Simulation of scanning tunneling microscopy from first principles

Ph.D. Thesis Booklet

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Research background

Scanning tunneling microscopy (STM) has been developed in the early 1980's based on the quantum-mechanical electron tunneling principle. Topographies of (110)-oriented surface reconstructions and monoatomic steps of $CaIrSn_4$ and Au were first reported in atomic resolution [1]. This development revolutionized the microscopy techniques of that time, and quickly resulted in a Nobel Prize in Physics awarded to Gerd Binnig and Heinrich Rohrer for the design of the STM in 1986. This scanning probe technique has clearly contributed to the rapid development of nanoscience and nanotechnology in the last 35 years, and has been actively used in many subfields of surface science to study a wide spectrum of materials' surfaces. Recent applications are concerning both physics and chemistry, and are ranging from studying complex topological spin states in magnetic surfaces and thin films with spin-polarized STM [2, 3, 4] for the purpose of the development of energy-efficient ultra-high-density magnetic data storage technologies to surface chemistry for investigating molecular and supramolecular structures [5], and even chemical reactions in the field of catalysis [6, 7]. The role of the STM in these studies is vital.

Another extremely useful feature of STM is that it can not only image but also manipulate surface structures with atomic precision [8, 9, 10, 11]. This latter functionality will definitely be used in future applications, for example in the design of a class of quantum computers.

Objectives

An important point is that the STM does not image the geometric structure of the surface, but the combination of the atomic geometry of the sample and the convolution of electron densities of states of the sample and the scanning tip. This, together with tip-surface interactions can highly complicate the interpretation of experimental STM images. For such reasons, theoretical modeling of the STM is highly required, which was the main topic of PhD research. Starting from existing electron tunneling models, such as the Bardeen method [12], Chen's method [13], the Tersoff-Hamann method [14, 15], or the atomic superposition method [16], the focus was on the development and implementation of computationally efficient electron tunneling theories capable of simulating high-resolution STM based on first-principles electronic structure methods (for example density-functional-theory), and the tests on various surface structures to validate the newly developed STM methods.

Thesis points

The major achievements of my research are summarized in the following thesis statements:

1. I made essential contributions to the theoretical development and implementation of the orbital-dependent 3D-WKB electron tunneling model for the simulation of high-resolution STM and SP-STM images in a computationally efficient way since the $k-$point samplings of the surface and the tip Brillouin zones do not affect the computational time in this new model [P1]. I demonstrated the validity of the model by investigating the corrugation inversion phenomenon depending on the tip-sample distance and bias voltage observed on the nonmagnetic W(110) [P1] and on the magnetic Fe(110) surfaces [P3]. I explained the observed STM contrast inversion based on the real-space shape of the electron orbitals involved in the tunneling, and in the magnetic SP-STM case based on the interplay of the real-space electron orbitals and the spin- and energy-dependent orbital-decomposed projected electron densities of states of the sample and the tip. In both cases, I found a good agreement by comparing STM images calculated by the 3D-WKB model to results obtained by Tersoff-Hamann and Bardeen theories [P1,P3].

2. I developed and implemented the treatment of asymmetric tips in the STM junction in a novel way by considering arbitrary tip orientations in the orbital-dependent 3D-WKB electron tunneling model [P2]. Focusing on the corrugation inversion phenomenon, I studied the W(110) surface with numerous tip orientations, and the complex dependence of the contrast inversion on the tip-sample distance, bias voltage, and tip orientation was uncovered and explained. I showed that – even in this case of a relatively simply structured surface – the relative orientation of the tip and sample has a considerable effect on characteristics of the corrugation inversion as well as on the STM images [P2]. I also studied the tip-rotational effects on the STM images of the highly oriented pyrolytic graphite (HOPG) surface. Focusing on the favorable conditions for tip stability, I pointed out that local tip-rotations maintaining a major contribution of the $d_{3z^2-r^2}$ tip-apex state to the STM current affect only the secondary features of the HOPG STM contrast resulting in 'stripe' formation and leaving the primary contrast unaltered [P4]. Conversely, tip-rotations leading to enhanced contributions from $m \neq 0$ tip-apex electronic states can cause a triangular-hexagonal change in the primary contrast [P4].

