Effective Kondo model for a trimer on a metallic surface

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I consider a Hubbard-Anderson model which describes localized orbitals in three different atoms hybridized both among themselves and with a continuum of extended states (ES). Using a generalized Schrieffer-Wolff transformation, I derive an effective Kondo model for the interaction between the doublet ground state of the isolated trimer and the ES. For an isosceles trimer with distances $a,l,l$ between the atoms, the Kondo temperature is very small for $l < a$ and has a maximum for finite $l > a$ when $a$ is small. The results agree with experiments for a Cr trimer on Au(111).

The study of many-body phenomena in nanoscale systems has attracted much attention in recent years. Progress in nanotechnology has made it possible to construct nanodevices in which the Kondo physics is clearly displayed [1–3]. Scanning tunneling spectroscopy has made it possible to probe the local density of states near a single impurity and Fano antiresonances have been observed for several magnetic impurities on metal surfaces [4–7]. These antiresonances observed in the differential conductance, reflect a dip in the spectral density of conduction states caused by the Kondo effect [8].

Furthermore, corrals built on the (111) surface of noble metals or Cu have been used to project the spectral features of the Fano-Kondo antiresonance (FKA) to remote places [5,8]. These antiresonances observed on these surfaces have been reproduced by many-body calculations [8–10].

The situation is however different for Cr trimers on the Au(111) surface [11]. Experimentally, no FKA is observed for a linear trimer, or a compact equilateral one in which the distance between any two Cr adatoms is believed to be the same as the Au-Au nearest-neighbor one ($a = 2.88$ Å). For a single Cr adatom, no FKA is observed either. This implies that in these cases, if a Kondo effect originating from localized moments exists, its characteristic temperature $T_K$ is less than the experimental temperature (7 K). On the other hand, surprisingly, for an isosceles trimer with one side of length $a$ and two sides of length $l \approx 5.2$ Å, the spectrum does display a FKA with a half width $T_K = 50 \pm 10$ K. This spectrum is similar to the one observed for one Co impurity on Cu(111) [5,7].

The origin of this puzzling dependence of $T_K$ of the Cr trimer with geometry is still unclear, in spite of recent theoretical efforts [12–14].

In this Letter, I start from a Hubbard-Anderson Hamiltonian that describes three Cr adatoms interacting with a continuum of extended states (ES). Using a generalized Schrieffer-Wolff transformation (SWT) [18], the model is mapped into the usual one-impurity Kondo model. The resulting effective Kondo interaction averaged over the Fermi energy $J$ depends on the geometry of the trimer. The ensuing Kondo temperature is consistent with the above experimental observations [11].

The form of the Hamiltonian is suggested by experimental evidence and previous theoretical work. The line shape observed for the isosceles Cr trimer with $T_K \approx 50$ K is rather symmetric, while calculations using Wilson’s renormalization group for the degenerate Anderson model obtain a strongly asymmetric Kondo resonance [15]. This suggests that there is only one relevant 3d orbital. The surface potential breaks the degeneracy of the d orbitals into two orbital doublets with angular momentum projection $m = \pm 1$ and $m = \pm 2$ and one orbital singlet with $m = 0$ (the $3d_{x^2−y^2}$ orbital). Therefore the latter, singly occupied, is the candidate for the formation of the Kondo state. A similar conclusion has been reached for Co atoms on Cu(111) [8–10]. The absence of a Kondo effect for Cr [11] or Co dimers on Au(111) at interatomic distances less than 6 Å [16] suggests a strong interatomic hopping leading to a spin singlet ground state.

Due to the symmetry breaking of the surface potential, the $3d_{x^2−y^2}$ orbital of the adatom hybridizes with the 4s orbital, and then one expects a decay $r^{−7}$ with distance $r$ of the hopping between hybrid localized orbitals [17]. Finally the fact that $T_K < 7$ K for a single Cr adatom points to a small hybridization between localized and ES, justifying the use of the SWT.

