Influence of Correlated Hybridization on the Conductance of Molecular Transistors

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We study the spin-1/2 single-channel Anderson impurity model with correlated (occupancy dependent) hybridization for molecular transistors using the numerical renormalization-group method. Correlated hybridization can induce nonuniversal deviations in the normalized zero-bias conductance and, for some parameters, modestly enhance the spin polarization of currents in applied magnetic field. Correlated hybridization can also explain a gate-voltage dependence to the Kondo scale similar to what has been observed in recent experiments.

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With the technological advances allowing for the construction of single-molecule transistors based upon transition-metal complexes \cite{1,2,3}, there is considerable interest in the out of equilibrium properties of the Anderson model. This model is used to describe the coupling of electrons in localized and strongly interacting states of an atom or molecule with electrons in weakly interacting extended states of the leads or host metal (see the schematic of Fig. 1). Most interest has focused on the resonant transport regime of the model associated with the local moment or Kondo limit of the Anderson model. In this case, correlated (occupancy dependent) hybridization has been invoked as a potential explanation for anomalies in the conductance \cite{4}, the unusual gate-voltage dependence of the measured Kondo temperature scale \cite{5} not described by the simplest version of the Anderson model, and to suggest a possible conductance enhancement via local pairing effects \cite{6}. In parallel, it has been demonstrated for transition metal-complexes that the correlated hybridization can be very large, comparable to the single-particle hybridization through the interatomic potential \cite{6}.

In this paper, we study the nonequilibrium spin-1/2 single-channel Anderson impurity model with correlated hybridization with the numerical renormalization-group (NRG) approach \cite{7,8,9}. We compute the universal zero-bias conductance vs. temperature curve of the Kondo regime, and show that deviations from universality can be induced by correlated hybridization even when the magnetic susceptibility appears universal. We find, as predicted earlier \cite{6}, that the spin polarization of the currents can be modestly enhanced by correlated hybridization in some parameter regimes, though not clearly enough to be useful in spintronics applications. We also find that the particle-hole symmetry breaking associated with correlated hybridization can induce a dependence of the Kondo scale upon gate voltage similar to what is observed in experiment \cite{1,3,3}.

To describe the couplings of electrons in the single-molecule transistor, we assume the leads are identical and consider the Hamiltonian for the spin-1/2 Anderson impurity model with correlated hybridization, as shown schematically in Fig. 1,

\begin{equation}
H = \sum_{k,\sigma} \epsilon_{k,\sigma} c_{k,\sigma}^\dagger c_{k,\sigma} + \sum_\sigma \epsilon_d d_{\sigma}^\dagger d_\sigma + Un_d n_{d\sigma} \tag{1}
\end{equation}

\begin{align}
&+ t_1 \sum_\sigma \left( 1 - n_{d,\sigma} \right) \left( d_{\sigma}^\dagger c_{\sigma 0} + c_{\sigma 0}^\dagger d_\sigma \right) \\
&+ t_2 \sum_\sigma n_{d,\sigma} \left( d_{\sigma}^\dagger c_{\sigma 0} + c_{\sigma 0}^\dagger d_\sigma \right),
\end{align}

where a conduction electron with momentum $k$ and spin $\sigma$ corresponding to an energy eigenvalue $\epsilon_k$ is created by $c_{k,\sigma}^\dagger$, and $d_{\sigma}^\dagger$ creates a conduction electron with spin $\sigma$ at the impurity site

\begin{equation}
c_{\sigma 0}^\dagger = \frac{1}{\sqrt{N}} \sum_k c_{k,\sigma}^\dagger. \tag{2}
\end{equation}

The operator $d_\sigma^\dagger$ creates an electron with spin $\sigma$ and energy $\epsilon_d$ at the d level of the impurity, while $U$ is the Coulomb interaction, and $n_{d,\sigma} = d_{\sigma}^\dagger d_\sigma$ is the occupancy of d orbital with spin $\sigma$.

\begin{figure}[ht]
\centering
\includegraphics[width=0.4\textwidth]{fig1.png}
\caption{Schematic for the spin-1/2 Anderson model with correlated (occupancy dependent) hybridization. Here $t_1$ describes transfer of an electron into an empty impurity orbital from the leads, and $t_2$ describes transfer of an electron into a singly occupied impurity orbital from the leads.}
\end{figure}
To solve the Hamiltonian, the numerical renormalization group method provides an excellent approach by mapping the Hamiltonian onto a tight-binding Hamiltonian in the Anderson model with correlated hybridization. We diagonalize the chain Hamiltonian iteratively while keeping the lowest 1500 states in each iteration. The band-structure analysis of the Anderson model with correlated hybridization may, however, change the steepness of the drop of \( T/\chi \) if the system goes from the free-orbital regime directly to the frozen-impurity regime, such as the cases of \( t_1 = t_2 = 1, \epsilon_d = -1 \)

and \( t_1 = 0.7, t_2 = 3, \epsilon_d = -3 \), where there is no Kondo universality.

