Long-range electronic interactions between adatoms on transition metal surfaces

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Abstract

Ab initio calculations of surface-state mediated interactions between Cu adatoms on transition metal surfaces are presented. We concentrate on Co/Cu(111) and Co(0001) substrates and compare results with our calculations for Cu(111). Our studies show that surface states of Co/Cu(111) and Co(0001) are spin-polarized. We reveal that long-range interactions between adatoms are mainly determined by sp-majority states. In contrast to Cu(111) and Co/Cu(111), the interaction between adatoms on Co(0001) is strongly suppressed at large adsorbate separations.

Key words: Ab initio calculations, spin-polarized surface states, long-range interactions

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In the last few years there has been a renewed interest in the study of indirect adsorbate interactions on metal surfaces predicted by Lau and Kohn in 1978[1]. This is at least in part due to the possibility to probe directly such interactions by scanning tunnelling microscopy (STM). A low temperature STM has allowed to resolve adsorbate interactions up to 80 Å[2,3]. It has been shown that oscillations of the electron density around adsorbates in a two-dimensional (2D) electron system can lead to a long-range, oscillatory, Friedel-type adsorbate-adsorbate interaction which decays as $1/d^2$. The required 2D nearly free electron gas could be realized in Shockley type surface states of metal surfaces. For example, surface-state electrons on the (111) surfaces of noble metals form a 2D nearly free electron gas. Several theoretical investigations have demonstrated that despite the fact that indirect adsorbate interactions are small (a few meV), they can significantly influence the growth of nanostructures[4,5,6].

Very recent STM experiments and ab initio calculations have revealed that surface states of transition metal nanostructures can be spin-polarized[7,8]. In particular, it has been shown that the electronic states of fcc Co monolayers and Co islands on Cu(111) are spin-polarized. Similar results have been reported for surface states of hcp Co(0001)[9]. In this paper, we present the first ab initio calculations of adsorbate-adsorbate interactions on transition metal surfaces. We concentrate on the interaction between Cu adatoms on the fcc Co/Cu(111) and the hcp Co(0001) substrates. Results are compared with the interaction on Cu(111). We demonstrate that the substrate-mediated interactions on magnetic substrates are mainly determined by $sp$-majority states. Our results show that adsorbate interactions on Co/Cu(111) are long-ranged and oscillatory. However, for Co(0001) we find that the substrate-mediated interactions are strongly suppressed at large distances.

Our calculations are based on the density functional theory and multiple-scattering approach using the Korringa-Kohn-Rostoker Green’s function method [6,7,10]. We treat the surface as an infinite two-dimensional perturbation of the bulk. Taking into account the 2D periodicity of the ideal surface, we calculate the structural Green’s function by solving a Dyson equation self-consistently. The consideration of adsorbate atoms on the surface destroys the translation symmetry. Therefore the Green’s function of the adsorbate adatom on the surface is calculated in a real space formulation. The structural Green’s function of the ideal surface in real space representation is then used as the reference Green’s function for the calculation of the adatom-surface system. Details of the method and its first applications for calculations of surface-state electrons and adsorbate-adsorbate interactions can be found in our previous work[6,7,10]. Calculations for the long-range interactions have been performed for the relaxed and unrelaxed positions of adatoms. However, we have found that the substrate-mediated interactions at large distances are essentially unmodified by the inclusion of the relaxation.
First, we present the results for the interaction between Cu adatoms on Cu(111). Our calculation for the Cu(111) surface gives a surface-state Fermi wavelength $\lambda_F = 29 \, \text{Å}$ and a surface-state band edge at $E_0 = -0.5 \, \text{eV}$ below the Fermi level. Due to the long Fermi-wavelength the confinement property of the Cu adatom should exist for large distances around the Cu adsorbate. The scattering of surface-state electrons by Cu adatoms leads to quantum interference patterns and to the long-range interactions between the two Cu adatoms[6]. Our calculations for the interaction energy between Cu adatoms on Cu(111) are presented in Fig.1.

