# Tunneling broadening of vibrational sidebands in molecular transistors

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Transport through molecular quantum dots coupled to a single vibration mode is studied in the case with strong coupling to the leads. We use an expansion in the correlation between electrons on the molecule and electrons in the leads, and show that the tunneling broadening is strongly suppressed by the combination of the Pauli principle and the quantization of the oscillator. As a consequence the first Frank-Condon step is sharper than the higher order ones, and its width, when compared to the bare tunneling strength, is reduced by the overlap between the ground states of the displaced and nondisplaced oscillators.

## I. INTRODUCTION

In recent years, the field of molecular electronics has renewed the interest in transport through mesoscopic systems with strong electron-phonon coupling. A number of experiments have been reported to demonstrate transport through single molecules,[1–6] some of which show signs of vibrational sidebands. In the pioneering experiments by Park *et al.*[1] it was shown that electron transport through a single $C_{60}$ molecule was strongly influenced by a single vibrational mode. The single phonon mode was associated with the motion of the molecule in the confining potential created by the van der Waals interactions with the electrodes. Later similar devices with more complicate molecules were investigated,[2,3] and they also showed excitation spectra which possibly could be associated with emission of vibrational quanta, so-called Frank-Condon peaks in the differential conductance. Some of these devices[2,5] furthermore exhibited a peak stemming from the Kondo effect, proving that the tunnel coupling to the leads was rather strong.

Theoretically there has been a large amount of work on the problem of tunneling through a single level with coupling to phonon modes. The approaches fall into two categories. The first category is the kinetic equation approach, which is relevant in the weak tunneling limit.[7,8] In the kinetic equation approach, it is essential that the excited vibrational levels are allowed to relax through coupling to a bath. For a large phonon relaxation rate one can assume an equilibrium phonon distribution; otherwise a nonequilibrium distribution function must be determined from the kinetic equations.[7] The coupling to the dissipative environment of the molecule leads to an additional broadening of phonon sidebands.[8]

The second category, into which this paper also falls, deals with the strong tunneling limit. The first approaches were an exact solution of a simplified situation, where only one electron is present,[9,10] i.e., the presence of the Fermi sea is ignored. The result of this exact solution is that the phonon sidebands in the tunneling density of states all are Lorentzians with the same width. The exact solution amounts to decoupling the electron and oscillator displacement operators. This decoupling approximation has been used in a number of papers.[11–13] Below we refer to this approximation as the "single particle approximation" (SPA), and we demon-

strate explicitly that this approximation is only valid for high energies, i.e., for electrons or holes sufficiently far from the Fermi surface, or in the weak tunneling limit where the rate equation is valid. For the many-body system many decay channels are in fact blocked by the Pauli principle. Other many-body works that include Fermi sea effects have been done,[14–16] and the blocking of the linewidth has also been alluded to.[14,15]

In this paper, we focus on the broadening of the Frank-Condon peaks in the differential conductance due to tunneling broadening, but in the non-Kondo regime. While this case cannot be solved exactly, an approximation, which is believed to be valid above the Kondo temperature and which includes the Pauli principle, but ignores correlations between lead electrons, is developed. The main result is that the combination of the Pauli principle and the splitting of the spectral weight into phonon sidebands severely limits the phase space for tunnel broadening. Hence the peaks are much narrower than the bare tunneling rate would suggest. We find a simple analytic result that describes this [see Eq. (38)], and compare with the SPA formula in Eq. (25). The approximation is exact in both the single particle limit and in the weak tunneling limit. Furthermore, we also support our conclusion by a perturbation theory in the electron-phonon coupling derived in Appendix B.

## II. MODEL HAMILTONIAN AND CURRENT FORMULA

We consider a model of a single electron level coupled to two leads. The single level is coupled to a vibrational mode of the molecule through the on-site energy. For simplicity we ignore the spin degree of freedom, which is not relevant unless Kondo-type effects are important. The model Hamiltonian is

$$H = H_k + H_D + H_{DB} + H_B + H_T, \qquad (1)$$

where

$$H_k = \sum_{k,\alpha=L,R} \xi_{k,\alpha} c_{k\alpha}^\dagger c_{k\alpha}, \quad H_D = \xi_0 d^\dagger d, \qquad (2)$$

$$H_{\mathrm{B}} = \frac{p_0^2}{2m_0} + \frac{1}{2} m_0 \omega_0^2 x_0^2, \quad H_{DB} = \lambda x_0 d^\dagger d, \tag{3}$$

$$H_T = \sum_{k,\alpha=L,R} t_{k\alpha}(c_{k\alpha}^\dagger d + d^\dagger c_{k\alpha}). \tag{4}$$

