Interactions mediated by surface states: from pairs and trios to adchains and ordered overlayers

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Abstract

Since metallic surface states on (1 1 1) noble metals are free-electron like, their propagators can be evaluated analytically. Since they are well-screened, one can use simple tight-binding formalism to study their effects. The needed phase shifts can be extracted from the experiment. Hence, one can now make quantitative predictions of these slowly-decaying, oscillatory indirect interactions. For the (isotropic!) pair interactions (which decay as the inverse square of adatom–adatom separation), remarkable agreement has been obtained with experiments by two groups. We have extended the formalism to consider the full indirect ("triple") interaction of 3 adsorbates, which is the sum of the 3 constituent pair interactions plus the non-pairwise "trio" contribution, which tends to decay with the $\frac{5}{2}$ power of perimeter. Here, we concentrate on interactions due to ordered overlayers and to linear defects, relating the latter to the interactions of $(n \times 1)$ ordered overlayers and both to the constituent pair and trio interactions. We compare with the experimental studies of interactions of adatoms with adchains and of consequent 1D motion of adatoms trapped between two such parallel chains. We discuss the implications for step–step interactions (on vicinal surfaces), with attention to the modification of the surface state itself for small terrace widths.
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1. Introduction and parameters

Metallic surface states, i.e. surface states crossing the Fermi level, have dramatic consequences

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that can be explored at the atomic scale by modern surface probes such as scanning-tunneling microscopy (STM). Here, we summarize our progress to date in understanding the consequences of these states for nanoscale interactions not only between adsorbed atoms, but also between chains of atoms and other atoms or chains. This work is

preparatory to extensions to step interactions. We also present some helpful tabulations not published previously.

While the simple asymptotic expressions for indirect interactions are valid only for separations larger than several/many atomic spacings, the more general expressions are valid for any surface-lattice separation (and could indeed be generalized to arbitrary separations by allowing different phase factors for the interacting species). On the other hand, for atoms at nearest-neighbor spacings, particularly for homoepitaxy (or for adatoms larger than substrate atoms), direct interactions should also come into play, and are then expected to overwhelm any indirect effects. Thus, for example, one must be cautious about using the formalism below to predict interactions between dimers or chains and atoms, specifically any indirect interactions that involve a propagator between the two members of the dimer (or neighboring atoms in a chain).

Table 1 summarizes key parameters that characterize the relevant isotropic Shockley surface states found on the (1 1 1) facet of the noble metals Cu and Ag. For both surfaces there now exist experimental investigations of the long-ranged adsorbate interactions [1,2]. The table compares experimental values of the surface-state band

parameters, obtained via STM [3], with our large sized-converged calculations by standard first-principles DFT [4,5]; the agreement is good. The table also shows STM measurements of the scattering-phase shifts $\delta_F \neq 0$ reported [1,2,6] for various adsorbates, e.g. from standing waves in "quantum corrals" [7]. Finally the table shows estimates for the Thomas–Fermi screening length k_{TF}^{-1} [8]. The surface-state electron response arises at much longer length scales, $\lambda_F/2 \gg k_{TF}^{-1}$, and so will dominate the long-range adsorbate interaction.

2. Pair interactions

The interaction between adsorbates on a metal surface can involve an elastic, an electrostatic, and an indirect coupling through electronic states of the substrate. The long history of theoretical investigation of indirect adsorbate interactions dates back nearly four decades [9]; the history of this oscillatory, long-range interaction has been amply documented [10]. Lau and Kohn [11] pointed out that the range of the interaction increases dramatically when the mediation is by a surface rather than a bulk states. Recent theory work [1,12] applied these ideas to the above-mentioned isotropic surface-state bands to find the

Table 1
Shockley surface-state parameters and Thomas–Fermi (bulk-screening) wavevectors of the Cu and Ag (1 1 1) surfaces

	Cu(1 1 1)-STM	Cu(1 1 1)-DFT	Ag(1 1 1)-STM	Ag(1 1 1)-DFT
ε_F (eV)	0.38[a]	0.42	0.065[a]	0.045
m_{eff}/m_e	0.44[a]	0.38	0.40[a]	—
q_F (Å^{-1})	0.21[a]	0.20	0.083[a]	—
$\lambda_F/2$ (Å)	15.0[a]	15.5	37.9[a]	—
k_{TF}^{-1} (Å)	0.552		0.588	
S adsorbate	$\delta_F = \pm\pi/2$[b]	—	—	—
Cu adsorbate	$\delta_F = \pm\pi/2$[c,d]	—	—	—
Co adsorbate	$\delta_F = \pm\pi/2$[d]	—	$\delta_F = \pi/3$[d]	—

