A Guide to simulation of STM images and spectra from first principles: bSKAN 3.6

W. A. Hofer
Surface Science Research Centre,
The University of Liverpool, Liverpool L69 3BX

August 25, 2005

Contents

Preface

This guide is intended as a hands on manual for the execution of bSKAN 3.6, an optimized and parallel code to simulate STM topographies and spectroscopies from first principles. The program is an open source package, it can be used free of charge. However, use of the program is limited to users complying with two conditions: (i) Acknowledgement of the source; and (ii) feeding back all improvements made to the code to the original author. These conditions are mandatory, and users who are found not to comply with these rules will be excluded from future releases. The program requires a minimum of 2GHz processors, with a memory of no less than 1GB. In parallel mode it has been tested for up to 64 processors. The memory requirement for high level computations of systems of medium size is about 200-500 MB.

Chapter 1

Versions

1.1 Additions version 3.6 (2005)

The main changes were in (i) the rewrite of the program to account for the newly developed theoretical method based on the Keldysh formalism, (ii) changes in the evaluation routines, and (iii) rewriting the symmetry analysis and the generation of symmetry, working now automatically. The default calculation is now with the standard Bardeen method (NKELDYSH = -1), the bias dependent corrections are computed with NKELDYSH = 1. The program now integrates the differential maps at the end of the calculation, the evaluation then can be performed with a setpoint taken from experiments (I,V values).

1.2 Additions version 3.5 (2004)

The main changes are the spectroscopy modules of bSKAN 3.5. Model calculations showed that (i) the reduced number of layers in the tip description, and (ii) the numerical stability on parameters for spectroscopy calculations is not satisfactory, if spectra are obtained by a numerical differentiation of I(V) maps. Version 3.5 therefore performs spectroscopy calculations differentially, the new routines allow to identify unambiguously the effect of the tip electronic structure.

1.3 Additions version 3.4 (2004)

Additional module for differential spectroscopy, in version 3.4 only as addition to the numerical differentiation of I(V) maps. Spectroscopy module optimized for calculations with more than thousand k-points per system. Included a method to calculate chemical interactions and their effect on tunneling currents, as described in PRL 92, 266101 (2004).

1.4 Additions version 3.3 (2003)

Much improved version of data representation by creating an interface which can be visualized with OpenDx throughout all calculation methods.

1.5 Additions version 3.1 (2003)

Tunneling topography and spectroscopy now equally implemented. Massive code optimization increased the speed of calculations by two orders of magnitude, which is particularly important for complicated metal systems. Parallel code optimized.

1.6 Additions version 2.1 (2000)

Optimization of the code and first high resolutions simulations. Parallel code developed.

1.7 Original version 1.0 (1999)

Based on FLAPW wavefunctions and only serial, this very first version could only calculate a few points on metal surfaces, with a rather limited resolution of k-space.

Chapter 2

Introduction

The program bSKAN is written in modular form and in the current implementation in Fortran 90. In contrast to Fortran 77 this allows to use derived memory structures like types, which in turn make the allocation of memory, the transfer of data, and the handling of large and complex structures much easier. For example, the whole package is programmed without a single common block, and all sizeable memory is allocated during runtime.

The main programming challenge was the reduction of operations. As the wavefunctions are given in a two dimensional Fourier grid of typically more than one hundred components, the integration involves handling of matrices of ten thousand components. This can only be accomplished in a reasonable timescale if all steps are highly optimized.

At present, and in a serial implementation, the program is a able to calculate a single gridpoint of the STM tip position in timescales of typically less than one minute, which makes the calculation of detailed images in high resolution possible within a few hours. In parallel execution e.g. on a SGI R10000 cluster, we have calculated the spectrum of one point on a magnetic surface, mapped with 3000 k-points in the IBZ, using a model tip with 400 k-points around the centre of the Brillouin zone, and an energy grid from -1V to +1V of 101 points in less than four hours. The program in this case uses about 2GB of memory.

2.1 Suitability and systems

So far simulations of STM and STS have been performed on a wide variety of systems: magnetic and non-magnetic metals, semiconductors, semiconductors with magnetic properties, molecules on metal and semiconductor surfaces, oxygen covered metals etc. In all cases the simulations agree reasonably well (same order of magnitude for the current in simulations and experiments for a given result) to spectacularly well (same current values). The qualifying facts for a given calculation seem to be: (i) Whether all effects are included in groundstate DFT calculations (here one can be sceptical, in particular if highly correlating systems are analyzed), and (ii) whether the experimental range is reasonable for perturbation methods (here, as a rule of thumb, we are limited to a maximum of about 5-10nA on metals for low voltages). Within this range the calculations should be generally safe and easy to perform.

2.2 Help utilities

2.2.1 Keywords and input

From the viewpoint of users it seemed important to structure the input in an easy manner. The main input is therefore reduced to a limited number of keywords (see Appendix), and the input routine provides help functionalities for input errors. The easiest way to get started is to provide an input file with a single line **HELP**, which invokes a routine writing a file **README** detailing all the options.

2.2.2 Input errors

The program contains a rudimentary - far from complete - check of input data for plausibility. In every run, where a problem is detected, a README file is created which specifies the problem. Mainly these are:

- The energy range of eigenvalues is smaller than the energy range of the calculation. Remedy: go back to the DFT calculation where the STM wavefunctions were created and increase the energy interval.
- The energy resolution of a spectroscopy calculation is too high for the input wavefunctions. This is usually correct for metals, where the eigenvalues are densely spaced, but not necessarily correct for semiconductors, where you have a bandgap. The routine checks whether every interval contains at least one eigenvalue. Remedy: increase the number of k-points.
- The k-points of either surface or tip do not cover the IBZ of the first Brillouin zone. This can be intended, if for example only a limited region of the IBZ is considered, or it can be an error, if the k-point sampling is incomplete. Remedy: check and if necessary change the k-point sampling in the DFT calculation.

