

Effect of exchange interaction on the spin-polarized bound states on metal surfaces: *Ab initio* study

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The exchange interaction between magnetic adatoms on a metal surface is known to significantly influence the magnetic characteristics of the system. In present study we analyze the effect of the exchange interaction on the spin-dependent localization of the surface state. Our *ab initio* study of spin-polarized bound states arising at pairs of magnetic adatoms shows that both the position and the shape of the bound-state peak are strongly affected by the spin coupling in the system. Moreover we demonstrate that the spin splitting of the bound-state peak can serve as a suitable tool for probing the exchange coupling in the system. By the example of Co pairs on a Cu(111) surface at different interatomic separations, we demonstrate that the presence of the spin splitting of the bound-state peak is a signature of a ferromagnetic coupling while its absence signifies an antiferromagnetic configuration of the system spins. Also, the amount of splitting can be regarded as a measure of the interaction's strength.

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Recent advances in experimental techniques concerning fabrication and manipulation of nanostructures brought the designers of spin-based devices very close to the single atomic limit. Fortunately, modern preparation and analysis techniques, such as the scanning tunneling microscopy (STM),^{1,2} allow for simultaneous manipulation of adsorbed nanostructures with atomic precision and measurement of their structural and electronic properties. This has greatly shifted the focus of theoretical and experimental studies to the subject of electronic and magnetic properties of atomic-scale systems such as adatom or cluster groups on surfaces. One of the key roles in these systems is played by magnetic interaction between constituent parts. The origin of interactions involved can be very different: direct interaction due to orbitals overlapping, direct magnetic coupling, or indirect coupling mediated by substrate or host, e.g., Ruderman-Kittel-Kasuya-Yosida (RKKY). Thus, it is vital for spintronics to be able to tune these interactions. This realization brought about the appearance of several methods of controlling the exchange interaction in subnanoscale systems utilizing precise geometry control³ and quantum confinement of system's electrons within artificially assembled nanostructures.⁴

However, the task of directly measuring the magnetic interaction between single adatoms remains rather poorly explored. Until recently, a direct measurement of the magnetic interaction between individual atoms has been impossible. First steps in this field were made by Hirjibehedin *et al.*⁵ as they managed to experimentally probe the spin-exchange interaction in linear manganese chains through spin-flip experiments. Another method, based on the analysis of the Kondo resonance, was proposed by Chen *et al.*⁶ for cobalt dimers on a Au(111) surface, and successfully extended and improved by Wahl *et al.*⁷ for Co on Cu(111). Moreover only recently a state of the art experiment by Meier *et al.*⁸ allowed direct mapping of the exchange coupling of single adatoms to their magnetization curves. The first two methods utilize the fact that the exchange interaction has its roots in the spin-

dependent scattering of conduction electrons of the system by interacting impurities. Thus it is logical to assume that other scattering-related phenomena might as well be affected by the exchange interaction of impurities on the surface. It is well known that (111) surfaces of some noble metals produce an electronic surface state, which in its properties resemble a free two-dimensional electron gas (2DEG). The origin of the surface state is the trapping of electrons between the vacuum barrier and the band gap of the metal bulk. An impurity immersed in such a 2DEG presents an additional potential for the surface-state electrons. The Simon theorem predicts that any two-dimensional (2D) attractive potential should have a bound state.⁹ Truly enough, it has been shown^{10–12} that the localization of a 2D Shockley surface state on an impurity potential manifests itself as a split-off bound state just below the surface-state band bottom. Similar states have been observed at nonmagnetic Cu chains.¹³

In present paper we study the interaction of surface-state electrons with Co adatoms adsorbed on a Cu(111) surface. We resort to first-principles calculations to prove that the bound state is strongly affected by the spin coupling in the system and that the spin splitting of the bound state can be utilized to probe the exchange coupling between single magnetic adatoms. Our calculations for Co pairs on a Cu(111) surface at various separations reveal that the ferromagnetic (FM) alignment of adatom spins results in strong spin splitting of the bound-state peak while an antiferromagnetic (AFM) alignment causes the bound-state peak to become spin degenerate.

