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Conductance of deformable molecules with interaction

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Zero temperature linear response conductance of molecules with Coulomb interaction and with various types of phonon modes is analyzed together with local occupation, local moment, and charge fluctuations. Particular emphasis is on deformation fluctuations, which are quantitatively related to charge fluctuations. Charge fluctuations are shown to exhibit similarity to static charge susceptibility.

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The evidence for phonon-assisted tunneling was found already in early conductance measurements in double-barrier heterostructures.[1] In conductance measurements of nanoscale systems such as quantum dots or real molecules, the Coulomb interaction leads to the Coulomb blockade or the Kondo effects.[2] The electron-phonon interaction also proved to play an essential role in such systems. In particular, in single organic molecules electronic transport is influenced by the vibrational fine structure.[3,4]

Phonon degrees of freedom lead to a mass enhancement of a single electron in the empty conduction band. The problem is known as the conventional polaron problem.[5] The local form of the polaron problem arises when the coupling between electrons and phonons is confined to only one site.[6,7] Here, the main effect of phonons is a narrowing of the level width, analogous to the electron-phonon mass enhancement and is similar to the level width renormalization due to electron-hole pairs.[8] Theoretical investigations of the combined effect, the electron-electron and the electron-phonon interaction, show that quite diverse impurity systems can be described by the Anderson model with renormalized effective parameters.[9]

Early studies of the conductance of various types of quantum systems with electron-phonon interaction were based on the calculation of the transmission probability as a function of incident energy for an electron interacting with Einstein phonons as it tunnels through a double-barrier structure.[10] The transmission probability for single injected electrons exhibits phonon-assisted transmission resonances—sidebands—at energies near the main elastic resonance.[10,11] Such sidebands appear also in the linear conductance calculation results if the coupling to the Fermi sea in the leads is not correctly taken into account.[12] However, vibrational sidebands would be discernible in nonlinear conductance measurements.[13,14] Recently, the numerical renormalization group method applied to a single-molecule device[15,16] showed that the problem can, in certain regimes, be mapped onto the anisotropic Kondo model.[17] Phonon effects in molecular transistors were also investigated in quantal and classical treatments.[18]

In this paper we concentrate on the deformation of a molecule in a linear response conductance measurement. In particular, the molecule is attached to the left and right noninteracting leads, schematically presented in Fig. 1, and described with the Anderson model

$$H_e = -\sum_{\langle ij\rangle\sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \epsilon_d n_d + U n_{d\uparrow} n_{d\downarrow}, \tag{1}$$

where $\langle ij\rangle$ represents nearest-neighbor hopping. In the leads $t_{ij}\equiv t$, and $t_{\pm 1,0}=t_{0,\pm 1}\equiv t'$ is the hopping matrix element from the leads to the molecule. The occupation of the molecule is $n_d=\Sigma_\sigma n_{d\sigma}$ with $n_{d\sigma}=d_\sigma^\dagger d_\sigma$, where $d_\sigma\equiv c_{0\sigma}$. The deformation of the molecule is modeled with a general form of linear electron-phonon coupling and the molecule coupled to the leads is described with

$$H = H_e + \sum_\alpha \Omega_\alpha a_\alpha^\dagger a_\alpha + \sum_\alpha \Big[M_\alpha (n_d - 1) + N_\alpha \sum_\sigma (d_\sigma^\dagger c_{-1\sigma} + d_\sigma^\dagger c_{1\sigma} + \text{H.c.}) \Big] x_\alpha, \tag{2}$$

where M_α and N_α are the local and nearest-neighbor electron-phonon coupling constants corresponding to an arbitrary number of orthogonal vibrational modes with energies Ω_α and corresponding displacements $x_\alpha=a_\alpha^\dagger+a_\alpha$. For simplicity, an assumption of linear coupling to displacements is taken. In various nanoelectromechanical systems (NEMS) and in many (bio)molecular applications, this assumption is not justified and the coupling should be treated more precisely. In this regard we want to stress that our numerical method can easily be adapted to a more general type of electron-phonon Hamiltonian.