2.3 Copyright and license issues

The copyright of the program rests with the authors. However, the program is distributed as open source program. This means that no licence fees apply, but also, that extensions and improvements of the programs should be made available to other users. Please include a reference to [1, 2] in every work which uses the Bardeen integration, a reference to [3], if you calculate spin-resolved currents, and a reference to [4], if you perform spectroscopy simulations. The extension to multiple scattering in the vacuum barrier is based on a publication in Journal of Physics [5].

Chapter 3

THEORETICAL BACKGROUND

STM theory, like STM experiment, has a history of at least twenty years, from the earliest papers of Binnig and Rohrer [6, 7, 8] on the origin of the instruments precision to the theoretical models of Büttiker and Landauer [9], Tersoff and Hamann [10, 11], Chen [12, 13], Sautet and Joachim [14], or Flores [15, 16]. Basically, there are two different philosophies concerning the importance of different effects on STM images and spectra:

On the one hand, it was thought that the scattering process itself contains the main physical parameters determining the images. This is reflected in all scattering approaches, where the exact electronic structure of the two surfaces is commonly treated in a very rudimentary fashion.

On the other hand, it is thought that the scattering process, due to the large timescales involved (the interval from one tunneling electron to the next is typically larger than picoseconds), makes a scattering approach redundant, as long as the electronic structures of the two surfaces are well described. bSKAN follows the second line of argument. The wavefunctions of both surfaces are determined by highly precise density functional calculations, while the transition process is described by perturbation theory. The theoretical model goes back to Bardeen's treatment of a metal-insulator-metal junction [17], and it has been used in the last years for a wide range of materials from metals and magnetic overlayers to semiconductors and molecules adsorbed on metals and semiconductors. For a review see [2].

3.1 Method

3.1.1 Bardeen approach

Within the Bardeen approach to tunneling the current between a surface and a tip is described by the sum over surface and tip states as follows:

$$I = \frac{4\pi e}{\hbar} \sum_{\mu,\nu} \left[f(E_\mu) - f(E_\nu + eV) \right] \left| -\frac{\hbar^2}{2m} \int_S dS \left(\chi_\nu^* \nabla \psi_\mu - \psi_\mu \nabla \chi_\nu^* \right) \right|^2 \delta \left(E_\nu - E_\mu + eV \right) \quad (3.1)$$

Here, ψ is the wavefunction of the single electron state (in DFT Kohn-Sham state) of the surface, χ a single electron state of the tip, f is the Fermi distribution function, the bias voltage between surface and tip equals V, and the integration surface is assumed to be in the vacuum region. The key variable in this relation is the integral over the separation surface, which is called the tunneling matrix element $M_{\mu\nu}$. It is defined by:

$$M_{\mu\nu} = \int_S dS \left(\chi_\nu^* \nabla \psi_\mu - \psi_\mu \nabla \chi_\nu^* \right) \quad (3.2)$$

The matrix element is a scalar quantity, which is equivalent to the overlap of the vacuum wavefunctions of surface and tip. To implement this approach within the periodic systems typical for groundstate DFT calculations, the following points have to be considered:

- The wavefunctions in DFT are given as Kohn-Sham states of specific points of the two dimensional Brillouin zone of the surface. Each k-point has its own range of eigenvalues and states.
- Since the lattice geometry of surface and tip are in general incommensurate, each k-point of the surface is inequivalent to each k-point of the tip.
- Most DFT codes reduce the number of operations to achieve convergence by utilizing symmetry properties of their systems. The k-points of a given mesh reflect these properties.

The method used in bSKAN accounts for these properties of groundstate DFT calculations in the following way: (i) The lateral k-value of a given state is not conserved in the transition. This means that all transitions are admissible as long as the electron energy is conserved. (ii) The wavefunctions of the DFT input are expanded over the whole Brillouin zone using the symmetry operations of the underlying lattice. For a lattice of hexagonal symmetry this means, for example, that every wavefunction read in is equivalent to six wavefunctions determined by the rotation of reciprocal lattice vectors.

The wavefunctions required by bSKAN have the following form:

$$\psi_\mu(\mathbf{k}_\parallel, \mathbf{r}_\parallel, z) = \sum_{\mathbf{G}_\parallel} C_\mu(\mathbf{G}_\parallel, z) \exp i(\mathbf{k}_\parallel + \mathbf{G}_\parallel)\mathbf{r}_\parallel \quad (3.3)$$

At present the grid in z-direction is hardwired in the program at 0.1 a.u. (0.05218 Å). It was found that this resolution is sufficient to reproduce corrugation values of metal surfaces precisely down to a corrugation amplitude of less than 1 pm, which is about the resolution of todays best instruments. Given the usual size of systems in DFT (topographies on metals: 10-40 k-points in the IBZ, six to eight symmetry operations, expansion up to 200 G-vectors), a point by point integration over the separation surface is ruled out for practical reasons. Therefore an additional assumption is made in bSKAN: The separation surface is a plane located in the middle between the tip and the surface. In this case the integration for a single Fourier component can be performed analytically, provided the region of the surface is limited. This is generally the case, if the tip consists not of a plane surface, but a surface with an attached microtip of one to a few atoms and one or more layers. It is established opinion today that such a tip is used in all high resolution scans. For calculated model tips under these assumptions see [2].