The Hamiltonian can be written as

$$H = H_{\text{Cr}} + H_{\text{Au}} + H_V,$$

$$H_{\text{Cr}} = \sum_{i\sigma} d_i^\dagger d_i + U \sum_{i\sigma} d_i^\dagger d_i + H_c,$$

$$H_{\text{Au}} = \sum_{k\sigma} c_k^\dagger c_{k\sigma},$$

$$H_V = \sum_{k\sigma} (V_k e^{-ik_{\text{R}}} d_{j\sigma}^\dagger c_{k\sigma} + \text{H.c.}).$$

$H_{\text{Cr}}$ is a Hubbard model that describes the isolated Cr trimer, with hopping that depends on the distance $r_{ij} = |\mathbf{R}_i - \mathbf{R}_j|$ between Cr adatoms as $t_{ij} = t_0 a/r_{ij}$. $H_{\text{Au}}$ describes a band of ES. $H_V$ describes a band of ES. I will discuss alternatively either bulk or Shockley surface states of the Au(111) surface. $H_V$ is the hybridization between localized and ES, assuming that the wave functions of the latter are plane waves [8].

If one eliminates $H_V$ by means of a SWT neglecting $t_{ij}$ and uses another canonical transformation to map
the half filled $H_{Cr}$ into a Heisenberg model, the resulting effective Hamiltonian becomes analogous to previously used ones [12,13]. As shown below, this approach misses some coherence effects that reduce $T_K$ strongly for the equilateral trimer.

I solve exactly $H_{Cr}$ retaining only the ground state doublet in the subspace of three particles $|3\sigma\rangle$, and then I perform a generalized SWT to eliminate $H_V$. The validity of the approach is discussed below. The resulting effective Hamiltonian has the form of a one-impurity Kondo model

$$H_K = H_{Au} + \sum_{kk'\sigma\sigma'} J_{kk'} c_{kk\sigma}^\dagger c_{kk'\sigma'} \cdot \mathbf{S},$$

(2)

where $\mathbf{S}$ describes the spin operators of the doublet $|3\sigma\rangle$ and $\sigma\sigma'$ is a vector with the three Pauli matrices. The effective exchange can be written in the form

$$J_{kk'} = \bar{V}_k V_k \sum_{\alpha} \left\{ \left( \frac{1}{E_{2sa} - E_3 + \epsilon_k} \right) \bar{A}_{2sa}^{k\sigma} A_{2sa}^{k'\sigma'} + \frac{1}{E_{2ta} - E_3 + \epsilon_k} \bar{A}_{2ta}^{k\sigma} A_{2ta}^{k'\sigma'} \right\},$$

(3)

and $\epsilon_k \to \epsilon_F$, with $\bar{A}_{ij} = \langle 3 \uparrow | d_{j\sigma}^\dagger | \nu \rangle$, $\bar{B}_{ij} = \langle \nu | d_{j\sigma}^\dagger | 3 \uparrow \rangle$, and $\beta_{ij}$ is the angular average of $\cos(k \cdot (\mathbf{R}_i - \mathbf{R}_j))$ with $\epsilon_k$ on the Fermi surface. For an isotropic two-dimensional (2D) band $\beta_{ij} = J_0(k_F R_{ij})$, where $J_0(x)$ is the zeroth order Bessel function and $k_F a \approx 0.6$. The corresponding 3D result is $\beta_{ij} = \sin(k_F R_{ij})/(k_F R_{ij})$, with $k_F a \approx 3.5$. However, free electrons with $\epsilon_k = \epsilon_F$ and small wave vector parallel to the surface (implying small $k \cdot (\mathbf{R}_i - \mathbf{R}_j)$) have a larger wave vector perpendicular to the surface. Naturally, one expects a larger extension of these states out of the surface and therefore a larger hybridization with the adatoms [8,10]. To simulate this effect I take $k_F a$ as a parameter smaller than or equal to 3.5 for the calculations in which bulk states are assumed to dominate the hybridization with the localized states.

In Fig. 1 I show the average exchange interaction $J$ for an isosceles trimer with $r_{23} = a$ and $r_{12} = r_{13} = l$, as $l$ is varied from $+\infty$ to $a$. I take $t_23 = t_{10}$ as the unit of energy. $E_d$ and $U$ were chosen to correspond to an electron-hole-symmetric situation for only one adatom. Taking surface states as the ES, and disregarding small oscillations coming from $J_0(x)$ at large argument, there is a moderate increase in $J$ as the Cr atom 1 approaches the dimer formed by Cr atoms 2 and 3, with a maximum near $l = 5a$. For smaller $l$, $J$ decreases monotonically until the equilateral shape is reached. The situation is qualitatively similar if the localized states are hybridized with bulk ES. The main difference is the larger value of $k_F$. As $k_F$ is increased, the maximum is shifted to smaller values of $l$ and larger values of $J$. For $k_F a = 3.5$, the average exchange always increases with decreasing $l$, except for the small initial oscillations, while for $k_F a = 0$, $J$ is a monotonically decreasing function [14].

