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Surface-state mediated three-adsorbate interaction: electronic nature and nanoscale consequences

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Abstract

The interaction energy of a three-adsorbate cluster on a surface consists of the sum of pair interactions *plus* a *trio* contribution. The trio interaction is produced by interference of electrons which propagate around the cluster perimeter, d_{123}. We investigate such interactions for a noble-metal (111) surface, where the isotropic Shockley surface-state band produces cluster-interaction energies significant for the low-temperature adsorbate dynamics. We provide experimentally testable interaction-energy predictions, specified by the s-wave phase shift δ_F that characterizes the standing-wave patterns seen in scanning-tunneling microscopy (STM) images. Compared with the adsorbate-pair interactions, the trio contribution exhibits a slightly weaker amplitude and a slightly faster asymptotic decay. We discuss how the trio interaction can

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affect the cluster geometry by introducing an additional angular dependence in the adsorbate interaction.

Keywords: Adsorbate, Impurity interactions, Surface states, Scanning tunneling microscopy

1. Introduction

Progress in scanning-tunneling microscopy (STM) has allowed atomistic studies of adsorbate interactions, dynamics, and growth. The STM can also probe the real-space variations of surface electrons and provides a direct measurement of the local density of state (LDOS) in the vicinity of both adsorbates and defects [1, 2]. The investigation of noble-metal surfaces (e.g., Cu(111)) supporting a surface-state electron band has been particularly fascinating as the surface waves are both strongly scattered from the adsorbates and defects and reflect the singular Friedel response present in a two-dimensional electron gas. Such STM investigations have thus revealed long-ranged standing surface-wave patterns formed, e.g., within "quantum corrals" [1]. These standing-wave patterns are characterized by a strong Fermi-level phase shift $\delta_F \approx \pm\pi/2$ and decay much slower than bulk-type electron states. The long-range oscillatory nature of the surface-state electron response opens the possibility for a mutual adsorbate and defect interaction at nanoscale separations. Theoretical investigations [3, 4, 5, 6, 7] and recent experimental verifications [8, 9], document that the interference of such standing-wave patterns produce such a finite mutual adsorbate interaction energy at nanoscale separations. Recent investigations also show how such very-long-ranged mutual-adsorbate interactions affect the low-temperature adsorbate dynamics [8, 9, 10].

The interaction between adsorbates on a metal surface can involve an elastic, an electrostatic,

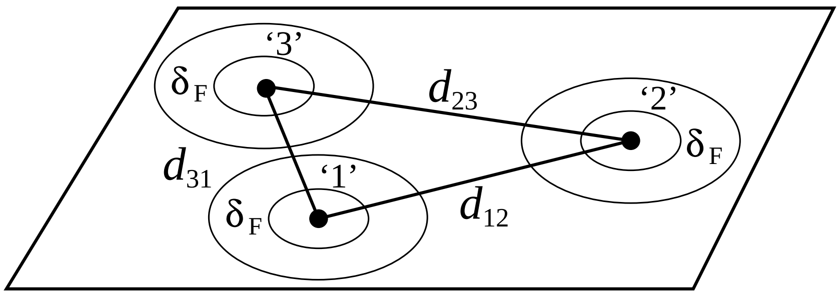

Figure 1: Schematics of the long-range triple-adsorbate interaction mediated by a surface-state band present, e.g., on a Cu(111) surface. The three adsorbates, at positions $i = 1, 2, 3$, each induce a strong screening response (Friedel oscillations) characterized by finite scattering phase shifts $\delta_F \neq 0$. A long-ranged (nanoscale) electronic interaction result from interference of such adsorbate-induced Friedel oscillations. We provide a nonperturbative estimate $\Delta E_{\mathrm{triple}}$ of the triple-adsorbate interaction given as a function of the mutual separations d_{ij} and of the phase shift $\delta_F \approx \pm\pi/2$ observable in scanning tunneling microscopy (STM) measurements.

and an indirect contribution arising from the singular screening response characterizing the Friedel oscillations. Indirect adsorbate interactions [5] have long received theoretical attention [3]. An early investigation by Lau and Kohn [4] stressed that the range of the indirect oscillatory adsorbate or defect interaction increases dramatically when it is mediated by a surface rather than a bulk state; here the indirect interaction can extend beyond both elastic and electrostatic contributions (which decays as $1/d^3$). Recent theory investigations [7, 8] applied these ideas to the special case of the isotropic surface-state bands found, e.g., on the (111) surface of a noble metal. Such surface-state bands are described by an effective mass m_{eff} in-surface Fermi wavevector q_{F} and Fermi level $\epsilon_{\mathrm{F}} = (\hbar q_{\mathrm{F}})^2/2m_{\mathrm{eff}}$. At asymptotic separation $d_{ij} > \lambda_F/2$, the nonperturbative result for the pair-interaction [7, 8] can be expressed analytically

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

Subsequent STM measurements of Cu and Co adsorbate dynamics on Cu(111) and Ag(111) [8, 9] have not only revealed a direct correlation between inter-adsorbate distances and 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 electronic adsorbate pair interaction.