The Shockley band is characterized by the effective electron mass m_{eff}, a Fermi energy ε_F (measured relative to the bottom of the surface-state band), and a corresponding in-surface Fermi wavevector $q_F = \hbar^{-1}\sqrt{2m_{eff}\varepsilon_F}$ and half wavelength $\lambda_F/2 = \pi/q_F$. The Thomas–Fermi screening lengths, k_{TF}^{-1}, are obtained as in Ref. [8]. Table adapted from Refs. [1,12–14].

[a]Ref. [3].
[b]Ref. [6].
[c]Ref. [1].
[d]Ref. [2].

pair-interaction [1,12]:

$$\Delta E_{\text{pair}}(d; \delta_F) = \frac{2}{\pi} \text{Im} \int_0^{\varepsilon_F} d\varepsilon$$
$$\times \ln(1 - [t_0(\varepsilon; \delta_F) g_0(qd)]^2) \qquad (1)$$

$$\sim \Delta E_{\text{pair}}^{\text{asym}}(d; \delta_F) = -\varepsilon_F \left(\frac{2 \sin(\delta_F)}{\pi} \right)^2$$
$$\times \frac{\sin(2q_F d + 2\delta_F)}{(q_F d)^2}. \qquad (2)$$

The simple analytic expression holds at asymptotic separation $d > \lambda_F/2$. The effective T-matrix $t_0(\varepsilon; \delta_F) = -(2\hbar/m_{\text{eff}}) \sin(\delta_0(\varepsilon)) \exp(i\delta_0(\varepsilon))$, is determined by the s-wave phase shift $\delta_0(\varepsilon)$ with the boundary condition $\delta_0(\varepsilon_F) = \delta_F$. The surface propagator $g_0(x)$ becomes basically the cylindrical Hankel function of the first kind ($H_0^{(1)}$):

$$g_0(x) = i \frac{m_{\text{eff}}}{2\hbar} H_0^{(1)}(x) \sim i \frac{m_{\text{eff}}}{\hbar} \frac{\exp(ix - i\pi/4)}{\sqrt{2\pi x}},$$
$$x \to \infty. \qquad (3)$$

To obtain the simple asymptotic expressions, tg must be small enough so that $\ln[1 - \cdots]$ can be expanded to leading order and x must be large enough to replace $H_0^{(1)}(x)$ by an outgoing circular wave.

Subsequent STM measurements of Cu and Co adsorbate dynamics on Cu(1 1 1) and Ag(1 1 1) [1,2] have verified that the interaction has period $\lambda_F/2 = \pi/q_F$ and the quadratic decay of the envelope with separation, both without adjustable parameters. Accounting for the overall magnitude requires insight into inelastic losses to bulk states.

3. Trio interactions

Study of the interaction of three adsorbates [13,14] serves as a bridge from pair interactions to multi-adsorbate interactions in clusters. The three adsorbates are taken to bond to substrate positions $i = 1, 2, 3$. The triple-adsorbate cluster adsorption energy is calculated [13] by combining a

formal expansion [10,15] of the adsorbate-cluster energy with scattering theory [12]:

$$\Delta E_{\text{triple}}(d_{12}, d_{23}, d_{31}; \delta_F)$$
$$\equiv \sum_{i>j=1}^{3} \Delta E_{\text{pair}}(d_{ij}; \delta_F)$$
$$+ \Delta E_{\text{trio}}(d_{12}, d_{23}, d_{31}; \delta_F)$$
$$= \frac{2}{\pi} \text{Im} \int_0^{\varepsilon_F} d\varepsilon \ln[1 - ((tg_{12})^2 + (tg_{23})^2$$
$$+ (tg_{31})^2) - 2(tg_{12})(tg_{23})(tg_{31})], \qquad (4)$$

where tg_{ij} is shorthand for $t_0(\varepsilon; \delta_F) g_0(qd_{ij})$. This triple-cluster interaction includes a new trio contribution ΔE_{trio} which arises from constructive interference of electrons which traverse the entire cluster parameter $d_{123} = d_{12} + d_{23} + d_{31}$. In the asymptotic limit, $d_{123} > 3\lambda_F$, we obtain the analytical result [13,14]:

