigma_F^{\text{R}}(\varepsilon) = i \sum_{\alpha=L,R} \mathcal{M} \left[ N_0 \mathbf{A}_\alpha(\varepsilon - \hbar \omega_0) f_\alpha(\varepsilon - \hbar \omega_0) \right. \\
+ (N_0 + 1) \mathbf{A}_\alpha(\varepsilon + \hbar \omega_0) f_\alpha(\varepsilon + \hbar \omega_0) \left. \right] \mathcal{M}
$$

$$
\Sigma_F^{\text{R}}(\varepsilon) = -i \sum_{\alpha=L,R} \mathcal{M} \left[ N_0 \mathbf{A}_\alpha(\varepsilon + \hbar \omega_0)(1 - f_\alpha(\varepsilon + \hbar \omega_0)) \right. \\
+ (N_0 + 1) \mathbf{A}_\alpha(\varepsilon - \hbar \omega_0)(1 - f_\alpha(\varepsilon - \hbar \omega_0)) \left. \right] \mathcal{M}
$$

The retarded self-energy can in turn be written in terms of the lesser and greater components using the identity $\Sigma_F^{\text{R}} = \Sigma_F^{\text{L}} - \Sigma_F^{\text{A}}$ and Kramers-Kronig relation $\text{Re}\Sigma_F^{\text{R}}(\varepsilon) = \mathcal{H}_{\varepsilon'} \left\{ \text{Im}\Sigma_F^{\text{R}}(\varepsilon') \right\}(\varepsilon)$. This leads to

$$
\text{Im}\Sigma'(\varepsilon) = -\frac{1}{2} \sum_{\alpha=L,R} \mathcal{M} \left[ N_0 \mathbf{A}_\alpha(\varepsilon - \hbar \omega_0) f_\alpha(\varepsilon - \hbar \omega_0) \right. \\
- \mathbf{A}_\alpha(\varepsilon - \hbar \omega_0) f_\alpha(\varepsilon - \hbar \omega_0) \left. \right] \mathcal{M},
$$

$$
\text{Re}\Sigma'(\varepsilon) = \mathcal{M} \left[ (N_0 + 1) \mathbf{g}_R(\varepsilon - \hbar \omega_0) + N_0 \mathbf{g}_R(\varepsilon + \hbar \omega_0) \right] \mathcal{M} \\
- \frac{1}{2} \sum_{\alpha=L,R} \mathcal{M} \mathcal{H}_{\varepsilon'} \left\{ \mathbf{A}_\alpha(\varepsilon') f_\alpha(\varepsilon') \right\}(\varepsilon + \hbar \omega_0) \\
- \mathcal{H}_{\varepsilon'} \left\{ \mathbf{A}_\alpha(\varepsilon') f_\alpha(\varepsilon') \right\}(\varepsilon - \hbar \omega_0) \mathcal{M},
$$

where we have used the identity $\mathcal{H}_{\varepsilon'} \{ \mathbf{A}(\varepsilon') \}(\varepsilon) = -2\mathcal{H}_{\varepsilon'} \{ \mathbf{g}_R(\varepsilon') \}(\varepsilon) = -2\mathbf{g}_R(\varepsilon)$, with $\mathbf{g}_R(\varepsilon)$, the real (imaginary) part of $\mathbf{g}_R$. We point out that the energy dependence of $\mathbf{g}_R^{(a)}$ cannot be disregarded while using Kramers-Kronig relations, as the Hilbert transform $\mathcal{H}_{\varepsilon'}$ generally involves integrals over infinitely extended range. However, in the limits $\Gamma \gg eV, \hbar \omega_0, \hbar \beta T$ or $|\varepsilon_{\text{res}} - EF| \gg \Gamma, eV, \hbar \omega_0, \hbar \beta T$ corresponding to the eWBL approximation the previous expressions take a simpler form

$$
\text{Im}\Sigma^{\text{R}}(\varepsilon) = -\frac{1}{2} \sum_{\alpha=L,R} \mathbf{M} \mathbf{A}_\alpha \mathbf{M} \left[ (2N_0 + 1) \\
+ f_\alpha(\varepsilon + \hbar \omega_0) - f_\alpha(\varepsilon - \hbar \omega_0) \right],
$$

$$
\text{Re}\Sigma^{\text{R}}(\varepsilon) = (2N_0 + 1) \mathbf{M} \mathbf{g}_R \mathbf{M} - \frac{1}{2} \sum_{\alpha=L,R} \mathbf{M} \mathbf{A}_\alpha \mathbf{M} \\
\times \mathcal{H}_{\varepsilon'} \left\{ f_\alpha(\varepsilon' + \hbar \omega_0) - f_\alpha(\varepsilon' - \hbar \omega_0) \right\}(\varepsilon).
$$

Note that the Hilbert transform now involves only a function with finite support. Inserting these expressions into Eq. [20], it is easy to show that the first term of Eq. [22] is the origin of the discrepancy between our result for $I_F$, Eq. [23], and the expression derived by Paulsson and coworkers. This discrepancy stems from the subtleties in the use of the eWBL mentioned above, and was already pointed out by Viljas et al., whose result agrees with ours.

