

Vibration-induced correction to the current through a single molecule

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We provide analytical results for the perturbative correction to the current-voltage relation through a vibrating molecule for weak electron-phonon coupling. The nonlinear conductance exhibits a steplike feature at $eV = \hbar\omega_0$, where ω_0 is the vibration frequency. We establish criteria for the sign change of the step in the conductance (up or down). This transition turns out to be nonuniversal and is governed by essentially all system parameters.

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Electronic transport through single molecules has attracted much attention lately; for recent reviews, see Refs. 1–5. Besides the technological promises raised by molecular electronics, this field also poses interesting questions to theory. In this Brief Report, we will revisit the problem of how the coupling to a vibrational mode (“phonon”) of frequency ω_0 and electron-phonon coupling strength g affects the current through a single molecule. The resulting features in the I - V characteristics are often referred to as inelastic electron tunneling spectroscopy.⁵ Theories for various aspects of this rich and diverse problem have been proposed over the past few years by a large number of authors,^{6–13} primarily motivated by groundbreaking experiments demonstrating the influence of vibrational degrees of freedom in single-molecule transport. To mention just a few key experiments, single-molecule transport has been studied using various organic molecules,¹⁴ fullerenes,^{15–17} carbon nanotubes,^{18,19} or single hydrogen molecules between Pt leads.²⁰ Phonon-assisted processes were shown to imply a step in the I - V characteristics once the dc bias V reaches the threshold value $\hbar\omega_0/e$ for excitation of a phonon mode. Related features can sometimes be seen at integer multiples of this value. Vibrational effects on single-molecule transport have recently been reviewed,⁵ including a discussion of the validity regime for our Hamiltonian below.

It is remarkable that the experimentally observed vibration-induced step features in the differential conductance can either *decrease*²⁰ or *increase* the conductance through the molecule near $eV = \hbar\omega_0$.^{14,15,17,18} This corresponds to dips versus peaks in the second derivative, d^2I/dV^2 . Such features have also been reported theoretically.^{5,21,22} Recent theoretical work on this question^{9,11} argues that the transparency \mathcal{T} of the single-molecule junction basically determines the step direction. The critical value was reported to be $\mathcal{T} = 1/2$, with a step down (up) in the differential conductance at $eV = \hbar\omega_0$ for $\mathcal{T} > 1/2$ ($\mathcal{T} < 1/2$). This conclusion seems roughly consistent with existing experimental data: For the H₂ measurements,²⁰ \mathcal{T} close to unity was reported, while typically $\mathcal{T} \lesssim 0.1$ in the other experiments. However, given the many parameters present in even the simplest Hamiltonian, one may question why the crossover should be universal in the sense that it is only determined by the transparency $\mathcal{T} = 1/2$. Here, we reexamine the question of current increase or decrease at the phonon exci-

tation threshold $eV = \hbar\omega_0$. We derive and discuss analytical results for the current correction δI perturbative in the electron-phonon coupling strength g . Experimental values for g are often very small, justifying a truncation of the perturbation series already at the lowest nontrivial order. For that reason, our expressions below are expected to provide useful estimates for many experiments. However, we will not attempt a detailed description of specific experiments, but instead aim at an *analytical* understanding of vibrational features in the I - V characteristics under a simple yet realistic model. In our opinion, a thorough understanding of the lowest-order feature is worthwhile, given the complexity of the physical processes involved. Most available results are obtained from lengthy numerical calculations and do not easily yield general insights. In addition, many calculations were based on essentially uncontrolled approximations, rendering their predictive power questionable. Moreover, some published theoretical work on this subject have used approximate schemes that are in conflict with the basic requirement of current conservation. Current conservation is automatically fulfilled under self-consistent approximations, but is generally violated otherwise (unless particle-hole symmetry is present), limiting the practical usefulness of many approximations to special parameter sets.²³ The lowest-order correction, however, can be evaluated exactly and, therefore, does not suffer from any such limitations. Although aspects of the lowest-order correction δI have been studied before,^{5,21,22} a complete and analytical discussion was not given so far. We show that besides the step feature caused by inelastic processes, quasielastic electron-phonon interactions are responsible for another singular term that logarithmically diverges at $eV = \hbar\omega_0$.