$$\Delta E_{\text{trio}}(d_{12}, d_{23}, d_{31}; \delta_F)$$
$$\simeq -\frac{4}{\pi} \text{Im} \int_0^{\varepsilon_F} d\varepsilon [t_0(\varepsilon; \delta_F)]^3 g_0(qd_{12})$$
$$\times g_0(qd_{23}) g_0(qd_{31})$$
$$\simeq -\varepsilon_F \sin^3(\delta_F) \left(\frac{16\sqrt{2}}{\pi^{5/2}} \right) \sqrt{\frac{d_{123}^3}{d_{12} d_{23} d_{31}}}$$
$$\times \frac{\sin(q_F d_{123} + 3\delta_F - 3\pi/4)}{(q_F d_{123})^{5/2}}. \qquad (5)$$

For completely absorbing scatterers the trio interaction result (5) is reduced by a factor of $\frac{1}{8}$ (see Ref. [13]). Since the scattering is taken to be s-wave, the trio interaction depends overwhelmingly on the perimeter d_{123} and is insensitive to the shape: the geometrical prefactor $\sqrt{d_{123}^3/d_{12} d_{23} d_{31}}$ varies little except for highly distorted arrangements [13,14]. Also [14], trio interactions can affect the barriers of atoms approaching growing clusters, an issue of recent theoretical study [16].

Our results are summarized in Table 2. We emphasize that our calculations are non-perturbative, resulting in the physically important phase shift δ_F absent in perturbative approaches (e.g. Ref. [11]). Since δ_F can differ for various adatom–substrate combinations (cf. Table 1), one can in principle, select a system that will have a minimum at an arbitrary lattice spacing.

Table 2
Comparison of indirect interactions on surfaces mediated by [metallic] surface and bulk states and as well as bulk interactions (mediated by bulk states). The pair and trio decays refer to the envelope of the oscillatory interaction in the asymptotic regime

	Surface via surface	Surface via bulk	Bulk
$\lambda_F/2$	~ 15.0 Å [Cu(1 1 1)]	~ 2.3 Å[Cu]	~ 2.3 Å[Cu]
Dispersion	Isotropic $\varepsilon \approx (\hbar k_\parallel)^2/2m^*$	Anisotropic $\varepsilon_n(k_\parallel)$	Anisotropic $\varepsilon_n(k)$
Computation	Simple: parabolic 2D band	Messy: multiple 3D bands	Messy
Pair decay	$\propto d^{-2} \Rightarrow$ observable	$\propto d^{-5} \Rightarrow$ insignificant	$\propto d^{-3}$ (RKKY)
Trio decay	$\propto d^{-5/2}$	$\propto d^{-7}$	$\propto d^{-4}$

While some evidence exists that the pair interaction alone is inadequate at non-asymptotic separations, there has not yet been a comparable experimental confirmation; trio interactions between adatoms and dimers are likely to be dwarfed by direct-interaction effects in the dimer, but other effects can be envisioned.

The preceding process can be extended to compute interactions between 4, 5, and more adatoms. The formalism for bulk impurities, readily convertible to surfaces, was worked out by Harrison [17]. Alternatively, one can consider the interaction energy of superlattices of adsorbates [10,18]. In this way, one can relate the integrand for ΔE of a fractional overlayer to that of a full monolayer. However, the simple expression for a full monolayer given in Ref. [18] involves "tricks" related to the simple model employed that are subtle to generalize.

4. Interactions with chains

By viewing a chain as the sum of its constituent atoms, one can readily add up these interactions [19] to show

$$
\begin{aligned}
\Delta E_{\text{chain-atom}}^{\text{asym}}(\ell) &\propto -\varepsilon_F \sin^2(\delta_F) \\
&\times \frac{\sin(2q_F\ell + 2\delta_F + \pi/4)}{(q_F\ell)^{3/2}},
\end{aligned} \tag{6}
$$

where ℓ is the distance from the atom to the chain. The remarkable $\frac{3}{2}$ power law was recognized over a decade ago [20]. A similar result should arise from consideration of the interaction energy of an

$(n \times 1)$ array of adatoms (but cf. warning at the end of Section 3).