Here we investigate the long-range indirect interaction for three adsorbates [13] as an initial effort to understand the multi-adsorbate interactions relevant for clusters on noble-metal surfaces. As illustrated in the schematic Fig. 1, each of the three adsorbates, at positions '$i = 1, 2, 3$,' causes a significant scattering and an oscillatory response (sets of concentric rings) in the local density of states due to presence of the surface-state Fermi surface. This scattering is characterized by a Fermi-level phase-shift $\delta_F \neq 0$ and the interference between such Friedel screening responses produces a nanoscale oscillatory adsorbate interaction. Based on the density-functional theory (DFT) [11, 12] concepts we present and compare analytical asymptotic estimates and exact model calculations for the long-ranged triple-adsorbate interaction mediated by an isotropic Shockley-type surface state at nanoscale separations. As in a previous investigation [7] of the pair-adsorbate interaction, our results are expressed in experimentally accessible parameters. For three adsorbates the asymptotic interaction consists of the sum of adsorbate-pair interactions [4, 5, 7, 8, 9], $\Delta E_{\mathrm{pair}}(d_{ij})$ plus an additional trio contribution $\Delta E_{\mathrm{trio}}(d_{123})$ [6, 13]. Our set of interaction results [6, 7, 8, 13], ΔE_{pair} and $\Delta E_{\mathrm{triple}}$ should be viewed as the initial steps in a calculation of the interacting energy of a general adsorbate- or defect cluster [14] at asymptotic adsorbate separations.

2. The noble-metal surface-state electron system

Table I summarizes key parameters that characterize the relevant isotropic Shockley surface states found on the (111) facet of the noble metals Cu and Ag. For both surfaces there now exist experimental investigations of the long-ranged adsorbate interactions [8, 9]. The table

Table 1: Shockley surface-state parameters and Thomas-Fermi (bulk-screening) wavevectors of the Cu and Ag (111) surfaces. The Shockley band is characterized by the effective electron mass $m_{\rm eff}$, a Fermi energy ϵ_F (measured relative to the bottom of the surface-state band), and a corresponding in-surface Fermi wavevector $q_F = \hbar^{-1}\sqrt{2m_{\rm eff}\epsilon_F}$ and half wavelength $\lambda_F/2 = \pi/q_F$. The Thomas-Fermi screening lengths, k_{TF}^{-1}, are obtained as in Ref. [17].

	Cu(111)-STM	Cu(111)-DFT	Ag(111)-STM	Ag(111)-DFT
ϵ_F (eV)	0.38^a	0.42	0.065^a	0.045
$m_{\rm eff}/m_e$	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	—
$k_{\rm TF}^{-1}$ (Å)	0.552		0.588	
S adsorbate	$\delta_F = \pm\pi/2^b$	—	—	—
Cu adsorbate	$\delta_F = \pm\pi/2^{c,d}$	—	—	—
Co adsorbate	$\delta_F = \pm\pi/2^d$	—	$\delta_F = \pi/3^d$	—

[a]Ref. [15] [b]Ref. [2] [c]Ref. [8] [d]Ref. [9].

compares measurements obtained by STM probing [15] of the surface-state band parameters with our large, sized-converged calculations by standard first-principles DFT [11, 16]. The table also shows STM measurements of the scattering phase shifts $\delta_F \neq 0$ reported [2, 8, 9] for various adsorbates. Finally the table shows estimates for the Thomas-Fermi screening length k_{TF}^{-1} [17]. The surface-state electron response arises at much longer length scales, $\lambda_F/2 \gg k_{TF}^{-1}$, and dominates the long-range adsorbate interaction.