The conductance for the single-molecule transistor with symmetric leads at zero bias can be expressed as

\[
G = \frac{e^2}{h} \rho_{F} \sum_{\sigma} \int d\omega \left( -\frac{\partial f(\omega)}{\partial \omega} \right) \rho_{\sigma}(\omega),
\]

where \( \rho_{F} \) is the Fermi-level density of states, \( f(\omega) \) is the Fermi distribution function, and \( \rho_{\sigma}(\omega) \) is the transmission density spectral function. We carry out the calculation of transmission density \( \rho_{\sigma}(\omega) \) in Lehmann representation,

\[
\rho_{\sigma}(\omega) = \frac{1}{\pi} \text{Im} \left[ \langle \langle A_{\sigma} | A_{\sigma}^\dagger \rangle \rangle (\omega - i\delta) \right]
\]

\[
= \frac{1}{Z} \sum_{n,m} (e^{-\beta E_n} + e^{-\beta E_m}) |\langle n | A_{\sigma} | m \rangle|^2 \delta(\omega + E_n - E_m),
\]

where the operator \( A_{\sigma} \) of the Green’s function \( \langle \langle A_{\sigma} | A_{\sigma}^\dagger \rangle \rangle (\omega - i\delta) \) is given by \( A_{\sigma} = t_1 |0 \rangle \langle \sigma - t_2 |\sigma \rangle |2 \rangle \) with \( |0 \rangle, |\sigma \rangle, |2 \rangle \) being the empty, singly, and doubly occupied impurity states, respectively. \( Z \) is the partition function, and \( |n \rangle, |m \rangle \) are the eigenstates of the Hamiltonian in Eq. 1. Therefore, the conductance can be obtained by

\[
G = \frac{e^2}{h} \frac{\beta}{Z} \rho_{F} \sum_{\sigma,n,m} |\langle n | A_{\sigma} | m \rangle|^2 \frac{e^{-\beta (E_n + E_m)}}{e^{-\beta E_m} + e^{-\beta E_n}}.
\]
of the NRG calculation. The influence of correlated hybridization on the conductance is investigated by studying the $\epsilon_d$ dependence of the conductance. In the molecular transistor, $\epsilon_d$ can be tuned with gate voltage. As a consequence of correlated hybridization, the symmetry of the $0 \leftrightarrow 1$ and $1 \leftrightarrow 2$ valence fluctuations in the conductance is broken, with the resonance widths proportional to $t^2$ accompanied by the shifts of the resonance positions. As the temperature decreases from high temperature to the Kondo temperature, we find the enhancement of the conductance, the broadening of the conductance peaks, and the shifts in their positions towards each other, which are characteristics of the Kondo effect. In the limit of $T \to 0$, the conductance per spin calculated by the NRG method is found to satisfy the unitary limit, $G_\sigma = 2e^2 \sin^2 \delta_\sigma$, and the peak of total conductance is always found $G_{\text{max}} = 2e^2/h$ to within $\Lambda$-dependent systematic corrections for different magnitudes of correlated hybridization. In the other words, the phase shift analysis using Friedel sum rule $[4]$ holds with correlated hybridization; the Fermi energy phase shift for an electron of spin $\sigma$ scattering off the impurity site can be obtained by $\delta_\sigma = \pi \langle n_{d,\sigma} \rangle$.

It has been believed that the conductance normalized to its zero-temperature value is universal in the Kondo regime $[5, 6]$ as well. Figure 3 shows $G/G_0$, where $G_0$ is the zero-temperature conductance, as a function of $T/T_K$. We find that for parameters within the range of Kondo regime, such as $t_1 = 0.3$, $t_2 = 1$, $-5 < \epsilon_d < -1$, the curves fall on top of those without correlated hybridization, showing the Kondo universality. However, we notice that in the case of $t_1 = 0.7$ and $t_2 = 3$, which has a magnitude of $|\sigma \to |2\rangle$ transition comparable to $U$, the conductance curves are obviously off the universality, while there is only slight variation in the $T \times \epsilon$ curves, as shown in Fig. 2. We also note that a perturbative treatment of correlated hybridization in Anderson Hamiltonian $[3]$ was used to explain the anomalous conductance plateau around $0.7(2e^2/h)$ observed in experiments on quantum point contacts. We do not see the 0.7 anomaly in the conductance calculated by this nonperturbative approach. In addition, there is no indication of the enhancement of the conductance in our calculation induced by local pairing $[3]$ associated with correlated hybridization.