The zero temperature linear response conductance through the molecule is calculated from the sine formula,[19,20] $G=G_0 \sin^2[(E_+-E_-)L/4t]$, where $G_0=2e^2/h$ and $E_\pm$ are the ground-state energies of a large auxiliary ring consisting of L noninteracting sites and an embedded interacting system (molecule), with periodic and antiperiodic boundary conditions, respectively. The chemical potential is set at the middle of the band in the leads, which corresponds to L

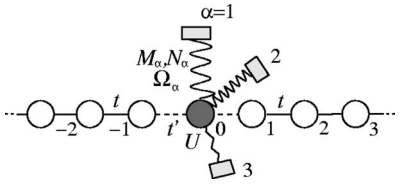

FIG. 1. Noninteracting leads attached to an Anderson site, e.g., molecule (gray-shaded site) with various phonon modes.

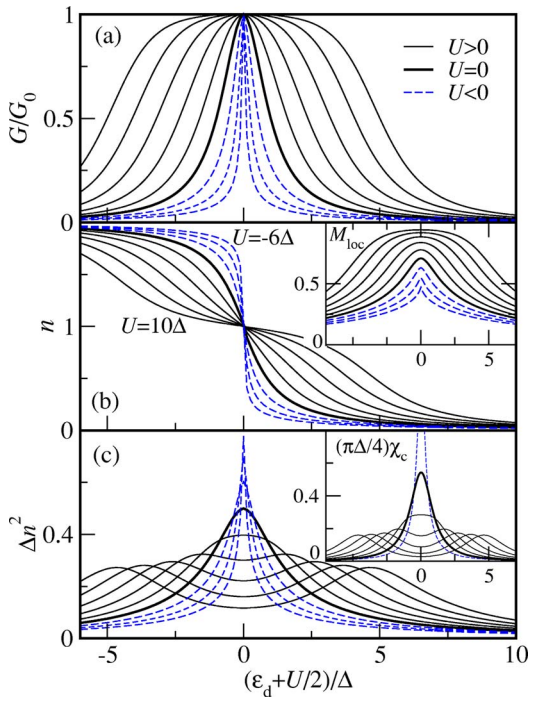

FIG. 2. (Color online) (a) Conductance for the bare Anderson model with $-6\Delta \leqslant U \leqslant 10\Delta$ in increments of 2Δ (full lines for $U>0$, dashed lines for $U<0$, and a thicker full line for $U=0$). (b) Local occupancy n and local moment M_{loc} (inset). (c) Charge fluctuations $\Delta n^2=2n-n^2-M_{\mathrm{loc}}^2$. Inset: renormalized charge susceptibility $(\pi\Delta/4)\chi_c$.

electrons in the system. To determine the ground-state energy, we generalized the projection-operator method proposed by Gunnarsson and Schönhammer.[21] The variational expression for the ground state is

$$|\Psi\rangle = \sum_{\lambda\{m_\alpha\}} C_{\lambda\{m_\alpha\}} P_\lambda \prod_\alpha a_\alpha^{\dagger m_\alpha} |\tilde{0}\rangle, \tag{3}$$

where P_λ are projection operators to the multielectron states of an isolated molecule, $P_0=(1-n_{d\uparrow})(1-n_{d\downarrow})$, $P_1=\Sigma_\sigma n_{d\sigma}(1-n_{d\bar{\sigma}})$, and $P_2=n_{d\uparrow}n_{d\downarrow}$, as well as additional operators involving the hopping of electrons between the molecule and leads (for details, see Ref. 21). The vacuum state $|\tilde{0}\rangle$ is the ground state of a decoupled, noninteracting electron-phonon system, described by renormalized matrix elements $\tilde{t}'$ and $\tilde{\epsilon}_d$. An approximation to the ground-state energy is obtained by minimizing the total energy with respect to coefficients $C_{\lambda\{m_\alpha\}}$ and parameters $\tilde{t}'$ and $\tilde{\epsilon}_d$ while allowing a sufficiently large number of excited phonons, in order to obtain a converged result.