Here $x_0$ is the oscillator degree of freedom and $\xi_0$ is the bare onsite energy. The lead electron energies are given by $\xi_{k\alpha} = \varepsilon_{k\alpha} - \mu_\alpha$, where $\mu_\alpha$ is the chemical potential of the lead $\alpha$. The tunneling amplitude between lead $\alpha$ and the molecule is $t_{k\alpha}$. The amplitudes could, in principle, also depend on the oscillator position. However, in the experimental realizations so far this is a negligible dependence and it is omitted here. Because of this, we can apply the current formula derived by Wingreen and Meir[17] who expressed the current in terms of the nonequilibrium Green's function of the molecule. The current through the system is

$$I = \frac{e}{h} \int \frac{d\xi}{2\pi} \frac{\Gamma_L \Gamma_R}{\Gamma_L + \Gamma_R} [n_L(\xi) - n_R(\xi)] A(\xi), \tag{5}$$

where the left and right distribution functions are

$$n_\alpha(\varepsilon) = n_F(\varepsilon - eV_\alpha), \tag{6}$$

and where $n_F(\epsilon) = (e^{\beta\epsilon} + 1)^{-1}$ is the usual Fermi-Dirac function. The spectral function $A$ is given by

$$A(\xi) = -2 \operatorname{Im} G^R(\xi), \tag{7}$$

where the retarded Green's $G^R$ functions are

$$G^R(t,t') = -i\theta(t-t')\langle\{d(t),d^\dagger(t')\}\rangle. \tag{8}$$

The widths of the level due to coupling to the leads are

$$\Gamma_\alpha(\xi) = 2\pi \sum_k t_{k\alpha}^2 \delta(\xi - \xi_{k\alpha}). \tag{9}$$

The Green's function $G^R$ must be calculated in nonequilibrium and in the presence of the leads.

It is often useful to eliminate the linear coupling terms of the Hamiltonian [Eq. (1)] by a unitary transformation similar to one used in the independent boson model.[18] The transformation is

$$\tilde{H} = SHS^\dagger, \quad S = e^{-ip_0\ell d^\dagger d}, \quad \ell = \frac{\lambda}{m_0\omega_0^2}, \tag{10}$$

and with this choice the Hamiltonian transforms into

$$\tilde{H} = H_k + H_B + \tilde{H}_D + \tilde{H}_T, \tag{11}$$

where

$$\tilde{H}_D = \varepsilon_0 d^\dagger d, \quad \varepsilon_0 = \xi_0 - \frac{1}{2}\lambda\ell, \tag{12}$$

and

$$\tilde{H}_T = \sum_{k\alpha} t_{k\alpha}(c_{k\alpha}^\dagger e^{ip_0\ell} d + d^\dagger e^{-ip_0\ell} c_{k\alpha}). \tag{13}$$

The retarded Green's function becomes after this transformation

$$G^R(t-t') = -i\theta(t-t')\langle\{e^{ip_0(t)\ell}d(t),d^\dagger(t')e^{-ip_0(t')\ell}\}\rangle_S, \tag{14}$$

where the average of course should be taken with respect to $\tilde{H}$, which is indicated by $\langle\cdots\rangle_S$.

## III. CALCULATION OF THE SPECTRAL FUNCTION

In this section, we calculate the spectral function, $A(\xi)$ that enters into the current formula [Eq. (5)]. As mentioned in introduction, the tunneling broadening of phonon assisted side bands has been considered before in the case when the presence of the Fermi sea is ignored (SPA). In this case the model can be solved exactly, at least in the so-called wide band limit.[9,10] For latter reference we start by quoting the SPA result

$$G^{R,\mathrm{SPA}}(t) = \exp(-t\Gamma/2)G_0^R(t), \tag{15}$$

where $G_0^R$ is the Green's function in the absence of tunneling. We see from this expression that the SPA implies that all conductance steps are smeared by the same amount.

### A. Dyson equation for $G^R$

In the following, we develop a method to calculate the broadened Green's function using a truncated equation of motion technique. Our starting point is the retarded Green's function in Eq. (14). We expand it in terms of eigenstates of the boson systems

$$G^R(t) = \sum G_{nn',mm'}^R(t) f_{nn'} f_{mm'}^*, \tag{16}$$

$$G_{nn',mm'}^R(t) = -i\theta(t)\langle[(|n\rangle\langle n'|d)(t),d^\dagger|m'\rangle\langle m|]\rangle_S, \tag{17}$$

where we have defined the overlap function between the oscillator states

$$f_{nn'} = \langle n|e^{ip_0\ell}|n'\rangle. \tag{18}$$

An expression for $f_{nn'}$ is given in Eq. (A12).

We now generate a series of equations of motion, starting with one for $G_{nn',mm'}^R$

$$(i\partial_t + E_{nn'} - \varepsilon_0)G_{nn',mm'}^R(t)$$
$$= L_{nn'}^R(t) + \delta(t)(\langle dd^\dagger|n\rangle\langle m|\rangle_S \delta_{n'm'}$$
$$+ \langle d^\dagger d|m'\rangle\langle n'|\rangle_S \delta_{nm}), \tag{19}$$

where $E_{nn'} = (n-n')\omega_0$, and $L_{nn'}^R$ is the contribution stemming from the tunneling Hamiltonian. The function $L^R$ is (see Appendix A for details of the derivations)

$$L_{nn'}^R(t) = \sum_{k\alpha,l} t_{k\alpha} f_{ln'}^* [G_{k\alpha,nl,mm'}^R(t) - G_{n_dk\alpha,nl,mm'}^R(t)]$$