### Appendix D: Fluctuation-dissipation theorem

The fluctuation-dissipation theorem relates the noise at zero voltage to the linear conductance of the system $G$

$$
S(V = 0) = \frac{2}{\beta} G.
$$

In the case of the contributions due to the Hartree term, it follows from Eqs. [32], [31] that $S_H^{(\text{mf})(V = 0)} = 0$ at zero voltage, while $S_H^{(\text{mf})}$ fulfills the fluctuation-dissipation theorem

$$
S_H(V = 0) = S_H^{(\text{mf})}(V = 0) = \frac{2}{\beta} G_H,
$$

with $G_H = e^2/h \text{Tr} \{ T_{H}^{(\text{rel})} \}$.

The situation is, however, different for the Fock term. In fact, in the limit $eV \rightarrow 0$, both the mean-field contribution $S_F^{(\text{mf})}$ and the vertex corrections $S_F^{(\text{ve})}$ are different from zero and reduce to

$$
S_F^{(\text{mf})}(V = 0) = \frac{2}{\beta} \text{Tr} \{ T_{F}^{(\text{rel})} \} \frac{U(h\omega_0)}{h\omega_0} + \frac{U(h\omega_0)^2 - (h\omega_0)^2}{h\omega_0} \\
\times \text{Tr} \{ T_{F}^{(\text{incl})} + \Gamma_L \mathbf{G}^\dagger \mathbf{M} \mathbf{A}_L \mathbf{M} \mathbf{g}^\dagger \},
$$

$$
S_F^{(\text{vc})}(V = 0) = -\text{Tr} \{ \Gamma_L \mathbf{G}^\dagger \mathbf{M} \mathbf{A}_L \mathbf{M} \mathbf{g}^\dagger \} \frac{U(h\omega_0)^2 - (h\omega_0)^2}{h\omega_0}.
$$

On the other hand, the correction to the linear conductance due to $\Sigma_F$ is given by

$$
\frac{G_F}{e^2/h} = \text{Tr} \{ T_{F}^{(\text{rel})} \} \frac{U(h\omega_0)}{h\omega_0} + \text{Tr} \{ T_{F}^{(\text{incl})} \} \frac{U(h\omega_0)^2 - (h\omega_0)^2}{h\omega_0}.
$$

Comparing the previous expressions one can see that

$$
S_F^{(\text{mf})}(V = 0) + S_F^{(\text{vc})}(V = 0) = \frac{2}{\beta} G_F.
$$

but the mean field contribution alone does not satisfy the fluctuation dissipation theorem $S_F^{(\text{mf})}(V = 0) \neq 2G_F/\beta$. This clearly shows that in general, even in the limit of weak $e$-ph coupling, vertex corrections must be included into the noise calculation in order to obtain consistent results.
FIG. 9. Upper panel: Plots of the dependencies of the functions $h_1(eV)$ and $h_2(eV)$ on the applied bias voltage (Eqs. (E3) and (E4), respectively). Lower panel: Same as above, but for the derivatives $\partial h_1/\partial V$ and $\partial h_2/\partial V$. In both panels $k_B T = \hbar \omega_0/30$.

Appendix E: Anti-symmetric contribution to $S_F$

In this appendix we give the complete expression for the terms of $S_F^{(mf/ve)}$ which are anti-symmetric with respect to the bias voltage. At finite temperature they are given by

$$
S_F^{(mf)} = \frac{h^2}{\hbar} \text{Tr}\{K_1^{(mf)}\} h_1(eV) + \frac{h^2}{\hbar} \text{Tr}\{K_2^{(mf)}\} h_2(eV),
$$

(E1a)

and

$$
S_F^{(ve)} = \frac{h^2}{\hbar} \text{Tr}\{K_1^{(ve)}\} h_1(eV) + \frac{h^2}{\hbar} \text{Tr}\{K_2^{(ve)}\} h_2(eV),
$$

(E1b)

where $K_1^{(mf/ve)}$ are those of Eqs. (10) and

$$
K_2^{(mf)} = \Gamma_L A_R \Gamma_L |A_R M (A_L - A_R) g^a + h.c.|, \quad (E2a)
$$

and

$$
K_2^{(ve)} = i M (A_R \Gamma_L g^r + h.c.) M (A_L \Gamma_R g^r - h.c.) - K_1^{(ve)}/2, \quad (E2b)
$$

The line shape of $S_{asym}^{(mf/ve)}$ is defined by the functions

$$
h_1(eV) = h(eV) \coth(\beta eV/2),
$$

(E3)

with $h(eV)$ given in Eq. (30) and

$$
h_2(eV) = \int d\varepsilon \left[ n_F(\varepsilon + eV) [1 - n_F(\varepsilon + eV)] \right]
\times \frac{\hbar}{\epsilon} \left| n_F(\varepsilon' - \hbar \omega_0) - n_F(\varepsilon' + \hbar \omega_0) \right| (\varepsilon).
$$

(E4)

We notice that $h_2(eV) = (e\beta)^{-1} \partial V h(eV)$, i.e. $h_2(eV)$ is directly proportional to the derivative of $h(eV)$ but it exhibits no divergencies and actually tends to zero in the limit $T \to 0$ due to the suppression factor $1/\beta$ with respect to $h(eV)$. Furthermore, we observe once again that $S_{asym}^{(mf/ve)}$ give a negligible contribution to the inelastic noise signal $\Delta S'$ at low temperatures, since $\partial V h_1$ is almost symmetric around the phonon emission threshold, i.e. $\partial V h_1 |_{eV \geq \hbar \omega_0} \approx \partial V h_1 |_{eV \leq \hbar \omega_0}$ and $\partial V h_2$ is suppressed by low temperature, see Fig. 9.
Based on a spin-less model, our results need to be multiplied by a factor of 2 when compared with works where spin degeneracy is explicitly taken into account.