Cluster Models for the Simulation of STM Images of Adsorbates: Origin of Non-Topographical Features

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1. INTRODUCTION

Scanning Tunneling Microscopy (STM) is a powerful technique to image atoms and small molecules adsorbed on conductive surfaces. The tunneling current bears the information about the structure of the adsorbate, its position on the adsorption site, and the energetics of the interaction with the surface. Although it would be extremely desirable to infer these quantities directly from the images, the occurence of non-topographical artifacts often prevent from a straightforward interpretation of the data. Simulations constitute an effective aid to overcome these difficulties and to provide insights in the mechanism of contrast.

In this context, we simulate STM images with a recently developed theory of the STM current (Kenkre et al. (1992)), which takes in account the detailed atomic structure of the adsorbate, the interaction of the adsorbate with the the substrate and the tip, and the complexity of the STM junction. We show how non topographical artifacts depend on i) the heterogeneous chemical nature of the adsorbate, and ii) tip-sample separation.

2. SIMULATION OF STM IMAGES

The STM junction is treated as three groups of states, tip (T), substrate (S), and molecule (M). T and S exchange carriers with two biased thermal reservoirs, which feed carriers according to a distribution P^{th}. The solution to the evolution equations in the steady-state limit provides the STM current as:

$$I = en_e \left\{ \frac{\eta_T^{th} - P_T^{th}}{\int_0^\infty dt[\Pi_{TT} - \Pi_{TS}](t)} - \frac{\eta_S^{th} - P_S^{th}}{\int_0^\infty dt[\Pi_{SS} - \Pi_{ST}](t)} \right\}, \quad (1)$$

where e is the magnitude of the electron charge, n_e is the number density of electrons, the driving force is the displacement from local equilibrium populations η^{th}. The probability propagators $\Pi_{MN}(t)$ are dynamical quantities that depend upon the system Hamiltonian and the interactions with the thermal bath. The current (1) is not restricted to weak tip-sample coupling, it embodies electronic structure effects as well as details of electron transport, and partly accounts for non-linear dependence in the bias voltage through the driving force term.

Here, this framework is implemented with cluster models of the STM junction. The tip is taken as a single Au atom, the substrate is a Au (111) single layer slab, each atom is represented by atomic orbitals. For each tip position, the configuration of the cluster is held fixed. The Hamiltonian is given by Extended Hückel Theory (Sautet and Joachim, (1991)), and dissipation is accounted with a Stochastic Liouville Equation *via* a local dephasing of the coherence at constant rate $\alpha = 1$ eV. Bias voltage is 20 mV, and temperature is 4 K.

3. ARTIFACTS IN STM IMAGES OF ADSORBATES

We have taken atoms with a single orbital mismatched with respect to the metal orbitals (viz. the Fermi level), and placed them at the experimental equilibrium distance on the hollow site. It turns out that while Na appears as a protrusion (Fig. 1b), H produces a slight non-topographical depression and a distortion in the image of the coordinating Au atoms (Fig. 1c compared to Fig. 1a). The hole in the case of H is due to destructive interference. The result in Fig. 1c differ from both the corresponding local density of states map (Tersoff and Hamann (1983)), and the current calculated according to a tip-sample partition of the system. This suggests that a perturbative framework might neglect important contributions to the current, and that local dephasing can be relevant for the description of electron transport across the STM junction.

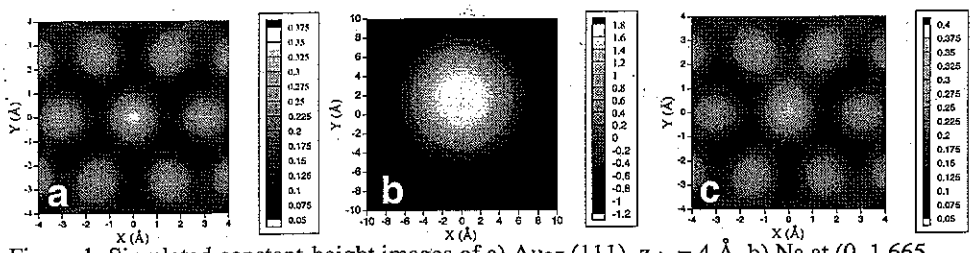

Figure 1: Simulated constant-height images of a) Au_{37} (111), z_{tip} = 4 Å, b) Na at (0, 1.665, 2.3) Å on Au_{97} (111), z_{tip} = 5 Å, and c) H at (0, 1.665, 0.532) Å on Au_{37}, z_{tip} = 4 Å Vertical bar is Log_{10}(I/nA). Height is measured from the plane of Au atoms.

Inversion of contrast, from bump to hole, as the tip-sample separation decreases has been observed experimentally for C on Al (111) (Brune et. al. (1990)) and predicted for O on Ni (110) (Doyen et al. (1988)). In Fig. 2, this effect is reproduced in the simulated images of O adsorbed on the hollow site of Au (111) substrate, as the tip approaches the sample. However, in our model it is not necessary to invoke resonances from virtual states of the adsorbate as responsible for the inversion of features.

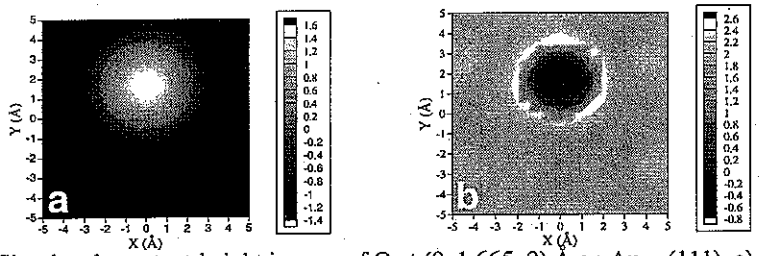

Figure 2: Simulated constant-height images of O at (0, 1.665, 2) Å on Au_{37} (111), a) z_{tip} = 5 Å, b) z_{tip} = 3.5 Å. Vertical bar is Log_{10}(I/nA).

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