Kondo and mixed valence regimes in multi-level quantum dots

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We investigate the dependence of the ground state of a multi-level quantum dot on the coupling to an external fermionic system and on the interactions in the dot. As the coupling to the external system increases, the rearrangement of the effective energy levels in the dot signals the transition from the Kondo regime to a mixed valence (MV) regime. The MV regime in a two level dot is characterized by an intrinsic mixing of the levels in the dot, resulting in non-perturbative sub- and super-tunneling phenomena that strongly influence the Kondo effect.

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The Kondo effect arises from the coherent screening between a localized spin and the spin of surrounding mobile electrons, producing for example anomalous transport properties in metals with magnetic impurities.1 Recently, however, there has been a great deal of experimental activity in systems where an individual localized spin is probed directly, either in small metallic clusters,2 in isolated magnetic atoms on metallic surfaces,3 and in quantum dots defined in semiconductor systems.4–9 This activity has been generated in great part by interesting and specific theoretical predictions.10–13

A great deal of information has been obtained about the Kondo effect in both the linear and non-linear transport regimes thanks to experiments in and theory for quantum dots. Several conditions have been analyzed, including large dots (with a quasi-continuous energy spectrum),4,5,14 one-level dots (well described by the Anderson impurity model),10–13,15,16 and the two- and multi-level quantum dots with discrete energy spectrum.17–19 The ability to change the structural parameters of the semiconductor quantum dot makes these systems particularly attractive for the experimental investigation of the Kondo effect. This flexibility invites the exploration of the transition from the Kondo to the non-Kondo ground state of the dot as either the shape, coupling to the external system or the gate voltage applied to the dot are changed. For instance, experiments show different sequences of Kondo and non-Kondo ground states in quantum dots, as the gate voltage (hence the number of electrons in the dot) is varied.4–9 To address these Kondo–non-Kondo transitions, we consider a model of a multilevel quantum dot with discrete energy spectrum. Our results are quite interesting, as they describe a rich behavior for different parameter values of experimental accessibility. Previous investigations on both single- and multi-level models have uncovered interesting features of the Kondo effect, including Kondo peaks in the conductance and the associated density of states, their temperature dependence, and other features.5,8,17–21 However, the typical approximation made in models of multilevel quantum dots with discrete energy levels is to neglect the strong mixing between the energy levels of the dot due to the interaction with the external fermionic system. This approximation incorporates the external fermionic system only as a broadening of the individual levels in the quantum dot.22

In this paper we show that the mixing among energy levels of the dot due to the coupling to the external system leads to a qualitative rearrangement of the levels at large coupling (in a regime we call ‘mixed valence’ (MV)). This is characterized by the appearance of effective dot levels exhibiting sub- and super-tunneling to the leads.23 In the linear regime, we explore the alternation between spinless and spinful ground states, as function of the interaction constants in the dot and the coupling to the external fermionic system, as the gate voltage (dot occupation) changes. Depending on the various dot parameters, we find two regimes for weak coupling to the leads: the “Hund’s rule” regime, where the dot tends to have maximal absolute value of spin, and successive addition of electrons does not cancel the Kondo effect;24,25 and the even-odd Kondo–non-Kondo regime, where the absolute spin of the dot is minimized, i.e., it is nonzero only if the number of electrons in the dot is odd.4 For strong coupling with the leads, the appearance of sub- and super-tunneling quasi-levels results in changes of the occupation sequence of the dot in the MV regime, in sharp contrast with the single-level quantum dot. This behavior may yield the observed different sequences of Kondo and non-Kondo ground states seen sometimes in experiments.7–9

In what follows we consider explicitly a two-level quantum dot in the linear regime at zero temperature, both for simplicity and ease of presentation. However, most of our description and conclusions are valid for higher level-multiplicity. Details will be shown elsewhere.26 The Hamiltonian of the model can be written as

$$H = \sum_{l,\sigma} (E_l \hat{c}_{l,\sigma}^\dagger \hat{c}_{l,\sigma} + U_1 \sum_{l \neq l'} \hat{n}_l \hat{n}_{l'} - U_2 (\hat{S}_l)^2) + J \hat{S}_1 \cdot \hat{S}_2$$
Here, the fermionic operators $c^+_{l\sigma}, \sigma$, describe the state (orbital) in the dot with index $l = 1, 2$, and spin index $\sigma$. $n_{l\sigma} = c^+_{l\sigma}c_{l\sigma}$ is the particle number operator of the state $(l, \sigma)$ and $\hat{n}_l = \sum_{\sigma} n_{l\sigma}$. $\hat{S}_l = \sum_{\alpha \beta} \sigma_{\alpha\beta} c^+_{l\alpha} c_{l\beta}$ is the spin operator for level $l$. The operators $\hat{a}^+_{r\sigma}, \hat{a}_{r\sigma}$ refer to the fermions in the external electron system (the leads). There is a tunnel coupling $\gamma$ between the dot and the external system at point $r = 0$, and $H_F$ is the Hamiltonian of the external fermionic system. This one-lead geometry is schematically depicted in the inset of Fig. 1.

