Many Body Effects on the Transport Properties of Single-Molecule Devices

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The conductance through a molecular device including electron-electron and electron-phonon interactions is calculated using the Numerical Renormalization Group method. At low temperatures and weak electron-phonon coupling the properties of the conductance can be explained in terms of the standard Kondo model with renormalized parameters. At large electron-phonon coupling a charge analog of the Kondo effect takes place that can be mapped into an anisotropic Kondo model. In this regime the molecule is strongly polarized by a gate voltage which leads to rectification in the current-voltage characteristics of the molecular junction.

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Electronic conduction through nanoscale systems connected to external electrodes exhibits a number of special features that are of great importance when one considers their potential as electronic devices.

The transport properties of such systems are strongly affected by (e-e) and electron-phonon (e-ph) interactions. For example, Coulomb blockade effects have been shown to dominate the transport in quantum dots [1] and even in single molecules weakly coupled to the electrodes [2]. The Kondo effect has been observed in quantum dots [3] and single molecules having well defined spin and charge states [2, 5, 6]. Furthermore the effects of e-ph coupling have been observed in Inelastic Electron Tunneling Spectra of small molecules adsorbed on surfaces [7] and in molecular-scale transistors made of C60 molecules [8]. Finally, e-ph coupling is also known to play an important role in the transport through organic conjugated molecules in which transport is mediated via polaron or soliton propagation [9].

It is usually assumed that energy scales for e-e interaction are much larger than those for e-ph interaction. However, it has been recently shown that Coulomb charging energies of single molecules can be considerably reduced by screening due to the electrodes [2]. These energies can be of the order of a few 100 meV (instead of a few eV for an isolated molecule) and therefore are of the same order of magnitude of the relaxation energies induced by e-ph coupling in the same systems. Interesting physics then arises when the energy scales of e-e and e-ph interactions merge. By studying such cases, insights on the origin of the features in the conductance can be brought and the influence of the e-ph coupling on the Kondo effect can be addressed.

Although there have been many theoretical investigations of electron transport in the presence of either e-e or e-ph interactions, the case in which both interactions are present has only been studied recently [10, 11, 12] either in the high temperature or weak e-ph coupling regimes.

In this Letter, we report results of non-perturbative calculations of the linear transport properties through a molecular device including e-e and e-ph interactions. The calculations are performed using the Numerical Renormalization Group (NRG) technique for a broad range of characteristic parameters.

We study a model of a molecule with a single relevant electronic level coupled linearly to a vibrational mode of frequency \(\omega_0\) and to the left (L) and right (R) metallic electrodes. The Hamiltonian of the system is

\[
H = H_M + H_E + H_{-E},
\]

where the first two terms describe the isolated molecule and electrodes, respectively, and the last term describes their coupling. We have

\[
H_M = \varepsilon_d n_d + Un_d^+ n_d - \lambda (n_d - 1) (a + a^\dagger)
\]

\[
+ \omega_0 a^\dagger a,
\]

\[
H_E = \sum_{k,\sigma,\alpha=L,R} \varepsilon_{\alpha}(k) c^\dagger_{k\sigma\alpha} c_{k\sigma\alpha},
\]

\[
H_{-E} = \sum_{k,\sigma,\alpha} V_{k\alpha} \left( d^\dagger_{\sigma} c_{k\sigma\alpha} + c^\dagger_{k\sigma\alpha} d_{\sigma} \right).
\]