3.1.2 Scattering method

From a theoretical point of view a tunneling electron, e.g. in a scanning tunneling microscopy measurement, is part of a system comprising two infinite metal leads and an interface, consisting of a vacuum barrier and, optionally, a molecule or a cluster of atoms with different properties than the infinite leads. The system can be said to be open - the number of charge carriers is not constant - and out of equilibrium - the applied potential and charge transport itself introduce polarizations and excitations within the system. The theoretical description of such a system has advanced significantly over the last years, to date the most comprehensive description is based either on a self-consistent solution of the Lippman-Schwinger equation or on the non-equilibrium Green's function approach. Within the vacuum barrier itself, inelastic effects play an insignificant role. Here, as in most experiments in scanning tunneling microscopy, the problem can be reduced to the description of the tunneling current between two leads - the surface S and the tip T - thought to be in thermal equilibrium. The bias potential of the circuit is in this case described by a modification of the chemical potentials of surface and tip system, symbolized by μ_S and μ_T. This reduces the tunneling problem to the Landauer-Büttiker formulation:

$$I = \frac{2e}{h} \int_{-\infty}^{+\infty} dE \left[f(\mu_S, E) - f(\mu_T, E) \right] \times Tr \left[\Gamma_T(E) G^R(E) \Gamma_S(E) G^A(E) \right]$$

Here, f denotes the Fermi distribution function, $G^{R(A)}(E)$ is the retarded (advanced) Green's function of the barrier, and Γ_S, Γ_T are the surface and tip contacts, respectively. They correspond to the difference of retarded and advanced self energy terms of surface and tip; we define them by their relation to the spectral function $A_{S(T)}$ of the surface (tip):

$$A_{S(T)}(E) = i \left[G^R_{S(T)}(E) - G^A_{S(T)}(E) \right] = G^R_{S(T)}(E) \Gamma_{S(T)}(E) G^A_{S(T)}(E) \quad (3.4)$$

The multiple scattering formalism can be evaluated in real space, with the help of an eigenvector expansion of the surface and tip Green's functions:

$$G_S^{R(A)}(\mathbf{r}_1, \mathbf{r}_2, E) = \sum_k \frac{\psi_k(\mathbf{r}_1)\psi_k^*(\mathbf{r}_2)}{E - E_k + (-)i\eta} \tag{3.5}$$

$$G_T^{R(A)}(\mathbf{r}_1, \mathbf{r}_2, E) = \sum_i \frac{\chi_i(\mathbf{r}_1)\chi_i^*(\mathbf{r}_2)}{E - E_i + (-)i\epsilon} \tag{3.6}$$

The zero order current results

$$I_{(0)} = \frac{4\pi e}{\hbar} \sum_{ik} \left[f\left(\mu_S, E_k - \frac{eV}{2}\right) - f\left(\mu_T, E_i + \frac{eV}{2}\right) \right] \left| \left(-\frac{\hbar^2}{2m} - \frac{eV}{\kappa_i^2 - \kappa_k^2} \right) M_{ik} \right|^2 \delta(E_i - E_k + eV). \tag{3.7}$$

The terms κ denote the vacuum decay of the surface (k) and tip (i) wavefunctions.
The result for the first order current, including only the terms for single electron paths (essentially the square of the matrix M_{ik}, while multiple scattering pathways will be described by four and six matrix multiplications), then involves also a term which depends on the bias voltage:

$$I_{(1)} = \frac{4\pi e}{\hbar} \sum_{ik} \left[f\left(\mu_S, E_k - \frac{eV}{2}\right) - f\left(\mu_T, E_i + \frac{eV}{2}\right) \right] \left| \left(-\frac{\hbar^2}{2m} + \frac{eV}{\kappa_i^2 - \kappa_k^2} \right) M_{ik} \right|^2 \delta(E_i - E_k + eV). \tag{3.8}$$

It can be seen that the zero and first order currents differ only in the sign of the explicit bias dependent part. Moreover, the obtained tunneling currents for higher voltages will increase more than linearly with the applied bias voltage and for both the special case of zero bias results us exactly the Bardeen current. The method is presented in [5].

3.2 Implementation

3.2.1 Topographic mode

The method is implemented in the program in the following way: first the lattice parameters of surface and tip are read in and the two lattices are expanded over the full Brillouin zone. Then a rectangular grid covering the surface unit cell is set up. The matrix elements $M_{G,G'}$ are calculated by analytically integrating the plane wave components over the surface of the tip unit cell:

$$M_{\mathbf{G}_S\mathbf{G}_T} = \int_S d\mathbf{S} \exp i(\mathbf{G}_S - \mathbf{G}_T)\mathbf{r} \qquad \mathbf{G}_{S/T} = \mathbf{k}_\parallel + \mathbf{G}_\parallel \tag{3.9}$$

For a given position R of the STM tip the matrix elements are multiplied by the phase of the surface wavefunctions:

$$N_{\mathbf{G}_S} = \exp i\mathbf{G}_S\mathbf{R} \tag{3.10}$$

The current of a given transition $\mu \rightarrow \nu$ and at a certain distance d is therefore the sum over all Fourier components of surface and tip wavefunctions. It contains three distinct components: (i) The z-dependent amplitudes; (ii) the integrals and phases depending on the lateral position of the STM tip; and (iii) the occupation numbers of electrons and a Gaussian, which mimicks the delta functional of elastic transport, and which depends on the tunneling conditions and the energy eigenvalues.

