Combining *Ab Initio* And Semi-Empirical Approaches For STM Simulations Of Molecules Weakly Bonded To Surfaces.

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The Scanning Tunneling Microscope is a remarkable tool to probe objects and materials at the atomic scale. It is widely used to characterize the adsorption of various molecules on metallic or semiconducting surfaces. STM can also be used to understand the precise relationship between electronic properties of materials and their structure at the atomic scale. Thus, the analysis of STM images allow, i) to study the structural parameters of the system; ii) to study the nature of the probed electronic states through the analysis of the bias dependent STM images. Also, complementary, Scanning Tunneling Spectroscopy (STS) measurements allow to scan the local density of states of the system. However, the correspondence between topographic or spectroscopic measurements and the underlying electronic structure is not always obvious. The bonding nature between the molecule and the substrate, the charge transfer or the interaction between several molecules are example of parameters that can modify the electronic properties of the system with respect to its isolated parts. There is therefore a crucial need for efficient theoretical tools to tackle these issues.

A theoretical model combining both *ab initio* and semi-empirical approaches for the simulation of STM experiments will be presented. The tunneling current will be calculated within the tight binding approximation, in the elastic scattering formalism[1]. This model is particularly well suited to the case of molecules weakly bonded to surfaces for which the effects of adsorption on the electronic properties of the molecule remain weak. The tunneling current can then be calculated, with a good accuracy, with no need for self-consistency. However, information about the geometrical structure and the electronic properties of the system remain essential and will first be extracted from first principles calculations[2]. The interests of the presented method lies in its simplicity to be implemented as well as in a low computational cost (examples will be given) so that very large system (several hundreds of atoms) can be studied in a short period of time (a few hours).

The method will be discussed and compared with STS spectra recently obtained for regioregular poly(3-dodecylthiophene) (P3DDT) chains adsorbed on highly oriented pyrolytic graphite (HOPG). Indeed, π-conjugated semiconducting polymers have emerged as a new class of materials which present both self-assembly and novel electronic features. A recent STM study of P3DDT adsorbed on HOPG[3] has been devoted to determine, at the local scale, the precise relationship between structural organization and electronic properties. In this talk, we will focus on the application of our method to the study of STS spectra obtained for a single defectless P3DDT chain.

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