Our *ab initio* calculations were done in the framework of the density-functional theory in local spin-density approximation. The Korringa-Kohn-Rostoker (KKR) Green's-function method in atomic spheres approximation^{14,15} was used to obtain the solution of Kohn-Sham equations in terms of Green's functions. The KKR approach exploits the properties of the Green's function of the Kohn-Sham operator, in particular the fact that the electronic density can be expressed through the imaginary part of the energy-dependent

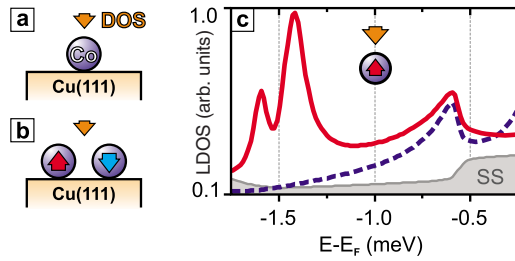


FIG. 1. (Color online) The geometry considered in calculations: (a) an adatom and (b) a dimer of Co adsorbed on a Cu(111) surface. The majority (red solid) and minority (blue dashed) LDOSs above (c) a single Co adatom. The gray-filled curve represents a surface state of a clean Cu(111) surface.

Green's function of the system. An arbitrary system can be regarded as the perturbation of an ideal one with a known Green's function. The Green's functions of those two systems can be linked through the Dyson equation.¹⁶ The bulk, surface, and impurity problems are consequently treated with a perturbative approach. At each stage a fully self-consistent Green's function is obtained, which is then used as a reference for the next step. We treat the surface as a 2D perturbation of an ideal crystal bulk with a slab of vacuum. Taking into account the translational symmetry of the surface geometry, the Green's functions are formulated in momentum space. Adatoms and addimers are considered as the perturbation of the clean surface. These calculations are performed in real space due to the reduction in the symmetry at the surface by the impurities. The local densities of states (LDOSs) presented in this work are calculated, in case of single noninteracting impurities, in vacuum space above the adatoms [Fig. 1(a)] or, in the case of two interacting adatoms, above the point halfway between them [Fig. 1(b)]. The point for LDOS calculation lies 2.62 Å above the surface.¹⁷ The choice of height is governed purely by the convenience of calculations and does not reflect any physical consideration.

To trace the effect of the exchange interaction on the bound state, we consider single Co adatoms and atomic pairs at different separations adsorbed on a Cu(111) surface. A clean Cu(111) surface has an intrinsic surface state of Shockley type. It manifests itself as an onset in the density of states at about -0.5 eV (below the Fermi energy). The density of states in vacuum above a clean Cu(111) surface is plotted in Fig. 1(c) as a gray curve with a filled area below. If we now adsorb a single Co adatom on the surface, the surface state becomes localized by the attractive potential of the impurity. The result of the LDOS calculation above a single Co adatom is presented in Fig. 1(c) for majority (red solid) and minority (blue dashed) electrons. The localization of the surface state has led to the formation of a narrow peak in both spin-up and spin-down channels at about -0.57 eV, which is just below the surface-state band bottom. Due to different scattering properties of the magnetic adatom for the spin-up and spin-down surface electrons, the bound state acquires a certain spin polarization. The position, the shape, and the spin splitting of the bound-state peak are in good agreement with the results obtained experimentally and theoretically by other groups.^{11,10,18,19} To be consequent, let us note that the majority peaks around -1.5 eV can be ascribed to the hy-

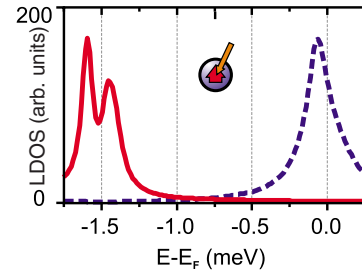


FIG. 2. (Color online) The majority (red solid) and minority (blue dashed) LDOSs at a single Co adatom. The peaks in both spin channels are mainly of a d character.

bridization of the surface electrons with the d orbitals of the Co adatom (the LDOS at the adatom is shown in Fig. 2).

