Quantum confinement on nanoislands as a tool for tailoring exchange interaction: An *ab initio* study

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We explore the influence of the quantum confinement of surface electrons by nanoscale paramagnetic islands on the exchange interaction between single adatoms adsorbed on top of the structure. We demonstrate that it is possible to enhance, reduce, or even reverse the exchange coupling at various adatom-adatom separations by deliberate choice of the island's size.

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I. INTRODUCTION

Throughout the evolution of nanoscience and nanotechnology there has hardly been a more elegant and yet efficient tool for surface studies and engineering than the surface-state electrons.[1] Surface states of a Shockley type are known to exist as a quasi-two-dimensional (quasi-2D) nearly free-electron gas at (111) surfaces of noble metals[2] trapped between the vacuum barrier and the inverted *L* gap of a metal bulk band. The scattering of surface-state electrons at point defects,[3,4] single adsorbates,[5,6] and extended structures[7–10] leads, due to high correlation and the intrinsic two dimensionality of the surface state, to the formation of interference patterns which manifest themselves as standing waves in the local density of electronic states (LDOS). These standing waves can be detected by various surface sensitive techniques such as the scanning tunneling microscopy/spectroscopy (STM/STS). Standing LDOS waves can induce palpable changes in adsorption and activation energies of surface impurities and are the cause of an indirect long-range interaction between them.[11–17] Recently it was realized that by deliberate arrangement of atomic scatterers[18,19] one can confine surface-state electrons to close geometries thus precisely tailoring their interference and consequently the effect they have on atomic motion and interatomic interaction.[20,21] With recent advances in experimental techniques allowing for a direct probing of the exchange interaction[22–24] a question naturally arose, whether it might be possible to utilize the quantum confinement to control the spin arrangement of single adatoms and nanoscale units. Theoretical investigations[25] have shown that, for example, quantum corrals indeed have a profound effect on the indirect magnetic exchange interaction between single adatoms adsorbed within. However, assembling atomic structures in an atom-by-atom fashion is still a rather taxing task. Fortunately, there exist natural or self-assembling structures which can also be utilized for surface electrons confinement. For instance, it is well known that at certain conditions an epitaxial growth of Ag on Ag(111) (Ref. 26) and Cu on Cu(111) (Ref. 27) results in the formation of hexagonal islands and vacancy craters. A quantitative study of the quantum confinement of surface electrons on nanoscale Ag islands on Ag(111) has been carried out by means of an STM/STS by Li *et al.*[28,29] These studies have confirmed that the confinement can be

observed at all island sizes down to the smallest ones. It has also been proposed[28,29] that an analogous effect should exist on Cu(111) and Au(111). True enough the confinement in hexagonal craters (vacancy islands) has been recently observed in an STM experiment on Cu(111) (Refs. 30 and 31) and the spin-dependent quantum confinement has been extensively studied on Co/Cu(111) nanoislands.[20,32]

In the present paper we discuss the possibility to utilize the quantum confinement on islands to tailor the exchange interaction of single adatoms adsorbed on top of them. Our *ab initio* calculations indicate that by deliberate variation of the island size it is possible to enhance, reduce, or even reverse the exchange coupling between adatoms adsorbed on top of the island at intermediate separations (Fig. 1). Moreover, by choosing different alignments for the adsorbates one can get yet another tool for exchange coupling adjustment.

II. CALCULATIONAL DETAILS

In our calculations we utilize the Korringa-Kohn-Rostoker (KKR) Green's function method in atomic spheres approximation.[33,34] This method is a implementation of the density-functional theory in local spin-density approximation. The KKR approach exploits the properties of the Green's function of the Kohn-Sham operator, particularly, the possibility to express the electronic density through the imaginary part of the energy-dependent 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.[35] We treat a 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 momen-
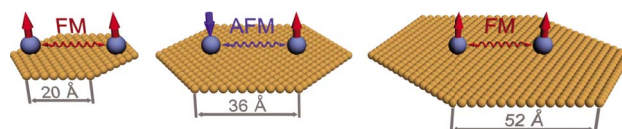

