Surface-State Mediated 3-Adsorbate Interaction: Exact & Numerical Results & Simple Asymptotic Expression

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Abstract

The interaction energy of three adsorbates on a surface consists of the sum of the three pair interactions plus a trio contribution produced primarily by interference of electrons which traverse the entire perimeter, d_{123}, of the three-adsorbate cluster. Here we investigate this 3-adatom interaction when mediated by the isotropic Shockley surface-state band found on noble-metal (111) surfaces, extending work on pair interactions. Our experimentally testable result depends on the s-wave phase shift, 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 exhibits a slightly weaker amplitude and a slightly faster asymptotic envelope decay, $d_{123}^{-5/2}$. It also has a different but well-defined oscillation period dependent on d_{123} and little dependence on the shape of the cluster. We finally compare the asymptotic description with exact model calculations assuming short-range interactions, which are viable even in the non-asymptotic range (when not outweighed by bulk-mediated interactions).

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The rich variety of ordered overlayers of chemisorbed atoms on metal surfaces caught the eye of experimentalists early in surface studies. These patterns are attributed to an indirect electronic interaction between the atoms [1,2] which evidently must be oscillatory in sign, rapidly decaying with separation, and generally decidedly anisotropic. Usually the interaction is carried by way of bulk electronic states which produce anisotropic interactions with a rapid $1/d_{ij}^5$ asymptotic decay with the separation d_{ij} between adsorbates "i" and "j" [3]. While the consequent qualitative features of the indirect interaction have been understood for decades [3], it has been difficult to establish quantitative agreement between theory and experiment beacuse of the complicated nature of the substrate electronic states and the interplay of all occupied energy levels at small d_{ij} [1]. At asymptotically large d_{ij}, when only states near the Fermi level ϵ_F are important [4]; however, these interactions usually cannot be measured because of the rapid decay.

When there are surface states near ϵ_F, the decay is much slower, going like d_{ij}^{-2} [5]. Recently, dramatic evidence of such surface-state electrons—long-range interference effects due to the slow decay of related response functions—has been found with scanning-tunneling microscopy (STM): on noble-metal (111) surfaces there are standing surface-wave patterns near adsorbates, defects, and steps [6]. Typically these surface states are Shockley-type, with free-particle-like dispersion. E.g. for Cu(111) the effective mass m_e is $0.46 m_e$, the in-surface Fermi wavevector q_F is 0.217Å, and $\epsilon_\mathrm{F} = (\hbar q_\mathrm{F})^2/2m_e$ is 0.39 eV. Corresponding $\lambda_\mathrm{F} = 2\pi/q_\mathrm{F}$, is over 6 times as large as the bulk λ_F. The resulting clear standing-wave patterns seen in STM indicate show strong scattering by adsorbates, with Fermi-level phase shift $\delta_F \approx -\pi/2$ for Cu/Cu [6,7].

Very recently Hyldgaard and Persson [8–10] put these ideas together to describe interactions on (111) noble metals mediated by these surface states. For $d_{ij} \gg \lambda_\mathrm{F}/2$, they worked out a simple expression for the adsorbate-pair interaction energy [8–10]

$$\Delta E_{\rm pair}(d_{ij};\delta_F) \sim \Delta E^{\rm asym}_{\rm pair}(d_{ij};\delta_F) = -\epsilon_{\rm F}\left(\frac{2\sin(\delta_F)}{\pi}\right)^2 \frac{\sin(2q_{\rm F}d_{\rm ij}+2\delta_F)}{(q_{\rm F}d_{\rm ij})^2} \tag{1}$$

Subsequent STM experiments considering Cu and Co on Cu(111) and Ag(111) [10,13] found impressive agreement with the periodicity, decay envelope, and magnitude of Eq. (1).

This short conference paper summarizes recent progress in analyzing *three*-adatom interactions as the first step in understanding multiadsorbate interactions on metal surfaces with isotropic surface-state bands [**?**]. Specifically,

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

defines the non-pairwise *trio* contribution. Such energies can be important in determining the shape of clusters, can be non-negligible ingredients in a lattice-gas parametrization of chemisorbed overlayers such as N/Fe(100) [15], and can lead to gross asymmetries in temperature-coverage phase diagrams by breaking the particle-hole symmetry of the lattice-gas Hamiltonian [16].