If another Co atom is introduced to the vicinity of the first one, the manner in which each of the adatoms interacts with the surrounding electrons becomes affected by the interatomic interaction. In this paper we discuss only the magnetic exchange interaction between the adatoms, as it is the magnetic coupling that is of the greatest interests for potential spintronic applications. At small interatomic separations (<3 Å) the main source of exchange interaction between adatoms is the direct overlap of atomic orbitals. At larger distances the magnetic interaction is mainly mediated by conduction electrons of the substrate (RKKY mechanism). It was shown²⁰ that the RKKY nature of the interaction causes the exchange coupling to oscillate with a wavelength determined by the copper surface-state Fermi wave vector and decay quadratically with the distance. The fact that the system is reasonably simple to produce and control experimentally and assumes a wide range of exchange coupling strength values makes such a system an ideal testing ground for both theoretical and experimental exchange interaction probing methods.

First of all, let us consider two Co atoms adsorbed on fcc hollow sites along the $[\bar{1}10]$ direction of a Cu(111) surface, forming a compact dimer. The LDOS above the middle of the dimer is shown in Fig. 3 for a (a) FM and an (b) antiferromagnetic AFM alignment of spins. The energetically stable configuration is the FM one. The total-energy calculations yield an exchange coupling energy of -432 meV. Let us analyze the origin of various peaks in the LDOS. If we con-

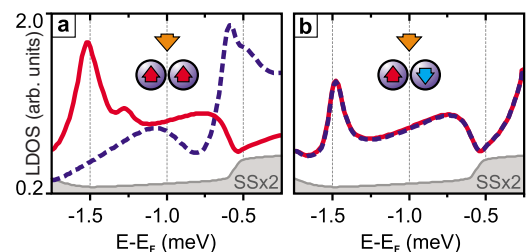


FIG. 3. (Color online) The majority (red solid) and minority (blue dashed) LDOSs above the middle of a compact Co dimer ($d=2.55$ Å), aligned along the $[\bar{1}10]$ direction of a Cu(111) surface, in (a) ferromagnetic and (b) antiferromagnetic configurations. The gray curve shows the surface state above a clean Cu(111) surface. It has been scaled by a factor of 2 for clarity.

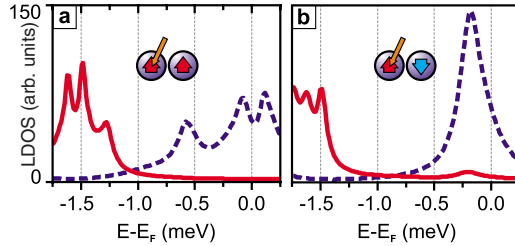


FIG. 4. (Color online) The majority (red solid) and minority (blue dashed) LDOSs at one of the atoms in a compact Co dimer ($d=2.55$ Å), aligned along the $[\bar{1}10]$ direction of a Cu(111) surface, in (a) ferromagnetic and (b) antiferromagnetic configurations. The peaks in the LDOS are mainly of the d character.

consider the LDOS at one of the atoms of the dimer (Fig. 4) in (a) FM and (b) AFM configurations, it immediately becomes evident that majority peaks around -1.5 eV and minority peaks around the surface-state band bottom (-0.5 eV) in the FM case are of atomic origin, i.e., arise from the hybridization of s surface electrons with majority and minority d states of Co, respectively. The remaining peaks (around -1.1 eV for minority and -0.8 eV for majority electrons) stem from the formation of the bound state. If we consider the position of the bound-state peaks it can be seen that the potential of the FM dimer has caused the bound state to acquire a larger splitting than in the case of a single adatom and become broadened. At the same time the LDOS for an AFM configuration displays no spin splitting at all.

This phenomenon can be easily understood if we consider the system in the framework of a two-state spin model. According to this model, one should expect that the interatomic interaction will cause localized electronic states to become split into a bonding-antibonding doublet in both the spin-up and the spin-down channels. However, the intrinsic width of the bound-state peak does not allow us to resolve the split resonances and thus we only observe a broadening of the localization peak. Moreover, the spin degeneracy in the AFM case is also a logical consequence of the theory. A similar idea and explanation were proposed for impurities on metal surfaces²¹ and in semiconductors,²² and have been experimentally proven to be quite feasible.²³

Another way to understand the results of the calculations is to consider the dimer as a single-scattering entity with a net spin being the sum of individual atom's spins. Then the AFM dimer can be regarded as a nonmagnetic scattering entity which immediately explains the spin degeneracy of the bound state. It also explains the increased spin splitting of the bound state arising at a FM dimer as compared to a bound state above a single adatom, as the net spin moment of the dimer is about twice the moment of a single magnetic impurity. Another thing that has to be mentioned in the context of a compact magnetic dimer is that the coupling in this case is governed by the direct overlap of the atomic wave functions; thus our reasoning might be slightly impaired by the fact that some magnetic dimers are known to have a noncollinear ground state (GS),^{24,25} in which case the two-state model for atomic spins is no longer applicable. However this does not hold for larger separations and therefore does not affect the reasoning in general.

