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Correlated adatom trimer on metal surface: 
A continuous time quantum Monte Carlo study

V. V. Savkin,1+, A. N. Rubtsov,2 M. I. Katsnelson,1 and A. I. Lichtenstein3
1Institute of Molecules and Materials, University of Nijmegen, 6525 ED Nijmegen, The Netherlands
2Department of Physics, Moscow State University, 119992 Moscow, Russia
3Institute of Theoretical Physics, University of Hamburg, 20355 Hamburg, Germany

The problem of three interacting Kondo impurities is solved within a numerically exact continuous
time quantum Monte Carlo scheme. A suppression of the Kondo resonance by interatomic exchange
interactions for different cluster geometries is investigated. It is shown that a drastic difference
between the Heisenberg and Ising cases appears for antiferromagnetically coupled adatoms. The
effects of magnetic frustrations in the adatom trimer are investigated, and possible connections with
available experimental data are discussed.

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The electronic structure of adatoms and clusters on
surfaces constitutes one of the most fascinating subjects in
condensed matter physics and modern nanotechnology
[1]. The scanning tunneling microscopy (STM) or spec-
troscopy technique allows the study of atomic structure,
the electronic energy spectrum, and magnetic properties
of different surfaces at an atomic scale. In particular,
STM gives the unique opportunity of directly investigat-
ing an essentially many-body phenomenon, namely
the Kondo effect [2, 3, 4]. Earlier only indirect meth-
ods such as analysis of temperature and magnetic field
dependencies of thermodynamic and transport proper-
ties were available [5, 6]. Recently STM studies of small
transition metal nanoclusters on different surfaces have
been performed, including Co dimers [7] and Cr trimers
[8] on a Au surface, and Co clusters on carbon nanotubes
[9]. The electron spectrum of these nanosystems, in par-
cular the existence of the Kondo resonance, turns out
to be very sensitive to the geometry of the clusters as
well as to the type of magnetic adatoms. The later can
be important for nanotechnological fine tuning of surface
electronic structure.

The “quantum-corral” type of STM-experiments pro-
vides an unique opportunity to investigate in detail
an interplay between the single-impurity Kondo effect
and interatomic magnetic interactions in nanoclusters
which is a key phenomenon in Kondo lattice physics
[10, 11, 12, 13, 14]. The interaction between itinerant
electrons and localized ones leads to the screening of the
magnetic impurity moment which is the Kondo effect;
on the other hand, the RKKY exchange interaction be-
 tween localized spins suppresses the Kondo resonance at
the Fermi level. As a result, a very complicated phase di-
mogram can be obtained with regions described by a strong
coupling regime, “normal” magnetic behavior with loga-
Quantum critical points at the boundary of different
phases is a subject of special interest [12, 14]. There
exists a general belief that anomalous features of many
f-electron systems such as heavy-fermion or non-Fermi-
liquid behavior can be treated in terms of the Kondo
lattice picture [6, 15, 16]. This is why non-perturbative
investigations of the basic physical features of few-atom
magnetic clusters in a metallic medium is of primary in-
terest. At the same time, due to the extreme complex-
ity of the problem, theoretical investigations of electronic
structure for several Kondo centers usually involve some
uncontrollable approximations, such as a replacement of
the Heisenberg interatomic exchange interactions by the
Ising ones [14] or a variational approach based on a sim-
ple trial function [17].

In this Letter we present results of a numerically ex-
act solution of the three Kondo impurity problem within
the recently developed continuous time quantum Monte
Carlo (CT-QMC) method [18]. For the antiferromagnetic
( AFM) exchange interatomic interaction, in contrast to
the ferromagnetic ( FM) one, the results for the Heisen-
berg and Ising systems differ essentially. Based on our
theoretical analysis, the recent paradoxical experimen-
tal results [8] where the Kondo resonance is observable
for an isoceles magnetic triangle but not for the perfect
Cr-trimer or individual Cr adatom will be discussed.