While the general expression for the change in the one-electron energies is rather complicated [11], to leading order (in $t_0 g_0$) the trio contribution $\Delta E_{\rm trio}$ comes from electrons which scatter at all three adsorbate locations and traverse the *perimeter*, $d_{123} \equiv d_{12}+d_{23}+d_{31}$. As we derive in [11],

$$\Delta E_{\rm trio}(d_{12},d_{23},d_{31};\delta_F) \simeq -\frac{2}{\pi}{\rm Im}\int_0^{\epsilon_{\rm F}} {\rm d}\epsilon\, 2[{\rm t}_0(\epsilon;\delta_{\rm F})]^3 {\rm g}_0({\rm qd}_{12}){\rm g}_0({\rm qd}_{23}){\rm g}_0({\rm qd}_{31}), \tag{3}$$

where the Green function $g_0(qd)$ describes the propagation a distance d along the surface at wavevector $q=\hbar^{-1}\sqrt{2m_{\rm eff}\epsilon}$ via the isotropic surface band. The effective T-matrix $t_0(\epsilon;\delta_F) = -(2\hbar/m_{\rm eff})\sin(\delta_0(\epsilon))\exp(i\delta_0(\epsilon))$, describes adsorbate scattering of surface-band electrons and is determined by the s-wave phase shift $\delta_0(\epsilon)$ with the boundary condition $\delta_0(\epsilon_F)=\delta_F$; δ_F is extracted from STM observations of standing waves. For our 2D parabolic band, the surface-state electron Green function g_0 amounts to a cylindrical Hankel function of the first kind: $-i(2\hbar/m_{\rm eff})g_0(x) = H_0^{(1)}(x) \simeq (2/\pi x)^{1/2}\exp(ix-i\pi/4)$ as $x\to\infty$. The slow decay of the amplitude for propagation in a 2-D surface state is illustrated by its asymptotic expansion; when only 3-D states contribute, the *surface* Green function typically decays as x^{-2} [1,4].

Assuming the adsorbates sit in the same type of binding site, identical phase-shifts δ_F describe them. Changing the integration variable from ϵ to q, we find the leading asymptotic term by just integrating the phase factor, which has the form $\exp(iq\mathcal{R})$, and evaluating it at the upper limit. The result is

$$\Delta E_{\rm trio}(d_{12}, d_{23}, d_{31}; \delta_F) \simeq -4 \left(\frac{2}{\pi}\right)^{5/2} \epsilon_{\rm F} \, \sin^3(\delta_F)\, \gamma_{123} \, \frac{\sin(q_{\rm F} d_{123} + 3\delta_F - 3\pi/4)}{(q_{\rm F} d_{123})^{5/2}}, \tag{4}$$

where the only shape dependence comes via the dimensionless ratio $\gamma_{123} \equiv d_{123}^{3/2}/\sqrt{d_{12}d_{23}d_{31}}$. For regular triple-cluster configurations (having comparable adsorbate separations), $\gamma_{123} \sim 5\frac{1}{2}$ [11]. The leading trio contribution (4) oscillates distinctly as a function of $q_{\rm F} d_{123}$, the Fermi wavevector times the perimeter, while decaying barely faster than the asymptotic pair interaction (1) and having roughly a quarter its magnitude. For special cluster configurations, with one triangle leg much smaller than the other two, our trio interaction result (4) reduces to an effective screening of the pair-interaction result (1) [11].

Fig. 1 shows our results for the 3-adsorbate interaction energies discussed above. While the actual perimeter has discrete values, the continuous depiction aids comprehension and generality. The top (bottom) panel compares estimates for the combined triple-adsorbate cluster (for the trio-interaction) energy. Previously [11,12], we considered an equilateral-triangle configuration. Here we show a linear (degenerate) isosceles configuration. The *solid curves* give our analytical asymptotic evaluation obtained using Eqs. (1) and (4). The *dashed curves* show separate interaction estimates, $\Delta E^{3\delta}_{\rm triple}$ and $\Delta E^{3\delta}_{\rm trio}$, which we obtain by numerically evaluating the adsorbate-induced change in DOS, Eq.(**??**), for $g_0(x) \propto H_0^{(1)}(x)$ with the reasonable assumption of a zero-range (δ-function) adsorbate potential [8,11]. The eventual approach to the analytical trio result of Eq. (4) is highlighted in the insert panel. We note in passing that straightforward computing of surface states using state-of-the-art density-functional techniques [18,19] would require about a dozen layers for proper convergence [12], well beyond current capabilities.

