Ab Initio STM and STS Simulations on Magnetic and Nonmagnetic Metallic Surfaces

Alexey Dick's PhD Dissertation

Abstract

An unambiguous understanding and control of the surfaces, of atoms or molecules positioned on a surface, and of their interaction with the environment is critical for an efficient development and engineering of future solid-state technology. One of the most celebrated experimental techniques to study surface properties with down to single-atom resolution is the scanning tunneling microscopy (STM), awarded with the Nobel Prize in 1986. The interpretation of the STM experiments is, however, frequently cumbersome because STM superimposes contributions from the surface topography and its electronic structure. Fortunately, modern *ab initio* methods like the Density Functional Theory (DFT) are capable to provide an accurate theoretical description of surface properties, and can be used to get a detailed understanding of STM experiments. Consequently, most state-of-the-art STM studies are joined efforts of experimental and theoretical groups.

The aim of this work was to provide an in-depth understanding of a new generation of scanning tunneling microscopy experiments, performed employing different regimes of the STM: the spectroscopy-mode (the so-called Fourier Transformed STM, FT-STM), and the spin-sensitive mode (the so-called spin-polarized STM, SP-STM). In the present thesis *ab initio* tools will be proposed that are based on DFT calculations to theoretically predict and analyze such types of the STM. All STM-relevant schemes were implemented into the multiscale library S/PHI/nX. These methods are general and can be applied to accurately predict and analyze STM images on various magnetic and nonmagnetic metallic surfaces.

The first part of this thesis focusses on the simulation of FT-STM, the mode that allows to probe local dispersion properties of the electrons at the surface. In order to provide the theoretical counterpart of the experimental FT-STM spectra we have introduced a new implicit approach that is derived from Tersoff-Hamann theory of the STM. Specifically, treating surface imperfections (that are necessary in FT-STM experiments) as ideally reflecting objects gave rise to a dramatic reduction of the computational complexity, since it requires explicit *ab initio* calculations only for the smallest (chemical) unit cell of the ideal unperturbed surface. The importance of an accurate description of surface wavefunctions at $5-15$ Å above the surface as well as the spurious quantum-size effects have been discussed in detail together with approaches to obtain converged FT-STM images. We applied our method to FT-STM experiments performed on Ag(110) surfaces. The resulting simulated FT-STM spectra are in excellent agreement with experimental data, and allow a complete interpretation even of specific experimental details. In particular, we have for the first time shown that STM, in contrast to common believe, is able to detect dynamic properties of the bulk electrons. The physical effect underlying this phenomenon was explained in detail.

In the second part of the thesis we discuss the modeling of the spin-resolved STM, the mode that allows to characterize the magnetic structure of a surface. As a case system we studied here the magnetically-ordered transition-metal nitride surface $Mn_3N_2(010)$. Because SP-STM experiments did not allow a conclusive understanding of the surface structure, we have first employed *ab initio* thermodynamics to figure out the most stable magnetic and atomic configuration of the surface that are consistent with experiments. To simulate SP-STM images on the most stable $Mn_3N_2(010)$ surface we have employed the spin-generalized transfer-Hamiltonian formalism, assuming that the tip wavefunctions have dominant radial symmetry (s-like tip). It was found that a real-space description of the vacuum region is essential in our case, and this method has been implemented into S/PHI/nX. The theoretical results have been found in excellent agreement with the measured profiles and allowed to resolve all open questions of the experiment, providing an in-depth understanding of all major effects such as the magnetic contrast reversal and the influence of the STM-tip on the measured profiles.

In summary, in this thesis we developed an approach for *ab initio* simulations of the FT-STM and SP-STM experiments, and applied it to a number of hitherto unsolved problems in recently reported STM experiments performed on magnetic and nonmagnetic surfaces. Most parts of the work presented here have been done in close collaboration with experimental groups from the Fritz-Haber-Institut der Max-Planck-Gesellschaft in Berlin and the Ohio University in USA.