The basic interactions in the quantum dot are the Hubbard-like repulsion between the electrons on a given level of the dot, represented here by the constant $U_2$, and the density-density repulsion between the charges on different energy levels via the interaction constant $U_1$. We also include an exchange interaction between the spins of the two levels via the interaction constant $J$. Typically, the range of $J$ is $0 \leq |J| \leq U_1$. In what follows we consider the antiferromagnetic exchange ($J > 0$), the role of the ferromagnetic exchange being less interesting. The various constants of these interactions depend mostly on the overlap integrals between the wave functions of the different energy levels. Therefore, they can be changed by changing the shape of the quantum dot, which is experimentally accessible.\(^4\)

To deal with the external fermionic system, we note that due to the $\delta(r)$-like interaction with the dot, one can consider only the $s$-wave scattering of the external electrons on the dot, and hence use a one-dimensional description of the external system.\(^27\) We use a discretized representation of the external electron system, so that the resulting problem reduces to the coupling of the quantum dot states to a 1D fermionic chain $H_F = \sum_{l=1}^{L} \left( \hat{a}^+_{l\uparrow} \hat{a}_{l+1\uparrow} + \hat{a}^+_{l\downarrow} \hat{a}_{l+1\downarrow} \right)$ (similar to the linear chain form for the $s$-$d$ model in Ref. [1]).

Integrating the fermionic degrees of freedom consecutively, starting from the site directly coupled to the quantum dot, we find that the influence of the external fermionic system on the quantum dot renormalizes the coupling constants in the system, and most importantly, gives rise to an additional term of the form $\kappa \sum_{l, l'} \tilde{c}^+_{l\sigma} \tilde{c}_{l'\sigma}$ in the effective Hamiltonian, where $\omega_n$ denotes the Matsubara frequency. Consecutive elimination of external degrees of freedom yields recurrent relations for the running interaction constants; we find

$$\omega_{j+1} = \omega_n + \tilde{\omega}_j t^2 / D_{nj}$$
$$\tilde{\gamma}_{j+1} = -\tilde{\gamma}_j t^2 / D_{nj}$$
$$\tilde{\kappa}_{j+1} = \tilde{\kappa}_j + i \omega_n \tilde{\gamma}_{j+1} / D_{nj},$$

where $D_{nj} = \omega_n \omega_j + t^2$, and $j$ is the integration step index.

These relations can be directly iterated. As we are interested in the interaction of the dot with infinite leads, we look for fixed points of the recurrent relations. This yields an effective dot coupling for small Matsubara frequencies given by $\kappa \approx (\gamma^2/2\pi)\tan(\omega_n)$, where the hopping in the fermionic chain $t$ is of the order of the bandwidth of the external fermionic system.\(^1,27\) While being approximately constant at small frequencies, the mixing $\kappa$ decays at large frequencies. This property insures the transition from the mixed valence regime for shallow energy levels, to the Kondo regime for deep levels.

The state of the quantum dot is characterized by the occupation of different energy levels. To determine the ground state of the dot, we treat the many particle interactions by means of the Hubbard – Stratonovich decoupling of the four-fermionic terms with subsequent mean field (Hartree) approximation for the bosonic decoupling fields.\(^26\) At the mean field level, the spin and occupation of a given level of the dot are characterized by the average values of the decoupling fields $\bar{M}_l$ (the average spin of the level $l = 1$ or $2$ – assumed frozen along the $z$-direction), and $R_l$ (the average charge/number of electrons on level $l$). The mean field solutions for the isolated quantum dot, $\kappa = 0$, allow us to classify the states of the quantum dot as follows: i) $M_1 = 0$, $R_1 = 0$: the level $1$ is empty; ii) $M_1 = \pm 1$, $R_1 = 1$: the level $1$ is singly occupied, spin $1/2$; iii) $M_1 = 0$, $R_1 = 2$: the level $1$ is doubly occupied, spin $0$. Further, we denote the states of the quantum dot as $(n, m)$ with $n$ and $m$ being the occupation of the first and the second energy levels, respectively.

In the mean field treatment, we replace the two level quantum dot with interactions by a non-interacting quantum dot with quasi-energy levels that depend on the ground state of the quantum dot. This approach allows one to describe correctly the properties of the quantum dot in the ground state and its gapless excitations, including the Kondo effect, which is the aim of our treatment. At the same time, the quasi-energy levels do not reproduce the gapped excitation spectrum of the quantum dot measured, for example, in optical experiments.