FIG. 1. (Color online) System setup used in our calculations to demonstrate the possibility of tailoring the exchange coupling between single adatoms adsorbed on islands by adjusting the island's size. The separation of adatoms remains constant.
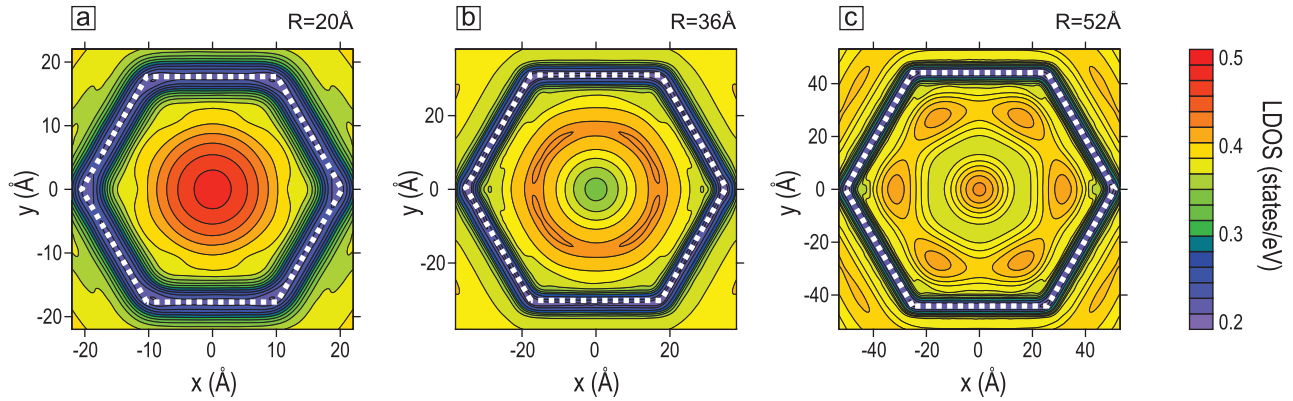
FIG. 2. (Color) LDOS distribution on islands with (a) $R=20$, (b) 36, and (c) 52 Å.

tum space. Adatoms and chains are considered as the perturbation of the clean surface. These calculations are performed in configurational space.

It has been shown[30] that KKR is a perfect tool for describing electronic confinement effects. Furthermore, exchange energy calculations are carried out according to the force theorem[36,37] from the single-particle energies, which allows one to resolve small energy differences with high accuracy.[38]

III. RESULTS AND DISCUSSION

As a model system for our studies we have chosen pairs of Co atoms adsorbed on top of hexagonal Cu islands of various sizes residing on a Cu(111) surface. The choice was governed mainly by the fact that such a system is relatively easy to produce experimentally yet represents a good model for a system of magnetic adatoms adsorbed on (111) surfaces of noble metals, which increases the generality of attained conclusions. To study the influence of the islands size on the electron confinement and the exchange coupling of adsorbed Co atoms we have selected hexagonal islands with circumscribed circle radii of 20, 36, and 52 Å (side lengths of 8, 14, and 20 Å atoms, respectively). To investigate the quantum confinement induced by islands we calculated the LDOS in vacuum some 2 Å above clean Cu islands.[39] The result is shown in Figs. 2(a)–2(c) for 20, 36, and 52 Å islands, respectively. The confining factor for the electrons in case of an island is the vacuum barrier existing at its boundaries. Thus the confinement region inherits the shape of the island's boundary and an electron confined in it behaves like a particle in a hexagonal box which clarifies the LDOS distributions shown in Figs. 2(a)–2(c).[28,29] Those distributions closely resemble the first three eigenmodes of a particle with a wavelength of about 30 Å which corresponds to the Fermi wavelength of Cu surface-state electrons. The first and the third distributions display a density maximum in the center of the hexagon with an additional maximum at the boundary on the 52 Å island. The second mode has its high-density region in the form of a ring with a diameter of about 30–35 Å and depletion zones both at the center and at the boundaries. The confinement causes the 20 Å island to acquire the highest (among the three) absolute local density of electronic states at the center while the LDOS map of the

52 Å island displays, as can be expected, the most profound hexagonal features. Similar LDOS distributions have been observed in hexagonal vacancy holes on Cu(111) (Ref. 30) and comprehensively analyzed in Ref. 31.

