EUROPHYSICS LETTERS 15 July 2002

Europhys. Lett., **59** (2), pp. 265–271 (2002)

Surface-state–mediated three-adsorbate interaction

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(received 31 December 2001; accepted in final form 16 April 2002)

PACS. 73.20.Hb – Impurity and defect levels; energy states of adsorbed species.
PACS. 73.20.At – Surface states, band structure, electron density of states.
PACS. 68.37.Ef – Scanning tunneling microscopy (including chemistry induced with STM).

Abstract. – The interaction energy of three adsorbates on a surface consists of the sum of the three pair interactions *plus* a *trio* contribution produced by interference of electrons which propagate the entire perimeter, d_{123}, of the three-adsorbate cluster. Here we investigate this triple-adsorbate interaction that is mediated by the isotropic Shockley surface-state band found on noble-metal (111) surfaces. Our experimentally testable result depends on the s-wave phase shift, $\delta_{\mathrm{F}} \neq 0$, characterizing the standing-wave patterns seen in scanning-tunneling microscopy (STM) images. Compared with the adsorbate-pair interactions, and in contrast to bulk-mediated interactions, the trio contribution has a slightly weaker amplitude and asymptotically decays slightly faster, $\propto d_{123}^{-5/2}$. It also has a distinctive oscillation period dependent on d_{123}. We finally compare the asymptotic description with exact model calculations.

Progress in scanning-tunneling microscopy (STM) has made possible the study of physical properties of surface-state electrons in real space, as revealed by standing surface-wave patterns formed in the vicinity of adsorbates, defects, and steps [1–5]. Most studies of these wave patterns have concerned Shockley-type surface states which on a clean surface are characterized by a free-particle–like dispersion with effective mass m_{e}, in-surface Fermi wave vector q_{F} and Fermi level $\epsilon_{\mathrm{F}} = (\hbar q_{\mathrm{F}})^2/2m_{\mathrm{e}}$. The corresponding in-surface Fermi wavelength, $\lambda_{\mathrm{F}} = 2\pi/q_{\mathrm{F}}$, significantly exceeds the bulk-electron counterpart, and the envelope of the response function decays far more slowly than for the bulk states. Such slow decay of the response functions opens the possibility for very-long-range interference and mutual defect-interaction effects mediated by the surface-state band. Exciting examples include "quantum corrals" formed by Fe atoms on Cu(111) [3] and small islands on Ag(111) [4]. Surface waves are strongly scattered from adsorbates, and most experiments reveal significant surface-state variation in the local density of state (LDOS) characterized by large Fermi-level phase shift, $\delta_{\mathrm{F}} \approx -\pi/2$ [2, 5].

The oscillatory nature of the indirect interaction between chemisorbed atoms on metal surfaces [6] has attracted theorical attention for over three decades [7]. Usually, the mediation is by bulk electronic states which produce anisotropic interactions with a rapid d_{ij}^{-5} decay with the adsorbate separation d_{ij} [8]. Although qualitative understanding of the features of the indirect interaction are known since long [8], quantitative agreement between theory and experiment proved elusive due to the complicated nature of the substrate electronic states and the interplay of all occupied energy levels at small d_{ij} [6]. While only states near the Fermi level ϵ_F are important at asymptotically large d_{ij} [9], the rapid decay renders these interactions unmeasurable. Lau and Kohn [10] recognized that when there are surface states near ϵ_F, the decay is much slower, going like d_{ij}^{-2}. However, only recently did theorists [11,12] apply these ideas to the surface states on (111) noble metals. These surface states consist of a single, circularly symmetric band. For two adsorbates, "i" and "j", at asymptotic separation, $d_{ij} \gg \lambda_F/2$, the single-adsorbate scattering can then be characterized by the *measurable* phase shift δ_F, leading to a simple expression for the adsorbate-pair interaction energy [11,12]:

$$\Delta E_{\text{pair}}(d_{ij};\delta_F) \simeq \Delta E^{\text{asym}}_{\text{pair}}(d_{ij};\delta_F) = -\epsilon_F \left(\frac{2\sin(\delta_F)}{\pi}\right)^2 \frac{\sin(2q_F d_{ij}+2\delta_F)}{(q_F d_{ij})^2}. \qquad (1)$$

