

Ab Initio Explanation of Tunneling Line Shapes for the Kondo Impurity State

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ABSTRACT

We report an ab initio study of the Kondo states formed from a Co adatom on Cu(111) and Cu(100). The model consists of a CoCu_n cluster ($n = 5\text{--}19$) embedded in (111) and (100) Cu slabs. An embedding potential derived from density functional theory treats the interaction between the periodic crystal surroundings and the CoCu_n cluster, while strong electron correlations within CoCu_n are explicitly accounted for via configuration interaction (CI) methods. Analysis of the embedded CI wave function provides insight into the nature of the Kondo state, specifically into the influence of the crystal host on the Co d-electronic structure. We predict that different d-orbitals are preferentially singly occupied in Co on Cu(111) versus Cu(100) as a result of the different crystalline environment. We propose that these variations in the local d-electronic structure on Co, not accounted for in previous theories, are responsible for the drastically different Kondo resonance line shapes observed in scanning tunneling microscopy experiments on these two surfaces.

In the past decade, scanning tunneling microscopy (STM) experiments of magnetic adsorbates on metal surfaces have provided direct measurements of the many-body Kondo state.^{1–3} This is a strongly correlated, spin-polarized singlet formed from a localized magnetic moment embedded in a quasi-continuum of conduction electrons. It is long known to be responsible for the anomalous, low-temperature behavior of bulk, nonmagnetic metals containing small amounts of magnetic impurities.⁴ Following this initial work involving single magnetic atoms on metallic surfaces, a variety of Kondo-like systems have been explored. These include assemblies of magnetic atoms on carbon nanotubes⁵ and metal surfaces,^{6–9} schemes to tune the impurity–substrate coupling via the attachment of molecular ligands,^{10–12} and a magnetic quantum dot coupled to conducting leads.^{13,14} These atomic-scale structures can be regarded as prototypical building blocks for practical devices that rely on the manipulation of spin. Thus, many of the insights gained here are relevant to the goal of manufacturing new spintronics devices that exploit Kondo physics.

The Kondo state manifests in STM as a sharp resonance in the differential conductance dI/dV near the Fermi level ϵ_F , detectable up to lateral distances of $\sim 10\text{--}60$ Å from the adsorbate. The resonance energy width is related to the Kondo temperature T_K , where $k_B T_K$ is the characteristic energy scale associated with low-lying excitations of the Kondo state. A sizable body of STM data now exists for

magnetic adatoms on (111) and (100) metal surfaces which clearly show that the Kondo resonance line shape is sensitive to the atomic-scale details of the adatom and substrate,¹⁵ thus motivating a more careful study of the underlying electronic structure. The differences are particularly striking for Co on Cu(111) and Cu(100): in the (111) case, the resonance is a single dip, while in the (100) case, it appears as an asymmetric dip followed by a peak.¹⁶

Theoretical interpretations of the STM data have largely relied on phenomenological approaches, most of which are based on the single-impurity Anderson model.^{2,17–19} In these cases, the impurity and substrate are reduced to a single, discrete impurity level in a model band structure representing the substrate. While efforts along these lines have largely focused on the role of surface and bulk states,^{20,21} relatively less attention has been paid to the nature of the magnetic impurity itself. In the case of a Co adatom, previous theoretical work typically neglected the 5-fold degeneracy of the d-levels, and assumed only the $d_{3z^2-r^2}$ is relevant in the behavior of the Kondo state. In principle such details are naturally included in first-principles descriptions; however, approaches based solely on density functional theory (DFT) are limited by the available approximations for exchange correlation, which cannot account for the strong electron correlation effects responsible for Kondo behavior. The use of DFT to make predictions about the impurity structure is further complicated by the fact that DFT typically yields the wrong atomic ground state for first-row transition metals.²²

In this Letter, we report an ab initio characterization of the Kondo state formed from a single Co adatom on Cu(111) and Cu(100). This is done using an embedded configuration

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interaction (CI) approach, whose accuracy has been benchmarked in previous studies of the chemisorption of a carbon monoxide molecule on metal surfaces.^{23–25} Here, the CI explicitly includes the d-orbital structure of the Co, along with the strong correlations involving localized Co d-electrons and surrounding metal sp-electrons. The effects of the periodic crystal background are accounted for with DFT. No assumptions about the nature or strengths of particular interactions are made, only that the essential correlation effects are localized near the impurity. Our calculations reveal that the Co d-electron configuration and symmetry differ when adsorbed on the (111) versus (100) surface of Cu. In particular, the common assumption of a local moment residing on the Co $d_{3z^2-r^2}$ orbital does not always hold, which has significant implications for understanding the origins of the resulting Kondo resonance line shape.

