



## NanoDMFT: Dynamical Mean-Field Theory for strongly correlated electrons at the nanoscale

D. Jacob

### Kondo effect in molecular devices from first principles

The Kondo effect is one of the most intriguing many-body phenomena [1]: It arises when a local magnetic moment is weakly coupled to a sea of non-interacting conduction electrons. Such a situation can be realized for example by a transition metal impurity in a metal host where the strongly interacting electrons within the open  $d$ - or  $f$ -shell of the impurity give rise to the formation of a local magnetic moment. Another possible realization is a molecule with an unpaired electron coupled to metallic leads.

At low temperatures the effective coupling between the magnetic moment and the conduction electrons becomes *antiferromagnetic* giving rise to the formation of a singlet state where the total spin  $S$  of the system is zero. Due to the formation of this so-called *Kondo singlet* state the magnetic moment of the impurity or molecule is effectively screened by the interaction with the conduction electrons. Hence the behavior becomes very different from that of a free magnetic moment. For example the magnetic susceptibility as a function of temperature does not obey the Curie-Weiss law anymore.

Another important consequence of the formation of the Kondo singlet state is the appearance of a sharp temperature dependent resonance in the spectral function right at the Fermi level. In the case of magnetic impurities in metal hosts the appearance of this *Kondo peak* leads to an increase in the resistance of the metal at low temperatures. Thus the Kondo effect solved the long-standing puzzle of the resistance minima at very low temperatures, first observed in the 1930s in Au metal samples [2] which were later traced back to the presence of magnetic impurities in the metal host [3].

Here we study theoretically the Kondo effect that occurs in atomic or molecular devices such as single magnetic atoms or molecules on metal surfaces or in

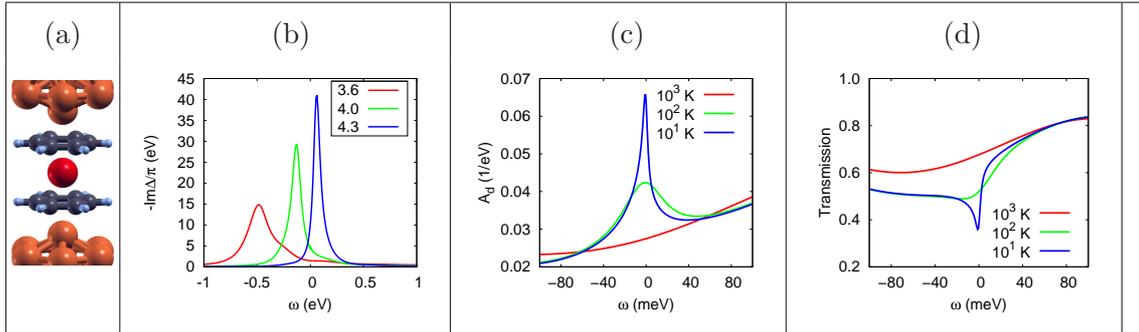


FIG. 1: Orbital Kondo effect in CoBz<sub>2</sub> sandwich molecule [7]. (a) Geometry of CoBz<sub>2</sub> sandwich molecule in Cu nanocontact. (b) Hybridization function calculated from the LDA electronic structure of the sandwich molecule in a Cu nanocontact as shown in (a) for different distances  $d$  between the tip atoms of the Cu nanocontact and the central Co atom of the sandwich molecule. (c) At low temperatures a sharp Kondo resonance appears in the spectral function of the Co  $3d$ -orbitals right at the Fermi level due to an *orbital Kondo effect* in the doubly degenerate  $E_2$ -orbitals. (d) Corresponding transmission function showing the typical Fano-lineshape resulting from the appearance of the Kondo resonance in the Co  $3d$  spectral function.

nanocontacts[4]. The challenge is to understand in detail how and under what circumstances the Kondo effect can emerge in a given system, and how the Kondo effect is altered by adding or changing the constituents. The ultimate goal is to being able to actually predict theoretically whether a given system will show the Kondo effect or not, and what type of Kondo effect.

To this end we have developed a novel approach for calculating the electronic structure and transport properties of a molecular device that explicitly takes into account the strong electronic correlations originating from the strongly interacting electrons within the open  $d$ - or  $f$ -shells of transition metal atoms that are ultimately responsible for the Kondo effect [5, 9]. This approach combines *ab initio* electronic structure calculations on the level of Density Functional Theory with sophisticated many body methods such as the One-Crossing Approximation (OCA) [5] and the Dynamical Mean-Field Theory (DMFT) [9] that account for the strong correlations of the  $d$ - or  $f$ -electrons.