Correlated hybridization has been proposed using mean-field treatment as a potential means to spin polarization of currents through transition-metal based molecular transistors in modest magnetic fields $[3]$. However, the effect on spin polarization in the low-temperature limit is still not clear. Here, we study the ratio of spin conductance at small magnetic field to total conductance at zero field in the zero-temperature limit, $\frac{(G_\sigma - G_\uparrow)}{G_{(H=0)}}$, as a function of single-particle energy. The magnetic field is set to $H = 0.1k_B T_K/(g\mu_B)$ for each set of parameters, as shown in Fig. 4. Without correlated hybridization, i.e. $t_1 = t_2 = 1$, the ratio is zero at $\epsilon_d = -5$, where there is particle-hole symmetry, and the zero-field phase shift $\delta_0 = \pi/2$. The ratio $\frac{(G_\uparrow - G_\downarrow)}{G_{(H=0)}}$ increases to about 0.06 and saturates in the empty and doubly occupied regime. When $t_1$ is reduced, the position of $\delta_0 = \pi/2$ is shifted towards $\epsilon_d = 0$ because the larger hybridization between singly and doubly occupied impurity states renormalizes their energy levels down relative to the level of empty impurity state. The spin polarization of currents can be enhanced depending upon the value of $\epsilon_d$. When $t_1 = 0.7$ and $t_2 = 3$, there is noticeable enhancement in the spin polarization in the regime between $\epsilon_d = -3$ and $\epsilon_d = -8$. Interestingly, the saturated value of the ratio of spin conductance to zero-field total conductance remains the same for different magnitudes of hybridization, and it seems to have universality.

One of the most interesting results with correlated hybridization is how it affects the $\epsilon_d$ dependence of the Kondo scale. Generally without correlated hybridization, as shown in Fig. 5(a), the Kondo temperature decreases when $\epsilon_d$ moves away from the charge degeneracy points, $\epsilon_d = 0$ and $\epsilon_d = -10$, towards the particle-hole symmetry point, $\epsilon_d = -5$. In the limit of $\Gamma \ll U$, the Kondo temperature has been well described by scaling theory $[13]$, $T_K \simeq 1/2\sqrt{U}\exp[\pi\epsilon_d/(\Gamma U)],$ in the Kondo regime. In the presence of correlated hybridization, the position of the minimum of Kondo temperature shifts away from $\epsilon_d = -5$. The shift is especially significant in the case of $t_1 = 0.7$ and $t_2 = 3$, where there is less $\epsilon_d$ dependence of Kondo temperature. The particle-hole symmetry breaking associated with correlated hybridization may explain the anom
FIG. 5: (color online) (a) Kondo temperature as a function of single-particle energy. (b) $T_K$ (normalized) as a function of $\epsilon_d$ normalized by the average hybridization $\Gamma$. The legend is the same as that in (a).

Previous results in a recent Letter [3] that the Kondo temperature is less dependent on gate voltage and even increases when moving away from the supposed charge degeneracy point, $\epsilon_d = 0$, in single-molecule transistors based upon transition-metal complexes. In fact, the true charge degeneracy point is shifted away due to the renormalization of the energy levels of the impurity states in the presence of correlated hybridization. Figure 5(b) shows $T_K/T_K(\epsilon_d/\Gamma=-1)$ as a function of $\epsilon_d/\Gamma$, where $\Gamma = \pi \rho [t_1(1-\langle n_{d,\sigma}\rangle) + t_2\langle n_{d,\sigma}\rangle]^2$ is the average hybridization which has occupancy dependency. How the Kondo scale changes with $\epsilon_d/\Gamma$ depends upon the magnitude of correlated hybridization. We see that in the mixed-valence regime ($-1 < \epsilon_d/\Gamma < 0$) the Kondo temperature decreases by about six folds in the case of $t_1 = 0.3$, $t_2 = 1$ when $\epsilon_d/\Gamma$ moves away from 0. The decrease of $T_K$ becomes less dramatic when $\epsilon_d/\Gamma$ goes into the Kondo regime ($\epsilon_d/\Gamma \ll -1$), and the dependence becomes much weaker when $\epsilon_d/\Gamma < -2$. The curve seems to capture the feature of the weak gate-voltage dependence of the Kondo temperature in the single-molecule transistor found by Liang et al. [1] We note that the orbital degeneracy which plays a role in Ref. [1] is absent in our model, so our calculation of Kondo temperature would have more dependency on $\epsilon_d/\Gamma$.

The present study shows that the correlated hybridization using spin-1/2 single-channel Anderson model can induce deviations in the normalized zero-bias conductance from universality, and it can modestly enhance the spin polarization of currents in small magnetic field. The particle-hole symmetry breaking associated with correlated hybridization provides an explanation for the weak gate-voltage dependence of the Kondo scale similar to what has been observed in transistion-metal based molecular transistors. Further investigations of correlated hybridization in the degenerate Anderson model are expected to provide detailed insight into electron transport through a more realistic single-molecule transistor with orbital degeneracy.

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