First Principles Embedding Theory. We partition the system into a cluster region containing the adatom and a few (<20) neighboring substrate atoms (I), and a background region comprised of the remaining periodic slab (II).^{23,24,26} The total energy is expressed as $E_{\text{tot}}[\rho_{\text{tot}}] = E_{\text{I}}[\rho_{\text{I}}] + E_{\text{II}}[\rho_{\text{II}}] + E_{\text{int}}$, where the E_i ($i = \text{tot}, \text{I}, \text{II}$) represents (exact) energy functionals for the total system, cluster, and background, respectively, and E_{int} is the cluster-background interaction. The densities ρ_i ($i = \text{tot}, \text{I}, \text{II}$) are defined similarly, with $\rho_{\text{tot}} = \rho_{\text{I}} + \rho_{\text{II}}$.

Our key assumptions are that the relevant correlation effects are encapsulated within the embedded cluster and that a good representation for ρ_{II} is available (defined further below). With ρ_{II} held fixed, the minimization of E_{tot} can be recast into a problem consisting of a finite cluster embedded in an effective one-electron potential v_{emb} .^{23,24,26}

$$[\hat{H}_{\text{I}} + \sum_{j=1}^{N_{\text{I}}} v_{\text{emb}}(\mathbf{r}_j)] \Psi_{\text{I}} = E \Psi_{\text{I}} \quad (1)$$

where \hat{H}_{I} is the many-body Hamiltonian involving the cluster atoms, N_{I} is the number of electrons in the cluster, and Ψ_{I} is a wave function that yields the density ρ_{I} . The quantity v_{emb} approximates the effect of the periodic background on the cluster. A density functional model for v_{emb} is adopted, and has the form^{23,24,26}

$$v_{\text{emb}}(\mathbf{r}) \equiv \frac{\delta E_{\text{int}}}{\delta \rho_{\text{I}}(\mathbf{r})} \approx \frac{E_{\text{tot}}^{\text{DFT}}[\rho_{\text{tot}}]}{\delta \rho_{\text{tot}}(\mathbf{r})} - \frac{E_{\text{I}}^{\text{DFT}}[\rho_{\text{I}}]}{\delta \rho_{\text{I}}(\mathbf{r})} \quad (2)$$

where E_i^{DFT} ($i = \text{tot}, \text{I}$) is defined as usual in DFT

$$E_i^{\text{DFT}}[\rho_i] = T_s[\rho_i] + J[\rho_i] + E_{\text{xc}}[\rho_i] + \int d\mathbf{r} \rho_i(\mathbf{r}) v_{\text{ion}}^i(\mathbf{r}) \quad (3)$$

T_s , J , and E_{xc} are the kinetic, Hartree, and exchange-correlation energies, respectively, and v_{ion}^i is the electron-ion potential. We employ the Thomas–Fermi (1/9)–von Weizsäcker model²⁷ for T_s and the local density approximation (LDA)²⁸ for E_{xc} .

It can be seen from eq 2 that $v_{\text{emb}} = v_{\text{emb}}[\rho_{\text{tot}}, \rho_{\text{I}}]$; i.e., it depends on both ρ_{tot} and ρ_{I} . Thus, eq 1 must be solved self-consistently for v_{emb} and Ψ_{I} . Starting with an initial guess for the cluster density $\rho_{\text{I}}^{(0)}$, the potential v_{emb} is updated at each iteration i of the self-consistency cycle as $v_{\text{emb}}[\rho_{\text{I}}^{(i)} + \rho_{\text{II}}, \rho_{\text{I}}^{(i)}]$, where ρ_{II} is the frozen approximation for the

extended background. This updated v_{emb} then yields a new $\rho_{\text{I}}^{(i+1)}$, and the cycle is repeated until self-consistency.

