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LETTER TO THE EDITOR

Long-ranged adsorbate–adsorbate interactions mediated by a surface-state band

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Abstract. The adsorbate–adsorbate interaction mediated by Shockley surface states on, for example, the (111) faces of noble metals, yields an oscillatory form modulated by a $1/d^2$ envelope at asymptotic adsorbate separations d . For this interaction we obtain a non-perturbative analytical estimate, specified by experimentally accessible Shockley-state parameters and the finite Fermi-level phase shift $\delta_F \neq 0$, which characterize the standing-wave patterns observed in scanning tunnelling microscopy (STM) images. We provide explicit interaction results for the phase shift value $\delta_F = -\pi/2$ suggested by the STM measurements of sulphur adsorbates on Cu(111), and we attempt to relate our results to the corresponding observations of correlations in the adsorbate distribution function.

The stunning progress in scanning tunnelling microscopy (STM) has made it possible to study the physical properties of surface-state electrons in real space. Their properties are revealed from standing surface wave patterns formed in the vicinity of defects such as adsorbates 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. Exciting examples include ‘quantum corrals’ formed by Fe atoms on Cu(111) [3], quantum wires formed by narrow terraces on a stepped Au(111) surfaces, and small islands on Ag(111) [4, 5]. A recent STM study of S segregation on Cu(111) [6] revealed a correlation between the inter-adsorbate distance and the period of the surface wave oscillations around the adsorbates. Surface waves are strongly scattered from adsorbates and the indirect adsorbate–adsorbate interaction mediated by the surface-state band could influence the spatial distribution of adsorbates, for example, during growth.

In this letter, we examine the indirect interaction mediated by a Shockley surface-state band between adsorbates on the (111) face of noble metal surfaces in the presence of bulk electrons. We stress the importance of screening by the finite density of the surrounding bulk (conduction-band) electrons. This bulk screening permits us to obtain a simple (but non-perturbative) description of the adsorbate-induced scattering within the surface-state band. In the asymptotic region of large adsorbate separations d we provide the analytical estimate

$$\Delta E_{int}(d) \simeq -\epsilon_F \left(\frac{2 \sin(\delta_F)}{\pi} \right)^2 \frac{\sin(2q_F d + 2\delta_F)}{(q_F d)^2}. \quad (1)$$

This estimate is specified by experimentally accessible parameters: the Fermi-level phase shift, δ_F , which characterizes the adsorbate-induced, standing surface-wave patterns (observed in STM images), the Fermi energy ϵ_F of the surface band (measured from the bottom of the

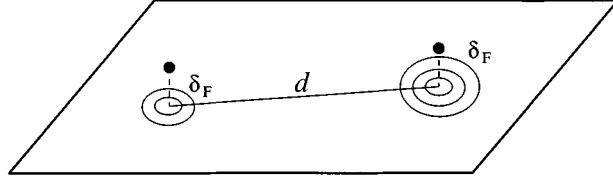


Figure 1. Schematic diagram of the adsorbate–adsorbate interaction geometry. A pair of adsorbates are separated by distance d and are located above a metal surface which supports a surface-state band. The scattering at each adsorbate causes oscillations (concentric rings) in the surface-state DOS. This scattering is characterized by a finite Fermi-level phase shift, $\delta_F \approx -\pi/2$.

Table 1. Shockley surface-state parameters and Thomas–Fermi (bulk-screening) wavevectors of the Cu(111), Ag(111), and Au(111) metal 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 wavevector $q_F = \sqrt{2m_{eff}\epsilon_F}$. The parameter values are taken from [7]. The Thomas–Fermi wavevectors, k_{TF} , are based on a (bulk) free-electron model [8].

	m_{eff}/m_e	ϵ_F (eV)	q_F (\AA^{-1})	k_{TF} (\AA^{-1})
Cu	0.46	0.39	0.217	1.81
Ag	0.53	0.12	0.129	1.70
Au	0.28	0.41	0.173	1.70

Shockley-state band), and the associated in-surface Fermi wavevector q_F . We present explicit interaction results for sulphur adsorbates on Cu(111), where STM images [6] show wave patterns consistent with the Fermi-level phase shift $\delta_F = -\pi/2$. We attempt to relate these to the adsorbate pair distribution function, also reported in [6]. Finally, we establish the reduction of the interaction result (1) by a finite electron scattering out of the surface-state band and into the bulk-electron conduction bands.