Here, \(n_d = \sum_{\sigma} d^\dagger_{\sigma} d_{\sigma}\) is the charge of the molecule, \(\varepsilon_d\) is the position of the electronic molecular level relative to the Fermi level of the electrodes and \(U\) is the Coulomb repulsion between two electrons that occupy the same molecular level. \(a\) creates a phonon of frequency \(\omega_0\) and \(\lambda\) is the e-ph coupling constant. We consider for simplicity the case of identical electrodes and contacts. In the wide-band limit the conductance \(G\) of the molecular junction at zero bias is

\[
G = \frac{dI}{dV}\bigg|_{V=0} = \frac{2e^2}{h} \pi \Delta \int_{-\infty}^{\infty} d\omega \left( -\frac{\partial f(\omega)}{\partial \omega} \right) \rho_d(\omega),
\]

where \(\rho_d(\omega) = -\pi^{-1}\text{Im} G_{dd}(\omega),\) \(G_{dd}(\omega)\) is the exact electronic Green function of the molecule in the presence of the leads, \(f(\omega)\) the Fermi distribution and \(\Delta = 2\pi\rho_0|V_{\text{FS}}|^2\). Here, \(\rho_0\) is the electrodes’ electronic density of states at the Fermi level and the brackets denote an average over the Fermi surface. Hamiltonian [1] is electron-hole symmetric for all values of \(\lambda\) at \(\varepsilon_d = \varepsilon_d^* = -U/2\) where \(\langle n_d \rangle = 1\). This point we will referred to as the symmetric point in the following.
where $G_0 = 2e^2/h$ is the quantum of conductance and the second equality follows from Luttinger’s theorem [15]. At $T = 0$ the conductance $G$ thus takes its maximum value $G_0$ at the symmetric point. Before presenting the results of a full numerical solution of the problem we discuss two limiting cases that can be treated analytically providing us with a qualitative picture of the dependence of $G$ upon $T$ and $\varepsilon_d$.

The Hamiltonian $H_M$ of the isolated molecule can be readily diagonalized. The eigenfunctions are direct products of electronic states (denoted by a subscript $e$) and oscillator states. The eigenstates and eigenvalues are

$$
\begin{align*}
|0,m\rangle &= |\bar{U}^-|0\rangle_e|m\rangle, \quad E^0_{m} = -\frac{\lambda^2}{\omega_0} + m\omega_0, \\
|\sigma,m\rangle &= |\sigma\rangle_e|m\rangle, \quad E^\sigma_{m} = \varepsilon_d + m\omega_0, \\
|2,m\rangle &= \bar{U}^+|\uparrow\downarrow\rangle_e|m\rangle, \quad E^2_{m} = -\frac{\lambda^2}{\omega_0} + 2\varepsilon_d + U + m\omega_0,
\end{align*}
$$

where $\bar{U}^\pm = \exp[\pm\lambda/\omega_0 (a^\dagger - a)]$ and $|m\rangle$ is the $m$-th excited state of the harmonic oscillator. Two limiting cases can be considered.

**Weak electron-phonon coupling**, $2\lambda^2/\omega_0 \ll U$. In this case the ground-state of the isolated molecule is the spin-doublet $|\sigma,0\rangle$. There is a large charge excitation gap $U_{\text{eff}} = U - 2\lambda^2/\omega_0$ at the symmetric point and the low-energy excitations of the full system are spin fluctuations described by the usual Kondo Hamiltonian [15]. Using standard second-order perturbation theory the coupling constant can be expressed in terms of a single matrix element: $\langle \sigma,0|H_{M-E}|0,m\rangle \langle 0,m|H_{M-E}|\sigma,0\rangle = \langle \sigma,0|H_{M-E}|0,m\rangle \langle 0,m|H_{M-E}|\sigma,0\rangle \approx \langle 0|\bar{U}^+|m\rangle|^2$. At $\varepsilon_d = \varepsilon^*_d$ we find the Kondo coupling constant [16]

$$
J_K(\lambda) \rho_0 \approx \frac{8\Delta}{\pi U} \sum_{m=0}^{\infty} \frac{\langle 0|\bar{U}^+|m\rangle^2}{1 - 2\frac{\lambda^2}{\omega_0} + 2\frac{\lambda^2}{U} + \frac{2\lambda^2}{U^{\text{eff}}}},
$$

where $\langle 0|\bar{U}^+|m\rangle|^2 = e^{-\lambda}(\lambda/\omega_0)^2(\lambda/\omega_0)^2/2m!$.