For the isolated quantum dot, the positions of the quasi-energy levels are given by $\epsilon_{\uparrow} = E_1 + \kappa U_1 \pm \left[ M_1 (2U_2 + J) - M_2 J \right]$, where $\kappa = E_2 - R_1 U_1 \pm \left[ M_2 (2U_2 + J) - M_1 J \right]$, the sign “+” (“−”) corresponds to $\uparrow$ (“$\downarrow$”) spin. As the gate voltage lowers, more electrons occupy the quantum dot. Whereas the spin of states with $0, 1, 3$ and $4$ electrons in the dot is defined uniquely, the state with 2 electrons in the dot can have total spin $1$, if the electrons occupy different energy levels (the state $(1,1)$), or total spin $0$ in the states $(0,2)$ or $(2,0)$. Which of these states is chosen depends on the relation between the interaction constants in the dot. Taking the degenerate case $E_1 = E_2$ and comparing the free energies of different states of the isolated dot with total occupation 2, we find, that the state $(1,1)$ is realized under the condition $U_1 < 2U_2 + 3J$, i.e., if the Hubbard and exchange inter-
actions that favor the magnetic state dominate over the density-density repulsion between the electrons on different levels. In the opposite case, the nonmagnetic (0,2) or (2,0) states of the quantum dot are realized for two electrons in the dot. Extending this result for the multilevel dot with almost degenerate single particle levels, the condition \( U_1 < 2U_2 + 3J \) corresponds to the Hund’s rule regime, hence a sequence of consecutive Kondo states as the dot charge increases. The opposite condition corresponds to the alternation of the Kondo and non-Kondo ground states for odd and even numbers of electrons, respectively, as one expects for separate single-level dots.

The coupling to the leads via a nonzero coupling \( \kappa \) results in the broadening and mixing of the energy levels that are given now by the expression:

\[
E_n = \epsilon_1^* + \epsilon_2^* \pm \sqrt{\left(\epsilon_1^* - \epsilon_2^*\right)^2 - 4\kappa^2} / 2 - i\kappa.
\]

In the limit of zero level mixing (zero tunneling), the values of \( E_n \) coincide with \( \epsilon_1^*, \epsilon_2^* \). Small level mixing \( \kappa \) leads to small deviations of the solutions from the above mentioned values, although the structure of the quasi-energy spectrum remains the same.

In contrast, in the case of strong level mixing, when the condition \( 2\kappa > |\epsilon_1 - \epsilon_2| \) is satisfied, the quasi-energy spectrum changes qualitatively, reflecting the transition into the regime we call mixed-valence (MV). This regime is realized if the level spacing in the noninteracting dot is small. Then the square root in the expression for the \( E_n \) turns out to be purely imaginary. The positions of the energy levels for a given spin direction coincide. It is convenient to rearrange the energies \( E_n \) introducing the values \( z_1 \) and \( z_2 \) in the following manner:

\[
z_1 = z_+\theta(\omega_n) + z_-\theta(-\omega_n), \quad z_2 = z_+\theta(-\omega_n) + z_-\theta(\omega_n).
\]

Then we obtain:

\[
z_{1,2} = (\epsilon_1 + \epsilon_2)/2 - i\left(\kappa \pm \sqrt{\kappa^2 - (\epsilon_1 - \epsilon_2)^2/4}\right)\text{sgn}(\omega_n).
\]

In the limit of large \( \kappa \) one has two degenerate levels for each spin projection, one strongly broadened \( (z_2) \) and the other one with strongly suppressed broadening \( (z_1) \).

Since in the MV regime the quasi-levels are degenerate (even in the presence of interactions), the electrons fill the dot pairwise, each pair containing two electrons with the same projection of the spin. (One could say that the strong mixing provides an effective ferromagnetic interaction between spins.) The sequence of ground states obtained by changing the gate voltage is modified correspondingly. For example, neglecting the exchange interaction, and in the regime \( E_1 - E_2 > 2U_2 - U_1 > 0 \), the sequence of ground states in the dot changes from “empty dot \( \rightarrow \) lower level singly occupied (Kondo state) \( \rightarrow \) lower level doubly occupied \( \rightarrow \) upper level singly occupied with lower level full (Kondo state) \( \rightarrow \) both levels doubly occupied in the weak coupling regime [or (0,0) \( \rightarrow \) (1,0) \( \rightarrow \) (2,0) \( \rightarrow \) (2,1) \( \rightarrow \) (2,2) in our \( (n,m) \) notation], to “empty dot \( \rightarrow \) both levels singly occupied (Kondo state with spin 1) \( \rightarrow \) both levels doubly occupied in the mixed valence regime [or (0,0) \( \rightarrow \) (1,1) \( \rightarrow \) (2,2)]”. The first sequence results in two Kondo peaks in the conductance (odd occupation) separated by two non-Kondo states (even occupation), whereas in the MV case one can see only one Kondo triplet-like peak (in the state with both levels singly occupied). This difference in ground state sequences will clearly have experimentally observable consequences. Notice, however, that the contribution to the Kondo effect from the two levels differs qualitatively. Whereas the broad supertunneling level results in behavior typical of the one-level dot in the MV regime (where charge fluctuations are strong, and one observes strong temperature dependence of the Kondo peak\(^7\)), the narrow subtunneling level contributes as a deep Kondo level in a one-level quantum dot (with large spin fluctuations and universal temperature dependence).