Recent STM investigations of Cu on Cu(111) [12,13] and Co on Cu(111) and Ag(111) [13] have not only revealed that inter-adsorbate distances depend on the period $\lambda_F/2 = \pi/q_F$ of the surface-wave oscillations around the adsorbates, but have also experimentally determined both the asymptotic decay and strength of this indirect electronic adsorbate-pair interaction.

In this letter, we begin the task of extending the analysis to multiadsorbate interactions on metal surfaces with isotropic surface-state bands. We investigate the mutual indirect electronic interaction of *three* adsorbates, focusing on the recently investigated [12,13] Cu(111) and Ag(111) surfaces. A simple tight-binding analysis provides the essential formalism [6,14], which can be adapted to provide a non-perturbative three-adsorbate interaction estimate,

$$\Delta E_{\text{triple}}(d_{12},d_{23},d_{31};\delta_F) \equiv \sum_{i>j=1}^{3} \Delta E_{\text{pair}}(d_{ij};\delta_F) + \Delta E_{\text{trio}}(d_{12},d_{23},d_{31};\delta_F). \qquad (2)$$

Such energies can be important in the formation of dilute superlattices [12,13], in determining the shape of clusters, can be non-negligible ingredients in a lattice-gas parametrization of chemisorbed overlayers [15], and can lead to gross asymmetries in temperature-coverage phase diagrams by breaking the particle-hole symmetry of the lattice-gas Hamiltonian [16].

To leading order in the adsorbate scattering, the trio contribution $\Delta E_{\text{trio}}(d_{12},d_{23},d_{31};\delta_F)$ comes from electrons which scatter at all three adsorbate locations and traverse the perimeter, $d_{123} \equiv d_{12}+d_{23}+d_{31}$. We expect the adsorbates to couple to the same local environment and so assume that identical phase-shifts, δ_F, (evaluated modulo π) describe them. (Otherwise, $3\delta_F \to \delta_{1F}+\delta_{2F}+\delta_{3F}$ below.) For asymptotic d_{ij} we derive the simple analytic result

$$\Delta E_{\text{trio}}(d_{12},d_{23},d_{31};\delta_F) \simeq -\epsilon_F \sin^3(\delta_F)\left(\frac{16\sqrt{2}}{\pi^{5/2}}\right)\gamma_{123}\,\frac{\sin(q_F d_{123}+3\delta_F-3\pi/4)}{(q_F d_{123})^{5/2}}, \qquad (3)$$

where $\gamma_{123} \equiv d_{123}^{3/2}/\sqrt{d_{12}d_{23}d_{31}}$ is a shape-dependent dimensionless ratio . For typical three-adatom configurations (*i.e.*, with comparable d_{12}, d_{23}, d_{31}), $\gamma_{123} \sim 5\frac{1}{2}$ [17], and the leading trio contribution of eq. (3) oscillates distinctly as $q_F d_{123}$ while decaying barely faster than the asymptotic-pair interaction of eq. (1). However, for an isosceles configuration with one leg, say d_s, much shorter than the other two legs of length d, $\gamma_{123} \simeq 2(2d/d_s)^{1/2}$; then ΔE_{trio} decays asymptotically with the identical envelope $1/d^2$ and oscillation period $2q_F d$ of (but different oscillation phase from) eq. (1), and thus effectively "screens" (or "antiscreens") ΔE_{pair}.