$$+ \sum_{k\alpha,l} t_{k\alpha} f_{nl}^* G_{n_dk\alpha,ln',mm'}^R(t), \qquad (20)$$

where we encounter two new Green's functions

$$G_{k\alpha,nl,mm'}^R(t) = -i\theta(t)\langle[(|n\rangle\langle n'|c_{k\alpha})(t), d^\dagger|m'\rangle\langle m|]\rangle_S, \qquad (21)$$

$$G_{n_dk\alpha,nl,mm'}^R(t) = -i\theta(t)\langle[(|n\rangle\langle n'|d^\dagger d c_{k\alpha})(t), d^\dagger|m'\rangle$$

$$\times \langle m|]\rangle_S. \qquad (22)$$

The equation of motion for the first one is

$$(i\partial_t + E_{nl} - \xi_{k\alpha})G_{k\alpha,nl,mm'}^R(t)$$

$$= L_{k\alpha,nl}^R(t) + \delta(t)(\langle c_{k\alpha}d^\dagger|n\rangle\langle m|\rangle_S\delta_{lm'}$$

$$+ \langle d^\dagger c_{k\alpha}|m'\rangle\langle l|\rangle_S\delta_{nm}), \qquad (23)$$

where again $L_{k\alpha,nl}^R$ is the contribution from the tunneling term. Again the tunneling term generates new higher order Green's functions, but at this point we truncate it using the following physical principles: we neglect correlations involving lead electrons, which means that we decouple terms lead electron operators using the Hartree-Fock approximation. Furthermore, we set $\langle c_{k\alpha}d^\dagger\rangle \approx 0$ in the equation of motion for Eqs. (21) and (22). With these approximations (see Appendix A for more details)

$$L_{k\alpha,nl}^R(t) \approx t_k \sum_j \langle n_{k\alpha}\rangle f_{jn} G_{jl,mm}^R$$

$$+ t_{k\alpha} \sum_j (1 - \langle n_{k\alpha}\rangle) f_{lj} G_{nj,mm}^R. \qquad (24)$$

It is now worth noting that in the case with only one electron, which is the SPA, the term $\langle n_k\rangle$ is exactly zero and Eq. (24) becomes exact for this case. In the same limit, $G_{n_dk\alpha,nl,mm'}^R = 0$, and the equations are easily solved. After setting the result back into Eq. (16) we get

$$G^{R,\text{SPA}}(\omega) = \sum_{nn'} |f_{nn'}|^2 \frac{(1-\bar{n})N_n + \bar{n}N_{n'}}{\omega + E_{nn'} - \varepsilon_0 + i\Gamma/2}, \qquad (25)$$

which is nothing but the SPA result in Eq. (15) written in the oscillator eigenstate basis. In doing this we have furthermore evaluated the last term in Eq. (19) as

$$\langle dd^\dagger|n\rangle\langle m|\rangle_S\delta_{n'm'} + \langle d^\dagger d|m'\rangle\langle n'|\rangle_S\delta_{nm}$$

$$= [(1-\bar{n})N_n + \bar{n}N_{n'}]\delta_{n'm'}\delta_{nm},$$

where $N_n = \langle|n\rangle\langle n|\rangle$ is the occupation of the $n$th oscillator level and $\bar{n} = \langle d^\dagger d\rangle$ is the average level occupation.

Here we want to go beyond the SPA and we continue by looking at the equation of motion for the last Green's function in Eq. (22). We have

$$(i\partial_t + E_{nl} - \xi_{k\alpha})G_{n_dk\alpha,nl,mm'}^R(t)$$

$$= L_{n_dk\alpha,nl}^R(t) + \delta(t)\langle c_{k\alpha}d^\dagger|n\rangle\langle m|\rangle\delta_{lm'}. \qquad (26)$$

The function $L_{n_dk\alpha,nl}^R(t)$ becomes after doing the same line of approximations as was done for $L_{k\alpha,nl}^R(t)$ (see Appendix A):

$$L_{n_dk\alpha,nl}^R(t) \approx t_{k\alpha}\langle n_{k\alpha}\rangle \sum_j f_{jn} G_{jl,mm'}^R. \qquad (27)$$

The set of equations now close. After integrating out the Green's function involving the lead electrons, we arrive at linear equations for the molecule Green's function,

$$(\omega + E_{nn'} - \varepsilon_0)G_{nn',mm'}^R(\omega)$$

$$= \langle dd^\dagger|n\rangle\langle m|\rangle_S\delta_{n'm'} + \langle d^\dagger d|m'\rangle\langle n'|\rangle_S\delta_{nm}$$

$$+ \sum_{lj} [\Lambda_{ln'}^e f_{nl}^* f_{jl} G_{jn',mm'}^R(\omega)$$

$$+ \Lambda_{nl}^h f_{ln'}^* f_{lj} G_{nj,mm'}^R(\omega)], \qquad (28)$$

where

$$\Lambda_{nl}^{e,h}(\omega) = \sum_\alpha \int d\xi \frac{\Gamma_\alpha}{2\pi}\begin{pmatrix} n_\alpha(\xi) \\ 1 - n_\alpha(\xi) \end{pmatrix}\frac{1}{\omega + E_{nl} - \xi + i\eta}. \qquad (29)$$