Table I reports good agreement between STM and our large-scale first-principle DFT calculations. Thus standard DFT could, *in principle,* account for the indirect adsorbate interactions [10]. However, a direct DFT investigation of interaction energies in adsorbate clusters at relevant nanoscale separations remains far beyond the scope of present computer capabilities. [2] The problem of long-ranged multi-adsorbate interactions requires instead a scattering-theory approach employed, e.g., in Refs. [6, 7]. Given the strong agreement between theory and experiments for the pair-adsorbate interaction problem [7, 8, 9], a corresponding analysis for the

[2]Our calculations show that slabs containing more than 18 atomic layers are required for an accurate calculation of the Cu(111) and Ag(111) surface-state parameters. Such 18-layer slab thickness makes a direct DFT-based calculation of nanoscale adsorbate-adsorbate interactions impossible.

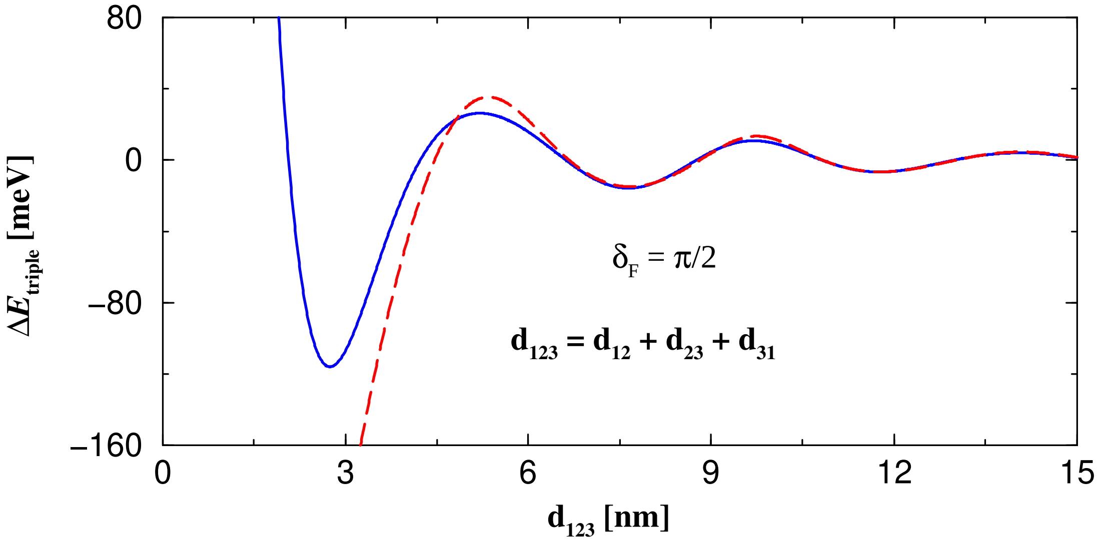

Figure 2: The long-range triple-adsorbate interaction mediated by a surface-state band. The figure illustrate our triple interaction result $\Delta E_{\text{triple}} = \Delta E_{\text{pairs}} + \Delta E_{\text{trio}}$ for an equilateral adsorbate configuration, $d_{ij} = d_{123}/3$, on a Cu(111) surface. The results also assumes the adsorbate-induced scattering phase-shift value, $\delta_F \approx -\pi/2$, experimentally observed in the standing-wave patterns of STM images of S, Cu, and Co adsorbates on the Cu(111) surface [8, 9]. The figure contrast our asymptotic analytic result, Eqs. (1-3), (solid curve,) against an exact numerical evaluation (dashed curve) obtained within a model treatment.

triple-adsorbate cluster interaction is warranted [13].

3. Nanoscale density-functional theory of the triple-cluster interaction

The triple-adsorbate cluster adsorption energy is calculated [13] by combining a formal expansion [5, 6] of the adsorbate-cluster energy with the scattering-theory approach used previously for pair interactions [7].

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

This triple-cluster interaction includes a new trio contribution $\Delta E_{\rm trio}$ 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 a analytical result [13]

$$\Delta E_{\rm trio}(d_{12}, d_{23}, d_{31}; \delta_F) \simeq -\epsilon_{\rm F} \sin^3(\delta_F) \left(\frac{16\sqrt{2}}{\pi^{5/2}}\right) \sqrt{\frac{d_{123}^3}{d_{12}d_{23}d_{31}}} \, \frac{\sin(q_{\rm F} d_{123} + 3\delta_F - 3\pi/4)}{(q_{\rm F} d_{123})^{5/2}}. \quad (3)$$

using formal results of Fourier transformation [18]. In the limit of completely absorbing scatterers the trio interaction result (3) is reduced by a factor of 1/8, see Ref. [13]. As in the corresponding asymptotic result (1) for the adsorbate-pair interaction [7, 8], this interaction estimate is given directly in terms of experimentally accessible parameters, Table I. Compared with the pair interaction (1), the trio interaction exhibits a slightly weaker amplitude (approximately one fourth at relevant adsorbate separations) and slightly faster asymptotic decay ($1/d_{123}^{5/2}$ versus $1/d_{ij}^2$).