Recasting as eq 1 allows for the inclusion of electron correlation via ab initio CI methods, while the effect of the extended background is accounted for via the periodic embedding potential v_{emb} . CI methods expand Ψ_{I} in a basis of Slater determinants (configurations), where the orbitals that constitute the Slater determinants are formed from a linear combination of Gaussian atomic orbitals (AOs). We employ here the complete active space self-consistent field (CASSCF) method,²⁹ which is a full CI expansion of all possible configurations within a chosen set of valence electrons and orbitals (the “active space”). Both CI expansion coefficients and AO coefficients are variationally optimized. Convergence of the CASSCF active space is established by a series of CASSCF calculations, where the size of the active space is systematically increased until no additional configurations with weights $|c_i|^2 \geq 0.01$ appear in the CASSCF wave function. In this manner, the CASSCF method is well-suited for describing the interaction between nearly degenerate configurations, particularly those arising from the various possible d-electron configurations of transition metals such as Co. Orbital hybridization is allowed for by the variation of AO coefficients.

Model and Numerical Details. Co adsorbs on the face-centered cubic (fcc) 3- and 4-fold hollow sites of Cu(111) and Cu(100), respectively. We adopt the notation $\text{CoCu}_n(111)$ or $\text{CoCu}_n(100)$ to denote a CoCu_n ($n = 5–19$) cluster embedded in Cu(111) or Cu(100). All clusters are embedded in a four-layer periodic slab, except $\text{CoCu}_{19}(111)$, whose larger size necessitates a six-layer slab. For $\text{CoCu}_n(111)$, a $n = 7$ cluster is formed from three Cu atoms from the top layer, three from the second, and one from the third. $n = 13$ has six top, six second, and one third layer Cu. $n = 19$ has three top, six second, seven third, and three fourth layer Cu. For $\text{CoCu}_n(100)$, the $n = 5$ cluster has four Cu atoms in the top layer and one in the second, directly below the Co. Four Cu neighbors in the second layer are added to form $n = 9$, and four top layer Cu are added for $n = 13$. $n = 17$ has 12 Cu in the top layer, and five in the second.

Our procedure follows that of refs 30 and 26; the difference here is in construction of the background density ρ_{II} , which is approximated as $\rho_{\text{II}} = \rho_{\text{clean}} - \rho_{\text{Cu}_n}$, where ρ_{clean} is the clean Cu slab (no adsorbate), and ρ_{Cu_n} is the Cu_n portion of the CoCu_n cluster. Each are obtained from separate plane-wave DFT calculations using the CASTEP code,³¹ the LDA for exchange-correlation,²⁸ Cu ultrasoft pseudopotentials especially constructed for the embedding,²⁶ and a plane-wave kinetic energy cutoff of $E_c = 1000$ eV.

A 1×1 primitive unit cell of the clean slab is first constructed by cleaving a bulk fcc structure with a lattice constant of $a_0 = 3.57$ Å, the equilibrium a_0 associated with our LDA Cu pseudopotential. A DFT-LDA calculation is done for this 1×1 cell, where integrations over \mathbf{k} are evaluated on a $16 \times 16 \times 1$ Monkhorst–Pack \mathbf{k} -point mesh over the irreducible Brillouin zone. The positions of the top two Cu layers are relaxed. For Cu(100), the distance between the top two layers decreases by 2% from bulk termination.

For Cu(111), the relaxation is <1%, so bulk-terminated positions are retained. ρ_{clean} is formed by replicating the primitive 1×1 density along both lateral directions, to give an 8×8 slab. ρ_{Cu_n} is evaluated in the same 8×8 lateral supercell via a separate DFT calculation, with Cu positions taken from the optimized clean slab structure. With both ρ_{clean} and ρ_{Cu_n} in the same supercell, the background density $\rho_{\text{II}} = \rho_{\text{clean}} - \rho_{\text{Cu}_n}$ is readily constructed.

The Co distance above a four-layer periodic slab, d_{Co} , is found from spin-polarized DFT calculations in a 3×3 lateral supercell, by holding the Cu positions at clean slab values and optimizing d_{Co} . This gives $d_{\text{Co}} = 1.79 \text{ \AA}$ for Co/Cu(111) and $d_{\text{Co}} = 1.51 \text{ \AA}$ for Co/Cu(100).