The functions $\Lambda^{e,h}$ are in the case of energy independent $\Gamma_\alpha$'s (which we assume henceforth) given by

$$\Lambda_{nl}^e(\omega) = \sum_\alpha \left[\frac{-i\Gamma_\alpha}{2}n_\alpha(\omega + E_{nl}) + \frac{\Gamma_\alpha}{2\pi}\psi(\omega + E_{nl})\right],$$

$$\Lambda_{nl}^h(\omega) = \sum_\alpha \left[\frac{-i\Gamma_\alpha}{2}n_\alpha(-\omega - E_{nl}) - \frac{\Gamma_\alpha}{2\pi}\psi(\omega + E_{nl})\right], \qquad (30)$$

where

$$\psi(\varepsilon) = \int d\xi n_F(\xi)\left[\frac{1}{\varepsilon - \xi} + \frac{1}{\xi}\right], \qquad (31)$$

where the last term has been added as a regularization of the integral at large energies. This is allowed because it cancels when adding the two $\psi$ terms in Eq. (28) (which is easily seen by noting that $\Sigma_l f_{nl}^* f_{jl} = \delta_{n,l}$). Note that $\psi(\varepsilon)$ is a function of $\varepsilon/kT$ only, and that $\psi(\varepsilon) = \psi(-\varepsilon)$. At large values of $\varepsilon/kT$ the $\psi$-function has the asymptotic form $\psi(\varepsilon) \approx -\ln(\varepsilon/kT)$, while for small $\varepsilon$ it goes as $\psi(\varepsilon) \approx -(\varepsilon/kT)^2 \times 0.213139\ldots$.

The only remaining question is how to evaluate the last term in Eq. (19). In the absence of tunneling or in the single particle approximation, we can decouple the electron and phonon degrees of freedom, such that $\langle dd^\dagger|n\rangle\langle m| \approx \langle dd^\dagger\rangle N_n\delta_{nm}$, where $N_n = \langle|n\rangle\langle n|\rangle$ is the occupation of the $n$th oscillator level and $\bar{n} = \langle d^\dagger d\rangle$ is the average level occupation. To leading order in $\Gamma$ this is a reasonable approxima-
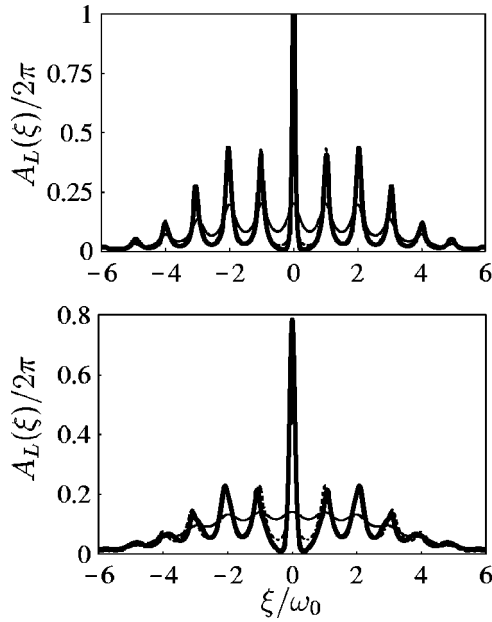
FIG. 1. The broadened tunnel density of states $A_L(\xi)$ for the resonance condition, $\epsilon_0 = 0$ and $g = 2$ and two different values of $\Gamma$. Top panel: $\Gamma/\omega_0 = 0.5$ and lower panel: $\Gamma/\omega_0 = 1$. The thick solid lines are the numerical solution of the full expression [Eq. (28)], while the thin lines are the single particle approximation. Also shown is the approximation expression [Eq. (38)] with dashed lines. The approximate expression is in fact bare distinguishable from the full result. It is clearly seen how the first Frank-Condon step remains sharp even for large values of tunnel broadening, in accordance with the estimate in Eq. (39). In all cases we take $kT/\omega_0 = 0.01$.

tion. However, in the more general case we should in principle solve the terms $\langle dd^\dagger |n\rangle\langle m|\rangle$ and $\langle d^\dagger d|m'\rangle\langle n'|\rangle$ on the first right hand of Eq. (28) self-consistently. In the general nonequilibrium case, it is, however, not possible to calculate these expectation values from the retarded Green's function alone. One must therefore invoke new approximations for this purpose. Instead of pursuing this, concentrate on a case where this is not necessary, namely, the situation of a strongly asymmetric device. This is done in Sec. III B.