Figure 2 compares our asymptotic triple-cluster interaction estimate (solid curve) — based on Eqs. (1) and (3) — with an exact model calculation (dashed curved) [13]. The figure shows interaction estimates for parameters appropriate for Cu, S, and Co on Cu(111) [8, 9], assuming here an equilateral cluster configuration. The non-vanishing interaction even at nanoscale separations suggests that it can affect the low-temperature assembly of adsorbate clusters.

4. Cluster geometry effects in the triple-adsorbate interaction

The triple-cluster interaction, Eqs. (1–3), could have important effects on the triple-adsorbate cluster geometry. The first and dominant term of the triple-cluster interaction involves a sum of three oscillatory pair interactions (1) which, therefore, must be sensitive to the triangle configuration of adsorbates. A corresponding configuration dependence is directly evident in the asymptotic result (3) for the trio interaction. For example, among adsorbate isosceles (two legs at d and one leg d_s) triangles with a fixed circumference d_{123}, the geometrical prefactor,

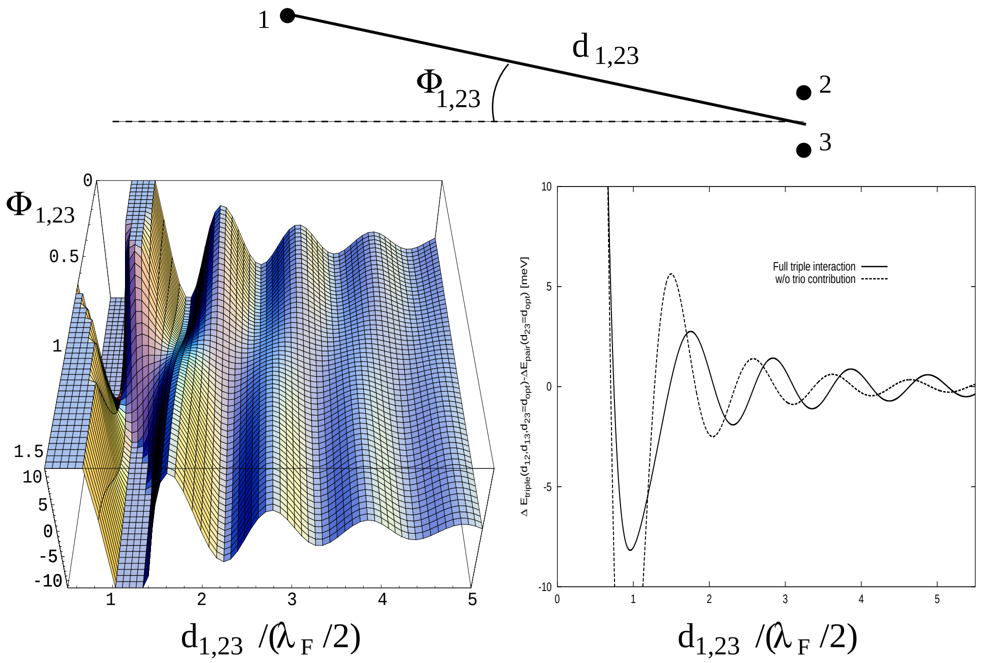

Figure 3: Triple-interaction effects on cluster assembly; geometry variation of the effective potential $\Delta E_{\rm triple}(d_{12}, d_{13}, d_{23} = d_{\rm opt}) - \Delta E_{\rm pair}(d_{23} = d_{opt})$ that determine the approach of a new adsorbate '1' toward an established (fixed) adsorbate pair '2-3' (sitting at optimal pair separation $d_{\rm opt}$). The left panel details significant variation with adsorbate/pair separation $d_{1,23}$ and with adsorbate-angle-of approach $\Phi_{1,23}$; This variation arises from both terms in $\Delta E_{\rm triple}$ (Eqs. (1-3)). The right panel documents the important role the new trio interaction (Eq. (3)) can play in modifying the interaction variation along the $\Phi_{1,23} = \pi/4$ angle of approach.