The magnitude and slow asymptotic decay of the predicted surface-state–mediated trio interaction (3) can have important effects at finite coverages of the noble-metal surfaces. While the sum of adsorbate-pair interaction contributions [11], $\Delta E_{\text{pair}}(d_{ij};\delta_F)$ dominates the

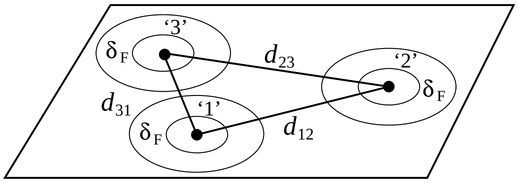

Fig. 1 – Schematics of the triple-adsorbate interaction. Three adsorbates couple at positions $i = 1, 2, 3$, separated by mutual distances d_{ij}, to a metal surface which supports a surface-state band near ϵ_F. The scattering at each adsorbate causes oscillations (concentric rings) in the surface-state density of state. This scattering is characterized by a finite Fermi-level phase shift, $\delta_F \approx -\pi/2$, corresponding to significant, slowly decaying Friedel oscillations induced in the surface-state electron gas.

general triple-adsorbate cluster energy (2), the trio interaction $\Delta E_{\text{trio}}(d_{12}, d_{23}, d_{31}; \delta_F)$ will contribute a non-negligible quarter of $\Delta E_{\text{triple}}(d_{12}, d_{23}, d_{31}; \delta_F)$ and decays only slightly faster than the pair interaction [11–13]. Previous attempts to compare theoretical and experimental values of trio energies have met with marginal success and have considered small separations between adsorbates [18, 19]. However, impressive agreement between theory and experiment regarding pair interactions mediated by surface states [12, 13] and preliminary indications of interactions in addition to those between pairs in multiadsorbate systems inspire us to revisit the trio interaction at intermediate and larger separations.

The schematic fig. 1 illustrates the experimental situation and identifies the adsorbate-adsorbate (Friedel) interaction mechanism. Three adsorbates are located above a (noble) metal surface, on which there is a surface-state band crossing ϵ_F. Table I identifies the key parameters which characterize the Shockley state on the (111) face of Cu, Ag, and Au. Table I also includes values for the effective mass m_{eff} which relates the Fermi energy to the Fermi wave vector, $q_F = \hbar^{-1}\sqrt{2m_{\text{eff}}\epsilon_F}$. Each adsorbate induces scattering and causes spatial oscillations in the surface-band density of states (DOS). At ϵ_F these DOS oscillations suffer a phase shift δ_F. The interference between such DOS variations produces a Friedel-type adsorbate-adsorbate interaction, which also oscillates with the mutual adsorbate separation d. Several theoretical studies have addressed this indirect adsorbate interaction mechanism [6,11]. The theoretical expression for the interaction becomes simple only in the asymptotic regime, where exclusively states at the Fermi level matter. While state-of-the-art first-principles calculations [23, 24] can compute the total energy of periodic overlayer structures, reaching the asymptotic regime requires cells bigger than current capabilities. Also, unless the interaction

TABLE I – *Shockley surface-state parameters and Thomas-Fermi (bulk-screening) lengths of the Cu, Ag, and Au* (111) *surfaces. 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 wave vector* $q_F = \hbar^{-1}\sqrt{2m_{\text{eff}}\epsilon_F}$ *and half wavelength* $\lambda_F/2 = \pi/q_F$.

	m_{eff}/m_e	ϵ_F (eV)	q_F (Å^{-1})	$\lambda_F/2$ (Å)	k_{TF}^{-1} (Å)
Cu	$0.44^a/0.46^b$	$0.38^a/0.39^b$	$0.21^a/0.217^b$	$15.0^a/14.5^b$	0.552^d
Ag	$0.40^a/0.53^b$	$0.065^a/0.12^b$	$0.083^a/0.129^b$	$37.9^a/24.4^b$	0.588^d
Au	0.28^b	0.41^b	0.173^b	18.2^b	0.588^d
Si-Ag $\sqrt{3}$	$0.15(7)^c$	$0.25(5)^c$	$0.010(3)^c$	$31(9)^c$	$[k_{\text{DH}}^{-1} \gg \lambda_F$ at 6 K$]^e$

[a]Ref. [20]. [b]Ref. [21]. [c]Ref. [22]. [d]Adapted from ref. [11]. [e]TF →Debye-Hückel (DH).

is transmitted by surface states, the interaction will be weak [24]. In contrast, in a scattering theory approach, the interaction energy is calculated by computing the propagators for the clean, high-symmetry surface. Lau and Kohn's landmark investigation of the asymptotic regime used a perturbative approach [10] but the LCAO tight-binding formalism produces equivalent results non-perturbatively [6,9]. Here we use the measured [2,5,12,13] phase shifts ($\delta_{\rm F} \approx \pm\pi/2, \pi/3$) for a non-perturbative evaluation of the triple-adsorbate interaction.