The lower panel shows that Eq. (4) underestimates the strength of the trio interaction for non-asymptotic perimeters. The specific curves—both solid (asymptotic) and dashed (as described above) are very similar to those for the previously displayed [11,12] equilateral triangles, as well as for obtuse (with apex angle 120°) isosceles and for rectangular (with perpendicular length ratio $\sqrt{3}$ configurations, consistent with the s-wave scattering.

In **??** we observed the comparison between $\Delta E_{\mathrm{triple,trio}}(d)$ and $\Delta E^{3\delta}_{\mathrm{triple,trio}}(d)$ (solid and dashed curves) as in in Fig. 1 documents that our asymptotic evaluations of both the triple-adsorbate the trio interactions become adequate for $q_F d_{123} > 6\pi$, corresponding to $d_{ij} > \lambda_F$. In contrast, the asymptotic pair-interaction result (1) becomes accurate already at $d_{12} > \lambda_F/2$ [8].

In Fig. 2 we show the triple interactions for the three previously unpublished configurations, the bottom panel being the top one of Fig. 1. Here there is noticeable dependence on shape, due to different pair contributions. Since the barriers for an adatom approaching a cluster evidently depends on more than just the distance from the cluster, we expect that full understanding of island growth will require more than just radial potentials for arriving adatoms. In contrast to [11,12], we use the *non-asymptotic* expression for the *pair* interaction to compute $\Delta E_{\mathrm{triple}}(d)$, so that the difference between the curves indicates more faithfully the correspondence between it and $\Delta E^{3\delta}_{\mathrm{triple}}(d)$. We find that the asymptotic approximation for the *trio* contribution alone provides a good approximation to smaller values of d.

In summary, we have recapitulated several results for the triple-adsorbate interaction energy mediated by an isotropic Shockley surface-state band, as found on noble-metal (111) surfaces, and included new results for different triangular shapes. We derive a general formalism for this energy expressed in terms of experimentally accessible parameters. We also provide an explicit numerical evaluation for several triangle shapes on Cu(111). While the sum of pair-interaction contributions dominates the triple-adsorbate interaction energy, we find 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 quattro 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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FIGURES

FIG. 1: For a linear configuration, three-adsorbate indirect interaction mediated by a surface-state band. The figure compares estimates both for the full (triple) interaction energy (top panel) and for the trio contribution (bottom panel) for a triangle with an obtuse isosceles configuration, for comparison with the previously computed equilateral configuration. *The solid curves* show our asymptotic result (4). *The dashed curves* show a numerical determination, $\Delta E^{3\delta}_{\mathrm{triple}}(d)$, which arises when we base the single-adsorbate scattering approximation on a zero-range (δ-function) approximation for the adsorbate potential **??**. *The insert* details the long-ranged asymptotic variation.

FIG. 2: Comparison of the triple interaction, corresponding to the top panel of Fig. 1, for rectangular (perpendicular sides with length ratio $\sqrt{3}$, obtuse isoceles (with apex angle 120°), and linear isosceles triangles. To make the comparison clear, the perimeter is taken to be continuous.