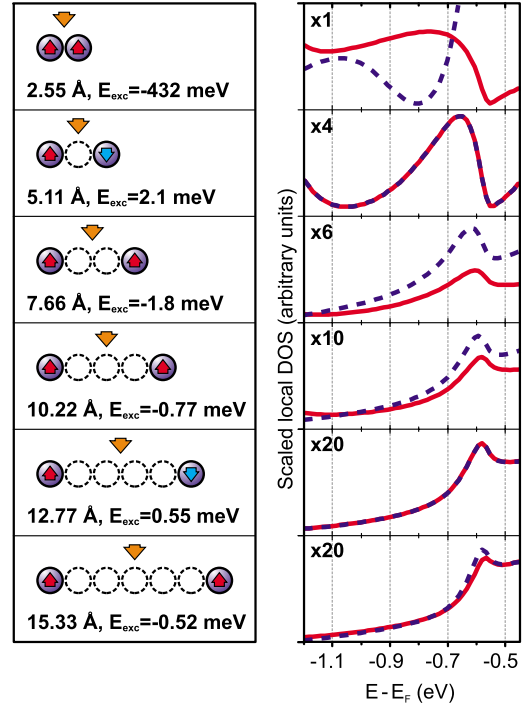


FIG. 5. (Color online) The majority (red solid) and minority (blue dashed) LDOSs above the middle of Co dimers at different separations (right panel), and the corresponding configurations, interatomic separations, and exchange coupling energies (left panel). LDOSs have been scaled for clarity. The scaling factors are given near each curve.

Let us now trace the changes in the surface-state localization as we gradually increase the distance between the Co adatoms. For each of the interatomic separations ranging from 2.55 to 15.33 Å, we determined the system ground state and the corresponding exchange coupling energy (left panel of Fig. 5). Then we calculated the LDOS above a point midway between the adatoms (right panel of Fig. 5) for the system in its ground state. As was already mentioned, the ground state for a compact dimer is a FM one. At the second-nearest-neighbor separation the Co pair in the ground state displays an AFM alignment of spins. The corresponding LDOS shows, as expected, no spin splitting. The width of the bound-state peak is decreased and its maximum is shifted to higher energies. At 7.66 Å separation (third nearest neighbors), the spin polarization of the ground-state LDOS is recovered and the corresponding spin coupling is a FM one. Both peaks are positioned at higher (with respect to the second-nearest-neighbor) energies. By further increasing the separation, we acquire a sequence of LDOSs and exchange coupling energies. As in the first three cases, it can be clearly seen that for all configurations with an AFM ground state the bound state is spin degenerate while for FM configurations it displays a splitting that decreases with increasing atom-atom separation. Thus the spin splitting of the bound state can serve as an indicator of the exchange coupling sign, being zero for antiferromagnetic alignment of spins and nonzero for the ferromagnetic one.

To get a grasp on the quantitative dependence of the bound-state peak position on the exchange coupling strength,

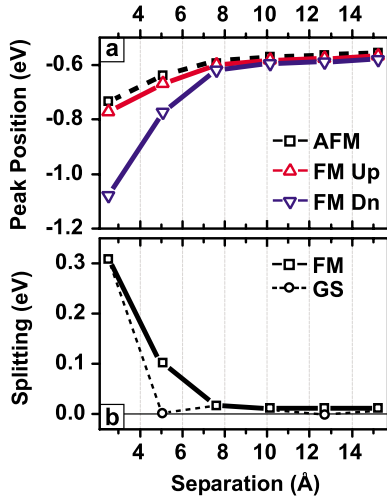


FIG. 6. (Color online) (a) The position of the bound state of Co dimers as a function of the interatomic separation for antiferromagnetic (dashed line, squares) and ferromagnetic (spin-up—solid red curve with triangles pointing up, spin-down—solid blue, triangles pointing down) configurations. (b) The amount of spin splitting of the bound state above a ferromagnetically coupled dimer (solid curve, squares) and a dimer in the GS configuration (dashed, circles) versus the interatomic distance.