### B. Asymmetric transistor, $\Gamma_L \gg \Gamma_R$

In the strongly asymmetric thermal case, things simplify considerably, because the dot states are in thermal equilibrium with one of the leads. For the case $\Gamma_L \gg \Gamma_R$, the current is

$$I = \frac{e}{h}\int \frac{d\xi}{2\pi}\Gamma_R[n_L(\xi) - n_R(\xi)]A_L(\xi), \quad (32)$$

where $A_L$ is the equilibrium spectral function in equilibrium with the left lead. Therefore, we can use the standard equilibrium expression for the self-consistent equations

$$\delta_{nm}\langle d^\dagger d|m'\rangle\langle n'|\rangle = \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}A_{nn',mm'}(\omega)n_F(\omega), \quad (33)$$
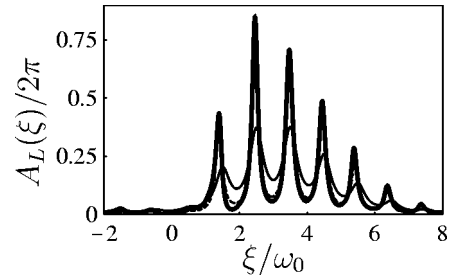


FIG. 2. Same plot as in Fig. 1 but with $\epsilon_0/\omega_0 = 1.5$ and $\Gamma/\omega_0 = 0.5$. Note that when compared to the $\epsilon_0 = 0$ curve in Fig. 1 with the same $\Gamma$ (top panel) the first step is broader because the blocking of the level broadening gradually disappears further away from the Fermi energy.

$$\delta_{n'm'}\langle dd^\dagger\rangle\langle|n\rangle\langle m|\rangle = \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}A_{nn',mm'}(\omega)n_F(-\omega), \quad (34)$$

where $A_{nn',mm'}(\omega) = i[G_{nn',mm'}^R(\omega) - G_{d,nn',mm'}^A(\omega)]$.

We have numerically solved these equations, and in Fig. 1 we plot the result for the spectral function, $A_L(\xi)$, for $\varepsilon_0 = 0$, and different values of the tunnel broadening. It is clearly seen how the Fermi surface effects sharpen the lines as compared to the SPA. This effect is more pronounced for the first peaks, which is also evident from Fig. 2, where we show the spectral function for the off-resonance condition.

### C. Approximate solution of the Dyson equations

In order to gain a more physical understanding of the narrowing of the lines seen above and to obtain analytical results, we now proceed to solve Eqs. (28) approximately. As is shown in the numerical plots, the approximate analytic solution, that is derived below, is in fact close to the full solution.

We look for a solution of Eq. (28) near one of the resonances, $\omega \approx \varepsilon_0 + n\omega_0$. Because the Green's function $G_{d,nn',mm'}^R(\omega)$ peaks at $\omega = \varepsilon_0 - E_{nn'}$, the two terms in the sum in Eq. (28) are dominated by, $E_{jn'} \approx E_{nn'}$ and $E_{nj} \approx E_{nn'}$, respectively. Hence we can set $j = n$ in the first one and $j = n'$ in the second one, which then gives the following diagonal equations

$$[\omega + E_{nn'} - \varepsilon_0 - \Sigma_{nn'}(\omega)]G_{nn',mm'}^R(\omega)$$
$$= \delta_{nm}\delta_{n'm'}\{(1-\bar{n})N_n + \bar{n}N_{n'}\}, \quad (35)$$

where the self-energy is

$$\Sigma_{nn'}(\omega) = \sum_l [\Lambda_{ln'}^e(\omega)|f_{nl}|^2 + \Lambda_{nl}^h(\omega)|f_{ln'}|^2]. \quad (36)$$

We have, furthermore, approximated

$$\langle dd^\dagger|n\rangle\langle m|\rangle_S\delta_{n'm'} + \langle d^\dagger d|m'\rangle\langle n'|\rangle_S\delta_{nm} \approx \delta_{nm}\delta_{n'm'}$$
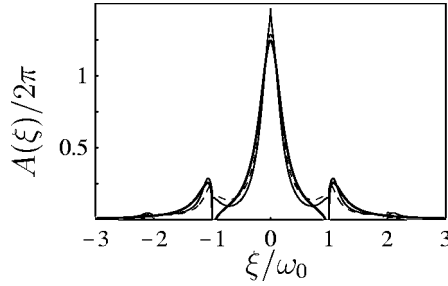$$\times\{(1-\bar{n})N_n + \bar{n}N_{n'}\}, \quad (37)$$

FIG. 3. The perturbative result for the spectral function (thick line) compared to the full solution of Eq. (28) (thin line) and the approximate solution [Eq. (38)] for the symmetric point $\epsilon_0 = 0$. The perturbative results, which is derived in Appendix B, treats the tunneling term exactly but the electron-phonon coupling only to linear order. The other parameters are $\Gamma/\omega_0 = 0.5$ and $g = 0.25$.

where $N_n = \exp(-n\beta\omega_0)$ and $\bar{n} = \langle d^\dagger d \rangle$. This approximation is valid for not too large $\Gamma$ and we have verified numerically, in the self-consistent calculation performed above, that it is indeed reasonably accurate for $\Gamma/\omega_0 \lesssim 1$. With these approximations, we obtain a closed expression for the Green's function $G^R$:

$$G^R(\omega) = \sum_{nn'} \frac{(1-\bar{n})N_n + \bar{n}N_{n'}}{\omega + E_{nn'} - \varepsilon_0 - \Sigma_{nn'}(\omega)} |f_{nn'}|^2. \quad (38)$$

The result in Eq. (38) thus generalizes the SPA approximation [Eq. (25)], by including the leading order effect of the Fermi sea. The new self-energy in Eq. (36) has a simple physical interpretation: the broadening, which is caused by tunneling out and tunneling in processes, can only occur if the state in the lead is either empty or occupied, respectively. For the noninteracting case, where in Eq. (36) we set $E_{nn'} = 0$ and use that $\Sigma_l |f_{nl}|^2 = 1$, the spectral functions reduces correctly to an Lorentzian with width $\Gamma$.