Note that the sub- and super-tunneling rearrangement of the energy levels and related changes in the state of the quantum dot described here can only occur in the multilevel (two-level here) dot. Moreover, this can be calculated theoretically only if one takes fully into account the effect of mixing of energy levels in the dot through the coupling to the external fermionic system. This non-perturbative effect is not present in other treatments, either because the strong coupling is explicitly neglected, or because it is treated only perturbatively.

A typical change of the state of the dot with gate voltage is shown in Fig. 1. Close to the Fermi level \( (E_F = 0) \), for \( E_1, E_2 \approx 0.84, 0.64 \) the spin and the occupation of both levels jump simultaneously, the values of the average spin and charge on both levels being equal, \( M_1 = M_2, R_1 = R_2 \). The dot is, therefore, in the MV regime. As the gate voltage lowers the levels in the dot, the MV regime breaks down (at \( E_1 \approx -3.9 \)), the level 2 becomes doubly occupied and nonmagnetic \( (R_2 \approx 2, M_2 = 0) \), whereas the level 1 remains singly occupied. The quantum dot is in the Kondo regime. Finally, the level 1 becomes doubly occupied also (at \( E_1 \approx -5.1 \)). The dot is completely filled. Note, that in the nonmagnetic states of the dot, the spin is identically zero, whereas the average charge assumes a continuously varying nonzero value due to the coupling to the external system. The different behavior of the spin and charge of the dot is similar to the quantization of the spin and the absence of quantization of the charge in a quantum dot, predicted recently in the limit of a large dot.

The exchange interaction generally favors the magnetic \((1,1)\) state of the quantum dot with both levels singly occupied. However, whereas the ferromagnetic exchange does not affect the transition between the Kondo and MV regimes, the AFM exchange suppresses the MV regime, effectively increasing the interlevel separation \( \epsilon_1^* - \epsilon_2^* \). At the same time, the Kondo effect is suppressed by the antiferromagnetic correlation of spins in the dot.\(^{11,15}\) The influence of the AFM exchange interaction on the MV regime is illustrated in Fig. 2. Here the change of the ground state of the dot is shown versus the tunneling amplitude \( \gamma \) for zero and nonzero values of the AFM
coupling $J$. We can see that at the transition to the MV regime the charge state of the dot changes from (1,2) (Kondo state with three electrons in the dot, spin 1/2) to (1,1) (Kondo state with two electrons in the dot, spin 1). Therefore, increasing the coupling to the external leads, resulting in a situation not described before: a strong-coupling MV regime, which produces Kondo-like behavior for even numbers of electrons in the dot. One can anticipate that if a sample exhibits consecutive Kondo peaks for both odd and even occupation, the signature of the MV regime would be a non-universal temperature dependence of the conductance, and its low-temperature unitary limit would clearly exceed the single-channel level.

Different ground state behavior has been identified in a two-level quantum dot (although most of our conclusions can be generalized to the multi-level case). This behavior depends on interaction parameters and coupling to the external leads, resulting in a situation not described before: a strong-coupling ‘mixed valence’ regime, which produces Kondo-like behavior for even numbers of electrons in the dot. One can anticipate that if a sample exhibits consecutive Kondo peaks for both odd and even occupation, the signature of the MV regime would be a non-universal temperature dependence of the conductance, and its low-temperature unitary limit would clearly exceed the single-channel level.

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FIG. 2. State of the quantum dot with changing tunneling amplitude $\gamma$ – transition from weak coupling regime to MV regime. $J = 1$ – solid lines; $J = 0$ – dashed lines. Nonzero antiferromagnetic exchange shifts the transition to the MV regime to larger coupling $\gamma$. 

$U_1=1$, $U_2=3$, $t=50$
$E_1=-4$, $E_2=-5$