

# Formation of the Kondo resonance in two-atom molecular systems for various interaction limits

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We consider a two-atom molecule connected to ferromagnetic leads, in the Kondo transport regime. To investigate the Kondo effect in the system, we use the slave-boson mean field approximation (SBMFA) techniques. Results are obtained for both the strong interaction limit, in which an infinite Coulomb repulsion  $U_{1-2}$  between atoms is assumed, and a finite  $U_{1-2}$  case. The transport is considered in the  $T = 0$  and  $V = 0$  equilibrium limit.

Key words: *Kondo resonance; interaction; two-atom molecule*

## 1. Introduction

In the last decade, the Kondo resonance has been observed in semiconductor nano-devices (quantum dots) [1, 2], and recently also in the molecular nanodevices [3]. Due to the different geometry of nanodevices, the Kondo effect observed varies from that for doped metals. The minimum at low temperatures is achieved not by the resistivity, but by conductance. The mechanism of forming of the resonance is, however, similar. Namely, second order processes like co-tunnelling enhance transmission through the system when an unpaired spin occurs on the quantum dot or a single molecule. These processes add coherently, which results in a correlated many-electron state coupling of the electrons from the electrodes and allows current to flow even in the Coulomb blockade regime.

## 2. The model and slave-boson techniques

We focus on non-equilibrium spin-dependent transport phenomena in devices based on two-atom molecules attached to para- and ferromagnetic leads. Such a model can be a useful tool helping us to understand transport through real systems with bi-partite

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molecules, like biphenyl, other similar aromatic-type molecules, or the divanadium molecule [3].

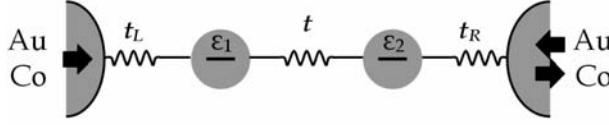


Fig. 1. Schematic view of a two-atom molecule connected to metallic leads. In the ferromagnetic case, it is possible to change the orientation of spin polarization in one of them

Figure 1 schematically shows a two-atom molecule connected to para- and ferromagnetic leads – Au and Co, respectively. The leads in the ferromagnetic system are spin-polarized, and one can change the polarization alignment in the system by changing the polarization orientation in one of the leads. For simplicity, each atom is represented by a single level. Such a system can be described with the double impurity Anderson Hamiltonian:

$$H = \sum_{i,j,\sigma} (t + \varepsilon_i \delta_{i,j}) c_{i\sigma}^+ c_{j\sigma} + U_{1-2} \sum_{i,j} n_i n_j + \sum_{k,\sigma} (t_{L1} c_{kL\sigma}^+ c_{1\sigma} + t_{R2} c_{kR\sigma}^+ c_{2\sigma} + h.c.) + \sum_{k,\sigma,\alpha \in L,R} \varepsilon_{k\alpha} c_{k\alpha,\sigma}^+ c_{k\alpha,\sigma} \quad (1)$$

The first two terms correspond to the two-atom molecule, the first describing the hopping of electrons between atoms and the potential energy  $\varepsilon_i$  of electrons on the site  $i$ , the second one includes the Coulomb interactions of two electrons on different sites,  $U_{1-2}$  being the Coulomb integral treated as an adjustable parameter. The on-site Coulomb repulsion is assumed to be infinite, and thus a double occupancy of the atom is forbidden.

We use the slave-boson mean field approximation (SBMFA) techniques in our calculations to include partially electronic correlations. The Coleman-Barnes representation of the auxiliary operators was chosen, as it gives reliable results for the paramagnetic case and describes the evolution of the physical quantities properly when magnetization appears in the leads. In the SBMFA Coleman-Barnes [4] representation, the electron creation operator reads  $c_{i\sigma}^+ = f_{i\sigma}^+ e_i$ , where  $f_{i\sigma}^+$  is the pseudo-fermion operator creating an electron at site  $i$  with spin  $\sigma$ , and  $e_i$  is the mean value of the boson operator creating an empty state at a site  $i$ . The condition  $Q_i = e_i^2 + f_{i\sigma}^+ f_{i\sigma} = 1$  limits the action of the auxiliary operators to physical space. This constraint enforces an additional term in the Hamiltonian:  $H \rightarrow H + \sum_i \lambda_i (Q_i - 1)$ ,