We can now in detail study the narrowing of the on-resonance line seen in Fig. 1. At resonance we have $\bar{n} = \frac{1}{2}$, and we then straightforwardly find

$$A(\omega) \approx \frac{|f_{00}|^2 \Gamma_{00}^2}{\omega^2 + (\Gamma_{00}/2)^2}, \quad \Gamma_{00} = |f_{00}|^2 \Gamma. \quad (39)$$

This result shows that the width of the resonance at $\varepsilon_0 = 0$ is considerably narrower than the bare tunnel broadening would suggest. For large values of $g$ $|f_{00}|^2$ becomes smaller and the lines narrows in. However, also the weight of the line goes down with $|f_{00}|^2$ as is evident from Eq. (39).

### D. Comparison with perturbation theory in $g$

It is interesting to compare the results where the tunneling is treated approximately but the electron-phonon coupling exactly, to the results of a perturbation theory, where the tunneling is treated exactly but the electron-phonon coupling to lowest order. This situation is solved in Appendix B, and Fig. 3 shows the result of the calculation. Note that both methods give qualitatively the same result, namely, that the

zero energy line is narrowed and that spectral function is suppressed between the two peaks.

## IV. CONCLUSIONS

We have presented results for transport through quantum dots with strong electron-phonon coupling and with a strong tunneling broadening of the phonon sidebands. This is not a solvable problem even when the spin degree of freedom is ignored, and we resorted to an approximation which incorporates the Fermi sea, but ignores correlation effects. The approximation is exact in both the single particle and weak tunneling cases. However, physical conclusions can be drawn from the approximate approach, namely, that the tunnel broadening is much weaker than expected from a model where the Pauli principle is not incorporated. We have, as mentioned, neglected the spin degree of freedom which is not expected to be important at temperatures above the Kondo temperature. It is, however, an interesting question to ask how the Kondo effect is influenced by the coupling between the electron occupancy and the vibrational mode of the molecule.

## APPENDIX A: DERIVATION OF THE EQUATIONS OF MOTION

Here we present the commutators and the methods used to derive the set of equations of motion in Sec. III A. We write the Hamiltonian in Eq. (11) as $H = H_0 + H_T$. In the oscillator eigenstate representation $H_T$ is

$$H_T = \sum_{k\alpha,ll'} t_{k\alpha}(d^\dagger c_{k\alpha}|l'\rangle\langle l|f^*_{ll'} + |l\rangle\langle l'|f_{ll'}c^\dagger_{k\alpha}d). \quad (A1)$$

Then Eqs. (19) and (20) follow from

$$[H_0, d|n\rangle\langle n'|] = (E_{nn'} - \varepsilon_0)d|n\rangle\langle n'|, \quad (A2)$$

$$[H_T, d|n\rangle\langle n'|] = \sum_{k\alpha,ll'} t_k f^*_{ll'}(-d^\dagger d c_{k\alpha}|l'\rangle$$
$$\times \langle n'|\delta_{nl} - dd^\dagger c_{k\alpha}|n\rangle\langle l|\delta_{n'l'}). \quad (A3)$$

The equation of motion in Eq. (23) follows from the commutators

$$[H_0, c_{k\alpha}|n\rangle\langle l|] = (E_{nl} - \xi_{k\alpha})c_{k\alpha}|n\rangle\langle l|, \quad (A4)$$

$$[H_T, c_{k\alpha}|n\rangle\langle l|] = \sum_{k'\alpha' jj'} t_{k'\alpha'}\{-f_{jj'}[|n\rangle\langle j'|\delta_{k\alpha,k'\alpha'}\delta_{jl}$$
$$+ c^\dagger_{k'\alpha'}c_{k\alpha}(|j\rangle\langle l|\delta_{j'n} - |n\rangle\langle j'|\delta_{jl})]d$$
$$+ f^*_{jj'}(|j'\rangle\langle l|\delta_{jn} - |n\rangle\langle j|\delta_{j'l})c_{k'\alpha'}c_{k\alpha}d^\dagger\}. \tag{A5}$$

At this point we truncate the equations of motion approximating the terms with three electron operators by the Hartree-Fock decomposition for the lead electrons. We have

$$c^\dagger_{k'\alpha'}c_{k\alpha}d \approx \langle c^\dagger_{k'\alpha'}c_{k\alpha}\rangle d - \langle c^\dagger_{k'\alpha'}d\rangle c_{k\alpha}, \tag{A6}$$

$$c_{k'\alpha'}c_{k\alpha}d^\dagger \approx c_{k'\alpha'}\langle c_{k\alpha}d^\dagger\rangle - c_{k\alpha}\langle c_{k'\alpha'}d^\dagger\rangle. \tag{A7}$$