The schematic diagram, figure 1, illustrates the experimental situation and identifies the adsorbate–adsorbate (Friedel) interaction mechanism. A pair of adsorbates is located above a (noble) metal surface, which supports a surface-state band. Table 1 identifies the key parameters which characterize the Shockley state in the (111) face of Cu, Ag, and Au. Table 1 also includes values for the effective mass m_{eff} which relates the Fermi energy to the Fermi wavevector, $q_F = \sqrt{2m_{eff}\epsilon_F}$. Each adsorbate induces scattering and causes spatial oscillations in the surface-band density of states (DOSs). These DOS oscillations can, at the Fermi level ϵ_F , be described by the phase shift δ_F . The interference between such DOS variations produce 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, as reviewed by Einstein [9]. Lau and Kohn [10] used a perturbative study to document how the presence of a two-dimensional (2D) electron gas significantly enhances the Friedel interaction and cause a long-range variation with asymptotic decay $1/d^2$. However, a perturbative analysis is not consistent with the observed significant Fermi-level phase shifts $\delta_F \approx -\pi/2$ [11]. Moreover, a complete analysis of the surface-state mediated adsorbate–adsorbate interaction must discuss the significant screening produced by the finite density of the surrounding bulk electrons.

Our interaction study is formally based on the Harris functional expression [11, 12]

$$\Delta E_{int}(d) = \Delta E_e(d) - \Delta \Phi_c(d) \quad (2)$$

which contains both a one-electron energy term, ΔE_e , and an electrostatic correction term[†],

$$\Delta\Phi_c(d) = \int d\mathbf{x} (-e\delta n_a(\mathbf{x}) - \delta\rho_i(\mathbf{x}))\phi_a(\mathbf{x} - \mathbf{d}). \quad (3)$$

This correction is defined by the adsorbate ion-core charge density, $\rho_i(\mathbf{x})$, the adsorbate-induced change in the electron density, $\delta n_a(\mathbf{x})$, and the corresponding electrostatic potential, $\phi_a(\mathbf{x} - \mathbf{d})$, produced by the second adsorbate. The electrostatic term, equation (3), corrects for the over-counting of the Coulomb energy in the contribution of the single-electron interaction ΔE_e .

We argue that the screening by the bulk electrons: (i) ensures a negligible correction, $\Delta\Phi_c(d) \sim 0$, because this screening implies a short-ranged electrostatic potential $\phi_a(\mathbf{x})$; and (ii) justifies a phase-shift scattering model for adsorbate scattering within the surface-state band. We identify the one-electron term $\Delta E_e(d)$ as the dominant contribution to our interaction result, $\Delta E_{int}(d)$, and find that the phase-shift model permits an asymptotic, but analytic, determination, equation (1), which is expressed in terms of experimentally accessible parameters.

The one-electron contribution ΔE_e is given by an energy integral

$$\Delta E_e(d) = 2 \int_{-\infty}^{\epsilon_F} d\epsilon (\epsilon - \epsilon_F) \Delta\rho(\epsilon; d). \quad (4)$$

The factor of two accounts for the spin degeneracy. An interference-related DOS difference [11].

$$\Delta\rho(\epsilon, d) = -\frac{1}{\pi} \frac{d}{d\epsilon} \text{Im} \int d\mathbf{x} \langle \mathbf{x} | \ln[1 - T_{a1}(\epsilon)G_0(\epsilon)T_{a2}(\epsilon)G_0(\epsilon)] | \mathbf{x} \rangle \quad (5)$$

identifies the change in level distribution at a finite adsorbate separation d compared to that induced by a pair of isolated adsorbates, at $d \rightarrow \infty$. This one-electron DOS difference, equation (5), should be calculated using frozen adsorbate-induced scattering potentials [12]. The screening by bulk electrons justifies an assumption that the pair of adsorbate scattering potentials are non-overlapping. We express the formal result, equation (5), in terms of the one-electron (retarded) Green function $G_0(\epsilon)$ for the bare surface and the T-matrices, $T_{ai}(\epsilon)$, which characterize the (non-perturbative) scattering at adsorbates $i = 1, 2$.