where  $\lambda_i$  is a Lagrange multiplier. The mean field approximation reduces the problem to the free electron Anderson model with shifted energies  $\tilde{\varepsilon}_{i\sigma} = \varepsilon_{i\sigma} + \lambda_i$ , and renormalized hopping parameters  $\tilde{t}_\alpha = e_i t_\alpha$  and  $\tilde{t} = e_i e_j t$ :

$$\begin{aligned}
H = & \sum_{i,j,\sigma} (\tilde{t} + \tilde{\epsilon}_i \delta_{i,j}) f_{i\sigma}^+ f_{j\sigma} + U_{1-2} \sum_{i,j} (1 - e_i^2) (1 - e_j^2) \\
& + \sum_{k,\sigma} (\tilde{t}_{L1} c_{kL\sigma}^+ f_{1\sigma} + \tilde{t}_{R2} c_{kR\sigma}^+ f_{2\sigma} + h.c.) + \sum_{k,\sigma,\alpha \in L,R} \epsilon_{k\alpha} c_{k\alpha,\sigma}^+ c_{k\alpha,\sigma} + \sum_i \lambda_i (e_i^2 - 1)
\end{aligned} \quad (2)$$

To obtain stable solutions for the considered system, one has to find the minima of the free energy  $F$  by solving a set of self-consistent equations:

$$\begin{cases} \frac{\partial F}{\partial \lambda_i} = 0, & \frac{\partial F}{\partial e_i} = 0 \end{cases} \quad (3)$$

with respect to the parameters  $e_i$  and  $\lambda_i$ . The boson part of the free energy reads  $F_b = \sum_i \lambda_i (e_i^2 - 1)$ . The fermion part of the free energy can be determined within the

Green functions techniques:  $F_f = \frac{2}{\pi} \int_{-\infty}^{+\infty} d\omega f_\alpha(\omega) \text{Im}[\ln G_{1\sigma,2\sigma}^r(\omega)]$ , where  $f_\alpha(\omega)$  is the Fermi function for the left ( $\alpha = L$ ) and right ( $\alpha = R$ ) lead, and the retarded Green function reads  $G_{1\sigma,2\sigma}^r(\omega) = \int d\omega \frac{\tilde{t} \tilde{\Gamma}_{L\sigma} \tilde{\Gamma}_{R\sigma}}{(\omega - \tilde{\epsilon}_{+\sigma})(\omega - \tilde{\epsilon}_{-\sigma})}$ . The coefficients  $\tilde{\Gamma}_{\alpha\sigma}$  denote renormalized molecule-lead tunnelling rates, and

$$\tilde{\epsilon}_{\pm\sigma} = \frac{1}{2} \left( \tilde{\epsilon}_{1\sigma} + \tilde{\epsilon}_{2\sigma} \pm \sqrt{(\tilde{\epsilon}_{1\sigma} - \tilde{\epsilon}_{2\sigma})^2 + 4\tilde{t}^2} \right)$$

are the effective energies of the bonding ( $-$ ) and antibonding ( $+$ ) levels of the molecule, which are formed in the diagonalisation of the Hamiltonian (2).

### 3. Transport in the limit of $U_{1-2} \rightarrow \infty$

In the strong interactions limit of  $U_{1-2} \rightarrow \infty$ , where only a single occupancy of the whole molecule is allowed, it is sufficient to use only one slave-boson  $e$  and one Lagrange multiplier  $\lambda$  to describe the system. The completeness relation and renormalization then reads:  $Q = e^2 + \sum_i f_{i\sigma}^+ f_{i\sigma} = 1$ . Two self-consistent equations (3) can be solved using the Green functions techniques:

$$\begin{aligned}
1 - e^2 &= \frac{2}{\pi} \sum_{\alpha,\sigma} \frac{\Gamma_{\alpha\sigma}}{\Gamma_\sigma} \int d\omega f_\alpha(\omega) \text{Im}[G_{1\sigma,2\sigma}^r(\omega)] \\
\lambda &= \frac{4}{\pi} \sum_{\alpha,\sigma} \Gamma_{\alpha\sigma} \int d\omega f_\alpha(\omega) \text{Re}[G_{1\sigma,2\sigma}^r(\omega)]
\end{aligned} \quad (4)$$

where  $\Gamma_\sigma = \Gamma_{L\sigma} + \Gamma_{R\sigma}$ . The conductance  $G$  is determined from:

$$G = \frac{e^2}{h} \sum_\sigma \frac{4\Gamma_{L\sigma}\Gamma_{R\sigma}}{\Gamma_\sigma^2} |G_{1\sigma,2\sigma}^r|^2 \quad (5)$$

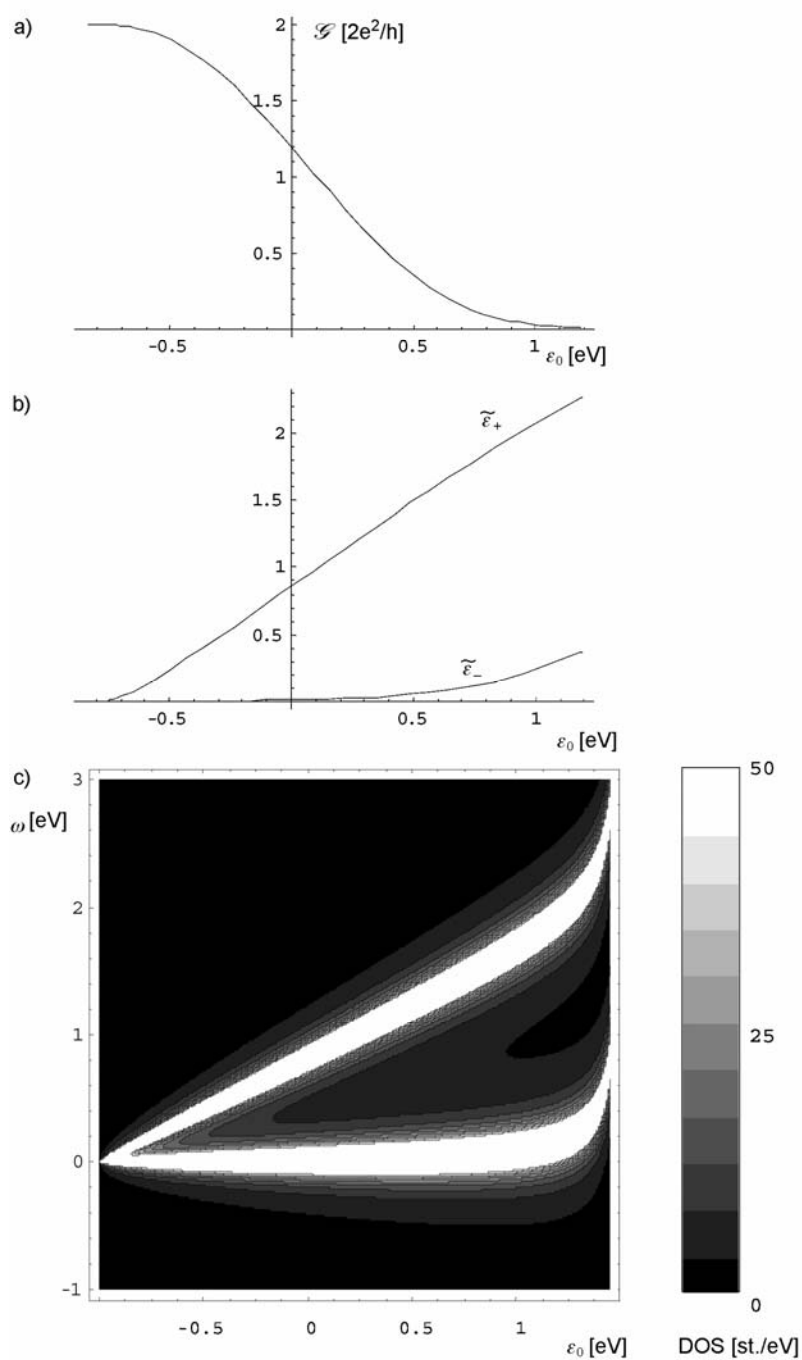


Fig. 2. Conductance in a symmetrical junction (a), effective positions of the molecular levels (b), and the grey-level plot of the densities of states in the leads. Densities of states in the leads are assumed  $\rho_\alpha = 0.294$  states/eV,  $t_L = t_R = 0.2$  eV