Our analysis starts with a Harris functional expression [11,25] and should include an electrostatic correction. However, as for the pair interaction [11], screening by the bulk electrons should make this correction neglible. Thus, the one-electron contributions determine the interaction, which, as in the tight-binding approach [6], is given by an energy integral

$$\Delta E_{\rm triple}(d_{12}, d_{23}, d_{31}; \delta_{\rm F}) = 2\int_{-\infty}^{\epsilon_{\rm F}} {\rm d}\epsilon\,(\epsilon-\epsilon_{\rm F})\Delta\rho_{\rm triple}(\epsilon; d_{12}, d_{23}, d_{31}) \tag{4}$$

of the change $\Delta\rho_{\rm triple}$ in the DOS of the three adsorbates relative to three isolated adsorbates. The factor of two comes from spin degeneracy. Adapting previous formalism [6,14], we find

$$\Delta\rho_{\rm triple}(\epsilon, d_{12}, d_{23}, d_{31}) = -\frac{1}{\pi}\frac{\rm d}{{\rm d}\epsilon}{\rm Im}\int {\rm d}\boldsymbol{x}\ \langle\boldsymbol{x}|\ln[1-\sum_{i>j}\mathcal{K}_{\rm pair}^{(i,j)} - \mathcal{K}_{\rm trio}]|\boldsymbol{x}\rangle, \tag{5}$$

$$\mathcal{K}_{\rm pair}^{(i,j)} = T_{a_i i}(\epsilon)G^0_{ij}(\epsilon)T_{a_j j}(\epsilon)G^0_{ji}(\epsilon),\quad \mathcal{K}_{\rm trio} = 2T_{a_1 1}(\epsilon)G^0_{12}(\epsilon)T_{a_2 2}(\epsilon)G^0_{23}(\epsilon)T_{a_3 3}(\epsilon)G^0_{31}(\epsilon). \tag{6}$$

The last contribution in eq. (6) contains a factor of 2 because the electrons can traverse the triple-cluster perimeter clockwise or counterclockwise. As noted above, eq. (5) should be calculated using frozen adsorbate-induced scattering potentials [25]. The screening by bulk electrons justifies an assumption that the adsorbate scattering potentials are non-overlapping. We express the formal result, eq. (5), in terms of the one-electron (retarded) Green function $G^0(\epsilon)$ for the bare surface and the T-matrices, $T_{a_i i}(\epsilon)$, which characterize the (non-perturbative) scattering at adsorbates a_i, where $i = 1,\ 2,\ 3$.

Mediation by a Shockley surface-state band greatly simplifies the evaluation of $\Delta\rho_{\rm triple}$ of eq. (5). First, at large adsorbate distances the dominant contribution to $\Delta\rho_{\rm triple}(\epsilon; d_{12}, d_{23}, d_{31})$ then arises from scattering of surface-state electrons: the amplitude for propagation along the surface in a 2D surface state has a significantly slower decay with distance than within the bulk electron bands. Second, the surface-state interaction is then dominated by s-wave scattering contributions because the Fermi wavelength $\lambda_{\rm F} = 2\pi/q_{\rm F}$ for the Shockley surface states typically is much larger than the bulk Thomas-Fermi screening length, $1/k_{\rm TF}$; cf. table I.