To estimate the Kondo temperature for $k_F a = 1.6$...
(dashed line), I take a density of states per spin and site \( \rho = 0.15/\text{eV}, t_0 = V = 0.5 \text{ eV}, \) a band width \( D = 10^5 \text{ K} \) [20], and use the expression [21]

\[ T_K = D \sqrt{\rho J} \exp \left( \frac{-1}{\rho J} \right). \] (6)

This gives \( T_K = 8.3 \text{ K} \) for the single adatom \( l \to \infty \), \( T_K = 9.7 \text{ K} \) for the equilateral trimer, and a maximum \( T_K = 45 \text{ K} \) for \( l = 2.3a \). This behavior is roughly consistent with the experimental observations [11]. While \( T_K \) for the monomer and equilateral triangle are larger than the experimental bound \( T_K < 7 \), it is possible that taking into account more precisely the wave vector dependence of \( J_{kk'} \) improves the agreement. A scenario leading to a more drastic change in \( T_K \) is discussed below.

For \( l \to \infty \), the average exchange coincides with the well known result for a single adatom as expected [18]: \( J = 2V^2 U/\{(E_d + U)(-E_d)\} \). The variation of \( J \) as \( l \) decreases is the result of mainly two competing effects: for \( \beta_{12} = \beta_{13} \approx 0 \), where there are no coherence effects between the atoms, the relevant matrix elements [Eqs. (5)] increase, while for \( l = a \) and \( \beta_{ij} = 1 \), they cancel by symmetry. Specifically, if \( \beta_{12} = \beta_{13} \) is not too close to 1, the largest contribution to \( J \) comes from the virtual state \( |2sg\rangle \), the ground state of \( H_{Cr} \) in the subspace of two particles, which is a singlet even under the mirror plane of symmetry of the isosceles triangle \( m \) [22]. For \( l \to \infty \), only the \( A^+_{j\nu} \), \( B^+_{j\nu} \) with \( j = 1 \) are different from zero. As \( l \) decreases, the sums in Eqs. (5) increase due to the increasing contribution of \( A^+_{j\nu} \), \( B^+_{j\nu} \) for \( j = 2, 3 \). Also, the energy level of adatom 1 is pushed up towards the Fermi level due to its mixture with the bonding combination of adatoms 2 and 3 (the denominator \( E_{2sg} - E_3 - \epsilon_F \) decreases). All effects tend to increase \( J \).

However, there is a competing effect due to symmetry, as the compact equilateral shape is approached when \( k_F l \) becomes small. For \( l = a \), the Hamiltonian is invariant under the operations of the point group \( C_{3v} \). For \( k_F \to 0 \) \( (\beta_{ij} \to 1) \), the operator entering Eqs. (4) becomes \( \sum_i d^a_{i\nu} \), which is invariant under the point group operations. The state \( |2sg\rangle \) is also invariant, while for \( l \to a \), the ground state for three particles becomes fourfold degenerate with two spin doublets belonging to the two-dimensional representation \( E \) of \( C_{3v} \). The matrix element of \( \sum_i d^a_{i\nu} \) between any of these four states and \( |2sg\rangle \) vanishes by symmetry [23]. Therefore, the contribution of virtual states containing \( |2sg\rangle \), which is the most important to \( J \) when \( \beta_{ij} \approx 0 \), vanishes when \( \beta_{ij} \to 1 \). This explains the decrease of \( J \) in Fig. 1 as \( l \to a \) [14].

The ground state for three particles \( |3g\rangle \) is even under \( m \) for \( l > a \) and odd for \( l < a \). As a consequence of this jump in the symmetry of the ground state, \( J \) becomes much smaller for an isosceles triangle with one side longer than the other two, including the linear trimer as a limit. In particular, the contribution of \( |2sg\rangle \) is negligible for \( l < a \), since all matrix elements between even and odd states are very small. This agrees nicely with the fact that no FKA is observed for the linear trimer [11]. These symmetry arguments are independent of the approximation made in the averaging over wave vectors.