For a positive U and $M_\alpha=N_\alpha=0$, the problem reduces to the standard Anderson impurity case. Here various numerical approaches reproduce basic properties: conductance exhibits a plateau in the Kondo regime and local electron density $n=\langle n_d\rangle$ is related to the conductance through the Friedel sum rule[24] and is also characterized with a plateau $n\sim 1$ in the Kondo regime, as presented in Fig. 2. The results of the present numerical method[19] accurately reproduce the exact solution based on the Bethe ansatz.[22] Kondo physics is signaled also with the increase of the local moment $M_{\mathrm{loc}}=\langle(n_{d\uparrow}-n_{d\downarrow})^2\rangle^{1/2}$, additionally presented in the inset of Fig. 2(b). Less investigated is the related occupancy (charge) fluctuation correlation function, $\Delta n^2=\langle(n_d-n)^2\rangle$, presented in Fig. 2(c) and in the inset the corresponding charge susceptibility, $\chi_c=-\partial n/\partial\epsilon_d$ is given. In accordance with the fluctuation-dissipation theorem, charge fluctuations are similar to the charge susceptibility, $\Delta n^2\sim(\pi\Delta/4)\chi_c$.[23] Fluctuations are suppressed in the Kondo regime, and are larger in the mixed valence regime, $|\epsilon_d|\lesssim\Delta$ or $|\epsilon_d+U|\lesssim\Delta$. We use throughout the paper fixed $\Delta=2t'^2/t=t/5$.

For attractive $U<0$, the situation is quite opposite to the more standard (spin) Kondo regime because at the impurity the system favors electron (hole) pairs rather than local moments due to single electrons.[7] This regime is not common in systems with strong Coulomb interaction as is, e.g., a quantum dot in the Coulomb blockade regime. Due to electron attraction, strong charge fluctuations emerge in the particle-hole symmetric point when the chemical potential is level with the local bipolaron energy leading to charge-fluctuation (anisotropic) Kondo effect.[17] In Fig. 2(a) the conductance for various $U<0$ is presented with dashed lines. The first observation is a narrowing of the conductance curve and the corresponding enhanced charge fluctuations [Fig. 2(c)], consistent with a sharp transition in the local occupation and a suppression of the local moment, Fig. 2(b). For increasing (negative) U, charge susceptibility is not limited and overshoots charge fluctuations. However, the comparison of Δn^2 and χ_c confirms at least qualitative proportionality. The regime of negative U is important in realistic systems with strong electron-phonon interaction. In the limit of large frequencies, Ω_α, finite M_α and $N_\alpha=0$, the model of Eqs. (1) and (2) is equivalent to the bare Anderson model with renormalized parameters $U_{\mathrm{eff}}=U-\Sigma_\alpha 2M_\alpha^2/\Omega_\alpha$ and $\epsilon_{d,\mathrm{eff}}=\epsilon_d-\Sigma_\alpha M_\alpha^2/\Omega_\alpha$,[6] and the results from Fig. 2 can also be regarded as the solution of the full Hamiltonian in this limit.

For general electron-phonon coupling the problem cannot be mapped onto a simple Anderson model. However, the main physics characterizing the quantities from Fig. 2 is at least qualitatively contained in the full solution of the Anderson-phonon problem. In particular, in Fig. 3 the results of the analysis of a molecule with a single vibrational mode using $U=10\Delta$ are presented. The coupling-frequency ratio is kept constant, $M_\alpha/\Omega_\alpha\equiv M/\Omega=1$, while the electron-phonon coupling M is varied from $M=\Delta$ to $M=6\Delta$ in increments of Δ. The results for conductance, occupancy, and occupancy fluctuations [Figs. 3(a)–3(c)] resemble the results of the bare Anderson model with renormalized parameters.[9] There are no discernible sidebands in the conductance. For comparison the result for undeformable molecule ($M=0$) is also presented. The molecule deformations, i.e., x_α, are related to the occupation of the impurity. The displacement of individual modes is, in general, given with $\langle x_\alpha\rangle=-2M_\alpha/\Omega_\alpha(n-1)-16N_\alpha/\Omega_\alpha\,\mathrm{Re}\langle d_\sigma^\dagger c_{1\sigma}\rangle$.[16] In NEMS the limit of displacement sensing is imposed by the fluctuations of the deformation, $\Delta x_\alpha^2=\langle(x_\alpha-\langle x_\alpha\rangle)^2\rangle$, related to the average number of particular phonons in the system, $\Delta x_\alpha^2=1+2\langle a_\alpha^\dagger a_\alpha\rangle+2\,\mathrm{Re}\langle a_\alpha^\dagger a_\alpha^\dagger\rangle-\langle x_\alpha\rangle^2$. A deviation of Δx_α^2 from unity signals deviations from the coherent state of the oscillator. In the limit of large