$$\begin{aligned} I_{\mu\nu}(d) &= \frac{4\pi e}{\hbar} w_{\mu\nu} \sum_{G_S,G_T} \left[C^*(G_T, d-z) \frac{dC_\mu(G_S,z)}{dz} - C_\mu(G_S,z) \frac{dC^*_\nu(G_T,d-z)}{dz} \right]_{z=d/2} \times \\ &\times \left|M_{G_S,G_T} N_{G_S}\right|^2 \times [f(E_\mu - f(E_\nu + eV)] \exp\left(-\frac{(E_\mu - E_\nu + eV)^2}{2\sigma^2} \right) \qquad (3.11) \end{aligned}$$

To speed up the program these three components are calculated separately in the simulation of topographies. The integral over the tip unit cell of the Fourier components is calculated initially and stored outside the loop changing the tip position. The calculation of the energy dependent components is also outside the loop over the tip positions in topographies. The phases are calculated after every shift of position of the STM tip. The sum over the z-dependent amplitudes and derivatives of the wavefunctions is in every case the innermost loop of the calculation. Simulations are routinely done over the whole range of z-values.

The weight of a given transition $w_{\mu\nu}$ depends on (i) the weight of surface and tip states, and (ii) the decay constants of the surface and tip states. These decay constants are calculated after the wavefunctions are read and stored in separate tables, which are used after the integration of Fourier coefficients to determine the weight of an individual transition. At present the program allows to calculate the current (topographies) and the differential spectrum (spectroscopies) either with the standard Bardeen method (no bias dependency), or with zero order or first order scattering methods, see section Method in this chapter.

3.2.2 Spectroscopies

Initially, spectroscopy functionality was built into the code by an additional loop over bias voltage. In this case the obtained results were topographies for every given bias voltage in a bias interval, e.g. from -1V to +1V. A comparison with experimental spectra (dI/DV spectra) was then simulated by a numerical differentiation of I(V) for every single point of the surface. The method proved to have several methodical problems:

1. The change of occupation numbers near the Fermi level due to the Fermi distribution function always shows up as a distinct spike in the spectrum.

2. The number of layers of the surface and tip electronic structure determines the spacing of eigenvalues and thus the ensuing spectrum (minimum number for noble metals about 23 layers). This is close to impossible to

calculate for the tip electronic structure, because the tip requires a very large unit cell of at least eight atoms per plane.

3. The ensuing I(V) curve and its numerical derivative do not allow a clear identification of surface and tip contributions and make it very difficult, if differences to experimental spectra are observed, to improve the representation.

For these methodical reasons the frontal attack of the problem was finally given up, after a large number of trial calculations on Fe, Cr, Mn/Fe systems and Cu, Ag, and Au surface states. Instead, the program now contains a comprehensively differential approach to the problem. The details of the theoretical analysis and the new approach are published in [4]. For the present purpose the relevant result is that the differential spectrum dI/dV is directly calculated and written to a file, which contains the dI/dV map for a defined surface grid. From this spectrum the I(V) map is obtained by integration. The incremental change in the current due to a change of bias from V to $V + dV$ is:

$$dI = \sum_{i_1 k_1} |M(\psi_{i_1}, \chi_{k_1})| + \sum_{i_2 k_2} |M(\psi_{i_2}, \chi_{k_2})| \tag{3.12}$$

where the eigenvalues of surface $E_{i_{1(2)}}$ and tip $E_{k_{1(2)}}$ states are within the intervals:

$$\begin{aligned} E_{i_1} &\in [E_F + eV - edV/2, E_F + eV + edV/2] \\ E_{k_1} &\in [E_F - edV/2, E_F + edV/2] \\ E_{i_2} &\in [E_F - edV/2, E_F + edV/2] \\ E_{k_2} &\in [E_F - eV - edV/2, E_F - eV + edV/2] \end{aligned} \tag{3.13}$$

Here, E_F denotes the Fermi level of surface and tip system, respectively. Then the total spectrum contains equally two distinct contributions due to the bandstructure of the surface and the tip system:

$$\frac{dI(V)}{dV} = \sum_{i_1 k_1} \frac{|M(\psi_{i_1}, \chi_{k_1})|}{dV} + \sum_{i_2 k_2} \frac{|M(\psi_{i_2}, \chi_{k_2})|}{dV} \tag{3.14}$$

The files containing the two separate contributions to the spectrum and the sum of these contributions. It is therefore possible to identify the origin of a feature in the spectrum and determine, whether it is due to the surface or the tip electronic structure. In general we find that surfaces with a very low density of states at the Fermi level lead to spectra with features unique of the surface. This is for example true for semiconductor surfaces. For metal surfaces we find that this is not the case and the ensuing spectra will show up both bandstructures. In this case there are two options to obtain a reliable result: (i) Limit the analysis to the surface contribution alone, which maps to the states at the Fermi level of the tip; or (ii) or increase the number of layers and the precision of the tip model so that its bandstructure is correctly represented in the calculation. In principle, this is feasible and will become routine once computing power has increased to this level. For the time being, we suggest to use the first approach.

3.3 Interfaces to DFT programs

The Kohn-Sham states can in principle be obtained from any DFT method, which describes the electron states in the vacuum range by a two dimensional Fourier expansion (x,y) and a real space grid (z). At present interfaces exist for VASP (see http://www.mpi.univie.ac.at/vasp/) and film FLAPW. Since FLAPW has been substantially altered during the last years by Michael Weinert and Raimund Podloucky, its interface is no longer up to date and will have to be rewritten in the future. It is also possible to use other methods like SIESTA or Wien2k for this purpose, specifications for the interfaces can be obtained from WH.

