Perturbative theory of the non-equilibrium singlet-triplet transition

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Abstract. We study equilibrium and non-equilibrium properties of a two-level quantum dot close to the singlet-triplet transition. We treat the on-site Coulomb interaction and Hund’s rule coupling perturbatively within the Keldysh formalism. We compute the spectral functions and the differential conductance of the dot. For moderate interactions our perturbative approach captures the Kondo effect and many of the experimentally observed properties.

1. Introduction
Handling strongly interacting multilevel systems under non-equilibrium conditions is of crucial importance for understanding transport properties of molecules and correlated mesoscopic structures. Although the theoretical description of these systems is rather satisfactory in equilibrium [1, 2, 3, 4, 5, 6], the success of non-equilibrium methods is rather limited [7]: In fact, most of the available methods are unable to capture the Kondo physics or are rather uncontrolled. Perturbation theory in this regard is of particular importance: Although it breaks down for strong interactions, for moderate interaction strengths it is able to capture the formation of the Kondo resonance and the Hubbard peaks [8], scales very well with the number of orbitals, and it is therefore a promising candidate to combine with ab initio calculations.

Motivated by experiments on lateral quantum dots [9] and carbon nanotubes [10], here we focus on a particular parameter range of multilevel quantum dots, and study the so-called singlet-triplet transition, i.e., the transition from a singlet state of the dot to a Kondo-screened triplet state, driven by the presence of Hund’s rule coupling. We show that the so-called interpolative perturbation theory (IPT) [2, 11, 12, 13] can be extended to include Hund’s rule coupling, and it captures such basic features of this transition as the splitting of the Kondo resonance [9]. A detailed analysis of the transition shall be published elsewhere [14].

2. Model and theoretical framework
We use the following two level Hamiltonian to investigate the transition, $H = H_0 + H_{\text{int}}$,

\begin{equation}
H_0 = \sum_{\xi,\alpha,\sigma} \xi c_{\xi \alpha \sigma}^\dagger c_{\xi \alpha \sigma} + \sum_{i,\sigma} \varepsilon_i d_i^\dagger d_i + \sum_{\alpha, i, \sigma} t_{\alpha i} (c_{\xi \alpha \sigma}^\dagger d_i + h.c.),
\end{equation}

\begin{equation}
H_{\text{int}} = U/2 \sum_{i \neq j} n_{i \sigma} n_{j \sigma'} - J S^2.
\end{equation}
Here $c_{i\alpha}^{\dagger}$ creates a conduction electron in the left or right lead with energy $\xi_{\alpha} = \xi + \mu_{\alpha}$ ($\mu_{\alpha} = eV_{\alpha}$ is the bias applied on lead $\alpha \in (L, R)$) and $d_{i\alpha}$ is the creation operator of an electron of spin $\sigma$ and energy $\varepsilon_{\pm}$ on the dot level $i \in (+, -)$. The $t_{ai}$ denote the tunneling matrix elements between lead $\alpha$ and dot level $i$. Throughout this paper we focus on a completely symmetrical lateral quantum dot, and assume that one of the dot levels is even (+), while the other is odd (-). As a consequence, the tunneling matrix elements have a simple structure: $t_{L,+} = t_{R,+} = v_{+}/\sqrt{2}$ and $t_{L,-} = -t_{R,-} = v_{-}/\sqrt{2}$ [4, 5]. The width of the dot-levels is given by $\Gamma_{\pm} = 2\pi\rho_{0}|v_{\pm}|^{2}$, with $\rho_{0}$ the density of states of the electrons in the leads. The coupling $U$ denotes the on-site Coulomb interaction, and accounts for the charging energy of the dot, while $J$ stands for the Hund’s rule coupling which favors a ferromagnetic alignment of the total spin of the dot, $\mathbf{S} = \frac{1}{2}\sum_{i\sigma}\sum_{i\sigma}d_{i\sigma}^{\dagger}d_{i\sigma}$.

The simple Hamiltonian (1) describes a variety of physical phenomena, and captures, e. g. the underscreened [15] and the SU(4) Kondo states [10, 16, 17, 18]. Here, however, we shall focus only to the regime with $<n_{+} + n_{-}> \approx 2$, and the vicinity of the singlet-triplet transition induced by the competition of the Hund’s rule coupling and the separation of the two levels, $\Delta \equiv \varepsilon_{+} - \varepsilon_{-}$.

We shall treat (1) by applying perturbation theory in $U$ and $J$. However, before doing so, we separate the Hartree contribution by introducing counterterms, $H_{0} = H_{0} + H_{\text{count}}$,

$$H_{0} = \sum_{\xi,\alpha,\sigma} \xi_{\alpha}c_{i\alpha\sigma}^{\dagger}c_{k\alpha\sigma} + \sum_{i,\sigma}\varepsilon_{\sigma}d_{i\sigma}^{\dagger}d_{i\sigma} + \sum_{a, i, \xi, \sigma} t_{ai}(c_{i\alpha\sigma}^{\dagger}d_{i\sigma} + \text{h.c.}) ,$$

We then use $H_{0}$ to obtain the unperturbed Keldysh Green’s functions, $G_{ii'}^{\sigma\sigma'}$, with $i$ and $i'$ dot-level labels and $\kappa$ and $\kappa' = \pm$ the usual Keldysh labels, and treat $H_{\text{count}} = \sum_{i,\sigma}(\varepsilon_{i} - \varepsilon_{\sigma})d_{i\sigma}^{\dagger}d_{i\sigma}$ as a perturbation.