The presence of a Shockley surface-state band introduces two important simplifications in the evaluation (equation (5)) of $\Delta\rho(\epsilon, d)$. First, at large adsorbate distances the dominant contribution to $\Delta\rho(\epsilon, d)$ will arise 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 will be dominated by s -wave scattering contributions because the Fermi wavelength $\lambda_F = 2\pi/q_F$ for the Shockley surface states is typically much larger than the bulk Thomas–Fermi screening length, $1/k_{TF}$. For example, for the Cu(111) surface we have from, table 1, $\lambda_F \approx 30 \text{ \AA}$, but $1/k_{TF} \approx 0.6 \text{ \AA}$.

At finite adsorbate separations d , the DOS difference (equation (5)) thus becomes dominated by

$$\Delta\rho(\epsilon, d) \approx -\frac{1}{\pi} \frac{d}{d\epsilon} \text{Im} \ln[1 - (t_0(\epsilon)g_0(qd))^2] \quad (6)$$

where $g_0(qd)$ describes the propagation d in the surface band at momentum, $q = \sqrt{2m_{eff}\epsilon}$ and a new effective T-matrix t_0 describes the adsorbate scattering within the surface band. The s -wave T-matrix energy dependence

$$t_0(\epsilon) = -\frac{2\hbar^2}{m_{eff}} \sin \delta_0(\epsilon) \exp(i\delta_0(\epsilon)) \quad (7)$$

[†] We neglect changes in the exchange-correlation energies produced by the adsorbate-introduced electron densities.

is, in turn, specified through the s-wave phase shift $\delta_0(\epsilon)$, for which we can obtain a model description. The Green function g_0 for the bare surface band is given by the cylindrical Hankel function, $H_0^{(1)}$, of the first kind

$$g_0(x) = i \frac{m_{eff}}{2\hbar} H_0^{(1)}(x) \simeq i \frac{m_{eff}}{\hbar} \frac{\exp(ix - i\pi/4)}{\sqrt{2\pi x}} \quad x \rightarrow \infty. \quad (8)$$

The slow decay of the amplitude for propagation in a 2D surface state is illustrated by its asymptotic expansion.

We obtain our formal interaction result (equation (1)) through an asymptotic evaluation of the one-electron energy integral, (4). Equation (6) is used to approximate the integrand $\Delta\rho(\epsilon)$ at finite adsorbate distances. In this asymptotic region, we find that the scattering-induced DOS change is essentially given by the first term in a logarithmic expansion of (6). Multiple adsorbate–adsorbate scattering effects provide only minor corrections to this difference in the adsorbate-induced DOS. We finally use Fourier analysis [13] to determine the one-electron energy integral, (4), which is dominated by integrand contributions around ϵ_F [11].

The predicted adsorbate interaction energy (equation (1)) can be evaluated directly from the information about the surface state parameters that is available from photoemission experiments and listed for Cu, Ag, and Au in table 1, and from measured STM images of the standing-wave patterns around isolated adsorbates. According to Tersoff–Hamann theory [14], STM images at low biases reflect the local adsorbate-induced DOS at the tip apex at the Fermi energy. This DOS is usually modelled by s-wave scattering with an s-wave phase shift, $\delta_F = \delta_0(\epsilon_F)$ [2, 5, 6]. For the surface-state scattering, the single-adsorbate-induced change in the DOS is

$$\Delta\rho_{as}(\mathbf{x}_{\parallel}; \epsilon) = -\frac{1}{\pi} [g_0(q|\mathbf{x}_{\parallel}|)^2 t_0(\epsilon)] \quad (9)$$

where \mathbf{x}_{\parallel} denotes a position along the surface. At large distances from the adsorbate the asymptotic result, (8), applies, i.e.

$$\Delta\rho_{as}(\mathbf{x}_{\parallel}; \epsilon) \propto \frac{\sin(\delta_0(\epsilon))}{2\pi q|\mathbf{x}_{\parallel}|} \cos(2q|\mathbf{x}_{\parallel}| + \delta_0(\epsilon)). \quad (10)$$

The phase shift $\delta_F \equiv \delta_0(\epsilon_F)$ can thus be extracted (modulus π) from the phase of the adsorbate-induced, standing-wave oscillations in the low-bias STM images. Note that the modulus- π ambiguity does not influence $\Delta E_{int}(d)$ in equation (1).