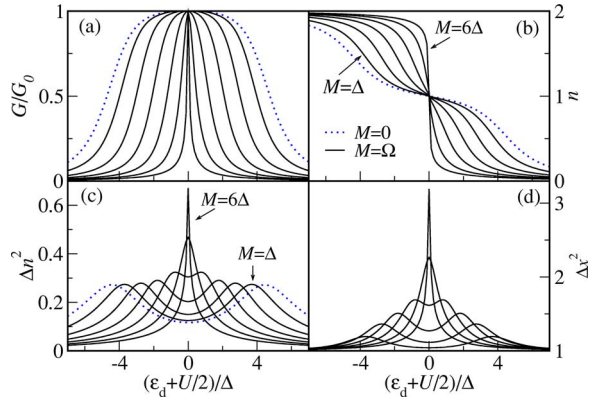

FIG. 3. (Color online) Results for $U=10\Delta$ and a single phonon mode with a fixed $M=\Omega$. (a) Conductance vs $(\epsilon_d+U/2)/\Delta$ for $0 \leqslant M \leqslant 6\Delta$ in increments of Δ. The dotted line represents the results for an undeformable molecule, $M=0$. (b) Occupation, (c) occupation fluctuations, and (d) deformation fluctuations.

phonon frequencies (fast modes) the oscillator deformations can follow charge fluctuations, $\Delta x_\alpha^2-1=(2M_\alpha/\Omega_\alpha)^2\Delta n^2$, while in general they are smaller than that. In the limit of small phonon frequencies (slow modes), phonons feel the average occupation of the molecule and $\Delta x_\alpha^2-1=0$. The fluctuations corresponding to a single mode system, $\Delta x_\alpha^2 \equiv \Delta x^2$, for the same set of parameters and labeled as above, are presented in Fig. 3(d).

Next we turn our attention to the case of a molecule with multiple vibrational modes. Here we give results for the case $U=10\Delta$ with mode 1 with frequency $\Omega_1=\Delta$ and mode 2 with frequency $\Omega_2=10\Delta$. The effective Coulomb interaction is reduced due to coupling to both modes $U_{\text{eff}}=U-2M_1^2/\Omega_1-2M_2^2/\Omega_2$. We take $N_\alpha=0$ and thus the system retains the particle-hole symmetry. Therefore, in Fig. 4 only the $\epsilon_d+U/2>0$ regime is shown. In order to study both the particular and mutual influence of different modes, we fix $U_{\text{eff}} \equiv 5\Delta$, and set $2M_1^2/\Omega_1=r(U-U_{\text{eff}})$, $2M_2^2/\Omega_2=(1-r)(U-U_{\text{eff}})$ where, by varying r, one can explore the effect of particular modes. For a single stiffer mode 2, $r=0$, the conductance curve, Fig. 4(a), is suppressed in the Kondo regime and enhanced in the empty orbital region compared to the softer mode 1, $r=1$. As a limiting case of this regime the bare Anderson model results for $U=5\Delta$ are presented.