In the CI calculations, both Co and Cu core electrons are represented with effective core potentials (ECPs), and valence orbitals (3d and 4s) are expanded in an optimized Gaussian AO basis set.³² The CoCu₁₉(111) cluster is modeled differently due to its size: only the Cu 3d electrons of the three surface Cu atoms are treated explicitly, while the remaining subsurface Cu 3d electrons are subsumed into a large-core ECP.³³ The Cu 3d-shell is filled and so Cu 3d-orbitals are assumed doubly occupied in all configurations.

Results and Discussion. Results for small CoCu_{*n*}(111) clusters ($n = 3, 7$) are reported in refs 30 and 26. There, ground- and excited-state energies were computed via the multireference singles and doubles CI (MRSDCI) method, which incorporates dynamical correlation effects involving all valence sp- and Co d-electrons, beyond that provided by CASSCF. The Co d- and Cu sp-orbitals mix to form metal-metal bonds, and a singlet ground state was found for $n = 7$, consistent with interpretations of the Kondo resonance seen in STM experiments for Co on Cu(111). While the computational demands of MRSDCI renders it inapplicable to larger clusters, these earlier studies established that CASSCF yields results in qualitative agreement with MRSDCI.³⁰ In particular, CASSCF captures the essential near-degeneracies due to the different possible Co d-electron configurations, which is the main subject of interest here.

In this work, low-lying singlet, triplet, and quintet CASSCF wave functions are evaluated for all embedded CoCu_{*n*} clusters described above. The CASSCF wave functions generally consist of a few dominant configurations with weights $|c_i|^2 \geq 0.01$, and a number of nearly degenerate configurations with significantly smaller weights arising from excitations between sp-orbitals. Examples of this are given in Tables 1 and 2, which list the dominant CASSCF configurations and their associated orbital occupations for CoCu₁₉(111) and CoCu₁₇(100), the largest clusters studied. As noted earlier,³⁰ the large deviation from unity of the dominant configuration's weight is consistent with the strongly correlated, multiconfiguration nature of the Kondo state.

Convergence of the Co d-electron configuration is determined by monitoring the occupations of the five Co d-orbitals with respect to cluster size n . For CoCu_{*n*}(111), cluster sizes of $n \geq 7$ yield the converged occupations shown in Table 3. Similarly, for CoCu_{*n*}(100), the occupations converge at $n \geq 13$, to the values in Table 3. These occupations are independent of spin-coupling: all low-lying singlet, triplet,

Table 1. Open-Shell Orbital Occupancies of Dominant $|c_i|^2 \geq 0.01$ CASSCF Configurations for CoCu₁₉(111)^a

spatial configuration	weight $ c_i ^2$
singlet	
$(1e_x)^2 (1e_y)^1 (2e_x)^1 (2e_y)^1 (3e_x)^1$	0.44
$(1e_x)^1 (1e_y)^2 (2e_x)^2 (2e_y)^1$	0.02
triplet	
$(1e_x)^1 (1e_y)^2 (2e_x)^1 (2e_y)^1 (3e_x)^1$	0.37
$(1e_x)^2 (1e_y)^1 (2e_x)^1 (2e_y)^1 (3e_x)^1$	0.10
$(1e_x)^2 (1e_y)^2 (2e_x)^1 (2e_y)^1$	0.04
quintet	
$(1e_x)^2 (1e_y)^1 (2e_x)^1 (2e_y)^1 (3e_x)^1$	0.40
$(1e_x)^1 (1e_y)^2 (2e_x)^1 (2e_y)^1 (3e_x)^1$	0.09

^a The 1e and 3e orbitals are a linear combination of Co/Cu atomic sp-orbitals, while the 2e orbitals are a hybridization of doubly degenerate $(d_{x^2-y^2}, d_{xy})$ and (d_{xz}, d_{yz}) orbitals with Co/Cu atomic sp-orbitals.^{34,35}