In Figure 2a, the conductance of the symmetrical junction ( $t_L = t_R$ ,  $\varepsilon_1 = \varepsilon_2 \equiv \varepsilon_0$ ) is shown. In the empty state regime, for large positive  $\varepsilon_0$ ,  $G$  tends to zero. With decreasing  $\varepsilon_0$ ,  $G$  increases and reaches its maximal theoretical value,  $2e^2/h$ , in the Kondo regime. The conductance behaviour reflects changes in the positions of the effective molecular levels, which are presented in Fig. 2b. In the empty state regime, the levels are not renormalized due to a lack of electronic correlations in the system. The energy gap is constant in this regime. With decreasing  $\varepsilon_0$ ,  $\tilde{\varepsilon}_\pm$  approaches the Fermi level ( $E_F = 0$ ). Due to renormalization,  $\tilde{\varepsilon}_-$  is strongly occupied and stays near  $E_F$ . The higher, antibonding level  $\tilde{\varepsilon}_+$  is still weakly renormalized. In the Kondo regime, for  $\varepsilon_0$  deeply below  $E_F$ , both levels are strongly renormalized and stay near  $E_F$ . In Figure 2c, a grey-level plot of the densities of states (DOS) of the effective molecular levels is presented. In the empty state regime, DOS peaks are separate and broad. The energy gap between them is constant. When approaching the Kondo resonance regime, the energy gap narrows, and eventually the DOS peaks merge and become extremely narrow and high.

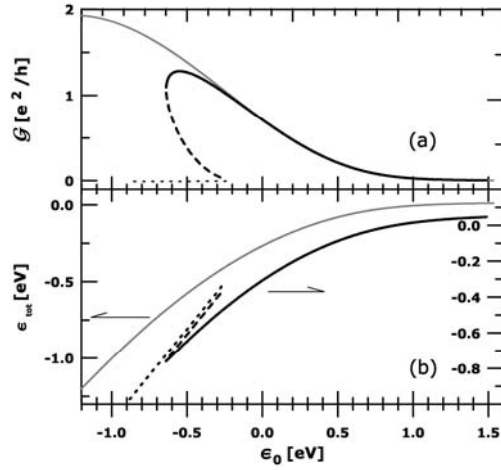


Fig. 3. Comparison of the conductance (a) in the symmetrical junction  $t_L = t_R = 0.2$  eV, for the cases  $\varepsilon_1 = \varepsilon_2$  and  $\varepsilon_1 \neq \varepsilon_2$ . A free energy plot (b) for the considered cases. The grey line denotes plots for the case  $\varepsilon_1 = \varepsilon_2$ , and the black for  $\varepsilon_1 \neq \varepsilon_2$ . Dotted and dashed lines correspond to unstable solutions

A comparison of the conductance in the asymmetrical and symmetrical junction is presented in Fig. 3a. For a non-zero gap between the local sites energies, the loop of  $G$  can be formed, because an unstable solutions appears. The system chooses a solution corresponding to the lowest energy. To decide which solution is stable, the total energy plot is shown in Fig 3b. The energy decreases monotonically with decreasing  $\varepsilon_0$  till the unstable regime, where three solutions appear. For very low  $\varepsilon_0$ , the levels are no longer renormalized, and the energy is equal to the occupied level energy. In the resonance regime,  $G$  exhibits a sudden drop to zero. The reason for such behaviour is the transport blockade in the system, when  $\varepsilon_1$  and  $\varepsilon_2$  are deeply below  $E_F$ . In such a case, the symmetry of the molecule is broken, and the lower level is occupied with the whole electron (as the double occupancy is forbidden). In a symmetric case, the

electron is distributed equally to the both levels; in the asymmetric case, it prefers the lower level. The result is a consequence of the approximation adopted.