We study the model of just one relevant molecular level (“dot”), the so-called local Holstein model, also employed by previous work,⁵

$$H = (\epsilon_0 + gQ)d^\dagger d + \hbar\omega_0 b^\dagger b + \sum_{k,\alpha=L/R=\pm} (\gamma_\alpha d^\dagger c_{k\alpha} + \text{H.c.}) + \sum_{k,\alpha} [\epsilon_k - \mu_\alpha] c_{k\alpha}^\dagger c_{k\alpha}, \quad (1)$$

which neglects the Coulomb interaction U and is formulated for spinless dot fermion operator d (we set $\hbar = 1$). The effect of the lowest-order correction in U , consistent with our g^2

calculation below, is anyway trivial and can be absorbed by a renormalization of the chemical potential. We take the standard wide-band limit for the leads, which is justified if the lead density of states ν_0 does not vary significantly in energy on the relevant scales. The lead modes are occupied according to Fermi functions $f_{L/R}(\epsilon) = f(\epsilon - \mu_{L/R})$, where $\mu_L - \mu_R = eV$ defines the bias voltage V . We introduce the hybridizations as $\Gamma_{L,R} = \pi\nu_0 |\gamma_{L/R}|^2$, and define $\Gamma = \Gamma_L + \Gamma_R$. Finally, the boson operator b describes an Einstein phonon mode (vibration mode) of frequency ω_0 , with linear coupling of strength g between the displacement operator $Q = b + b^\dagger$ and the dot occupation operator $d^\dagger d$. The electrical current through the dot can be computed from the retarded dot Green's function (GF) evaluated in the presence of the leads and the phonon, $G^r(\omega)$, according to the well-known expression²⁴

$$I(V) = -\frac{4e\Gamma_L\Gamma_R}{h\Gamma} \int d\omega [f_L(\omega) - f_R(\omega)] \text{Im} G^r(\omega). \quad (2)$$

The noninteracting ($g=0$) Keldysh GF describing the out-of-equilibrium dot coupled to the leads is

$$\hat{G}_0(\omega) = \frac{1}{(\omega - \epsilon_0)^2 + \Gamma^2} \begin{bmatrix} (\omega - \epsilon_0) \text{diag}(1, -1) \\ -i \sum_{\alpha} \Gamma_{\alpha} \begin{pmatrix} 2f_{\alpha}(\omega) - 1 & -2f_{\alpha}(\omega) \\ 2 - 2f_{\alpha}(\omega) & 2f_{\alpha}(\omega) - 1 \end{pmatrix} \end{bmatrix}. \quad (3)$$

Note that we use the unrotated Keldysh notation, where the connection to retarded or advanced GFs $G^{r/a}$ and the lesser GF $G^<$ is established by

$$\begin{pmatrix} G^{--} & G^{+-} \\ G^{+-} & G^{++} \end{pmatrix} = \begin{pmatrix} G^r + G^< & G^< \\ G^r - G^a + G^< & -G^a + G^< \end{pmatrix},$$

such that $G_0^r(\omega) = (\omega - \epsilon_0 + i\Gamma)^{-1}$. Since G^r obeys its own Dyson equation, we only need to compute the retarded self-energy $\Sigma^r(\omega)$ to order g^2 , resulting in

$$G^r(\omega) = G_0^r(\omega) + G_0^r(\omega) \Sigma^r(\omega) G_0^r(\omega), \quad (4)$$

where the second term defines the correction δI in Eq. (2). We will focus on the most interesting $T=0$ limit from now on, where the Fermi function is $f(\omega) = \Theta(-\omega)$. Defining

$$\bar{\mu} = \frac{\mu_L + \mu_R}{2} - \epsilon_0, \quad \bar{\mu}_{\alpha=L/R=\pm} = \bar{\mu} \pm eV/2, \quad (5)$$

the first ($g=0$) term yields

$$I_0(V) = \frac{e4\Gamma_L\Gamma_R}{h\Gamma} [\tan^{-1}(\bar{\mu}_L/\Gamma) - \tan^{-1}(\bar{\mu}_R/\Gamma)]. \quad (6)$$

The $V \rightarrow 0$ transparency of the junction, $\mathcal{T} = (h/e^2)dI/dV$, follows as

$$\mathcal{T} = \frac{4\Gamma_L\Gamma_R}{\Gamma^2} \frac{1}{1 + (\bar{\mu}/\Gamma)^2} \leq 1. \quad (7)$$

Note that ϵ_0 and the mean chemical potential always appear in the combined scale $\bar{\mu}$.