Below the Kondo temperature $T_K \propto \exp[-1/(J_K\rho_0)]$, $G(\varepsilon^*_d) \sim G_0$. Expanding Eq. 5 around $\lambda = 0$ we find $J_K/J_K(0) \approx 1 + 2\frac{1}{U} (\lambda/\omega_0)^2 \frac{\lambda^2}{U^{\text{eff}}}$. The e-ph coupling thus leads to an increase of the Kondo temperature in this regime. For $T > T_K$, Coulomb blockade peaks separated by $U_{\text{eff}}$ are expected at gate voltages $\varepsilon_d \approx -\lambda^2/\omega_0$ and $\varepsilon_d \approx -U + \lambda^2/\omega_0$.

Expanding Eq. 5 around the symmetric point we have $G(\varepsilon_d) \sim G(\varepsilon^*_d) \sim -G_0 (\chi_e \pi/2)^2 (\varepsilon_d - \varepsilon^*_d)^2$, where $\chi_e$ is the charge susceptibility, inversely proportional to the charge gap. The width of the $T = 0$ conductance peak, $\Delta\varepsilon_d \approx \chi_e^{-1} \approx U_{\text{eff}}$, decreases with increasing $\lambda$ in the weak coupling regime.

**Strong electron-phonon coupling**, $2\lambda^2/\omega_0 \gg U$. In this regime the ground-state doublet of the isolated molecule is composed of the states $|2,0\rangle$ and $|0,0\rangle$, degenerate at the symmetric point. The low-energy excitations of the full system are now charge fluctuations and there is a large gap for spin fluctuations. The low-energy excitations are described by an effective Kondo model in which the role of the spin is played by a pseudo-spin variable that represents the two states of the lowest lying doublet. *A priori* there is no rotational invariance in pseudo-spin space and, in fact, in the effective Hamiltonian the two different matrix elements appear: $\langle 2,0|H_{M-E}|\sigma,m\rangle \langle \sigma,m|H_{M-E}|2,0\rangle \propto \langle 0|\bar{U}^+|m\rangle|^2$ and $\langle 2,0|H_{M-E}|\sigma,m\rangle \langle \sigma,m|H_{M-E}|0,0\rangle \propto \langle 0|\bar{U}^+|m\rangle|^2$. The effective model is thus the anisotropic Kondo model (AKM) with couplings $J_{\parallel}$ and $J_{\perp}$ given by

$$
J_{(\parallel,\perp)} \rho_0 \approx \frac{8\Delta}{\pi U} \sum_{m=0}^{\infty} \frac{\langle 0|\bar{U}^+|m\rangle^2}{\frac{2\lambda^2}{\omega_0} - 1 + 2\frac{\lambda^2}{U}}.
$$

Asymptotically, $J_{\parallel}/J_{\parallel} \approx \exp[-2(\lambda/\omega_0)^2]$ and $T_{\text{AKM}} \approx \exp[-\alpha(\lambda/\omega_0)^2]$ with $\alpha = \pi\omega_0/\Delta$. In this regime the Kondo temperature decreases sharply with increasing $\lambda$. In contrast to the weak e-ph coupling case, no Coulomb blockade peaks are expected for $T > T_{\text{AKM}}$. Another important difference from the weak $\lambda$ case is that, now, the charge susceptibility ($\propto T_{\text{AKM}}$) is very large. Then, the width of the conductance peak versus gate voltage $\Delta\varepsilon_d \approx T_{\text{AKM}}$ also decreases sharply as $\lambda$ increases. The region in the $T - \varepsilon_d$ plane where $G \approx G_0$ is thus strongly suppressed by a strong e-ph coupling.

We now turn to the discussion of our numerical results obtained using the NRG method [18, 19]. The original NRG method has been modified to include e-ph coupling [20] and to calculate the spectral density $\rho_0(\omega)$ according to Ref. [21]. We have performed calculations for a broad range of parameters. We set $k_B = 1$ and take the half-bandwidth of the electrodes as the unit of energy. In the following, we present results for the set of parameters $\Delta = 0.016$, $\omega_0 = 0.05$ and $U = 0.1$.