![Fig. 1. Calculated interaction energies between two Cu adatoms on Cu(111). Inset shows the long-range oscillatory interaction at large distances.](image)

These results show that the interaction energy is oscillatory with a period of about 15 Å. The envelope of the magnitude decays as $1/d^2$ in agreement with the prediction of Lau and Kohn[1].

In recent STM experiments on large Co islands supported on Cu(111) the standing wave patterns in the local density of states (LDOS) due to the quantum interference of surface-state electrons have been observed[7,8]. Ab initio calculations[7] have revealed that a majority free-electron like surface states give rise to LDOS oscillations on Co islands. In Fig.2, as an example we show the contour plot for majority and minority spectral densities of two monolayers of Co on Cu(111).

We find that the majority $sp$ states have a parabolic dispersion relation, described by an onset below the Fermi level at $E_0 = 0.28 \, \text{eV}$ and an effective mass $m^* = 0.50m_e$. Compared to Cu(111), a surface-state Fermi wavelength for 2Co/Cu(111) is found to be significantly larger ($\lambda_F = 48 \, \text{Å}$). In the mi-
Fig. 2. Contour plot for majority(a) and minority(b) spectral densities of surface-state electrons on the fcc 2Co/Cu(111); the Fermi-energy is choosen as zero.

Minority channel the $d$ contribution is found to be dominant. The strong feature below the Fermi level (cf. Fig.2b) is mainly determined by the $d$-states with a small $sp$ contribution. These states lead to a strong localized peak at about 0.4 eV below the Fermi energy observed in experiments[7,8].

Our calculations show that the LDOS around a single Cu adatom on 2Co/Cu(001) displays the long-range Friedel oscillations caused by the quantum interference of the $sp$-majority surface-state electrons. These oscillations lead to a long-range interaction between adatoms. Results presented in Fig.3. clearly demonstrate that the interaction between Cu adatoms is oscillatory with a period of about 24 Å corresponding to the Fermi wavelength of the majority $sp$ states of fcc Co (cf. Fig.2a). It is important to note that our studies for different number of Co layers on Cu(111) have shown that the surface-state band edge of the majority electrons increases with coverage[7]. Therefore, there is the possibility of tailoring the long-range interactions on Co/Cu(111) by variation of the coverage. Our results for different number of Co monolayers on Cu(111) will be presented elsewhere.

Finally, we discuss our results for the hcp Co(0001) substrate. Recent spin-polarized STM experiments of Okuno et al.[9] have found a spin-polarized surface state at -0.43 eV relative to the Fermi energy. Our calculations of the spectral densities for majority and minority states are shown in Fig.4.

One can see that a minority surface state exists and the energy of its minimum agrees well with the experiment[9]. Our analysis shows that this state has $d$ character similar to the minority state of fcc Co (cf. Fig.2b). However, in
Fig. 3. Calculated interaction energies between two Cu adatoms on the fcc 2Co/Cu(111). Inset shows the long-range oscillatory interaction at large distances.

Fig. 4. Contour plot for majority(a) and minority(b) spectral densities of surface-state electrons on the hcp Co(0001).

Contrast to the fcc Co, the sp-majority states of the hcp Co(0001) are strongly shifted to higher energies and become unoccupied. These results suggest that the substrate-mediated interaction between adatoms on Co(0001) could be very much different from that on Cu(111) and fcc Co substrates. Our calculations presented in Fig.5 show that the interaction energy between Cu adatoms
on Co(0001) decays very fast and practically vanishes for adatom-adatom separation larger than 15 Å.

\[ \text{Interaction Energy (meV)} \]

\[ \text{distance (Å)} \]

\[ E_{int} \text{(meV)} \]

\[ \text{distance (Å)} \]

Fig. 5. Calculated interaction energies between two Cu adatoms on the hcp Co(0001). Inset shows the interaction at large distances.

In summary, we have performed first ab initio calculations for the substrate mediated adsorbate-adsorbate interactions on transition metal surfaces. We have found that the surface states on the fcc Co and the hcp Co substrates are spin-polarized. Our results predict that the spin-polarization of surface-state electrons can strongly affect interactions between adatoms. We reveal that mainly majority sp-states determine the interaction at large adatom-adatom separations.

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