We start with the system of three impurity correlated
sites with Hubbard repulsion $U$ in a metallic bath and
with an effective exchange interaction $J_{ij}$ between them,
a minimal model which however includes all relevant in-
teractions necessary to describe magnetic nanoclusters on
a metallic surface. The effective action for such cluster
in a metallic medium has the following form:

$$ S = S_0 + W, $$

$$ S_0 = -\int_0^\beta \int_0^\beta d\tau d\tau' \sum_{i,j,\sigma} c^\dagger_{i\sigma}(\tau) G^{-1}_{ij}(\tau - \tau') c^\dagger_{j\sigma}(\tau'), $$

$$ W = \int_0^\beta d\tau \left( U \sum_i n_i(\tau)n_i(\tau) + \sum_{i,j} J_{ij} S_i(\tau) S_j(\tau) \right). $$

The last term in the right-hand-side of Eq.(1) allows us
to consider the most important “Kondo lattice” feature,
that is, the mutual suppression of the Kondo screening
and intersite exchange interactions [10, 11]. Another fac-
tor, the coherence of the resonant Kondo scattering, is
taken into account by the introduction of inter-impurity hopping terms $t_{ij}$ to the bath Green function which is supposed to be $G_{ij}^{-1} = G_{ij}^{-1} \delta_{ij} - t_{ij}$. Here $G_{i}^{-1}(i\omega_n) = \mu + i(\omega_n + \sqrt{\omega_n^2 + 1})/2$ corresponds to the semicircular density of states (DOS) with band-width 2 and $t_{ij}$ are inter-impurity hopping integrals. For real adatom clusters the exchange interactions are mediated by conduction electrons (RKKY interactions) which are dependent on the specific electronic structure of both adatoms and host metal. To simulate this effect we will consider $J_{ij}$ as independent parameters which is a common practice in the Kondo lattice problem [10, 11, 14]; otherwise for the half-filled non-degenerate Hubbard model used in our calculations the exchange is always antiferromagnetic. In the model (1) the geometry of the problem is specified by the values of exchange integrals $J_{ij}$ and hopping parameters $t_{ij}[19]$. We will concentrate on the case of equilateral triangle when $J_{ij} = J$ and $t_{ij} = t$; to compare with the experimental situation in Ref. 8 also an isosceles triangle will be considered. To check an approximation used in Ref. 14 we will investigate the case when all spin-flip exchange terms are ignored and the Heisenberg (SS) form of interaction $J_{ij} S_i(t) S_j(t)$ is transformed into the Ising ($S_i S_j$) one $J_{ij} S_i^z(t) S_j^z(t)$.

The later can be presented in the form $\sum \frac{n!}{i!j!} \sum \int d\tau_1...d\tau_n \text{Tr} \left( T_{c_i^+ c_j} w_1(\tau_1)...w_n(\tau_k) \right)$.

Here $Z$ is the partition function and $I$ denotes the set $i, j, j', j''$. Our algorithm performs the random-walk in a space of all possible values for $k; \tau_1...\tau_k; I_1...I_k$. The numerical averaging of Eq.(2) over this random walk gives the desired Green function for the interacting system with the action (1). Typical value for $k$ in our calculation is $k \approx \int dt \sum \|w_i(t)\| \approx N \beta U + N^2 \beta J$, where $\beta$ is the inverse temperature and $N$ is number of atoms in the cluster. One can see that for the case $U \gg NJ$ the exchange interaction indeed does not slow the calculation down, its complexity is determined by the local (Coulomb) interaction.

In order to check the CT-QMC algorithm for a system with complicated Heisenberg interactions we apply this method to a simple Hamiltonian analogue of the model (1), i.e. for $G_{ij}^{-1}(i\omega_n) = \mu + i\omega_n$. We compare our CT-QMC approach with the solution obtained using the exact diagonalization method. Results for the system with AFM $J (J > 0)$ are shown in Fig.1 for $S_i S_j$ and SS interactions. The estimated errorbar in numerical data is $10^{-3}$ or less.

Although the problem of DOS-calculations from $G(\tau)$ data is ill-defined, quite reliable estimations can be made at our level of the numerical accuracy. For example, DOS of the above-mentioned Hamiltonian models is at most contributed by the four $\delta$-peaks located at $\pm U/2, \pm (U/2 + J)$ for Ising and $\pm U/2, \pm (U/2 + 2J)$ for Heisenberg interaction. Fit of the numerical data with several $\delta$-peaks indeed resolves their positions (with a 5% errorbar) and relative heights (with a 20% errorbar). Further, we study models with a continuous DOS, and standard maximum-entropy analytical continuation method [21] is used to recover DOS. Normally it resolves the DOS features from imaginary time QMC data with a similar accuracy.

Let us discuss correlated adatom trimer in the metallic bath depending on type of the effective exchange interaction ($S_i S_j$ or SS) for AFM and FM cases. First we show that SS type of interaction suppresses the reso-
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FIr. 2: Imaginary part of the Green functions at Matsubara frequencies for the correlated adatom equilateral triangle in the metallic bath for AFM (upper figure) and FM (lower figure) types of effective exchange interaction. Parameters: $U = 2, J = \pm 0.2, \beta = 16, \mu = U/2$. There are three dependencies on each picture for SS, $S_zS_z$ and $J = 0$ (which corresponds to single atom in the metallic bath) types of interaction. The insets show DOS.