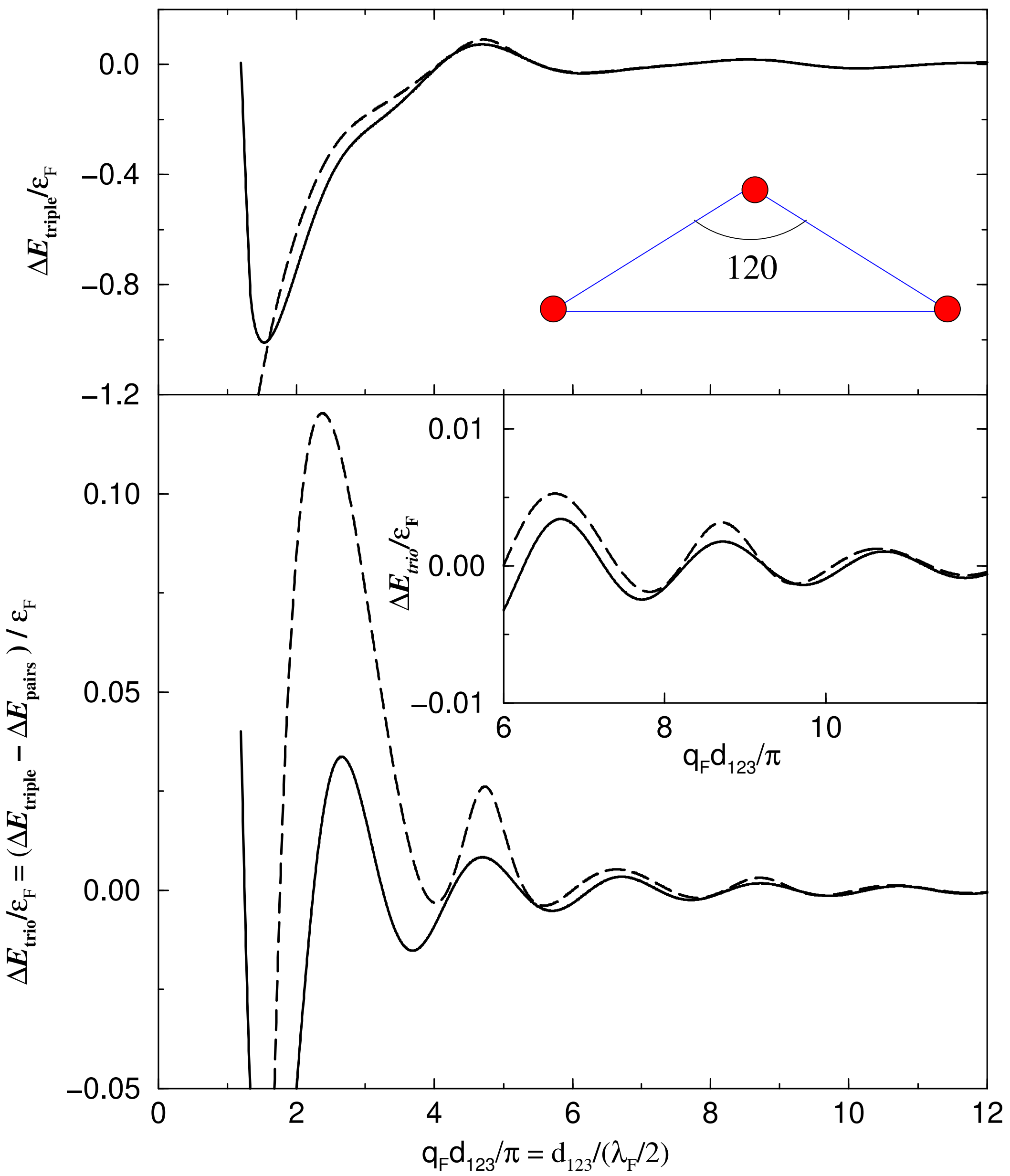
0.0
−0.4
−0.8
−1.2
$\Delta E_{\mathrm{triple}}/\varepsilon_F$
120
0.10
0.05
0.00
−0.05
$\Delta E_{\mathrm{trio}}/\varepsilon_F = (\Delta E_{\mathrm{triple}} - \Delta E_{\mathrm{pairs}})\ /\ \varepsilon_F$
0.01
0.00
−0.01
$\Delta E_{trio}/\varepsilon_F$
6
8
10
$q_F d_{123}/\pi$
0
2
4
6
8
10
12
$q_F d_{123}/\pi = d_{123}/(\lambda_F/2)$