As mentioned in the main text, we will at this level neglect the terms $\langle c_{k\alpha}d^\dagger\rangle$ and therefore only $c^\dagger_{k'\alpha'}c_{k\alpha}d$ contributes and gives $\langle c^\dagger_{k'\alpha'}c_{k\alpha}\rangle d \approx \delta_{k\alpha,k'\alpha'}\langle c^\dagger_{k\alpha}c_{k\alpha}\rangle d$. The last approximate sign here means up to order $\Gamma$, which is consistent with neglecting $\langle c_{k\alpha}d^\dagger\rangle$. When this is inserted back into Eq. (A5), we get

$$[H_T, c_{k\alpha}|n\rangle\langle l|] \approx \sum_{jj'} t_{k\alpha}\{-f_{jj'}[|n\rangle\langle j'|\delta_{jl} + \langle c^\dagger_{k\alpha}c_{k\alpha}\rangle(|j\rangle$$
$$\times\langle l|\delta_{j'n} - |n\rangle\langle j'|\delta_{jl})]d\}, \tag{A8}$$

which then leads to Eq. (24). Finally, the last equation of motion in Eq. (23) follows from

$$[H_0, d^\dagger dc_{k\alpha}|n\rangle\langle l|] = (E_{nl} - \xi_{k\alpha})d^\dagger dc_{k\alpha}|n\rangle\langle l|, \tag{A9}$$

$$[H_T, d^\dagger dc_k|n\rangle\langle l|] = \sum_{k'\alpha', jj'} t_{k'\alpha'}[-f_{jj'}|j\rangle\langle l|c^\dagger_{k'\alpha'}c_{k\alpha}d\delta_{j'n}$$
$$- f^*_{jj'}|n\rangle\langle j|c_{k\alpha}c_{k'\alpha'}d^\dagger\delta_{j'l}], \tag{A10}$$

and after using the same arguments as before, we obtain

$$[H_T, d^\dagger dc_{k\alpha}|n\rangle\langle l|] \approx -\sum_j t_k f_{jn}|j\rangle\langle l|\langle c^\dagger_{k\alpha}c_{k\alpha}\rangle d, \tag{A11}$$

which leads to Eq. (27). Furthermore, when the oscillator states are chosen real the function $f_{nn'}$ is

$$f_{nn'} = \sqrt{\frac{1}{2^n 2^{n'} n! n'!}} e^{-g/2}$$
$$\times\left[\text{sign}(n'-n)\sqrt{\frac{g}{2}}\right]^{|n-n'|} 2^{\max(n,n')}L^{\min(n,n')}_{|n-n'|}(g). \tag{A12}$$

## APPENDIX B: PERTURBATION THEORY IN $g$

In this appendix we derive a perturbative result for the spectral function to first order in the coupling constant but to all orders in the tunneling matrix element. We do, however, also assume a constant bare tunneling density of states and

also take the asymmetric case, $\Gamma_R \ll \Gamma_L = \Gamma$. We want to compute $G^R$ in Eq. (8) and for the perturbative calculation it is more convenient to use Hamiltonian (1) instead of the transformed Hamiltonian. We will start from the equations of motion for the Green's function $G^R_d$. Here we use the notation $G^R_y = -i\theta(t)\langle[y(t), d^\dagger]\rangle$. We obtain

$$\left(\omega - \xi_0 + i\frac{\Gamma}{2}\right)G^R_d(\omega) = 1 + \lambda G^R_{xd}(\omega). \tag{B1}$$

The equation of motion for the function $G^R_{xd}$ is

$$\begin{pmatrix} \omega - \xi_0 & -i/m \\ im\omega_0^2 & \omega - \xi_0 \end{pmatrix}\begin{pmatrix} G^R_{xd} \\ G^R_{pd} \end{pmatrix}$$
$$= \begin{pmatrix} \langle x\rangle \\ 0 \end{pmatrix} + \sum_k t_k\begin{pmatrix} G^R_{xk} \\ G^R_{pk} \end{pmatrix} + \frac{\lambda}{2}\begin{pmatrix} \ell_0^2 \\ -i \end{pmatrix}G^R_{d,\lambda=0}(\omega), \tag{B2}$$

and

$$\begin{pmatrix} \omega - \xi_k + i\eta & -i/m \\ im\omega_0^2 & \omega - \xi_k + i\eta \end{pmatrix}\begin{pmatrix} cG^R_{xk} \\ G^R_{pk} \end{pmatrix}$$
$$= t_k\begin{pmatrix} G^R_{xd} \\ G^R_{pd} \end{pmatrix} - i\lambda\begin{pmatrix} 0 \\ 1 \end{pmatrix}G^R_{nk,\lambda=0}(\omega), \tag{B3}$$