Table 2. Open-Shell Orbital Occupancies of Dominant $(|c_i|^2 \geq 0.01)$ CASSCF Configurations for CoCu₁₇(100)^a

spatial configuration	weight $ c_i ^2$
singlet	
$(1b_1)^2 (1e_x)^2 (1e_y)^1 (1b_2)^1 (1a_1)^1 (3e_x)^1$	0.42
$(1e_x)^1 (1e_y)^2 (1b_2)^1 (1a_1)^1 (3e_x)^2 (3e_y)^1$	0.02
$(1b_1)^2 (1e_x)^2 (1b_2)^1 (1a_1)^1 (3e_x)^1 (3e_y)^1$	0.01
triplet	
$(1b_1)^2 (1e_x)^2 (1e_y)^2 (1b_2)^1 (1a_1)^1$	0.83
$(1e_x)^2 (1e_y)^2 (1b_2)^1 (1a_1)^1 (3e_x)^2$	0.03
quintet	
$(1b_1)^2 (1e_x)^2 (1e_y)^1 (1b_2)^1 (1a_1)^1 (3e_x)^1$	0.42
$(1e_x)^1 (1e_y)^2 (1b_2)^1 (1a_1)^1 (3e_x)^2 (3e_y)^1$	0.02
$(1b_1)^2 (1e_x)^2 (1b_2)^1 (1a_1)^1 (3e_x)^1 (3e_y)^1$	0.01

^a The $1b_2$ is the Co d_{xy} orbital, $1a_1$ is a hybridization of Co $d_{3z^2-r^2}$ and Co/Cu atomic sp-orbitals, and the remaining orbitals are linear combinations of Co/Cu atomic sp-orbitals.^{34,35}

Table 3. Cluster-size-converged Co *d*-orbital occupations from Mulliken population analyses of CoCu_{*n*}(111) ($n \geq 7$) and CoCu_{*n*}(100) ($n \geq 13$) CASSCF wavefunctions.^a

	$d_{x^2-y^2}$	d_{xy}	d_{xz}	d_{yz}	$d_{3z^2-r^2}$
Co/Cu(111)	1.6	1.6	1.4	1.4	2.0
Co/Cu(100)	1.9	1.1	2.0	2.0	1.0

^a Note that for Co/Cu(111), the $(d_{x^2-y^2}, d_{xy})$ and (d_{xz}, d_{yz}) are doubly degenerate, while for Co/Cu(100), the (d_{xz}, d_{yz}) are doubly degenerate. The total d-orbital occupation in both cases is $n_d = 8.0$.

and quintet states exhibit the same occupation. Our observations are consistent with Co in the local moment regime in the sense that excitations involving a change in Co d-electron configuration are much higher in energy than spin excitations of the surrounding metal sp-electrons. Different Co d-electron configurations occur on the (111) and (100) surfaces due to the different symmetries of the 3- and 4-fold adsorption sites. For Co on Cu(111), the 3-fold site splits the Co d-orbitals into two sets of doubly degenerate pairs with e symmetry $(d_{x^2-y^2}, d_{xy})$ and (d_{xz}, d_{yz}) and an a_1 ($d_{3z^2-r^2}$). The a_1 is doubly occupied, while hybridization of the e-orbitals leads to an average occupation of ~ 1.5 each. On the 4-fold hollow site of Cu(100), the Co d-orbitals are split into states with a_1 ($d_{3z^2-r^2}$), b_1 ($d_{x^2-y^2}$), b_2 (d_{xy}), and e (d_{xz}, d_{yz}) symmetry, where the a_1 and b_2 are singly occupied while the rest have double occupation.

The Co d-electron configurations predicted here have important implications for the interpretation of the STM

Kondo resonance line shapes seen for Co on Cu(111) and Cu(100). Typically, phenomenological descriptions for the Kondo resonance^{2,17-19} reduce the magnetic adsorbate and metallic substrate to an Anderson model, which consists of a single discrete impurity level embedded in a band of conduction states. The tunneling of electrons between the STM tip and the discrete impurity plus conduction states is analogous to a similar problem considered by Fano,³⁶ involving resonant electron scattering off a discrete, excited atomic level interacting with a continuum of ionization states. In the STM case, for energies near ϵ_F and temperatures $T < T_K$, the dI/dV spectrum has the form

$$\frac{dI}{dV} \propto \frac{(\epsilon' + q)^2}{1 + \epsilon'^2} \quad (4)$$

where $\epsilon' = (eV + \Delta\epsilon)/k_B T_K$, $\Delta\epsilon$ is a small constant shift in the energy, and V is the applied bias. Treating q , $\Delta\epsilon$, and T_K as fit parameters, eq 4 provides a good fit for the experimentally measured Kondo resonance line shape. Strikingly different values of q are obtained from fits to dI/dV spectra for Co on Cu(111) and Cu(100), where $q = 0.18$ and $q = 1.13$, respectively.¹⁶