Figure 4 shows the linear conductance $G$ as a function of the gate voltage $\varepsilon_d$ for $T = 0$ and $T = \Delta$ and several values of the e-ph coupling $\lambda$. For $\lambda = 0$ [Fig.4a)] and $T = \Delta$ the Coulomb blockade peaks [22, 23] separated by the charging energy $U$ are clearly seen. With decreasing $T$ the conductance in the Coulomb blockade valley increases as the Kondo effect develops. At zero temperature $G$ has a single peak of width $\Delta\varepsilon_d \sim U$ centered at $\varepsilon^*_d$. The main effect of a weak coupling to the vibrational mode at finite $T$ [Fig.4b)] is a reduction of the distance between the Coulomb blockade peaks, now given by $U_{\text{eff}}$ as anticipated above. The width of the $T = 0$ peak is also of the order of $U_{\text{eff}}$. This large width is a consequence of
Parameters are $U$, $G$, and $FIG. 1$: Conductance $\lambda$ for different values of $-\Delta$. A single peak is observed in the conductance with $T = 0$, thin lines: $T = 0.016$. Parameters are $U = 0.1$, $\Delta = 0.016$ and $\omega_0 = 0.05$.

![FIG. 1](image)

FIG. 2: Zero-bias conductance $G$ versus temperature $T$ for different values of $\lambda$. (a) Symmetric point $\varepsilon_d = -U/2 = -0.05$. (b) Asymmetric case, $\delta\varepsilon_d = \varepsilon_d - \varepsilon_d^* = 0.01$. Other parameters as in Fig. 1.

The rigidity of the ground state of the molecule against charge fluctuations.

For strong $e$-$ph$ coupling [Fig. 1(d)] the features change qualitatively. A single peak is observed in the conductance at all temperatures and its width sharply decreases with $T$. The peak narrowing results from the dramatic increase of the charge susceptibility of the molecule in the strong coupling regime. Moving away from the symmetric point by application of a gate voltage produces an effect similar to that of applying a magnetic field in the standard Kondo effect: the degeneracy of the ground-state doublet is broken and the Kondo resonance in the spectral density is destroyed.

For $U_{\text{eff}} \lesssim \Delta$ [Fig. 1(c)] the system is in a mixed valence regime in which the four charge states of the molecule are nearly degenerate for $\varepsilon_d \sim \varepsilon_d^*$. A single peak is then observed in the conductance at all temperatures with a $T = 0$ width that is determined by the hybridization $\Delta$.

In all regimes discussed so far, the $T = 0$ conductance at $\varepsilon_d^*$ is perfect as required by Eq. (6).

Figure 2 shows the $T$-dependence of $G$ for several values of $\lambda$. At the symmetric point [Fig. 2(a)] $G \sim G_0$ below a temperature scale that depends on the coupling. This scale varies non-monotonically with $\lambda$, first increasing and then decreasing. For very small $\lambda$ the behavior in the asymmetric case [Fig. 2(b)] is similar to the previous one. For the larger couplings, however, $G \ll G_0$ at all temperatures.

![FIG. 3](image)

FIG. 3: Full width at half maximum $\Gamma$ of the central peak in the spectral density $\rho_d$ versus $\lambda$ at the symmetric point $\varepsilon_d = \varepsilon_d^*$. Solid lines are fits based on the given analytical expressions (see text). Inset: $\rho_d(\omega)$ for three values of $\lambda$. Other parameters as in Fig. 1.