Chapter 4

INSTALLATION

The program is delivered in a compressed tar.gz file, which needs to be uncompressed either with gunzip (the Unix utility), or any other of available utilities like WinZip etc. Once the Fortran 90 modules (named *.F) and the makefiles are stored in a directory, the executable can be compiled with any suitable compiler. The current implementation supports Intel Fortran Compilers (Makefile.ifc), Sun clusters (Makefile.sun) and Silicon Graphics clusters (Makefile.sgi). Portation to other systems should be unproblematic, because the program does not depend on external libraries. All routines use standard Fortran 90. The commands to unzip and to extract the program files are:

```
gunzip BSKAN.360.tar.gz tar -vxf BSKAN.360.tar
```

After this the makefile.xxx needs to be copied onto makefile, e.g. for a Silicon Graphics environment with:

```
cp makefile.sgi parallel makefile
```

Then the (parallel) executable can be compiled with:

```
make bskan
```

For serial executables other makefiles with the tag serial have to be used. Please note that the location of the libraries as well as the switches generally depend on the setup of your cluster. The easiest way to find out about your environment is to ask the system administrator. There should be no error messages during compilation. If, however, the compilation ends with an error, please check first that the correct makefile was used. If this is the case and the errors do not disappear, please contact your system administrator.

4.1 Parallel version

The problems with parallel coding are well known: there exists no standard implementation of the MPI interface e.g. for Linux clusters. The necessary libraries (LAPACK, BLAS, SCALAPACK) need to be compiled for the computer environment. However, this is not usually trivial and will best be done by the administrator. I therefore follow the usual practice not to provide explicit advice for MPI implementation. The parallel compilation, as provided for the computer environment the code has been running so far, can be seen in the makefiles. The location of the libraries will invariably vary, as will the compiler used (for example, I used a PGF90 compiler on Linux 2.7.2 clusters, built from AMD Athlon processors). The makefile therefore has to be modified. Again, this is best done in cooperation with the computer administrators.

4.2 Input features

Generally, it was sought to minimize the input to the bare essentials for a run. The program therefore provides a number of default settings, which are written at the beginning of the output file. It was also sought to make the input format as free as possible. However, there is a limit, where coding becomes rather demanding, without a substantial gain in efficiency or flexibility. The input routines of bSKAN are aimed at a compromise: a command usually consists of one word plus zero or more values. The first command in the input file should always be the method command. Apart from that the order of commands is optional.

Chapter 5

PROGRAM EXECUTION

The name of the executable is bskan36, it can be either executed in interactive mode by bskan36 or bskan36 &. Initially, the program searches in the same directory for five files: INSCAN, WAVSAMPLE, WAVTIP, ASAMPLE and ATIP. The first contains all the input parameters, the second two the wavefunctions of the sample surface and tip, respectively, and the last two contain the atomic positions in direct coordinates for the surface and tip, respectively (see section FILES). Please note that WAVTIP and ATIP files are not needed in case of a Tersoff-Hamann calculation.

For most applications the program will be executed in a queueing system. Please remind that it might take some time (up to a few minutes, depending on the system), for the program to produce any output. In case the program stops by writing a README file, it detected some input error in the file INSCAN. In case it stops without such a message, the file OUTSCAN should contain a message detailing an error in a read operation on the wavefunction files. In this case the files are probably corrupt and have to be generated again. Depending on the tasks defined in INSCAN, the program generates various output files. These are listed in the section FILES.

Chapter 6

TOPOGRAPHIES

In topographic mode an STM scans across the surface while the tunneling current is kept constant. This could be mimicked by a suitable feedback within the program. However, the feedback algorithm is tricky to program and convergence then becomes a major issue. Therefore it was decided to compute a complete 3D matrix of tunneling currents on the surface. This is still manageable, computationally, and it makes the program substantially simpler. The vertical extension depends on the input files, generally all z values of the smaller file are included. If, for example, the WAVSAMPLE file includes 50 z-values, and the WAVTIP file 100, then only the first 50 gridpoints of the tip electronic structure are included in the calculation. bSKAN provides two different routines:

6.1 Tersoff-Hamann method

Since this is included in practically all DFT codes, it also provides a handy check of the surface electronic structure and subsequent calculations with a model tip. The input in the file INSCAN is the following:

```
TERSOFF HAMANN MODEL
BIAS VOLTAGE = -0.01
LIMITS = -0.05 0.05
GRIDPOINTS = 61
CELL = 1.0 1.0
PIVOT POINT = 0.0 0.0
NKELDYSH = 1
ZVACUUM = 11.2
```

BIAS VOLTAGE and LIMITS values are in eV. The limit describes an ambient environment, it determines the states included in the summation outside the energy window defined by the bias voltage. The number of gridpoints applies to the longest axis. For a square lattice, this means a quadratic grid of the surface mesh. For a rectangular lattice the shorter direction is covered by proportionally less gridpoints, so that the mesh is equally spaced in both directions. For a hexagonal lattice it creates a rectangular mesh, where the rectangular lattice vectors (ARs) are

AR1 = A1 + A2
AR2 = A1 - A2,

with A1 and A2 being the lattice vectors of the hexagonal lattice. It is easily seen that the rectangular cell has an area of two hexagonal unit cells. The default without an input of GRIDPOINTS is 31. The image size can be varied with the keyword CELL. The bSKAN default here is one rectangular unit cell. The keyword PIVOT POINT determines the lower left point of the created surface image. The default, if no value is given, is the point (-0.5,-0.5). NKELDYSH determines whether the scattering approach is used. Finally, the ZVACUUM parameter describes the vacuum boundary of the sample surface (in Å), in the above example it is 11.2 Å. For more details on keywords, see chapter KEYWORDS. The program creates two output files: OUTSCAN provides the information about the system and the run, the file CURMAT contains the binary 3D matrix of local density of states. The file CURMAT can be used to evaluate the relevant properties like surface CORRUGATION, the apparent height of atoms on this surface, it can also be used to create constant density or constant height contours which can be compared to the experiments. This is described in the chapter EVALUATION.