A physical interpretation for the observed line shape can be made by considering the microscopic expression for the asymmetry parameter $q = A/B$, where

$$A = M_{at} + \sum_{\mathbf{k}} M_{kt} V_{ak} P \left(\frac{1}{\epsilon - \epsilon_{\mathbf{k}}} \right) \quad (5)$$

$$B = \pi \sum_{\mathbf{k}} M_{kt} V_{ak} \delta(\epsilon - \epsilon_{\mathbf{k}}) \quad (6)$$

and P denotes the principal value.¹⁸ V_{ak} is a hybridization matrix element for the discrete impurity level and a conduction level \mathbf{k} , while M_{at} and M_{kt} are tip-impurity and tip-conduction tunneling matrix elements, respectively. The numerator A represents a coupling between the tip and the impurity, either directly or indirectly via conduction states that are hybridized with the impurity, while the denominator B is a tip-substrate coupling. Thus, a small q suggests that the tip-impurity channel is weak compared to the tip-substrate channel, while a value of $q \sim 1$ indicates both pathways contribute. While various generalizations of this picture have been put forth,^{17,19} the basic features summarized here remain unchanged.

Our analysis goes beyond the single-impurity Anderson model to include the full set of d-orbitals on the Co. If we assume the tip states are dominated by s-waves, as is typically done in models of STM tunneling, by symmetry the coupling between the STM tip and Co is strongest to states with a_1 symmetry,³⁷ i.e., the $d_{3z^2-r^2} + sp$ hybrid orbital. Thus, this state is expected to make the dominant contribution to the tunneling current relative to the other d-orbitals. In Co/Cu(111), we find this state to be doubly occupied, and so an electron from the STM is excluded from tunneling into this state. Tunneling into substrate states is expected to dominate instead, thus explaining the small value for q derived from experiments. In Co/Cu(100), this a_1 state is singly occupied, and tunneling may proceed via this state. It has been pointed out that direct tunneling onto the Co $d_{3z^2-r^2}$ is not likely because d-orbitals are very localized around the atomic core,

and the STM line shapes are relatively insensitive to tip-impurity height.¹⁸ But we see that the $d_{3z^2-r^2}$ orbital is also hybridized to the neighboring Cu sp-orbitals, which are diffuse, and so indirect tunneling via this hybridized state is possible. Thus, both tip-impurity and tip-substrate pathways are possible, which explains the value of $q \sim 1$ seen in experiments.

In summary, we have applied an ab initio, many-body wave function theory to the Co on Cu(111) and Cu(100) Kondo states. The differing STM Kondo resonance line shapes can be understood as a consequence of the different Co d-electron configurations that arise due to interaction with the different local environments provided by the (111) and (100) surfaces of Cu. Low-lying spin excitations involve fluctuations in Co/Cu sp-states, while Co d-orbital occupations remain unchanged. Our work suggests that the adatom d-orbital structure plays a key role in the STM tunneling process, whose outcome can potentially be controlled by switching the adatom electronic state. One possible strategy is via the coordination of organic ligands, whose perturbation is expected to alter the Co electronic structure. Some efforts along this direction has already been demonstrated experimentally,¹⁰⁻¹² and further ab initio calculations of metal-ligand complexes on surfaces would provide valuable guidance in the design of novel Kondo-based devices.

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- (34) For spatial configurations with four open-shell electrons, there are two distinct singlet spin eigenfunctions, three triplet eigenfunctions, and one quintet eigenfunction; thus, the singlet and triplet weights shown are a sum over all configurations with identical orbital occupations, but different spin couplings.
- (35) Configurations related by symmetry, e.g., $(1e_x)^2 (1e_y)^1$ and $(1e_x)^1 (1e_y)^2$, have identical CI weights and are not shown.
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