Considering that surface electrons act as mediators of the indirect exchange interaction it is most likely that a change in the LDOS up to 30% (0.5 st/eV in the center of the 20 Å island versus 0.35 st/eV on the 35 Å one) will lead to a significant modulation of the exchange coupling of magnetic atoms adsorbed on top. However, it should be noted here that besides the intrinsic electron-density redistribution the coupling constant is effectively determined by the phase relation of surface-state electrons scattered at both impurities which is in turn profoundly affected by the introduction of reflective vacuum barriers at the boundary of the island. By changing the island's size we alter both the intrinsic density of surface-state electrons and the scattering geometry. However, although the results of *ab initio* calculations incorporate both effects, it is virtually impossible to separate those two contributions.

To study the cumulative impact of the quantum confinement of surface electrons on the exchange interaction of magnetic atoms adsorbed on top of an island we have calculated the exchange coupling energies between single Co atoms residing on hexagonal Cu islands of the three above-
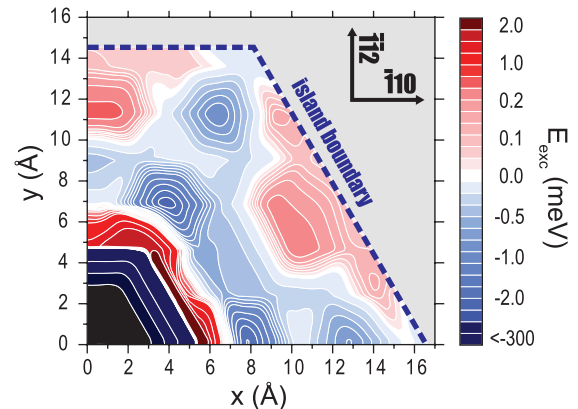

FIG. 3. (Color) A map of the exchange interaction energy of two Co adatoms adsorbed on a hexagonal Cu island of 20 Å in radius, given that one of the adatoms is residing in the island's center.
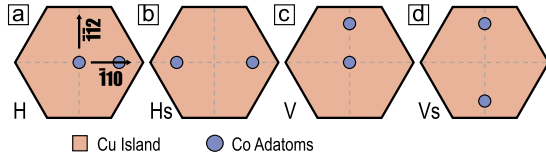
FIG. 4. (Color online) A scheme of principal arrangements of Co adatoms on an island chosen for investigation: (a) horizontal (h), (b) horizontal symmetric (Hs), (c) vertical (V), and (d) vertical symmetric (Vs).

mentioned sizes. In regard of the fact that the placement of two adatoms on a nanometer-scale island allows for a vast amount of variants let us consider first one of the most logical choices, namely, the case when one of the adatoms is placed in the center of the island and the other occupies one of the remaining adsorption sites. The resulting exchange energy landscape $E_{exc}(x,y) = E_{exc}(x_1 = 0, \ y_1 = 0, \ x_2 = x, \ y_2 = y)$ [where (x_1, y_1) and (x_2, y_2) are the in-plane coordinates of the first and the second Co adatoms] for the 20 Å island is given in Fig. 3. It must be noted that the coordinate zero does not precisely coincide with the geometrical center of the island but rather with an adsorption site closest to it which is situated some 1.5 Å away. It can be seen that starting from intermediate separations of ∼8 Å the map exhibits two principal directions that differ significantly along the $[\bar{1}10]$ and the $[\bar{1}\bar{1}2]$ vectors of the surface. Those directions are dictated

by the sixfold symmetry of the islands. Most intermediate directions reveal an exchange behavior closely resembling that along one of the principal directions. Relying on this fact we have chosen to limit our investigations to four main arrangements aligned along those two main directions. For each direction the two adatoms were either aligned symmetrically with respect to the center of the hexagon or one of them was placed at the center and the other at various separations along the respective direction. A sketch of all four configurations is given in Fig. 4. For ease of notation let us designate those configurations as "horizontal" (H), "horizontal symmetric" (Hs), "vertical" (V), and "vertical symmetric" (Vs) [Figs. 4(a)–4(d), respectively].