$\gamma_{123} \equiv \sqrt{d_{123}/d_{12}d_{23}d_{31}}$ in the trio estimate Eq. (3), still contains a noteworthy shape dependence, particularly for highly distorted arrangements. Specifically, $\gamma_{123} = 3^{3/2}$ for an equilateral configuration while the case $d_s \ll d$ yields $\gamma_{123} \approx 2(2d/d_s)^{1/2}$ thus producing a trio interaction with the same asymptotic decay $(1/d^2)$ — but different oscillation phase from that found for pair interactions.

An interesting variation with triangle configuration arises, for example, at the above-mentioned case of $d_s \ll d$ describing the important case where one new adsorbate approaches an existing adsorbate pair. Since adsorbates at low temperatures are known [8, 9] to retain a finite (nanoscale) minimal separation on the Cu and Ag surfaces our asymptotic triple-adsorbate interaction results (1–3) can be used to investigate the consequences for such low-temperature cluster growth.

Figure 3 illustrates such consequences of the indirect adsorbate interaction on the growth and assembly of (well-separated) adsorbate clusters on a Cu(111) surface. The figure reports the geometry effects on the triple-adsorbate interaction Eqs. (1–3). Assuming an optimal configuration of one adsorbate pair, the figure compares the (triple) interaction potential for one additional adsorbate approaching along different angles (specified relative to the axis of the adsorbate pair).

5. Conclusions

In summary, we present both an asymptotic evaluation and an exact model calculation for the triple-adsorbate interaction energy mediated by an isotropic Shockley surface-state band, as found on noble-metal (111) surfaces. This interaction consists of a sum of pair interactions and a trio correction. We stress that the trio and analogous quattro and higher-order interaction contributions could play an important role for larger clusters and affect the total interaction energy of relatively dense (ordered) overlayers. Equally important, we conclude that the trio contribution and the triple-adsorbate interaction can play a role in the low-temperature adsorbate assembly [5, 10].

6. Acknowledgments

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FIGURE CAPTIONS

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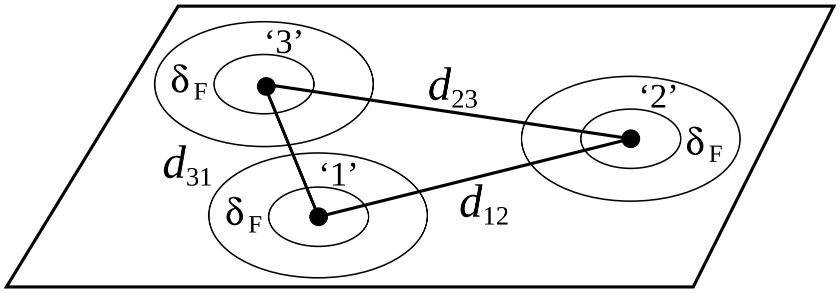
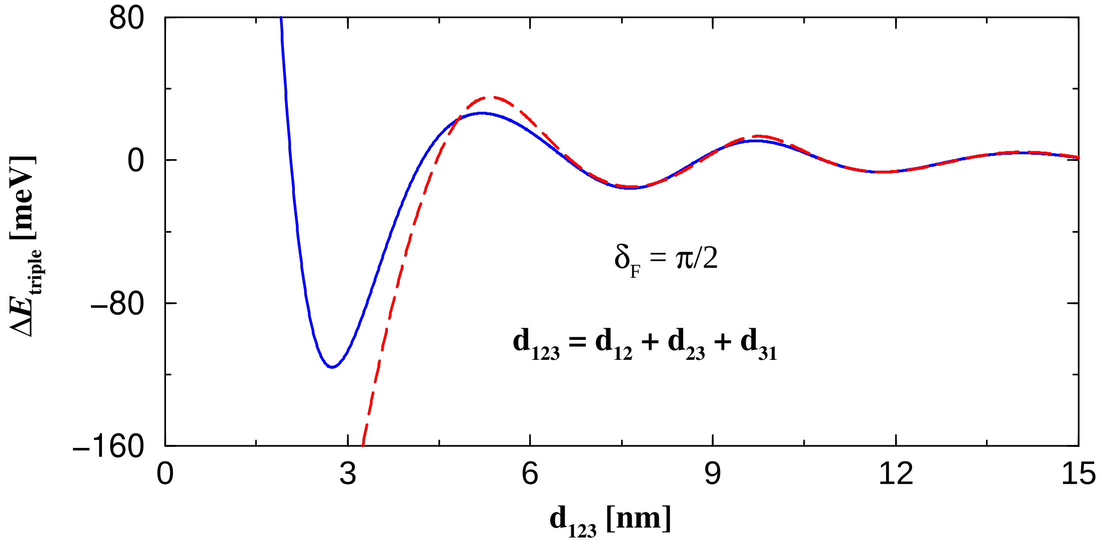