At finite adsorbate separations, the change in the DOS (5) due to the indirect interaction between the three adsorbates thus becomes dominated by

$$\Delta\rho_{\rm triple}(\epsilon; d_{12}, d_{23}, d_{31}) \approx -\frac{1}{\pi}\frac{\rm d}{{\rm d}\epsilon}{\rm Im}\ln\left[1-\sum_{i>j}K_{\rm pair}(d_{ij};\delta_{\rm F}) - K_{\rm trio}(d_{12}, d_{23}, d_{31};\delta_{\rm F})\right]. \tag{7}$$

To obtain $K_{\rm pair}(d_{ij};\delta_{\rm F})$ from $\mathcal{K}_{\rm pair}^{(i,j)}$ and $K_{\rm trio}(d_{12}, d_{23}, d_{31};\delta_{\rm F})$ from $\mathcal{K}_{\rm trio}$, replace $T_{a_i i}(\epsilon)$ by $t_0(\epsilon;\delta_{\rm F})$ and $G^0_{ij}(\epsilon)$ by $g_0(qd_{ij})$, where the Green function $g_0(qd)$ describes the propagation a distance d along the surface at wave vector $q = \hbar^{-1}\sqrt{2m_{\rm eff}\epsilon}$ via the isotropic surface band. Describing adsorbate scattering of surface-band electrons, the new effective T-matrix, $t_0(\epsilon;\delta_{\rm F}) = -(2\hbar/m_{\rm eff})\sin\{\delta_0(\epsilon)\}\exp[i\delta_0(\epsilon)]$, is determined by the s-wave phase shift $\delta_0(\epsilon)$ which, in turn, is specified by the boundary condition $\delta_0(\epsilon_{\rm F}) = \delta_{\rm F}$. The cylindrical Hankel function of the first kind, $H_0^{(1)}$, solves the Helmholtz equation in two dimension, so that

$$g_0(x) = i\frac{m_{\text{eff}}}{2\hbar} H_0^{(1)}(x) \simeq i\frac{m_{\text{eff}}}{\hbar}\frac{\exp[ix - i\pi/4]}{\sqrt{2\pi x}} \qquad \text{for } x \to \infty. \tag{8}$$

The expansion emphasize the slow amplitude decay for propagation in a 2D surface state; when only 3D states contribute, the *surface* Green function typically decays as x^{-2} [6, 9].

Our simple formulas for the adsorbate interaction (1) and (3) follow from an asymptotic evaluation of one-electron energy integrals like eq. (4). In the asymptotic region, K_{trio} and K_{pair} become small, allowing expansion of the logarithm in ΔE_{triple}. To order t_0^3 we get an integral of each of three K_{pair}, corresponding to the asymptotic-constituent-pair interactions ΔE_{pair} of eq. (1), plus the *asymptotic limit* of the trio contribution $\Delta E_{\text{trio}}(d_{12}, d_{23}, d_{31}; \delta_{\text{F}})$:

$$-\frac{2}{\pi}\text{Im}\int_0^{\epsilon_{\text{F}}} \text{d}\epsilon\, K_{\text{trio}} = -\frac{4}{\pi}\text{Im}\int_0^{\epsilon_{\text{F}}} \text{d}\epsilon\, [t_0(\epsilon;\delta_{\text{F}})]^3 g_0(qd_{12}) g_0(qd_{23}) g_0(qd_{31}). \tag{9}$$

For parabolic dispersion, the Jacobian for changing the integration variable from ϵ to q is simple. The leading asymptotic term comes from simply integrating the phase factor, which has the generic form $\exp[iq\mathcal{R}]$, and evaluating it at the upper limit. The result, $-(2/\pi)\text{Im}K_{\text{trio}}(\epsilon_{\text{F}})/q\mathcal{R}$ [26], is just our asymptotic trio-interaction contribution, eq. (3).