Figure 1

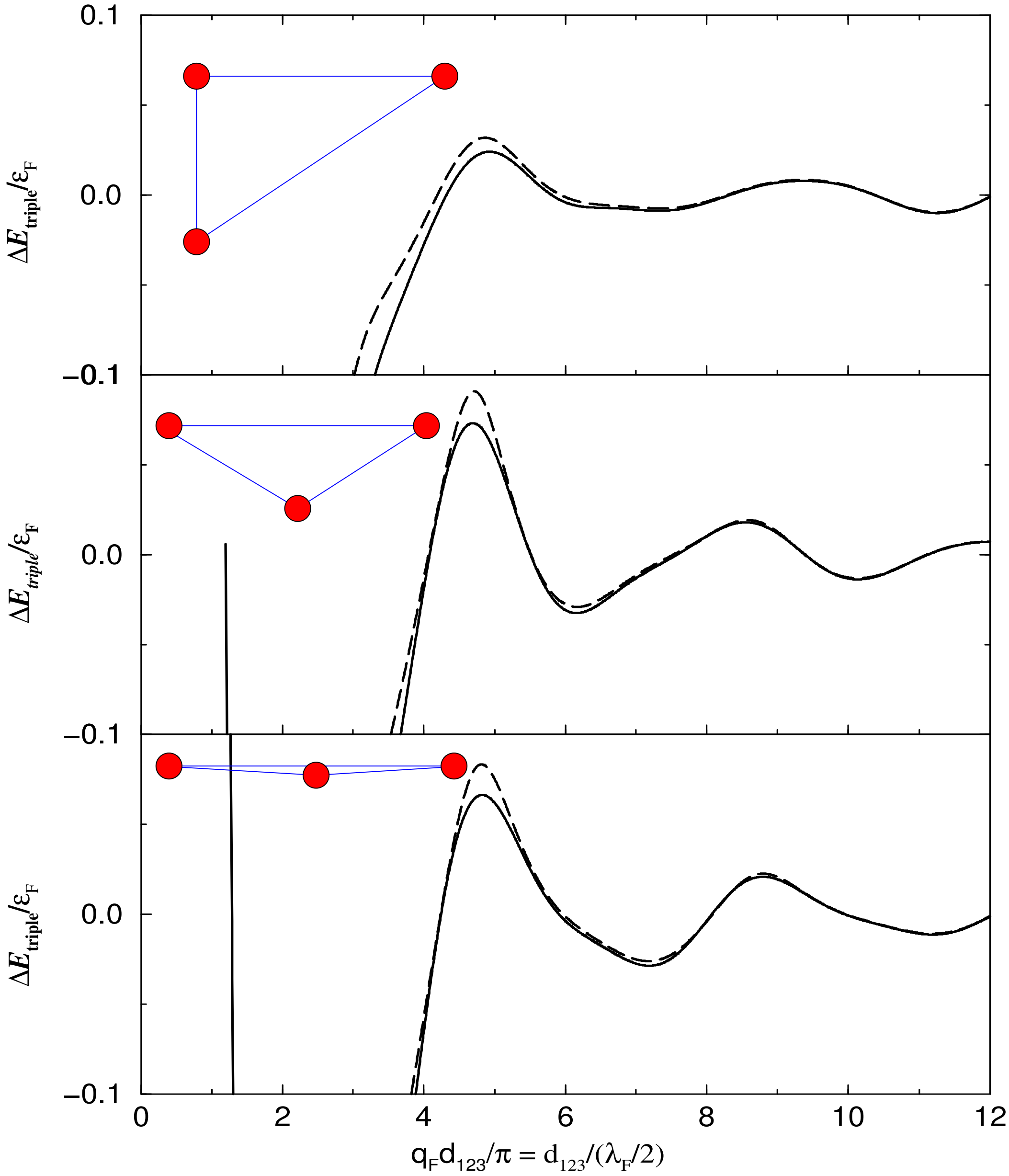
0.1
0.0
−0.1
0.0
−0.1
0.0
−0.1
$\Delta E_{triple}/\varepsilon_F$
$\Delta E_{triple}/\varepsilon_F$
$\Delta E_{triple}/\varepsilon_F$
0
2
4
6
8
10
12
$q_F d_{123}/\pi = d_{123}/(\lambda_F/2)$

Figure 2