As a representative of the opposite limit, we consider very soft phonons with $\Omega=\Delta/100$. In the Kondo regime the conductance is close to the unrenormalized Anderson model result with $U=10\Delta$. In the mixed valence regime the curve is much steeper, due to the strong renormalization of hopping parameter $\tilde{t}'$. In the empty-orbital regime the conductance approaches the result obtained with doubly reduced electron-electron interaction $\tilde{U}=U-4M^2/\Omega$, which can be understood as follows. First the oscillator displacement is shifted, $x \rightarrow \tilde{x}+2\lambda$, thus the Hamiltonian is transformed into $\tilde{H}=(\epsilon_d+2\lambda M)n_d+\tilde{x}[M(n_d-1)+\Omega\lambda]+\Omega\tilde{a}^\dagger\tilde{a}+\cdots$, where $\lambda=-M(n-1)/\Omega$, with vanishing transformed displacement. This Hamiltonian can be solved with trial wave functions with $m_\alpha=0$. Renormalized local energies are then ϵ_d+2M^2/Ω, ϵ_d, and ϵ_d-2M^2/Ω for $n=0,1,2$, respectively. The shifts of ϵ_d where $n=0,2$ in turn correspond to reduced $\tilde{U}=U-4M^2/\Omega$ and to $\tilde{U}=U$ for $n=1$.

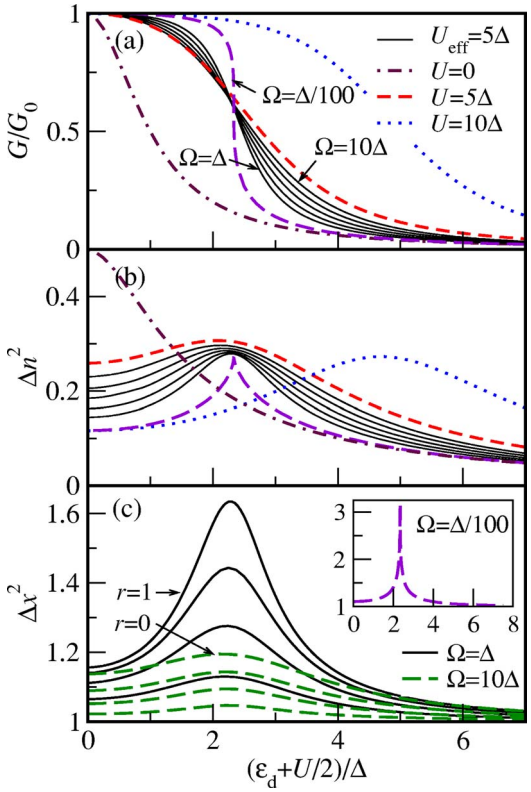

FIG. 4. (Color online) A fixed $U_{\text{eff}}=5\Delta$ with $U=10\Delta$ and $\Omega_1=\Delta$, $\Omega_2=10\Delta$ for various $M_{1,2}$ (corresponding to $r=0$, 1/4, 1/2, 3/4, and 1) (full lines). Also plotted are the results for a bare Anderson model with $U=10\Delta$, $U=5\Delta$, and $U=0$ (dotted, short-dashed, and dashed-dotted lines, respectively). Long-dashed lines correspond to a single softer mode with $\Omega=\Delta/100$ and the same $U_{\text{eff}}=5\Delta$. (a) Conductance, (b) occupation fluctuations, and (c) deformation fluctuations for modes 1 and 2. In the inset, the deformation fluctuations for a single softer mode are shown.

Occupancy n is related to the conductance similarly as in the previous figures and is not presented for this case. Charge fluctuations, Fig. 4(b), are similar to the relation between Δn^2 and χ_c as in the above single mode case: The fluctuations are larger for stiffer phonon modes, except in the mixed-valence regime, where Δn^2 is very weakly dependent of Ω_α. Charge fluctuations for the case of softer mode $\Omega=\Delta/100$ exhibit limiting behavior consistent with G as discussed above. Deformation fluctuations, $\Delta x_{\alpha=1,2}^2$, are shown in Fig. 4(c). As expected, the fluctuations of the softer mode 1 are enhanced in comparison with the stiffer mode 2. This effect is even more pronounced for $\Omega=\Delta/100$ [inset of Fig. 4(d)].