As described in ref. [11] adsorbate scattering into the bulk band can be addressed by allowing the phase shift to become complex: $\delta_0(\epsilon) = \delta_0'(\epsilon) + i\delta_0''(\epsilon)$. Then eq. (3) becomes

$$\Delta E_{\text{trio}} \simeq -\epsilon_{\text{F}} \left(r \sin^2\{\delta_0'(\epsilon_{\text{F}})\} + \frac{(1-r)^2}{4} \right)^{3/2} \left(\frac{16\sqrt{2}}{\pi^{5/2}} \right) \gamma_{123} \frac{\sin(q_{\text{F}} d_{123} + 3\theta_0 - 3\pi/4)}{(q_{\text{F}} d_{123})^{5/2}}, \tag{10}$$

where $r = \exp[-2\delta_0''(\epsilon_{\text{F}})]$ is the intra-surface-band reflection and θ_0 (determined by $\tan(\theta_0) = (1/r)\csc\{2\delta_0'(\epsilon_{\text{F}})\} - \cot\{2\delta_0'(\epsilon_{\text{F}})\}$) is the phase shift of standing waves around adsorbates. Thus, for maximal limit of "black" scattering ($r \to 0$), ΔE_{trio} is reduced by a factor of 1/8.

Figure 2 shows our results for the three-adsorbate interaction energy mediated by the surface-state band assuming the Fermi-level phase shift $\delta_{\text{F}} = -\pi/2$. The top (bottom) panel compares estimates for the combined triple-adsorbate cluster (for the trio-interaction) energy. For specificity, we assume an equilateral-triangle configuration. The *solid curves* show our analytical asymptotic evaluation obtained using eqs. (1) and (3). The *dashed curves* show separate interaction estimates, $\Delta E_{\text{triple}}^{3\delta}$ and $\Delta E_{\text{trio}}^{3\delta}$, which we obtain by numerically evaluating the adsorbate-induced change in DOS, eq. (7), for $g_0(x) \propto H_0^{(1)}(x)$ with the additional assumption of a zero-range (δ-function) adsorbate potential [11]. This model assumption of δ-function scattering provides a semiquantitative approximation for describing defects in metals [27]. For a two-dimensional free-electron–like band, the s-wave phase shift [27] takes the simple analytic form given in ref. [11], $\delta_0(\epsilon) = \text{arccot}[\pi^{-1}\ln(\epsilon/\epsilon_{\text{F}}) + \cot(\delta_{\text{F}})]$; thus, $\delta_0(\epsilon)$ is uniquely specified by the experimentally observed δ_{F}. As for the asymptotic-pair interaction [6, 8–11], the asymptotic trio interaction is determined by the behavior of the integrand around ϵ_{F} and hence eventually approaches the analytical trio result of eq. (3), as illustrated in the insert panel. For non-asymptotic d, the numerical $\Delta E^{3\delta}(d)$ results are still valid, although they may become outweighed by *bulk*-state–mediated indirect interactions.

The comparison between $\Delta E_{\text{triple,trio}}(d)$ and $\Delta E_{\text{triple,trio}}^{3\delta}(d)$ (solid and dashed curves) in fig. 2 documents that our asymptotic evaluations of both the triple-adsorbate energy and of the trio contributions become adequate for $q_{\text{F}} d_{123} > 6\pi$, corresponding to $d_{ij} > \lambda_{\text{F}}$. In contrast, for the simpler two-adsorbate interaction problem, the asymptotic-pair interaction result (1)