where we used that since $G^R_{xd}$ in (B1) is multiplied by $\lambda$, the last term of Eq. (B3) should be calculate without electron phonon coupling. Therefore, for temperatures $kT \ll \omega_0$ the following replacements were made in that term $\lambda x^2 d = \lambda\langle x^2\rangle_0 d = \frac{1}{2}\ell_0^2 d$, and $\lambda pxd = \lambda\langle px\rangle_0 d = (-i/2)d$. The average value $\langle x\rangle$ appearing in Eq. (B2) follows from $\langle\ddot{x}\rangle = -\omega_0^2\langle x\rangle - \langle n_d\rangle\lambda/m = 0$. Expressing the functions $G^R_{xk}$ and $G^R_{pk}$ in Eq. (B3) in terms of $G^R_{xd}$ and $G^R_{pd}$ and inserting this back into Eqs. (B2) and (B1), we obtain

$$G^R_d(\omega) = \frac{1-g}{N_0} - \frac{g\omega_0}{N_0^2} + \frac{gn}{N_{+1}} + \frac{g(1-n)}{N_{-1}} + \frac{\lambda^2}{m}\frac{1}{N_{+1}N_{-1}N_0}$$
$$\times\sum_k \frac{t_k(N_0 + \omega - \xi_k)}{(\omega - \xi_k + i\eta)^2 - \omega_0^2}G^R_{nk,\lambda=0}(\omega), \tag{B4}$$

where $N_p = \omega - \xi_0 + p\omega_0 + i(\Gamma/2)$. The first four terms in (B4) are nothing but the SPA result in Eq. (25) expanded to lowest order in $g$. *Therefore, it is evident that the last term of Eq. (B4) constitutes the correction to the SPA.* The Green's function $G^R_{nk,\lambda=0}$ can be evaluated using Wick's theorem

$$G^R_{nk,\lambda=0}(\omega) = \langle n_d\rangle_0 G^R_{k,\lambda=0}(\omega) - \langle d^\dagger c_k\rangle_0 G^R_{d,\lambda=0}(\omega), \tag{B5}$$

where

$$G^R_{k,\lambda=0}(\omega) = t_k\frac{1}{\omega - \xi_k + i\eta}G^R_d(\omega),$$

$$\langle d^\dagger c_k \rangle_0 = i \int \frac{d\omega'}{\pi} n_F(\omega') [G^R_{k,\lambda=0}(\omega') - G^A_{k,\lambda=0}(\omega')].$$
$$(B6)$$

The integrant in Eq. (B4) is analytic in the upper half-plane of the complex $\xi_k$ plane, and when performing the integral by a contour in the lower half-plane only one term in Eq. (B6) contributes. The last term in Eq. (B4), which was the correction to the SPA result, then reads

$$\delta G^R_d(\omega) = \frac{-g\omega_0^2 \Gamma}{N_{+1}N_{-1}N_0^2} \gamma(\omega),$$
$$(B7)$$

where

$$\gamma(\omega) = \omega_0 \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} n_F(\omega') \frac{1}{\omega' - \xi_0 - i\Gamma/2}$$
$$\times \frac{2\omega - \xi_0 - \omega'}{(\omega' - \omega - i\eta)^2 - \omega_0^2}.$$
$$(B8)$$

The SPA is restored when the energy is either far above or far below the Fermi surface, because the model is then similar to a single electron or a single hole. This is clearly seen in the limit $|\xi_0|, \omega_0 \gg \max(\Gamma, kT)$, where we can replace $n_F$ by either one or zero. For the first cases it is clear that $\delta G$ is 0. When $n_F = 1$, we have also get zero because the integrant is analytic in one half-plane.

Finally, at $T = 0$, we have

$$\gamma(\omega) = \frac{\omega_0}{2\pi} \frac{2\omega - 2\xi_0 - i\Gamma/2}{(\omega - \xi_0 - i\Gamma/2)^2 - \omega_0^2}$$
$$\times \{2i\pi n_0 + \ln[(\xi_0/\omega_0)^2 + (\Gamma/2\omega_0)^2]\}$$
$$+ \frac{\omega - \xi_0 - \omega_0}{2\pi(\omega - \xi_0 + \omega_0 - i\Gamma/2)}[i\pi\theta(-\omega_0 - \omega)$$
$$+ \ln|(\omega_0 + \omega)/\omega_0|] - \frac{\omega - \xi_0 + \omega_0}{2\pi(\omega - \xi_0 - \omega_0 - i\Gamma/2)}$$
$$\times [i\pi\theta(\omega_0 - \omega) + \ln|(\omega_0 - \omega)/\omega_0|],$$

where

$$n_0 = \frac{1}{\pi} \tan^{-1}\left(\frac{-2\xi_0}{\Gamma}\right) + \frac{1}{2}.$$
$$(B9)$$

The zero temperature expression for the SPA correction is seen to diverge at $|\omega| = \omega_0$. This divergence is, however, cut-off at finite temperatures. If Fig. 3 we show the result of the perturbation theory compared to the approximate spectral function derived in the main text. The plot is at the symmetric point $\varepsilon_0 = \xi_0 - g\omega_0 = 0$. One should note that when expanding $\varepsilon_0$ to linear order it cancels off the term $-g\omega_0/N_0^2$ in Eq. (B4).

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