In Fig. 5 we present as an example of more general interaction with $N_\alpha \neq 0$ the case of single electron-phonon mode coupling with $U=10\Delta$ and $\Omega=5\Delta$. As pointed out by Cornaglia *et al.*,[16] N_α terms together with M_α break the particle-hole symmetry, while the symmetry is conserved if only one of the terms is nonvanishing. In Fig. 5(a) the conductance for three typical cases is shown. The full line represents the $M=0$ and $N=5\Delta$ results where the resonance width is severely increased, because the N terms increase the effective t'. If both electron-phonon coupling terms are relevant, e.g., $M=3.5\Delta$ and $N=3\Delta$, the conductance exhibits asymmetry

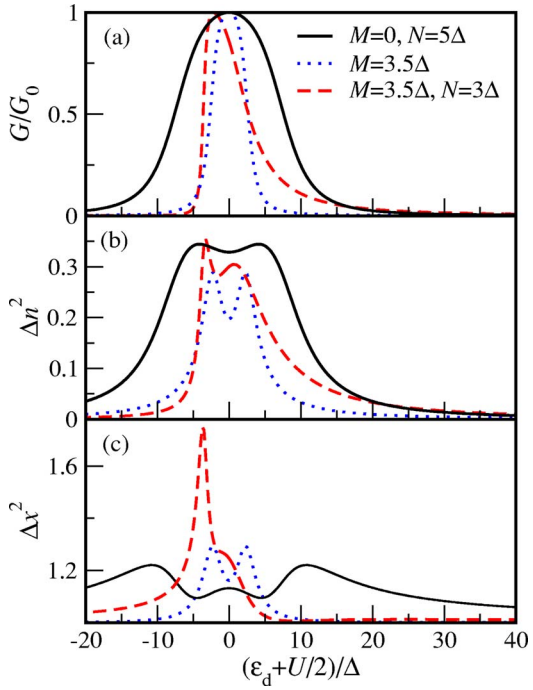

FIG. 5. (Color online) (a) Conductance, (b) occupation fluctuations, and (c) deformation fluctuations for various types of electron-phonon interaction ($U=10\Delta$, $\Omega=5\Delta$).

(dashed line), compared to the $N=0$ case (dotted line). In Fig. 5(b) the corresponding occupation fluctuations are presented. Displacement fluctuations Δx_α, Fig. 5(c), in this case are not related solely to occupation fluctuations, but also to fluctuations of the hopping operator $d_\sigma^\dagger c_{1\sigma}$ (not shown here).

We have presented results of the analysis of linear response conductance through a deformable molecule with electron-electron interaction and different orthogonal phonon modes. In general, the conductance does not exhibit sidebands and is related to the Anderson model with renormalized parameters for the single- or multiple-phonon interaction. Additionally, the emphasis of our analysis was on the deformation fluctuations of the molecule due to multiple phonon modes. Such current-induced displacement fluctuations could, e.g., increase the uncertainty of displacement sensing in NEMS. Phonons in slow phonon modes are permanently in a coherent state corresponding to the average occupation of the molecule and the deformation fluctuations are minimal in this limit (except close to the charge fluctuations maxima). In the opposite limit of a fast phonon mode, phonons form a coherent state corresponding to the occupation at a given moment in time. Therefore, deformation fluctuations are enhanced proportionally to charge fluctuations, the proportionality coefficient being $-(2M_\alpha/\Omega_\alpha)^2$. In general, the deformation fluctuations take a value between these two limits. It was also shown that charge fluctuations are approximately proportional to static charge susceptibility of the molecule. The method used here proved to be robust and appropriate for a wide range of generalizations due to specific electron-phonon interaction or the topology of the interaction region, for example, a molecule with several interconnected sites.

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[23] Strictly, $\langle n_d^2\rangle$ is given with the integral of imaginary part of dynamic charge susceptibility, $\chi_c''(\omega)$, therefore the relation to static χ_c is only qualitative (even at $U=0$). We should note that for large U limit we found reasonable agreement with $1/\mathcal{N}$-expansion result $\chi_c \sim (\pi/\mathcal{N}\Delta)n^2(1-n)$.
[24] $G=G_0 \sin^2(\pi/2)n$ for $t\to\infty$.