In the ferromagnetic system, DOS in the leads are approximated with constant values on the Fermi level:  $\rho_{\uparrow} = 0.174$  and  $\rho_{\downarrow} = 1.735$  st./eV [5]. The magnetizations of the leads can be aligned parallel (P configuration) or antiparallel (AP configuration). The conductance in the symmetrical and asymmetrical junctions is shown in Fig. 4a. Unlike in the

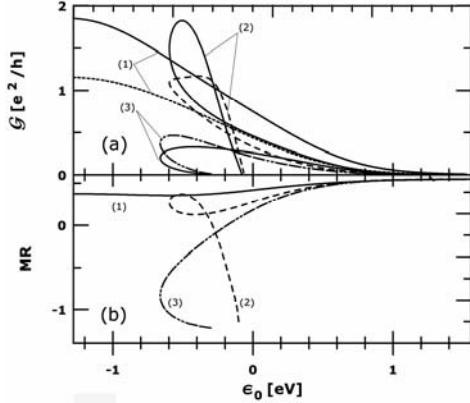


Fig. 4. Conductance (a) and magnetoresistance (b) for the system with ferromagnetic leads.

Curves (1) denote the symmetric junction  $\varepsilon_1 = \varepsilon_2$ ,  $t_L = t_R = 0.2$  eV; (2) – asymmetric junction with  $\varepsilon_1 - \varepsilon_2 = 0.1$  eV and  $t_L - t_R = -0.13$  eV; (3) – asymmetric junction with  $\varepsilon_1 - \varepsilon_2 = 0.1$  eV and  $t_L - t_R = +0.13$  eV. The solid lines in (a) denote a parallel (P) alignment of magnetization in the leads, and dashed lines an antiparallel alignment (AP)

P configuration,  $G$  does not reach a value of  $2e^2/h$  in the AP configuration due to lower contact efficiencies. For the asymmetric case, loops of  $G$  can be observed in the unstable solution regime; in the empty state regime,  $G$  tends to zero in all cases.  $G_{AP}$  can be larger than  $G_P$  when differences in  $t_a$  and  $\varepsilon_i$  are opposite in sign and minority spin transfer is preferred. Magnetoresistance, shown in Fig. 4b, is defined as the relative difference in conductance between the P and AP configurations,  $MR = (G_P - G_{AP})/G_P$ . In the resonance regime, MR can be positive or negative due to the asymmetry of the junction; in the empty state regime, MR tends to the value determined by the Julliere formula for the given DOS values,  $MR_{\text{Julliere}} = 2p^2/(1 + p^2) \approx 0.55$  for all considered cases, where  $p = (\rho_{\downarrow} - \rho_{\uparrow})/(\rho_{\downarrow} + \rho_{\uparrow})$  is the magnetic polarization of the leads.

#### 4. Transport in the finite $U_{1-2}$ limit

In the finite  $U_{1-2}$  limit, double occupancy of the molecule is allowed. In such a case, we apply two slave-bosons and two Lagrange multipliers to describe the system. The completeness and renormalization relations then read:  $Q_i = e_i^2 + f_{i\sigma}^+ f_{i\sigma} = 1$  and  $\tilde{t} = e_1 e_2 t$ ,  $\tilde{t}_L = e_1 t_L$ ,  $\tilde{t}_R = e_2 t_R$ ,  $\tilde{\varepsilon}_{i\sigma} = \varepsilon_{i\sigma} + \lambda_i$ ,  $i = 1, 2$ . In this case, the four self-consistent equations (3) can only be solved numerically. Conductance  $G$  is again determined from (5). We consider only the symmetric paramagnetic junction, as the calculations for the asymmetrical junction and ferromagnetic cases are still in pro-