Let us now analyze the lowest-order correction δI to the current. It arises from the retarded self-energy $\Sigma^r(\omega)$ evalu-

ated to order g^2 due to phonon processes, entering Eqs. (4) and (2). There are two contributions coming from the real (imaginary) parts Σ_R^r (Σ_I^r), corresponding to quasielastic (inelastic) processes,

$$\delta I_{\text{qel}} = \frac{e4\Gamma_L\Gamma_R}{h\Gamma} \int_{\bar{\mu}_R}^{\bar{\mu}_L} d\omega \frac{2\omega\Gamma}{(\omega^2 + \Gamma^2)^2} \Sigma_R^r(\omega), \quad (8)$$

$$\delta I_{\text{inel}} = \frac{e4\Gamma_L\Gamma_R}{h\Gamma} \int_{\bar{\mu}_R}^{\bar{\mu}_L} d\omega \frac{\Gamma^2 - \omega^2}{(\omega^2 + \Gamma^2)^2} \Sigma_I^r(\omega). \quad (9)$$

The self-energy is readily computed on the perturbative level, where two diagrams are present in order g^2 . The ‘‘tadpole’’ diagram does not carry frequency dependence and can be absorbed by a renormalization of $\bar{\mu}$. We, therefore, keep only the standard ‘‘rainbow’’ diagram, which gives the retarded self-energy $\Sigma^r(\omega) = \Sigma^-(\omega) + \Sigma^+(\omega)$ from

$$\Sigma^{\pm}(\omega) = \mp ig^2 \int \frac{d\Omega}{2\pi} D_0^{\mp}(\Omega) G_0^{\pm}(\omega - \Omega). \quad (10)$$

Here, $\hat{D}_0(\omega)$ is the $g=0$ GF of the displacement operator Q , which for $T=0$ is given by

$$\hat{D}_0(\omega) = \begin{pmatrix} \sum_{s=\pm} \frac{1}{s\omega - \omega_0 + i0^+} & -2\pi i \delta(\omega + \omega_0) \\ -2\pi i \delta(\omega - \omega_0) & -\sum_s \frac{s}{s\omega - \omega_0 + i0^+} \end{pmatrix}. \quad (11)$$

Using a Wiener-Hopf decomposition of $G_0^-(\omega)$ into the parts analytic in the upper or lower complex frequency plane, one arrives at the result (cf. also Ref. 7)

$$\Sigma_R^r(\omega) = \sum_{\alpha,s=\pm} \frac{g^2\Gamma_{\alpha}}{\Gamma^2 + (\omega + s\omega_0)^2} \left[\frac{s}{\pi} \ln \frac{\sqrt{\Gamma^2 + \bar{\mu}_{\alpha}^2}}{|\omega + s\omega_0 - \bar{\mu}_{\alpha}|} + \frac{\omega + s\omega_0}{2\Gamma} \left(1 + \frac{2s}{\pi} \tan^{-1}(\bar{\mu}_{\alpha}/\Gamma) \right) \right], \quad (12)$$

$$\Sigma_I^r(\omega) = -\sum_{\alpha,s} \frac{g^2\Gamma_{\alpha} \Theta[s(\bar{\mu}_{\alpha} - \omega) - \omega_0]}{(\omega + s\omega_0)^2 + \Gamma^2}. \quad (13)$$

The computation of δI is then reduced to a single frequency integration. We see that due to the phonon mode, the retarded electron self-energy contains directly the Fermi functions shifted by $\pm\omega_0$. Hence, a singular (step) dependence of its imaginary part on the energy results, which must be accompanied by a logarithmic singularity in the real part due to analytic properties. These singularities have been discovered first by Engelsberg and Schrieffer in their study of bulk Einstein phonons.²⁵ With the above self-energies, it is easy to check that the requirement for current conservation,²³

$$\int d\omega [G^<(\omega)\Sigma^>(\omega) - G^>(\omega)\Sigma^<(\omega)] = 0,$$

is fulfilled (also at finite T) to the required g^2 order. Let us first discuss the inelastic part, δI_{inel} . Using the auxiliary relation for an arbitrary function $F(\omega, V)$,

$$\frac{d}{dV} \int_{\bar{\mu}_R}^{\bar{\mu}_L} d\omega F(\omega, V) = \frac{e}{2} \sum_{\alpha} F(\bar{\mu}_{\alpha}, V) + \int_{\bar{\mu}_R}^{\bar{\mu}_L} d\omega \frac{\partial F(\omega, V)}{\partial V}, \quad (14)$$

some algebra gives the g^2 inelastic correction to the $T=0$ nonlinear conductance for arbitrary parameters in closed form,