3. I introduced a novel correlation analysis method to quantitatively evaluate the degree of agreement between STM images obtained by different theoretical methods or experimental data [P5]. I applied the method on the HOPG surface in combination with different tungsten tips, and a detailed comparison among 3D-WKB and Bardeen theoretical methods and experimental data was provided. I found that both theoretical methods provide the same quantitative reliability of correlation coefficients in comparison with the experimental STM images [P5]. Moreover, I introduced a statistical correlation analysis method to obtain information on the local geometry and orientation of the tip used in STM experiments based on large scale simulations. I demonstrated the applicability of the method considering the HOPG surface in combination with tungsten tip models of two different apex geometries, each in close to 20000 different orientations. I found that a blunt tip model provides better correlation with the experiment for a wider range of tip orientations and bias voltages than a sharp tip model [P5].

4. I revised Chen's derivative rule for electron tunneling for the purpose of computationally efficient simulations of STM based on first-principles electronic structure data and implemented it in the bSKAN code [P6]. The revised model allows the weighting of tunneling matrix elements of different tip-orbital characters by an arbitrary energy-independent choice or based on energy-dependent weighting coefficients obtained by an expansion of the tip single-electron wave functions/density of states projected onto the tip-apex atom. The reliability of the model was demonstrated by applying it to two functionalized surfaces where quantum interference effects play an important role in the STM imaging process: N-doped graphene and a magnetic Mn_2H complex on the Ag(111) surface [P6]. I showed that the electronic structure of the tip has a considerable effect on STM images, especially the interference between s and p_z tip orbitals that can cause a significant contrast change in both studied systems, which cannot be captured by the widely used Tersoff-Hamann method [P6]. Moreover, the revised Chen's model turned out to be 25 times faster than the Bardeen method concerning computational time, while maintaining good agreement, thus proved to be a fast and reliable tool for calculating STM images taking into account the electronic structure and local geometry by arbitrary tip orientations [P6].

List of publications

Publications related to the thesis points

[P1] K. Palotás, **G. Mándi**, L. Szunyogh, "Orbital-dependent electron tunneling within the atom superposition approach: Theory and application to W(110)" *Physical Review B* **86**, 235415/1-11 (2012)

[P2] **G. Mándi**, N. Nagy, and K. Palotás, "Arbitrary tip orientation in STM simulations: 3D WKB theory and application to W(110)" *Journal of Physics: Condensed Matter* **25**, 445009/1-10 (2013)

[P3] **G. Mándi** and K. Palotás, "STM contrast inversion of the Fe(110) surface" *Applied Surface Science* **304**, 65-72 (2014)

[P4] **G. Mándi**, G. Teobaldi, and K. Palotás, "Contrast stability and "stripe" formation in Scanning tunneling Microscopy imaging of highly oriented pyrolytic graphite: The role of STM-tip orientations" *Journal of Physics: Condensed Matter* **26**, 485007/1-11 (2014)

[P5] **G. Mándi**, G. Teobaldi, and K. Palotás, "What is the orientation of the tip in a scanning tunneling microscope?" *Progress in Surface Science* **90**, 223–238 (2015)

[P6] **G. Mándi** and K. Palotás, "Chen's derivative rule revisited: Role of tip-orbital interference in STM" *Physical Review B* **91**, 165406/1-12 (2015)

Other publications

[P7] K. Palotás, **G. Mándi**, and W. A. Hofer, "Three-dimensional Wentzel-Kramers-Brillouin approach for the simulation of scanning tunneling microscopy and spectroscopy" *Frontiers of Physics* **9**, 711-747 (2014)

[P8] K. Palotás, **G. Mándi**, L. Szunyogh, "Enhancement of the spin transfer torque efficiency in magnetic STM junctions" *Physical Review B* **94**, 064434/1-13 (2016)

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