We stress that our formal result for the adsorbate interaction energy permits a simple discussion of materials' dependence. Our result, equation (1), provides an explicit determination for the interaction strength (given by ϵ_F and δ_F) and oscillation phase (specified by $2\delta_F$). In general, a more favourable interaction strength is obtained for Cu and Au than for Ag, as shown by their values for ϵ_F in table 1. As a specific example, we consider the case of maximum repulsive scattering, $\delta_0(\epsilon_F) = -\pi/2$. According to the Friedel sum rule [15], this phase-shift value corresponds to a depletion in the surface-state band of one electronic charge, $-e$. Our choice of δ_F is consistent with the values 1.5 ± 0.2 (modulus π) and -1.15 obtained from an analysis of the observed adsorbate-induced, standing-wave oscillations by Crommie *et al* [2] and by Wahlström *et al* [6], respectively. In both cases the adsorbates were interpreted as sulphur atoms.

Figure 2 shows our results for the adsorbate–adsorbate interaction energy mediated by the surface-state band in Cu(111) and assuming the Fermi-level phase shift $\delta_F = -\pi/2$. The *full curve* shows our asymptotic analytical result, equation (1), produced by the one-electron energy term in equation (4). The *broken curve* shows a separate interaction estimate, $\Delta E_{int}^{2\delta}(d)$, which we obtain by numerically evaluating the full 2D result for the DOS in (6), using a zero-range

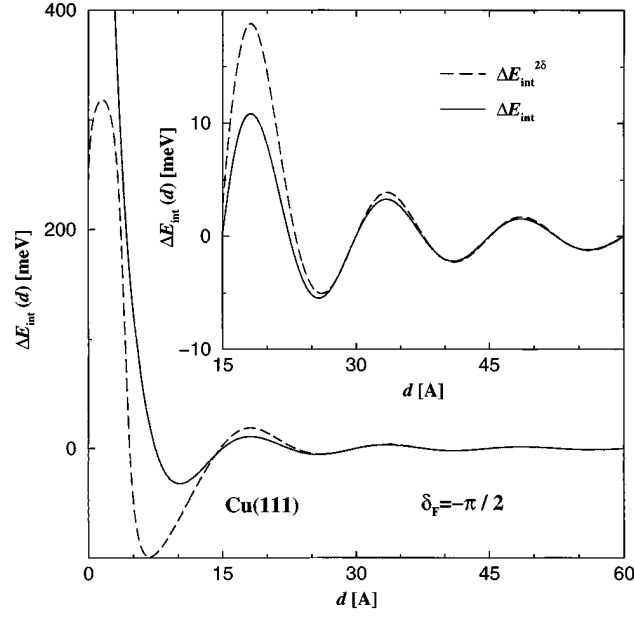


Figure 2. Calculated adsorbate–adsorbate interaction energy mediated by the surface-state band. We show our non-perturbative interaction results at the phase-shift value $\delta_F = -\pi/2$. This phase shift is consistent with experimentally observed standing-wave patterns of sulphur at Cu(111). The full curve shows our main asymptotic result, equation (1). The broken curve shows a numerical determination, $\Delta E_{int}^{2\delta}(d)$, which arises when we base the single-adsorbate scattering approximation, equation (6), on a zero-range (δ -function) approximation for the adsorbate potential and obtain the s -wave phase-shift variation specified in (11). The insert details the long-ranged asymptotic variation and is used in a comparison against the experimentally observed pair correlation in the adsorbate distribution.

(δ -function) potential model for the phase shift,

$$\delta_0(\epsilon) = \text{arccot} \left[\frac{1}{\pi} \ln \left(\frac{\epsilon}{\epsilon_F} \right) \right]. \quad (11)$$

The comparison between $\Delta E_{int}(d)$ and $\Delta E_{int}^{2\delta}(d)$ (full and broken curves) in figure 2 shows that our asymptotic expression, equation (1), is accurate, even down to a distance of $\lambda_F/2$. The deviation at closer distances is primarily caused by a breakdown of the asymptotic evaluation in the energy integral, equation (4).