$$\begin{aligned} \frac{d\delta I_{\text{inel}}}{dV} = & -\frac{e^2}{h} \Theta\left(V - \frac{\hbar\omega_0}{e}\right) g^2 \frac{2\Gamma_L\Gamma_R}{\Gamma} \sum_{\alpha} \Gamma_{\alpha} \\ & \times \left(\frac{\Gamma^2 - \bar{\mu}_{-\alpha}^2}{(\Gamma^2 + \bar{\mu}_{-\alpha}^2)^2 [(\bar{\mu}_{-\alpha} + \alpha\omega_0)^2 + \Gamma^2]} \right. \\ & \left. + \frac{\Gamma^2 - (\bar{\mu}_{\alpha} - \alpha\omega_0)^2}{[\Gamma^2 + (\bar{\mu}_{\alpha} - \alpha\omega_0)^2]^2 (\bar{\mu}_{\alpha}^2 + \Gamma^2)} \right). \end{aligned} \quad (15)$$

We focus now on the singular contribution at $eV = \hbar\omega_0$, which is best illustrated by analyzing $d^2\delta I/dV^2$. Singular terms come from the derivative acting on the Heaviside function in Eq. (15), and produce a delta peak,

$$\left. \frac{d^2\delta I_{\text{inel}}}{dV^2} \right|_{\text{sing}} = -\frac{e^2}{h} \left(\frac{g}{\Gamma}\right)^2 \frac{4\Gamma_R\Gamma_L}{\Gamma^2} c_{\text{inel}} \delta\left(V - \frac{\hbar\omega_0}{e}\right) \quad (16)$$

with the dimensionless coefficient

$$c_{\text{inel}} = \frac{1 - [(\bar{\mu}/\Gamma)^2 - (\omega_0/2\Gamma)^2]^2 + [2\omega_0(\Gamma_L - \Gamma_R)\bar{\mu}/\Gamma^3]}{[1 + (\bar{\mu}/\Gamma + \omega_0/2\Gamma)^2]^2 [1 + (\bar{\mu}/\Gamma - \omega_0/2\Gamma)^2]^2}, \quad (17)$$

which is the main result of this Brief Report. We will discuss this result below, but first turn to the quasielastic contribution δI_{qel} due to the real part (12) of the self-energy. Using Eq. (14), we find again a singular contribution in the differential conductance at $V = \hbar\omega_0/e$. We obtain the analytical result, valid for $V \approx \hbar\omega_0/e$,

$$\left. \frac{d\delta I_{\text{qel}}}{dV} \right|_{\text{sing}} = -\frac{2}{\pi} \frac{e^2}{h} \left(\frac{g}{\Gamma}\right)^2 \frac{4\Gamma_R\Gamma_L}{\Gamma^2} c_{\text{qel}} \ln \left| \frac{\Gamma}{eV - \hbar\omega_0} \right|, \quad (18)$$

with the dimensionless coefficient

$$c_{\text{qel}} = \sum_{\alpha} \frac{-\alpha \frac{\Gamma_{\alpha}\bar{\mu} - \alpha\omega_0/2}{\Gamma} (1 + [\bar{\mu}/\Gamma + \alpha\omega_0/2\Gamma]^2)}{[1 + (\bar{\mu}/\Gamma + \omega_0/2\Gamma)^2]^2 [1 + (\bar{\mu}/\Gamma - \omega_0/2\Gamma)^2]^2}. \quad (19)$$

It is worth mentioning that $c_{\text{qel}}=0$ for large $\Gamma \gg \omega_0$ at the symmetric point $\Gamma_L = \Gamma_R$. Away from this limit, however, the logarithmic term in Eq. (18) will be present. All other contributions to δI_{qel} beyond Eq. (18) are smooth and featureless at $eV \approx \hbar\omega_0$, and do not affect the characteristic feature in

d^2I/dV^2 , whereas the singular contribution (18) is logarithmically divergent at the threshold. Note that this logarithmic divergence due to quasielastic processes creates a symmetric dip or peak (depending on the sign of c_{qel}) in the differential conductance at $eV = \hbar\omega_0$, while the inelastic contributions are responsible for a step feature. In the full d^2I/dV^2 curve, this translates to *asymmetric* dips or peaks. The relative importance of inelastic versus quasielastic contributions can be judged from the ratio $c_{\text{inel}}/c_{\text{qel}}$. For the symmetric case, $\Gamma_L = \Gamma_R = \Gamma/2$, a simple result follows from Eqs. (17) and (19),

$$r = \left| \frac{c_{\text{inel}}}{c_{\text{qel}}} \right| = \left| \frac{\Gamma^2 + \bar{\mu}^2 - \omega_0^2/4}{\Gamma\omega_0/2} \right|. \quad (20)$$