Let us now take a closer look at how the quantum confinement on islands influences the exchange interaction. Figure 5(a) shows the exchange energies of two Co adatoms adsorbed in an "H" (see Fig. 4) configuration at various separations as a function of the island's size R_{island}. For comparison exchange energies of the same adatoms at the same separation on a clean Cu(111) surface are given as the last point of each curve marked on the R_{island} axis by ∞. The figure indicates that at smaller separations of 7.6 Å (black squares) the exchange energy is gradually reduced [increasing the ferromagnetic (FM) coupling] with increasing island's size in the range of 20%–25% of the clean surface value. At intermediate separations of 10.2 and 12.8 Å [red (dark gray) circles and blue (gray) triangles pointing up, respectively] the dependence becomes irregular in its behavior allowing either for a switching (at 10.2 Å) or for a 20% increase (at
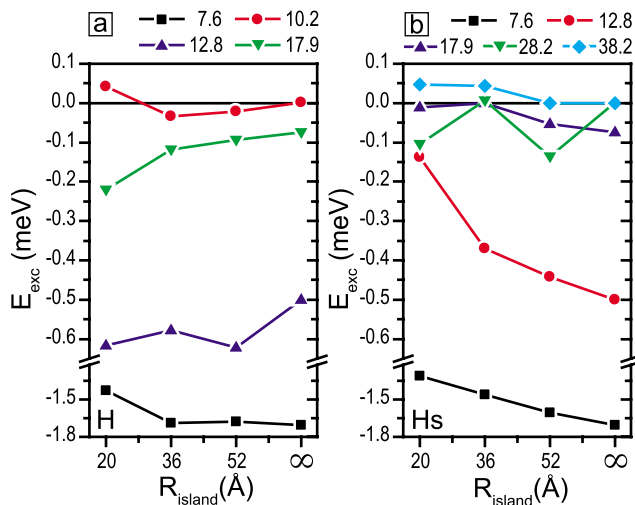

FIG. 5. (Color online) (a) Exchange coupling energies of two Co adatoms aligned according to configuration H (see Fig. 4) at separations of 7.6 Å (black squares), 10.2 Å [red (dark gray) circles], 12.8 Å [blue (gray) triangles pointing up], and 17.9 Å [green (light gray) triangles pointing down] as a function of the island's size R_{island}. (b) Exchange coupling energies of two Co adatoms aligned according to configuration Hs (see Fig. 4) at separations of 7.6 Å (black squares), 12.8 Å [red (dark gray) circles], 17.9 Å [blue (gray) triangles pointing up], 28.2 Å [green (light gray) triangles pointing down], and 38.2 Å [cyan (light gray) diamonds] as a function of the island's size. In both cases corresponding exchange energy values on a clean surface are given as a last point of each curve (denoted on the horizontal axis as ∞). Connecting lines are only there to guide the eyes.
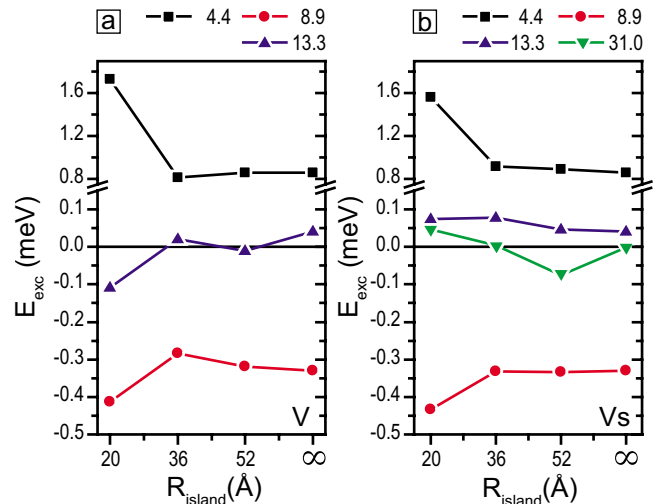

