

Application of SPAGS-STM to the formation of thin organic semiconducting layer

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Abstract: A new computational tool named SPAGS-STM has been developed to produce STM images in a very short time. Major improvement over standard STM software was made possible through the development of a strongly parallel computational approach, and by introducing new iterative algorithms for space discretization steps. This powerful technique has been used to reveal complex features in organized thin films built from organic semiconducting molecular species.

1. Introduction

A series of theoretical frameworks have already been proposed to evaluate the tunnel current with intimate goals of understanding and explaining STM image contrasts. Even a simple theoretical approach can predict and explain the various changes in intermolecular interactions with respect to the specific STM image topology [1]. Generally, the choice of a STM solver arises from a compromise between the accuracy level needed for the calculated tunnel current and the simulation time needed to reach a targeted image resolution. In terms of theoretical complexity, the Tersoff-Hamann model is a basic technique that considers the tip-surface interaction within a first order perturbative approach of tunnelling. More sophisticated and accurate models use the Landauer formulation of tunnelling in conjunction with Green's function and tight-binding Hamiltonians [2,3] or ultimately a non-equilibrium (Keldysh) approach with the help of Green's function and fully ab-initio Hamiltonians [4]. In fact, this last approach is still mostly impractical for large-scale molecular systems that may contain several hundred atoms.

In this contribution, we present the *SPAGS-STM* (Strongly Parallel Adaptive Grid Solvers – Scanning Tunnelling Microscope) software that produces accurate STM images within a short time. More specifically, we will present i) the parallel strategies implemented in the tunnel current calculations, ii) the adaptive algorithms used to minimize the amount of computed tunnel currents in the domain without affecting the image resolution, and iii) the theoretical investigation of structural properties of rubrene molecule adsorbed on low index faces of copper.

2. Method

Although *SPAGS-STM* includes several solvers, the computational technique we used to predict the present STM images employs a Green's function approach within the Landauer-Büttiker formalism in conjunction with a tight-binding Hamiltonian that originates from a generalization of extended Hückel parameters. In this theoretical framework, the tunnel current is obtained after solving appropriate propagation of electron through several layers including the tunnelling region that separate the two semi-infinite electrodes, i.e. the STM tip and the surface. Starting from an existing software (*Green*) [3], our first effort was to develop an efficient parallel strategy to evaluate the currents that are not completely numerically decoupled. Among the available possibilities, we adopted a master-slave strategy in which a server rules the distribution of tasks to the available processors. More demanding parallelized tasks are the calculation and storage of matrix elements related to the surface and tip electrodes during initialization step, and the splitting of tunnel current calculations forming the pixel of the STM image. This first generation of parallel STM simulator called *STM-Green* was used to simultaneously evaluate several tunnel currents on up to 512 nodes of a multi-processors computer [5].

The second effort to speed up the simulation was to reduce the number of currents to compute without affecting the final image resolution. This speed improvement was done by redefining the discretization scheme of the scanned domain. Instead of using a typical high-resolution square grid, we use a non-uniform meshing that concentrates mesh nodes in the zones of interest such as where high contrasts related to adsorbed molecules are present. More specifically, we build iteratively an optimized mesh from a previous coarse STM image solution. The process is a step by step differential analysis in which the image contrasts are identified using edge detection on a Delaunay

mesh. These edge detectors are built using a first and second order derivatives obtained by quadratic fit [6]. For example, Figure 1 shows a series of consecutive STM snapshots of a benzene molecule adsorbed on a Cu(100) surface obtained upon the adaptive meshing algorithm that gradually uncovers the STM image as new pixels are computed. It is also noteworthy to mention that the software (*MAMI*, Molecular Adaptive Mesher for Imagery) developed is generic, and could be applied to other type of imaging techniques [7].