For small ω_0/Γ or large $\bar{\mu}$, we have $r \gg 1$ and the inelastic channel always dominates, while for large ω_0 , quasielastic processes can be more important. The perturbative results (18) and (16) obviously break down close to the threshold voltage. At $T=0$ and in the absence of an external bath, the only way to account for the finite lifetime of the phonon, and hence the smearing of the step and/or peak features, is to take into account the electronic polarization in the phonon GF. The retarded polarization function $\chi^r(\omega)$ will then result in a damping $\gamma \approx -g^2\chi^r(\omega_0)$ of the phonon mode. We obtain after some algebra the nonequilibrium electronic polarization function in analytical form. In the particle-hole symmetric case, this result simplifies to

$$\chi^r(\omega) = \frac{\Gamma}{\pi\omega(\omega + 2i\Gamma)} \ln \left(1 - \frac{\omega(\omega + 2i\Gamma)}{\Gamma^2 + V^2/4} \right). \quad (21)$$

This implies the estimate $\gamma \approx g^2\omega_0/\pi\Gamma^2$ in the limit of a soft phonon $\omega_0 \ll \Gamma$, and $\gamma \approx g^2\Gamma/\omega_0^2$ for a hard phonon $\omega_0 \gg \Gamma$. However, phonon damping is, in fact, a higher-order effect in the electron-phonon coupling, and to consistently account for the finite damping γ while keeping current conservation intact remains a theoretical challenge. Other effects of higher-order diagrams include the proliferation of steps and/or peaks at multiples of the phonon frequency ω_0 . Indeed, it is easy to see that the g^{2n} -th-order rainbow diagram in the electronic self-energy produces a step feature in the differential conductance at the voltage $V = n\hbar\omega_0/e$. The appearance of such step features at multiples of ω_0 is closely related to the strong-coupling picture obtained through a polaron transformation.²⁶ However, when going beyond the lowest order in g , vertex corrections are also expected to be important. Unfortunately, the proper treatment of such nonequilibrium many-body effects (respecting the requirements posed by current conservation) remains a challenging task and is beyond the scope of this work. For weak electron-phonon coupling, which appears to be appropriate for many experiments, none of these fine details matter in any case, and the g^2 calculation is sufficient. The d^2I/dV^2 feature is then determined by Eqs. (16) and (18), where the damping γ in the phonon mode acts to broaden the delta function in Eq. (16) within a phenomenological description.

The above results allow us to clarify the question of peak vs dip in the second derivative, d^2I/dV^2 , which arises due to the singular inelastic correction (16). For $\Gamma_L = \Gamma_R$ and $\bar{\mu}=0$, where the transparency (7) is ideal, $T=1$, we observe from

Eq. (17) that for $\omega_0 > 2\Gamma$, instead of the expected dip ($c_{\text{inel}} > 0$), one actually observes a peak. For $\bar{\mu} \neq 0$, once $|\bar{\mu}| > \sqrt{\Gamma^2 + \omega_0^2/4}$, one finds a peak. Note that for $\bar{\mu} = \pm\Gamma$, the transparency (7) is precisely 1/2, thereby allowing us to rationalize why previous numerical studies for related models^{9,11} reported a $\mathcal{T}=1/2$ criterion for the transition from peak to dip. This value correctly describes the transition in the limit of a soft phonon, $\omega_0 \ll \Gamma$, and assuming symmetric contacts, $\Gamma_L = \Gamma_R$. The value $\mathcal{T}=1/2$ was, in fact, established precisely in this parameter regime.^{9,11} Our analytical result (17), shows, however, that, in general, the transition is non-universal and determined by all parameters. For example, it can be achieved either by tuning \mathcal{T} —where the precise transition value depends also on ω_0 and the asymmetry $\Gamma_L - \Gamma_R$, and is only approximately given by $\mathcal{T}=1/2$ —or by changing other parameters, such as $\Gamma_R - \Gamma_L$ or the ratio between phonon frequency and hybridization, ω_0/Γ . The nonuniversality

of the step is also implicit in the early work on phonon-assisted tunneling through a resonant level by Glazman and Shekhter.²⁷ On top of this peak or dip structure due to inelastic processes, the quasielastic contribution causes a singular response near the threshold value $eV = \hbar\omega_0$. This logarithmic correction to the differential conductance implies an asymmetric line shape in d^2I/dV^2 as discussed above. Such asymmetries have frequently been reported experimentally and in numerical calculations,⁵ and they are a direct consequence of the Engelsberg-Schrieffer singularity.

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