Inserting parameters for Cu(1 1 1) into Eq. (6), we find minima when ℓ is 9, 24, 39, and 54 Å. In counting the occurrences of atoms between 20 and 30 Å from a chain, Repp [21] did indeed find the behavior of Eq. (6). _The chain–chain interaction has the same form as Eq._ (6) since the second chain can (also) be viewed as the sum of individual atoms, each of which have this interaction.

An atom between two parallel chains will experience a 1D corrugation potential parallel to the chains. Repp constructed such a situation for Cu atoms on Cu(1 1 1) with atomic manipulation [21] and produced STM movies of atoms wandering along the trough. Since the chains are of finite length, the well depth decreases near the ends of the chain. Hence, the atom is trapped in this furrow. If the chains are far enough apart, there are multiple furrows. Repp [21] observed two atoms, in furrows nanometers apart, moving back and forth individually.

One can imagine the extensions of these ideas such as producing gridworks of chains with a regular set of traps for atoms or a maze of walls through which atoms might move as stupid rats. Computing the corresponding potential surface is then a fairly well-defined task.

5. Complications in going from chains to steps

Surface states are not so robust as bulk states, so one cannot blithely view them as unaffected by the adsorption process. Baumberger et al. [24] show

that, on vicinal Cu(1 1 1), the surface state is shifted up (and so q_F reduced) as the terrace width ℓ decreases. However, when the steps are decorated with CO, the energy shift becomes downward with decreasing ℓ!

Furthermore, Ortega et al. [25] find that when ℓ decreases sufficiently (in particular, when the misorientation of Cu(1 1 1) increases beyond 7°), the surface state is no longer that of the (1 1 1) facet but is determined by the vicinal surface itself. The periodic potential of the steps then opens a gap in the parabolic band structure.

Both these arguments assume implicitly that the steps are straight and uniformly spaced, neither of which are generally true. It is not clear how the meandering of steps or the fluctuations in ℓ alter these results or, conversely, how the interactions affect the meandering and distribution of the steps. (In concise words, are the steps "actors or spectators?" [26].)

The existence of slowly decaying oscillatory interactions should have profound implications for the distribution of terrace widths $P(\ell)$. In general the dominant interaction between steps comes from entropic and elastic repulsions, both of which vary as ℓ^{-2}. As a consequence $P(\ell)$ has a "universal" form depending only on the ratio $\ell/\langle \ell \rangle$ (and the strength of the ℓ^{-2} repulsion) but not on the mean spacing $\langle \ell \rangle$, i.e., not on the misorientation. With surface states, this scaling breaks down, as has been observed experimentally [27].

Furthermore, the oscillatory interaction introduces a new length scale λ_F. Thus, the equilibrium crystal shape, which is expected to be independent of crystal size, would seem to acquire some size-dependent behavior, at least for small crystallites. Since the $\ell^{-3/2}$ decay of the envelope is slower than the ℓ^{-2} of the pure repulsion, it is not clear what changes arise in the Pokrovsky–Talapov [28] "critical behavior" of the curved regions near the edges of facets.

6. Conclusions

In summary, we present both an asymptotic evaluation and an exact model calculation for adsorbate interaction energies mediated by an isotropic Shockley surface-state band, as found on noble-metal (1 1 1) surfaces. While this interaction is primarily the sum of pair interactions, there can be significant trio corrections. Such interactions can play a role in the low-temperature adsorbate assembly [10,16,22] and efforts are being made to investigate them directly [2,23]. We can on this basis evaluate the interaction between a chain of adatoms and another chain and/or other adatoms. Novel nanostructures can be imagined and actually constructed [21] by skilled experimentalists.

As noted, the slowly decaying oscillatory interactions should affect a broad range of phenomena and should apply to any situations in which defects create localized perturbations on surfaces with surface states, e.g., magnetic interactions. Thus, the exchange coupling should oscillate with the same period $\lambda_F/2$ as the adatom–adatom interaction; however, there is no a priori reason to expect that the phase shift δ_F will be the same. Thus, one can imagine a rich phase diagram.

In subsequent papers, we will present a detailed investigation [19] of the surface-state-derived interactions associated with chains and nanostructures. We will also produce a careful and thorough analysis and assessment of the assumptions involved in our approach [29], with comments about extensions to systems in which, for example, rapid screening of the adsorption bond is questionable.

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