To explain these results we need to calculate the spectral density $D(\omega)$ of the on-site spin-flip operators $S^\pm$ for an AFM equilateral triangle $D_{SS}(\omega) = \frac{3}{2}\delta(\omega) + \frac{1}{2}\delta(\omega - 3J)$, $D_{S_zS_z}(\omega) = \frac{1}{2}\delta(\omega) + \frac{1}{2}\delta(\omega - 2J)$. In both cases there is a part of the spectral density with zero frequency due to degeneracy of the ground state and spin-flip transitions between its components, but for the SS case this part is twice as large. For the case $J > T_K$ ($T_K$ is one-site Kondo temperature) only this “soft” component of the spectral density will lead to Kondo screening which means that the suppression of the Kondo effect is twice more efficient for the SS case than for the $S_zS_z$ one. Since the trimer as a whole has a degenerate ground state there is still a strong-coupling regime and an effective Kondo temperature $T^*_K$ which however is much smaller than $T_K$.

Scaling considerations similar to one proposed in Ref.11 gives an estimation of $T^*_K \approx T^3_K/J^{1/2}$ and $T^*_K \approx T^3_K/J^2$ for the SS and $S_zS_z$ case respectively. We assume that this quantity is too small to be visible in our simulations (as well as in the experimental data [8]) so what is observed corresponds to the one-site Kondo resonance at the condition $T_K > J$. Similar estimation for the case of FM interactions shows that there is no difference between the $S_zS_z$ and SS model there and $T^*_K \approx T^3_K/J$ as in the AFM $S_zS_z$ case.

In order to describe the experimental situation we changed the geometry of the adatom trimer. An observation of the Kondo resonance reconstruction was reported for one isosceles geometry of three Cr atoms on a gold surface [8]. Thus we study the isosceles triangles for AFM and FM types of effective exchange interaction. We have chosen the following parameters of $J_{ij}$ to imitate the experimental system: $J_{23} = J, J_{12} = J/3, J_{13} = J/3$. The computational results are presented in Fig. 3, where one can see the reconstruction of resonance in AFM and FM cases in accordance with experimental data. Note that the Kondo resonance appears only for the more weakly bonded adatom in AFM case.

The observed picture can be drastically changed by introducing a non-zero value of the hopping parameter $t_{ij}$. As noted above the trimer ground state is degenerate at $t_{ij} = 0$, however this degeneracy is lifted for $t_{ij} \neq 0$. If one of the obtained states lies below the Fermi level, DOS can be changed drastically and at certain parameters it leads to the appearance of a resonance on the Fermi level (see Fig.4). In Fig.4, DOS is shown for various values of filling in the system and at nonzero $t_{ij}$. It is necessary to point out that the introduction of the parameter $t_{ij}$, the variation of the filling in the system ($\mu$), and different geometries ($J_{ij}$) can lead to various results in DOS. This can be used as one of the possible explanations of the experimental data regarding the Cr trimer on an Au surface which look initially appear counter-intuitive: the Kondo temperature for the trimer is much larger than for the single site, despite the suppression of the Kondo effect by $J_{ij}$. One can assume that this is a consequence of the change of the number of $d$-electrons in ground-state configuration for the Cr atom in the trimer in comparison...
FIG. 3: DOS for equilateral triangle (ET) and isosceles triangle (IT) geometries with AFM (upper figure) and FM (lower figure) types of effective exchange interaction. Parameters are the same as in Fig. 2. Values of the effective exchange integrals for IT are as follows: $J_{23} = J$, $J_{12} = J/3$, $J_{13} = J/3$. There are two dependencies in case of IT: one for adatom 1 and another for equivalent adatoms 2 and 3. All adatoms are equivalent in the case of ET (one dependence).

In conclusion, we have shown that the electronic structure of a correlated adatom trimer on a metallic surface drastically depends on the symmetry of magnetic interactions. The effective exchange interaction of SS type leads to more efficient suppression of the Kondo resonance in the AFM case than in the case of $S_zS_z$ interactions. The experimental STM data [8] can be reproduced qualitatively well by variation of the geometry of the problem, hopping integrals and electronic filling for magnetic nanostructures.

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FIG. 4: DOS for equilateral triangle with an AFM type of effective exchange interaction at various values of filling in the system. Parameters: $U = 2, J = 0.2, t = 0.3, \beta = 16$. Corresponding numbers of particles are $n = 0.8$, $n = 1$ (half-filled case) and $n = 1.3$.

* Electronic address: savkin@sci.kun.nl