We then need to do second order perturbation theory in $H_{\text{int}}$. To treat both the Coulomb interaction and the Hund’s rule coupling on equal footing, we merge them into a single interaction vertex, $\Gamma^{j\sigma' m\sigma}_{i\sigma n\sigma'}$, as diagramatically shown in Fig. 1. Then the second order self-energy can be expressed in time domain as follows,

$$\Sigma^{(2)}_{ii'\sigma\sigma'}(t) = \sum_{j, j', m, m', n, n', \sigma, \sigma'} \Gamma^{j\sigma' m\sigma}_{i\sigma n\sigma' j'\sigma' m\sigma'} g_{ij'}^{\sigma\sigma'}(t) g_{nn'}^{\sigma'\sigma}(t) g_{nn'}^{\kappa\kappa'}(-t) .$$

Up to second order, the frequency dependent Green’s functions can be obtained from the following Dyson’s equation

$$\left[G_{ii'\sigma}^{\kappa\kappa'}(\omega)\right]^{-1} = \left[g_{ii'\sigma}^{\kappa\kappa'}(\omega)\right]^{-1} - \Sigma^{(1)}_{ii'\sigma}(\omega) - \Sigma^{(2)}_{ii'\sigma}(\omega) ,$$

where $\Sigma^{(1)}_{ii'\sigma}(\omega)$ contains the self-energy part coming from the counterterm and the first order Hartree contribution, also shown in Fig. 1.
Eqs. (3) and (4) give a complete perturbative description of the quantum dot, however, they depend parametrically on the so far unspecified levels, $\tilde{\varepsilon}_{i\sigma}$. These are determined selfconsistently from Eqs. (3) and (4) by requiring that $g$ and $G$ give the same occupation numbers [2]

$$n_{i\sigma}^{(0)}[\tilde{\varepsilon}_{i\sigma}] = \frac{1}{2\pi i} \int_{-\infty}^{\infty} g_{ii\sigma}(\omega) d\omega \equiv \frac{1}{2\pi i} \int_{-\infty}^{\infty} G_{ii\sigma}^{12}(\omega) d\omega = n_{i\sigma}^{(2)}[\tilde{\varepsilon}_{i\sigma}] . \quad (5)$$

**Equilibrium results:** For simplicity, here we focus on the electron-hole symmetric case, where $\varepsilon_{\pm} = -1.5U \pm \Delta/2$. First we consider the equilibrium spectral functions of the two levels:

$$\rho_{i\sigma}(\omega) = -\frac{1}{\pi} \Im G_{ii\sigma}^{R}(\omega) = -\frac{1}{2\pi i} \left( G_{ii\sigma}^{>}(\omega) - G_{ii\sigma}^{<}(\omega) \right) , \quad (6)$$

the sum of which, $\rho_T(\omega) \equiv \sum_{i,\sigma} \rho_{i\sigma}(\omega)$, is plotted in Fig. 2. Consider first the case $J = 0$ (Fig. 2a). In the absence of hybridization, the ground state is highly degenerate for $\Delta = 0$, and turning on a finite hybridization leads to the appearance of a Rondo resonance. Changing the value of the level splitting ($\Delta/U$) the two electrons are forced to stay on the lower level, $\varepsilon_{-}$, and a dip opens in the spectral function, corresponding to a singlet ground state.

In Fig. 2b we analyze the effect of Hund’s rule coupling, $J$. For $J \gtrsim \Delta$ a triplet ground state is favored, and a Kondo effect develops, where the spin $S = 1$ of the dot is screened by the even and odd combinations of the conduction states. A clear signal of the singlet-triplet transition is that the zero bias dip of the spectral function closes and a Kondo peak develops on the triplet side. These features are surprisingly well captured by the simple perturbative calculation presented here.

**Out of equilibrium results:** Equations (3), (4) and (5) also provide a closed set of equations for the local Green’s function in non-equilibrium. Solving them we can then compute transport properties of the dot using the Meir–Wingreen formula [19]. In our calculations the effective energies were fixed in equilibrium for a given parameter set, and we used these equilibrium values for all bias voltages.

In Fig. 3 the current is plotted as a function of bias, $\delta \mu = \mu_L - \mu_R = eV$, for two different parameter sets. In case of $J/U = 0$ and $\Delta/U = 0$ the current is suppressed and the linear conductance vanishes. This is due to the destructive interference between the even and odd channels, which both acquire a phase shift $\delta_{\pm} = \pi/2$ in this Kondo regime. The other current plot (red crosses) corresponds to a dot with singlet ground state. The differential conductance displays a dip at zero bias (see inset of Fig. 3), which is a clear fingerprint of the non-equilibrium singlet-triplet transition.

**Figure 2.** Total spectral function, $\rho_T(\omega) \equiv \sum_{i,\sigma} \rho_{i\sigma}(\omega)$. Evolution of (a) spectral functions as a function of level splitting, $\Delta$, (b) spectral functions as a function of Hund’s rule coupling, $J$. 

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Figure 3. Current versus dimensionless bias, $\delta \mu / U = eV/U$, for a singlet ground state ($J/U = 0$, $\Delta/U = 1.2$) and for the highly degenerate ground state ($J/U = 0$, $\Delta/U = 0$). Inset: differential conductance for $J/U = 0$, $\Delta/U = 1.2$. In all cases $\Gamma_+ = \Gamma_- = \Gamma = 0.564\, U$.

3. Conclusions
In summary, we find that self-consistent second order perturbation theory captures qualitatively the transport properties of a two-level quantum dot throughout the singlet-triplet transition, and the splitting of the Kondo resonance.

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