6.1.1 Possible errors

There are essentially two classes of errors: either the program stops, without creating the matrix, or it creates the matrix but gives unexpected results. In the first case it will either create a README file, then the parameter input contained an error and the file should contain information to correct the error. Or if it does not, then the wavefunction file is corrupted and should be generated again. In the second case the possible sources of error are the input range of eigenvalues. If the limits and the bias voltage lead to an energy range which is beyond the limits defined in the wavefunction file, the result will be an error message but no stop of the program.

6.2 Bardeen method

In this method the tip is included in the calculation. Two files, WAVTIP and ATIP are needed in the working directory containing the electronic structure of the STM tip model, and the atomic positions of the tip in direct coordinates, respectively. The input parameters are the following:

```
NUMERICAL EVALUATION
BIAS VOLTAGE = -0.01
LIMITS = -0.05 0.05
GRIDPOINTS = 61
CELL = 1.0 1.0
PIVOT POINT = 0.0 0.0
```

NKELDYSH = 1
ZVACUUM = 11.2

The program in this case sets up a surface grid, computes the matrix of integrated Fourier components, and determines the eigenvalues to be included before looping over the surface grid. The time needed for a gridpoint scales nearly linearly with the bias voltage, since this determines the number of included states. For low bias scans on metal surfaces it is commonly in the range of seconds, for semiconductors the duration is considerably higher and can be as long as a few minutes. The program produces the usual output files OUTSCAN and CURMAT, and in addition a formatted file CURSAVE, which should be saved, since binary files like CURMAT do not always port easily from one system to the other. By playing around with different model tips it can be seen that the Bardeen integration makes tunneling topographies tip dependent to quite a high degree. This means that the inclusion of the tip adds an additional dimension in the comparison between experiments and simulations. A good agreement between them requires that the experimental input (current, bias voltage), and output (corrugation, shape of a structure) agrees with the input and output in the simulation.

6.2.1 Possible errors

The energy range of tip and surface electronic structures determines the range of possible bias potentials. A bias potential outside the range of eigenvalues of either surface or tip will lead to an error message in the output.

6.3 Magnetic surfaces

While tunneling currents into paramagnetic tips made of tungsten are not spin-selective - both electron states of a magnetic surface tunnel into the same states of the tip -, the situation changes for magnetic tips. Here, the spin-up and spin-down states find a different electronic structure, with commonly a higher density of spin-down states at the Fermi level. This favors transitions of spin-down electrons, which leads to a magnetic image of the surface, or an image, predominantly, of the electronic structure of the minority band. bSKAN includes functionalities both, for the calculation of spin-polarized currents, and for the evaluation of contours if the magnetization direction of surface and tip are not collinear. To make a non-collinear calculation it is first necessary to determine the currents for both ferromagnetic (up states into up states) and antiferromagnetic transitions (up states into down states). This is done by adding the keyword:

FERROMAGNETIC (ANTIFERROMAGNETIC) ORDERING

The two runs will yield two different current matrices, which are merged, in a second step, under the assumption of an angle between the magnetization vector of surface and tip (see [2]). This step is described in the section EVALUATION.

Chapter 7

SPECTROSCOPIES

In the spectroscopic mode the STM tip is stabilized at a point above the surface, this point is usually described by a bias voltage/current combination. After stabilization the feedback loop is disengaged, and the bias voltage ramped from a lower limit to an upper limit. The current/voltage curves in this case look rather bland, but their first and second derivatives contain information about the surface electronic structure (e.g. surface states on (111) noble metals or (100) iron) and the dynamic changes due to electron-electron and electron-phonon interactions. Within bSKAN a spectroscopy is a topography over a range of bias voltages. This makes it possible to study not only the spectroscopies at fixed points of the surface, but also to study their change with the STM tip position, which in turn can yield valuable information about local electronic properties.

7.1 Tersoff-Hamann model

The input is similar to the input used for topographies and with the TH-method. The minimum input for a spectrum is the following:

```
STERSOFF = -1.0 1.0
LIMITS = -0.05 0.05
NSPECTRUM = 101
GRID = 1
NKELDYSH = 1
ZVACUUM = 11.2
```

Here, the spectrum covers the interval from -1.0 to 1.0 Volt, the surface is probed at only one gridpoint (the TOP point, which is (0.0,0.0) in default, and the energy interval from -1.0 to +1.0 eV is computed with 101 values. The variables NSPECTRUM and GRID could in principle also be omitted, the defaults within bSKAN are 11 energy gridpoints (NSPECTRUM) and 31 surface gridpoints (GRID) along the major axis. NKELDYSH determines whether the scattering approach is used, since ZVACUUM sets the vacuum boundary. For more details on keywords, see chapter KEYWORDS. The output of such a run consists of three files. OUTSCAN gives, as usual, the information about the system and the tunneling parameters as well as the included states. The files CURSPEC and CURSAVE contain the current matrix for all local and energy gridpoints, the faster loop in this case runs over the energies.