The insert of figure 2 details the long-range oscillations of our interaction prediction, equation (1), and permits a comparison with the experimental observation of the pair correlations in the sulphur adsorbate on the Cu(111) distribution function [6]. This adsorbate correlation was reported at experimental temperatures in the range $T = 85\text{--}300$ K and showed very pronounced maxima at 21 ± 3 , 36 ± 4 , and 66 ± 7 Å (specified by the period 15 Å for the surface-state Friedel oscillations, except for a missing maximum at 51 Å). In contrast, our predicted adsorbate–adsorbate interaction (figure 2, inset panel) shows potential-energy minima at 26, 41, and 56 Å. Moreover, these potential minima are only separated by a set of very shallow barrier heights (9, 4, and 2 meV). Even at the lowest experimental temperature $T = 85$ K, such barrier would yield, *at most*, a 60% decrease in the relative barrier to potential-minima population[†]. Although evaluated at the experimentally motivated choice of phase shift

[†] We note that our experimental comparison applies, when we assume that the cooling of surface-segregated adsorbates occurs sufficiently slow to establish a thermally equilibrated adsorbate distribution.

$\delta_F = -\pi/2$, our interaction prediction is not consistent with the corresponding experimental observation of the adsorbate pair correlation [6].

Adsorbate scattering into the bulk band produces an important further reduction of the adsorbate–adsorbate interaction energy. Up to now we have used an inherent assumption that the adsorbate scattering remains within the surface-state band. Such an assumption disagrees with the calculated scattering of the surface-state electrons off a row of adsorbate atoms and into the bulk-like electron states [16]. However, the bulk-scattering constitutes an effective ‘absorption’ of surface-state electrons and can be represented by imparting a positive imaginary part to the phase shift, $\delta_0 = \delta'_0 + i\delta''_0$. This complex phase shift in turn produces a (intra-surface-band) reflection amplitude $r = \exp(-2\delta''_0)$, which is less than unity. Using a polar representation of the T-matrix $t_0(\epsilon)$, we find that the phase θ_0 of the standing wave around an adsorbate is now determined by

$$\tan(\theta_0) = \frac{1 - r \cos(2\delta'_0)}{r \sin(2\delta'_0)} \quad (12)$$

but reduces to $\theta_0 = \delta_0$ at $r = 1$. In general, it is difficult to determine r and δ'_0 uniquely, as one would then need to experimentally establish the absolute amplitude of the standing-wave patterns. However, the polar representation of t_0 still permit important qualitative statements about the resulting modified adsorbate–adsorbate interaction

$$\Delta E_{int}^{r < 1}(d) \simeq -\epsilon_F \left(\frac{(r-1)^2}{4} + r \sin^2(\delta'_0) \right) \times \left(\frac{2}{\pi} \right)^2 \frac{\sin(2q_F d + 2\theta_0)}{(q_F d)^2}. \quad (13)$$

The phase of the interaction oscillations remains unchanged whereas the amplitude is reduced. A peculiarity of the phase-shift value $-\pi/2$ is that inclusion of the surface-state ‘adsorption’ does not affect δ'_0 , but simply causes the reduction $(r+1)^2/4$ of the interaction strength. The bulk-scattering reduction effect is at most one-quarter in the ‘black dot’ limit, $r \rightarrow 0$ [17].

In summary, we have developed a simple analytical result for the adsorbate–adsorbate interaction energy mediated by a Shockley surface-state band on the (111) face of noble metals. Our model is based on the assumption that the screening by the bulk electrons makes the adsorbate-induced potentials short ranged, so that (i) the electrostatic correction within our Harris functional approach can be neglected, and (ii) the scattering of the long-wavelength, surface-state electrons is dominated by s-wave scattering. The dominant interaction contribution arises from the interference-related difference in the one-electron DOS produced by the multiple adsorbate scattering. In the asymptotic region of large adsorbate–adsorbate distances, this energy is determined by experimentally accessible parameters. We find that any scattering of the surface-state electrons from the adsorbates into the bulk states tends to reduce the interaction. We present explicit results for the interaction energy in the case of the most favourable value of the phase shift, $\delta_F = -\pi/2$, a choice suggested by STM observations of standing-wave patterns induced by sulphur adsorbates at Cu(111). Our prediction for the adsorbate–adsorbate interaction is not consistent with recent observations of the pair correlation in the sulphur adsorbate distribution.

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