we present the bound-state energies in Fig. 6(a) as a function of the distance between Co adatoms. The black-dashed curve shows the position of the bound state for AFM aligned dimers. With increasing interaction at smaller separations, the peak gets shifted to lower energies. In the case of a ferromagnetic configuration, the spin-up bound state (solid red curve with triangles pointing up) displays a similar behavior. However, the spin-down bound state (solid blue with triangles pointing down) occupies a lower energy at all interatomic distances. Moreover, the amount of splitting also increases with the interaction strength. The values of the splitting for the ferromagnetic configuration are given in Fig. 6(b) by a solid curve and square markers. The dashed curve represents the spin splitting in the ground-state configuration. The shift of the bound-state peak position (with respect to the position of the bound state above a single adatom) shows a monotonous decrease with increasing interatomic separation. This is valid for both FM and AFM configurations. However, in absence of a reference point the position of the localization peak alone cannot be regarded as a reliable measure of the exchange coupling. The spin splitting of the bound states provides a more reliable source of information. One could expect that the splitting amount would decay with interatomic distance, following a power law, as is usual for values describing conduction-electrons mediated processes; however, the investigated distances are not large enough and the amount of splitting is too small to make any conclusive statement. Still, it is clear that both the position of the bound state and the amount of its splitting provide a valuable source of information about the magnetic exchange interaction between single adatoms on a surface.

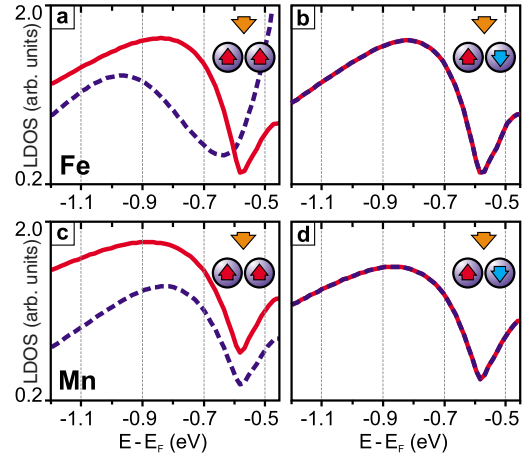


FIG. 7. (Color online) The majority (red solid) and minority (blue dashed) LDOSs above the middle of compact [(a) and (b)] Fe and [(c) and (d)] Mn dimers ($d=2.55$ Å), aligned along the $[\bar{1}10]$ direction of a Cu(111) surface, in [(a) and (c)] ferromagnetic and [(b) and (d)] antiferromagnetic configurations.

The application of this approach is by no means restricted to particular adatom species. Our calculations show that the bound-state peak demonstrates the same behavior for most of $3d$ adatoms. For example, LDOS above the middle of compact Fe and Mn dimers is shown in Fig. 7. We also assume that this approach can be generally applied to any surface possessing a surface state and any kind of magnetic dimers.

Another aspect worth mentioning is the stability of the approach with respect to the location of the point of measurements/calculation, as this might be relevant for its experimental application. The deviation from the axes of symmetry of the dimer causes the LDOS of an AFM configuration to start losing the spin degeneracy. However, due to the s character of the localized electrons, the susceptibility of the LDOS to the symmetry breaking is only moderate in the AFM case and hardly noticeable in the FM case. Therefore, at small and intermediate separations, which are the relevant ones for technological applications, the proposed approach should be stable against small variations in the point of measurement and thus retain its validity.

In conclusion, we have shown that the localization of the surface state is strongly affected by the interaction of atomic spins and can possibly be utilized to determine the exchange coupling between single impurities adsorbed on metallic surfaces. The presence (or absence) of a spin splitting of the bound state indicates a ferromagnetic (respectively, antiferromagnetic) alignment of spins in the system. Moreover, the amount of splitting can be regarded as an indicator of the exchange coupling's strength. This approach may provide suitable means of exchange coupling probing at small and intermediate separations for future spintronic applications.

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