7.2 Bardeen method

The only difference is the method keyword, which has to be changed. The input for a spectroscopy calculation with the Bardeen method is the following:

```
SPECTROSCOPY = -1.0 1.0
LIMITS = -0.05 0.05
NSPECTRUM = 101
GRID = 1
NKELDYSH = 1
ZVACUUM = 11.2
```

The output is the same as above. It is recommended to save the file CURSAVE since the binary CURMAT file is not generally transferable to other platforms.

In case of spectroscopies the representation of the bandstructure becomes the most important parameter for the quality of the spectrum. In general, a too low number of k-points leads to a loss of resolution and even to a complete distortion of the spectrum. The necessary number of k-points depends to some extent on the desired resolution, i.e. the energy grid in the calculation. To analyze the grid the information about the number of states in every interval are printed out in the file TRANSLOG. In case the grid is too small, the number of states in an interval approaches one or even reaches zero. In this case a warning message is printed in the OUTSCAN file. It is recommended to increase the k-point sampling until this warning disappears.

7.3 Magnetic surfaces

The only additional information needed is the magnetic ordering. The bSKAN default is ferromagnetic, the explicit keyword for ferromagnetic and antiferromagnetic ordering are the following:

```
FERROMAGNETIC (ANTIFERROMAGNETIC) ORDERING
```

7.4 Differential Spectroscopy

In general it is desirable to have a clear representation of the STM tip, which can be inferred from experimental spectra and gives the correct contributions to a spectrum over a limited voltage around the Fermi level. However, such a tip cannot be calculated today even with high performance computers. The reason is twofold: (i) The electronic bandstructure of a metal film is discrete due to the limited number of layers in the film. The spacing of the eigenvalues at a given point of the Brillouin zone reflects this limitation. (ii) The number of two dimensional k-points is also limited, which reduces the precision of the bandstructure map also in two dimensions.

Chapter 8

EVALUATION

8.0.1 Creating current maps and current contours

The keyword for evaluating the current maps is CURRENT. In connection with a real number it has two different meanings:

CURRENT = 0.0

will create a file CURRENT, which contains the current map in a format compatible with OpenDx (this means that the current is given in nested loop of three indices).

If the keyword is used with a positive value, e.g.

CURRENT = 1.5

then the program constructs a current contour of the surface with this input value (generally in nA, for TH topographies in units of the LDOS). This contour is written to the file PLOTCON, which contains in the first line the information about the contour maximum and minimum as well as the current value.

8.1 Corrugation

The main information contained in an STM image is the corrugation height, or the difference of the vertical position of the STM tip between a hollow site and an on top site. This information can be extracted from the current matrix with the commands:

CORRUGATION

TOP = 0.0 0.0

HOLLOW = 0.5 0.5

The first keyword defines the task, the other keywords define the position of the ion and the hollow site. The file written is called PLOTCOR, it contains the z-dependent current values at both sites, the apparent barrier height due to the current decay, and the corrugation value in Å.

8.2 Two dimensional maps in parallel planes

The current can also be plotted in 2dim maps at preset z values from the surface. This is done with the following commands:

PLOTS = 5
FPLOT = PLT
ZPLOT = 10 20 30 40 50

The program creates five output files, called PLT.001 to PLT.005, containing the currents in the parallel planes for z = 10 to z = 50. The first line of each file gives the distance and the maximum current value in this plane.

8.3 I/V spectra of a surface

The spectra of the surface are contained in the file CURSPEC, they cover all current values over the surface grid for bias voltages within the predefined range. To extract the currents for a given position of the tip, the bias voltage and the current value, at which the tip was stabilized, have to be defined. The command lines to this end are the following:

BIAS VOLTAGE = - 0.3
CURRENT = 1.5
TOP = 0.0 0.0

This creates four output files. The file PLOTSPC contains the current, the normalized derivative and the second normalized derivative of the current at the point TOP. The vertical position of the tip in this case is preset to the value defined by the bias/current values. In addition, a two dimensional map of currents, first and second derivatives is written to the files PLOT.01 to PLOT.03, where the map is determined by the position TOP and the bias/current values from the input.

8.4 Magnetic calculations

Here, two separate outputs can be created with the keywords FERROMAGNETIC or ANTIFERROMAGNETIC. These result of the calculations have to be merged under the assumption of an angle PHI between the magnetization vector of surface and tip. The two results are merged in the following way. For topographies, first create two separate current maps, for ferromagnetic and antiferromagnetic ordering. Then, move the two CURMAT files to CURFM and CURAFM, respectively. Now execute bSKAN with the following added command lines:

MERGE = T
PHI = 45

The angle is given in degree. The result of the calculation is a new file CURMAT containing the merged current maps under this angle. This file can then be evaluated in the usual manner, extracting current contours, corrugations, or current planes. For tunneling spectra the names of the input files to merge are CURSFM and CURSAFM, apart from that, the procedure is identical.

Chapter 9

FILES

All input and output files are written in capital letters. The first two or three letters generally specify the information contained. For example, all files related to the Kohn-Sham states begin with WAV-, files describing the geometry with A-, input parameters are contained in files named IN-, the output in files OUT-. Current maps are stored in CUR- files, while plots generally are called PLOT or PLT.

9.1 Input

Note that we make a difference between essential files (which are necessary for every run) and non-essential ones (which are usually optional). The input files are described in Table 13.1 at the end of the guide. The keywords used in INSCAN file are found in chapter KEYWORDS. For more details on wavefunctions and geometry input files, see chapters WAVEFUNCTIONS and Geometry files, respectively.