The inset in Fig. 3 shows the spectral density $\rho_d(\omega)$ at the symmetric point for three values of the $e$-$ph$ coupling. The width of the central peak is renormalized by the interaction. It is also non-monotonic as a function of $\lambda$ as shown in the main plot where fits to the theoretical expressions discussed above are also shown. For weak coupling region we use $\Gamma = A \exp[-1/(J_K \rho_0)]$ with $J_K$ given by Eq. (8). For strong coupling we use $\Gamma = A' \Gamma_{\text{AKM}}$ with $\Gamma_{\text{AKM}}$ given by Eq. (10), instead. Only the amplitudes $A, A'$ are fitting parameters. It can be seen from Fig. 3 that the agreement with the predicted widths $\Gamma(\lambda)$ is excellent. For intermediate couplings the charge fluctuations are no longer blocked by the Coulomb interaction and the system is in the mixed valence regime where $\Gamma = \mathcal{O}(\Delta)$.

Figure 4 shows the spectral density for strong $e$-$ph$ coupling and several values of $\delta\varepsilon_d \leq 0$. At the symmetric point there are peaks at the energies of the isolated molecule given by Eq. (7). There is also a peak at the Fermi level associated with the charge Kondo effect. Its width is proportional to $\Gamma_{\text{AKM}}$ [Eq. (10)]. For $|\delta\varepsilon_d| \ll \Gamma_{\text{AKM}}$ there is little change in the spectral density. When the asymmetry increases, spectral weight is transferred from positive to negative energies $\omega$ and $\rho_d(0)$ is suppressed. For $|\delta\varepsilon_d| > \Gamma_{\text{AKM}}$, the central peak disappears and almost all the spectral weight is concentrated in the negative $\omega$ region. The behavior for positive $\delta\varepsilon_d$ is obtained through the transformation $\omega \to -\omega$. This spectral polarization is the result of the strong charge fluctuations.
FIG. 4: Spectral density $\rho_d$ for different values of the asymmetry $\delta\varepsilon_d = \varepsilon_d - \varepsilon_d^0$ in the strong $e$-$ph$ coupling regime ($\lambda = 1.2\omega_0$). Here $T_{AKM} \sim 0.0012$. Left inset: average charge $\langle n_d \rangle$ in the molecule as a function of the asymmetry. Right inset: current-voltage curves showing rectification in the asymmetric case. Other parameters as in Fig. 1.

polarization induced by the asymmetry. It is illustrated in the left inset to Figure 4 that shows the ground-state charge of the molecule $\langle n_d \rangle$ as a function of $\delta\varepsilon_d$. It can be seen that charge fluctuations in the molecule are rapidly suppressed for $|\delta\varepsilon_d| \gtrsim T_{AKM}$.

An interesting consequence of this spectral asymmetry is that the molecular device exhibits strong rectifying properties in the strong $e$-$ph$ coupling limit. The right inset to Fig. 4 shows the current-voltage $(I-V)$ characteristics for the device in this regime. At the symmetric point, the $I-V$ curve is symmetric around zero bias $V$ and it exhibits some structures associated to the peaks in the spectral density. In the asymmetric case (with $\delta\varepsilon_d < 0$), the molecule is polarized and the $I-V$ curve is asymmetric: the current for negative bias is much larger than for positive $V$ (the opposite occurs for $\delta\varepsilon_d > 0$).

In summary, we have studied the transport properties of a molecular device including $e$-$e$ and $e$-$ph$ interactions. We have shown that at low temperatures and weak $e$-$ph$ coupling, the conductance properties of the molecular junction are described by the standard Kondo model with renormalized parameters. At large $e$-$ph$ coupling, new physics appears: the properties of the device are described in terms of a charge analog of the Kondo effect. In this regime the transport properties of the molecular junction are controlled by the large charge polarizability of the molecule. The latter induces a strong spectral polarization that leads to a rectifying behaviour of the current-voltage characteristics of the molecular junction.

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[26] Here we simply assume that $\rho_d(\varepsilon, V) \sim \rho_d(\varepsilon, V = 0)$, assumption valid for small $V$ and calculate the current using $I \propto \int d\varepsilon \left( f(\varepsilon + eV) - f(\varepsilon) \right) \rho_d(\varepsilon)$. 