FIG. 6. (Color online) (a) Exchange coupling energies of two Co adatoms aligned according to configuration V (see Fig. 4) at separations of 4.4 Å (black squares), 8.9 Å [red (dark gray) circles], and 13.3 Å [blue (gray) triangles pointing up] as a function of the island's size R_{island}. (b) Exchange coupling energies of two Co adatoms aligned according to configuration Vs (see Fig. 4) at separations of 4.4 Å (black squares), 8.9 Å [red (dark gray) circles], 13.3 Å [blue (gray) triangles pointing up], and 28.2 Å [green (light gray) triangles pointing down] as a function of the island's size. In both cases corresponding exchange energy values on a clean surface are given as a last point of each curve (denoted on the horizontal axis as ∞). Connecting lines are meant as a guidance for the eyes only.

12.8 Å) in the exchange coupling between the adsorbates. At larger separations of 17.9 Å [green (light gray) triangles pointing down] the quantum confinement allows one to increase the FM coupling energy to up to twice its value on a clean surface. Similar exchange dependencies for the "Hs" configuration are presented in Fig. 5(b). Here as well, at small and intermediate separations of 7.6 Å (black squares), 12.8 Å [red (dark gray) circles], and 17.9 Å [blue (gray) triangles pointing up] the exchange energy is reduced by the confinement decreasing the coupling. But an even more significant effect can be observed at large separations of 28.2 and 38.4 Å [green (light gray) triangles pointing down and cyan (light gray) diamonds, respectively]. At a clean surface the exchange coupling at such separations is negligibly small. The quantum confinement on an island, however, allows one through reflection and focusing of scattered electrons by the island's boundaries to restore the coupling to values reaching up to over 100 μeV.

To generalize the picture even further let us take a look at both the "V" and "Vs" configurations. The exchange coupling dependencies for those configurations are presented in Figs. 6(a) and 6(b), respectively. Though different values of interatomic separations superimposed by the fcc lattice do not allow us to make a one-to-one comparison with H and Hs cases the dependencies show a rather similar behavior and tendencies. Once again at small separation a deliberate choice of the island size can allow us to either reduce or increase the interatomic coupling between the adsorbates. At intermediate separations we yet again have the possibility to

switch the exchange coupling by adjusting the island size. And at larger separations of about 30 Å the initially small coupling at a clean surface can be restored to palpable values.

IV. CONCLUSIONS

In conclusion, it might be noted that the quantum confinement of surface electrons to nanoislands is a suitable tool for tailoring the exchange interaction of magnetic adsorbates. In some systems [for instance, Cu/Cu(111) or Ag/Ag(111)] such islands can be relatively easily obtained by epitaxial growth and their size distribution can be controlled by growth conditions. The dependence of the surface electron-density distribution and the phase relations of scattered electrons on the island's size makes the latter a convenient adjustment parameter. Besides the island size, the alignment of magnetic adsorbates with respect to the island has a notable effect on the interatomic exchange interaction and thus can be varied to achieve a desired effect. This fact might make the quantum confinement on islands a good candidate for future spintronic applications.

ACKNOWLEDGMENT

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[39] To produce LDOS maps the integrated density of electronic states at the Fermi energy in each atomic sphere of the first vacuum layer above the island has been calculated. For a clearer picture the values have then been interpolated to produce the $\eta = \eta(x, y)$ (where x and y are the in-plane coordinates and η is the local density of states) contour map shown in Figs. 2(a)–2(c).