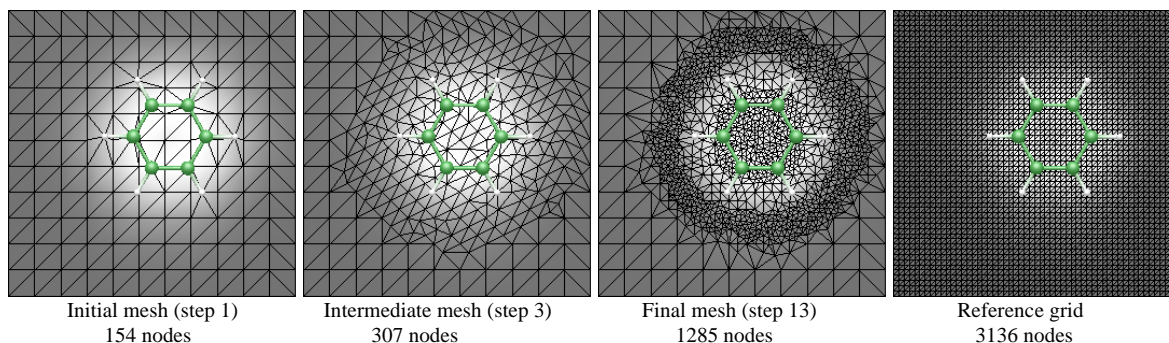


Figure 1 A progressive rendering, from step 1 (154 nodes) to step 13 (1285 nodes), of a STM image (constant-height mode, bias 0.5 V, height 5 Å) of a benzene molecule sitting on a hollow site of a Cu(100) surface. The adapted solution is obtained by computing 1285 tunnel currents with comparison to a reference grid of equivalent resolution that necessitates the computation of 3136 tunnel currents.

3. Results and Discussion

Electronic structure studies focusing on the adsorption of large and complex organic systems still constitute a remarkable task with first-principles approaches. This reality becomes amplified for STM imaging in which the minimal effort needed to produce an image, even for the lowest level of STM theory, is similar to electronic structure calculations. In this work, we considered the adsorption of the semiconducting rubrene molecule (see Fig. 2 (a)) on different copper surfaces. The interest for rubrene is mainly related to its very promising electronic and electrical properties such as its impressive high charge carrier mobility around $15 \text{ cm}^2/\text{Vs}$ [8]. Prior to the STM simulations, accurate DFT calculations are performed to determine the optimized adsorption conformation of rubrene on the Cu surface, and also on isolated species to obtain an estimation of the adsorption energy. Then, as shown in Fig. 2 (b), different pattern of rubrene are developed, and for which STM images are computed. The comparison between experimental and theoretical STM images is then performed to identify the most probable molecular arrangement on the surface, and furthermore to characterize the electronic properties of the adsorbates within the monolayer.

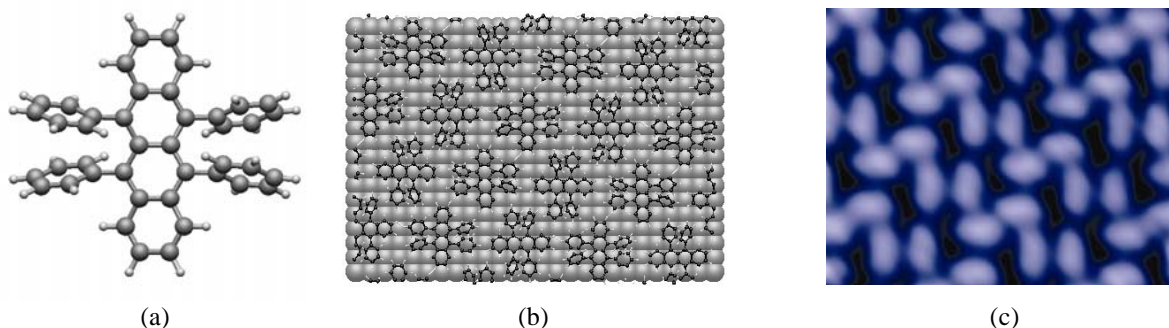


Figure 2 (a) Gaseous form of a rubrene molecule ($\text{C}_{42}\text{H}_{28}$) obtained by DFT calculations. (b) A periodic system that shows a rubrene monolayer on a Cu(100) surface. Experimental STM image of a rubrene monolayer adsorbed on a Cu(100) surface.

4. References

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