Figure 1


80
0
−80
−160
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3
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9
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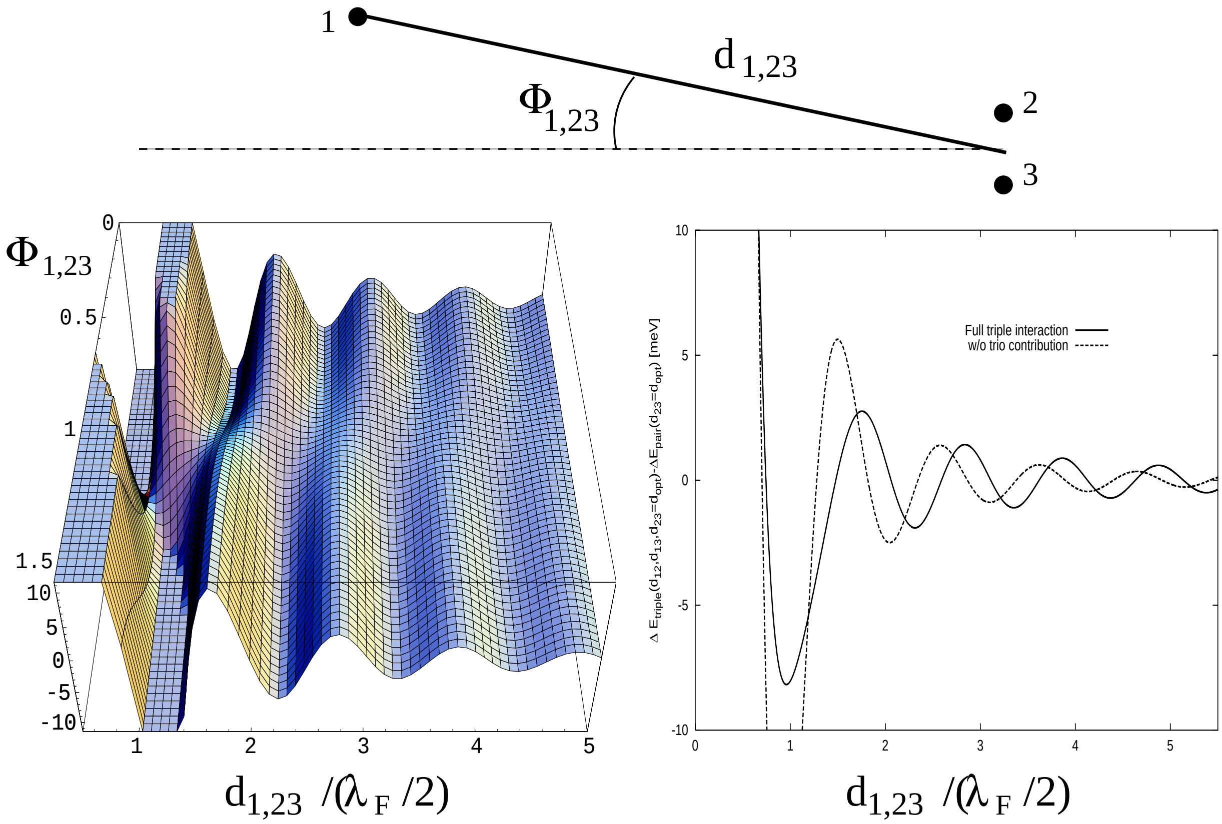
15
ΔE_triple [meV]
d_123 [nm]
δ_F = π/2
d_123 = d_12 + d_23 + d_31

Figure 2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$d_{1,23}$
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-5
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5
$d_{1,23}\ /(\lambda_F\ /2)$
Full triple interaction
w/o trio contribution
$\Delta E_{triple}(d_{12},d_{13},d_{23}=d_{opt})-\Delta E_{pair}(d_{23}=d_{opt})$ [meV]
$d_{1,23}\ /(\lambda_F\ /2)$

Figure 3