The SWT is valid when the matrix elements connecting the ground states with excited states \( (V_{kk'} A^+_{k\nu}, V_{kk'} B^+_{k\nu}) \) are smaller than the corresponding denominators. In addition, since I retained only the ground state of \( H_{Cr} \) in the three-particle sector, the effective matrix elements connecting different states in this subspace should be smaller than the corresponding energy difference. For reasonable values of \( U \), the eight states with one particle per site are well separated from those of higher energy. These eight states are degenerate if the separation between any two adatoms is large. However, in the situations of interest at least two adatoms interact, and then the spin quadruplet is well separated from the two spin doublets and can safely be neglected. Precisely at the equilateral shape, the two spin doublets are degenerate and our approach is invalid. However a very small distortion towards an isosceles shape is enough to recover the validity of the SWT. This is because the distortion splits the spin doublets even and odd under \( m \) and the matrix elements between any even and any odd state are very small (they vanish for \( k_F a \to 0 \)). For the parameters used above to estimate \( T_K \), a 1% change in the length of one side suffices.

As mentioned before, the difference \( E_{2sg} - E_3 + \epsilon_F \) decreases as \( l \) decreases from \( \infty \) to \( a \), but is always positive and significant for the parameters of Fig. 1. However, for \( E_d \) nearer to \( \epsilon_F \) (for example \( \epsilon_F - E_d < t_0 \) if \( U = 0 \)) there is a crossing point and the ground state of \( H_{Cr} \) in the equilateral trimer is the two-particle singlet \( |2sg\rangle \). As a consequence of the decrease in the corresponding denominator in \( J \), there is a dramatic increase in \( T_K \) for decreasing \( l \) near the crossing point, until the system enters an intermediate valence regime (where the SWT ceases to be valid) and for further decrease in \( l \) the singlet dominates the physics and there is no Kondo effect. The dependence of \( J \) on \( l \) in a situation like this, taking surface states as the ES is illustrated in Fig. 2. The crossing point is at \( a/l = 0.576 \). Taking \( \rho l^2/V = 0.04 \), the resulting Kondo temperature given by Eq. (6) is
$T_K = 0.33 \text{ K}$ for the single Cr adatom, has a relative maximum $T_K = 14 \text{ K}$ at $a/l = 0.2$, and after a minimum near $7K$, reaches $44$ K at $a/l = 0.47$ and $174$ K at $a/l = 0.50$. However, at this point the quantitative validity of the approach becomes questionable.

Fig. 3 shows a similar situation when bulk ES states dominate the hybridization with the localized ones. The crossing point is at $a/l = 0.75$. The behavior of $J$ is more monotonic than in the previous case. Taking again $\rho V^2/t_0 = 0.04$, one obtains $T_K = 0.05 \text{ K}$ for $l \rightarrow \infty$. For small $ak_F = 1.1$, $T_K$ reaches $51$ K at $a/l = 0.47$ and $106$ K at $a/l = 0.55$. For $ak_F = 3.5$, $T_K = 50$ K at $a/l = 0.52$ and $169$ K at $a/l = 0.55$, where the SWT is at the limit of its validity. Beyond the crossing point ($a/l > 0.75$), no Kondo effect takes place.

In summary, I have constructed an effective Kondo model for a Cr trimer on a Au(111) surface. For an isosceles trimer with one short side and two longer sides of length $l$ and reasonable parameters, the model provides two scenarios in which $T_K$ first increases with decreasing $l$ and then decreases as the equilateral shape is approached. In the first one, this decrease is due to symmetry effects and in the second one (which requires smaller $E_F - E_d$), the ground state of the isolated equilateral trimer is a singlet and no Kondo compensation of a localized spin takes place. For an isosceles trimer with one side longer than the other two, or a linear trimer, $T_K$ is very small due to the odd mirror symmetry of the ground state. While these results are qualitatively consistent with experiment [11], a quantitative agreement with all the different experimental observations seems to favor the second scenario, which is more robust under changes in the parameters, and that bulk states dominate the hybridization with the localized states of the Cr adatoms. Since in the second scenario the electronic occupation of each Cr atom in the compact equilateral trimer decreases by $\sim 1/3$, it is in principle possible that X-ray experiments [24] which are sensitive to the Cr valence can distinguish between the two scenarios.

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