gress. The conductance for  $U_{1-2} \approx 0$  is presented in Fig. 5a. In the empty state regime, the conductance is close to zero. With decreasing  $\epsilon_0$ ,  $G$  increases. Unlike the strong interaction limit,  $G$  drops to zero for very low  $\epsilon_0$  after attaining the value of  $2e^2/h$  near the Fermi level  $E_F = 0$ . Conductance for higher values of  $U_{1-2}$  shows the behaviour similar to that of  $U_{1-2} \approx 0$ ; the  $G$  peak, however, is broadened and shifted toward lower  $\epsilon_0$ . The positions of the effective molecular levels are shown in Fig. 5b. In the empty state regime, the levels behave like in the strong interaction cases. In both

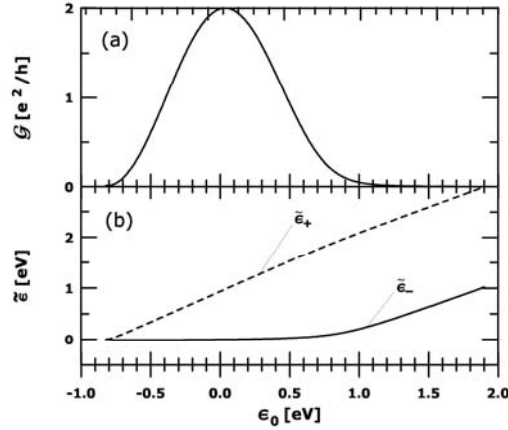


Fig. 5. Conductance (a) and positions of the effective molecular levels (b) for the symmetric paramagnetic junction in the limit of  $U_{1-2} \rightarrow 0$ . All parameters are the same as in Fig. 2

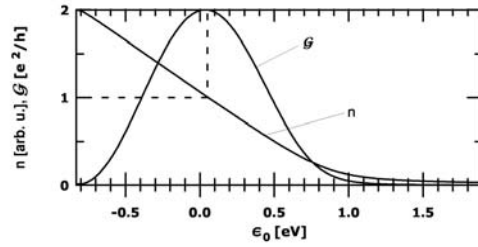


Fig. 6. Conductance and total number of electrons for the symmetric junction in the case of  $U_{1-2} = 0$ . The dotted line is just a guide for the eye

cases, when the resonance regime is approached,  $\tilde{\epsilon}_-$  (which is closer to the Fermi level) is fully occupied and pushed down below  $E_F$  due to renormalization between the effective levels. Now, the transport takes place only through  $\tilde{\epsilon}_+$  now. A further filling of  $\tilde{\epsilon}_+$  renormalizes hopping to the leads, and transport gradually drops to zero. In Figure 6, the conductance and number of electrons are shown, proving that the resonance and therefore  $G$  have maxima of  $2e^2/h$  exactly for  $n = 1$ .

## 5. Conclusions

We have analysed the electronic transport in systems of two-atom molecules connected to para- and ferromagnetic leads, including electronic correlations for the molecule by applying the SBMFA techniques. The Kondo resonance and finite Coulomb repulsion between sites were observed in systems with a strong interaction limit of  $U_{1-2} \rightarrow \infty$ . We have shown that the resonance is formed when the local atomic levels are deeply below the Fermi level. The conductance can form loops when a difference in the atomic energy levels appears due to energetically unstable solutions. In the magnetic system, conductance for a parallel alignment of the magnetization of the leads is larger than for the antiparallel case, due to larger contact efficiencies in the symmetric junction. The situation, however, can be reversed in the asymmetric system. In the case of a non-zero energy levels gap, unstable solutions appear similarly to the paramagnetic case. Depending on the asymmetry of the system, its magnetoresistance positive or negative values in the Kondo regime.

In the empty state regime, it tends to the Julliere value for all considered cases. For finite values of  $U_{1-2}$ , the Kondo resonance arises for levels positions corresponding to an occupancy of the molecule of  $n = 1$ , which can also be observed as a maximum in conductance. When the system is occupied by two electrons ( $n = 2$ ), electronic correlations are irrelevant due to electron-hole symmetry, and the conductance behaviour is the same as for the empty state limit ( $n = 0$ ).

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