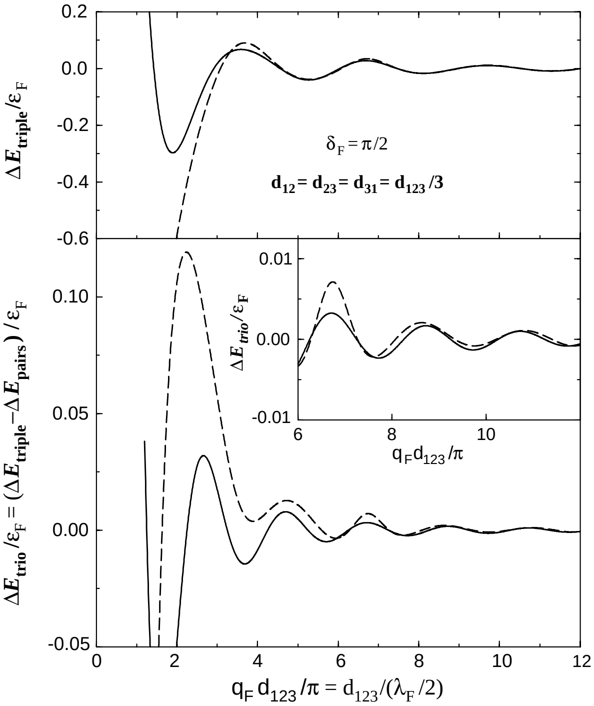

Fig. 2 – Three-adatom indirect interaction mediated by a surface-state band. The figure compares estimates both for the full interaction energy ΔE_{triple} of three adatoms (top panel) and for the trio-interaction energy (bottom panel), *i.e.* the energy by which ΔE_{triple} differs from the sum of the three constituent-pair interactions. Our non-perturbative results use the phase-shift $\delta_F = -\pi/2$, consistent with experimentally observed standing wave patterns of S, Cu, and Co on Cu(111). The *solid curves* show our asymptotic results, eqs. (1) and (3). The *dashed curves* show a numerical determination, $\Delta E^{3\delta}_{\text{triple}}(d)$, which arises when we base the single-adsorbate scattering approximation, eq. (7), on a zero-range (δ-function) approximation for the adsorbate potential and obtain the s-wave phase shift $\delta_0(\epsilon) = \text{arccot}[\pi^{-1}\ln(\epsilon/\epsilon_F) + \cot(\delta_F)]$. The *insert* details the long-range asymptotic variation.

becomes accurate already at $d_{12} > \lambda_F/2$ [11]. This difference in the onset of validity of the two asymptotic formulas (3) and (1) reflects the intrinsic complexity of the multiterm logarithmic integrand which defines ΔE_{triple} and hence ΔE_{trio} in eqs. (2)-(6). There is, in general, no simple way to express the trio-interaction result without an explicit subtraction; unlike for the pair interaction problem [6,11], there is no concise expression for a $\Delta\rho_{\text{trio}}$ that can be inserted into eq. (4) to obtain the trio interaction. It is the single-integral approximative result (9) itself which only becomes applicable at $q_F d_{123} > 6\pi$.

Isotropic, free-electron-like, partially filled surface states are also found on semiconductor surfaces with partial overlayers of metals, *e.g.*, Si(111)-$\sqrt{3}\times\sqrt{3}$-Ag [22]. The relevant parameters are included in table I. STM measurements at 6 K reveal a remarkable ordered adsorbate phase with interatomic spacings much smaller than the asymptotic limit. The absence of bulk screening, however, makes it unclear if the concepts developed here and/or in preceding works and resting on a Harris functional analysis can be directly applied.

In summary, we have presented results for the triple-adsorbate interaction energy mediated by an isotropic Shockley surface-state band, as found on noble-metal (111) surfaces. We derive a general formalism for this energy expressed in terms of experimentally accessible parameters. We also provide an explicit numerical evaluation for the equilateral-triangle configuration on Cu(111). While the sum of pair interaction contributions dominates the triple-adsorbate interaction energy, our work indicates that the additional trio contribution accounts for about a quarter of the interaction and exhibits only a marginally slower asymptotic decay. We also derive a simple analytic expression for the asymptotic limit of the trio interaction. It depends essentially only on the perimeter of the three-adsorbate "triangle" and so has its own characteristic oscillation wavelength and decay envelope. We assess its range of validity. The trio and analogous quarto and higher-order interaction contributions can play an important role for larger clusters and affect the total interaction energy of relatively dense (ordered) overlayers for which adsorbate interactions are mediated primarily by surface states.

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PH gratefully acknowledges financial support from the Wilhelm and Martina Lundgrens Foundation and from the Swedish Foundation for Strategic Research (SSF) through Materials Consortium ATOMICS. TLE's work was supported by NSF Grant EEC-0085604, with supplemental support from University of Maryland NSF-MRSEC, Grant 00-80008.

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