Fig. 1 shows results of an LDA+OCA calculation of the electronic structure and transport properties of Co-Benzene sandwich molecule (CoBz<sub>2</sub>) trapped between the

tips of a Cu nanocontact [7]. Our calculation predict that the strong correlations in the co 3d-shell give rise to a so-called *orbital Kondo effects* which stems from the orbital degeneracy of the doubly degenerate  $E_2$ -levels in the Co 3d-shell. Here the *pseudospin* labeling the two degenerate  $E_2$ -levels is screened instead of the normal electron spin as in the usual Kondo effect.

Using our LDA+OCA methodology we have also studied the Kondo effect of Co atoms on graphene sheets [6], and the Kondo effect of metallic nanocontacts hosting magnetic impurities in the contact region [5].

### **Dynamical mean-field theory for nanoscale conductors**

When a nanoscale device contains several transition metal atoms that exhibit strong electronic correlations, the direct application of the above mentioned LDA+OCA methodology [5] is computationally not feasible anymore. Therefore we have recently adapted the so-called Dynamical Mean-Field Theory (DMFT) originally conceived to describe strong electronic correlations in bulk materials [8] to the case of nanoscopic conductors such as nanocontacts and molecules attached to electrodes [9]. The basic assumption of DMFT is that *non-local electron correlations*, i.e. correlations between electrons on different atoms are small and hence can be neglected. In this case it is easy to show that the problem of many interacting electrons on a lattice can be mapped on an Anderson impurity model, that is an interacting site coupled to a “bath” of non-interacting electrons. This problem can then be solved with an impurity solver, for example the above mentioned OCA impurity solver. However, since the “bath” depends on the electronic structure of each site and thus on the local correlations on each site, the problem has to be solved self-consistently. This is the so-called DMFT self-consistency condition.

In the case of a molecular conductor (i.e. a nanocontact or a molecule connected to bulk electrodes) we are dealing with a finite region (the molecule or nanocontact) and hence a finite set of correlated atomic sites in contrast to a solid for which DMFT was originally developed. Also in contrast to a crystalline solid, each of the correlated atoms of the molecular conductor in principle has a different environment. Hence for each correlated atom in the conductor we have to solve an individual Anderson impurity problem in each step of the NanoDMFT self-consistency. This is illustrated in Fig. 2a.

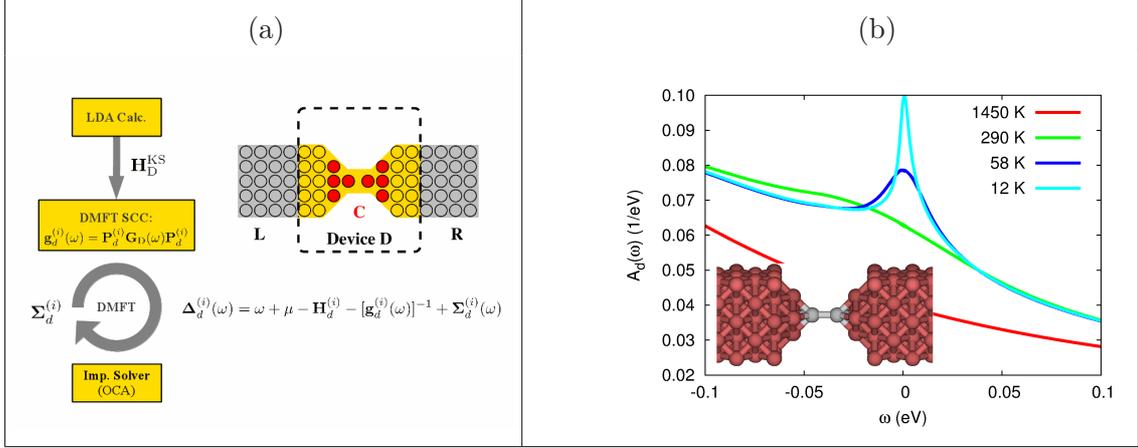


FIG. 2: Dynamical Mean-Field Theory for nanoscale devices (NanoDMFT). (a) Illustration of NanoDMFT self-consistency cycle for a molecular conductor [9] and schematic drawing of a molecular conductor showing the division of the system into left (L) and right (R) electrodes and device region (D) that hosts the strongly correlated subspace (C) consisting of the  $d$ -orbitals of the magnetic atoms (red circles). (b) Application of NanoDMFT method to a Ni dimer hosted in a Cu nanocontact: Spectral function calculated with NanoDMFT method near the Fermi level for different temperatures. The inset shows the geometry of the system.

Fig. 2b shows the application of the NanoDMFT self-consistency procedure to the case of a Ni dimer suspended between the tips of a Cu nanocontact [9]. The strong correlations of the  $3d$ -electrons of the two Ni atoms give rise to a Kondo effect signaled by a sharp Kondo peak in the  $3d$ -spectral function at the Fermi level and the concomitant Fano lineshape in the low-bias conductance characteristics of the nanocontact. Such a system has recently been realized experimentally [10].

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