9.2 Output

Output files are either for information on the run, contain the simulation data, or contain an extracted sample of the simulation data for visualizing. They are described in Table 13.2

Chapter 10

KEYWORDS

The program only uses the first three characters of a keyword, the rest is omitted. In the following table these essential characters are given in capitals. The list of essential keywords and their usage can be printed out by executing the program with only one line in the INSCAN file:

HELP

The current keywords are described in Table 13.3.

10.1 METHOD

10.1.1 TERSOFF-HAMANN

The Tersoff-Hamann method is standard in many DFT simulations, where the charge within an energy window can be integrated and displayed. The difference between the bSKAN implementation and DFT implementations is:

1. The surface unit cell is arbitary and can be changed by the keyword CELL = X Y, which allows in principle to compute an area of multiple unit cells
2. The surface unit cell does not have to be rectangular, while the computed unit cell is always rectangular. This is an advantage for visualisation programs like OpenDx
3. The bias dependency can be included from the formulation found for the first order scattering approach by setting NKELDYSH = 0 (zero order scattering) or NKELDYSH = 1 (first order scattering).

The line in the INSCAN file has the format:
TERSOFF-HAMANN

10.1.2 STERSOFF

The differential spectrum in this case is calculated with the same model, the bias dependency for the zero and first order scattering approximation is included via the NKELDYSH switch. The spectrum can be extended over the whole unit cell with arbitrary resolution, which allows to compare differential spectra with locally resolved spectroscopy experiments. The advantages are the same as for TH spectroscopies.

The line in the INSCAN file has the format:

STERSOFF = V_1 V_2

here V_1 and V_2 describe the lower and upper limit of the spectrum. Note that the bias interval is assumed to contain the zero bias value.

10.1.3 NUMERICAL

Bardeen topographies are based on the wavefunctions of surface and tip; it is assumed that the z-grid of both systems is equally spaced (0.1 a.u) and that the distance from the surface nuclei at a given gridpoint i is roughly the same for surface and tip systems (symmetric setup). The advantage of Bardeen topographies is that they include the electronic structure of the tip explicitly; for topographies, where typically only a limited number of states around the Fermi level contributes to the tunneling current, this leads to effects like contrast inversion or contrast changes due to different tip models, a feature well documented in STM experiments. The bias dependency of the current can be included by changing NKELDYSH from -1 (the default) to 1 (the first order approximation in the scattering approach).

The line in the INSCAN file has the format:

NUMERICAL

10.1.4 SPECTROSCOPY

Bardeen spectroscopies include surface and tip electronic structures. The method is described to some extent in the methods chapter, it is based on differential increments of the current due to a differential change of the bias voltage. In this case the dI/dV values are written to a file and then integrated from the point of zero bias. It is therefore essential that zero bias is included in the calculation. The binary files CURDSPEC and CURSPEC contain three separate values: one for the contributions from the surface bandstructure mapped onto the tip Fermi level, one from the contributions of the tip bandstructure, mapped onto the Fermi level of the surface, and the sum of the two values.

The line in the INSCAN file has the format:

SPECTROSCOPY = V_1 V_2

As in the previous cases the bias dependency in the calculation is included with an appropriate switch NKELDYSH.

10.1.5 FORCE

From version 3.5 the chemical interactions have been included in the simulation routines. To correct a given CURMAT file for interactions, one needs first to determine the harmonic constant of surface atoms, and the Wigner Seitz radius of surface and tip atoms. The ratio between current and interaction energy is parametrized with respect to the Wigner Seitz radii, the parametrization has the form (see PRL 91, 036803 (2003)):

$$\alpha = 0.02563 \cdot \exp[1.1 \cdot (r_S + r_T)] \tag{10.1}$$

The harmonic constants, the distance between nuclei and vacuum boundary of surface and tip, as well as the lateral position of surface atom and tip apex are needed to be given in the file INFORCE. At present, the program can only account for primitive surface cells (one atom only). Then the current values in CURMAT are used as the basis for a calculation of a file CURMATF, which contains the currents, corrected for displacement of the surface atoms.

The line in the INSCAN file:
FORCES = T
The default is FORCES = F.

10.1.6 WAVE

Sometimes it is desirable to plot the decay characteristics of a single surface state. The functionality is provided in the program, in this case the charge density of a single state, defined by its energy eigenvalue, is plotted for the on-top position of the unit cell.

The line in the INSCAN file:
WAVE = E_k [htr]

The energy eigenvalue has to be defined precisely enough, so that only a single state is chosen.

10.2 SETUP

The setup of the calculation involves, apart from the chosen method, the following parameters: bias voltage, bias dependency, scan area, thermal broadening, ferromagnetic and antiferromagnetic transitions, absolute Fermi level, energy and local resolution of the scan.

10.2.1 ANTIFERROMAGNETIC

In magnetic systems the vector of magnetization will have a direction in space, which means that spin is no longer isotropic. In this case the calculation of two separate scans, one with FERROMAGNETIC, the other with ANTIFERROMAGNETIC ordering allows to simulate STM scan on magnetic systems, where the angle between surface and tip magnetization vectors is used as an input in the subsequent evaluation runs. In non-magnetic systems this parameter is ignored.

The line in the INSCAN file:
ANTIFERROMAGNETIC
The default in a scan is ferromagnetic ordering of surface and tip states.

10.2.2 AREA

The tip unit cell is typically made up of a film with a single atomic or a pyramid apex. This geometry guarantees that the amplitude of the wavefunctions at the edges of the tip unit cell are negligible compared to the amplitude at the apex. In this case an integration over the tip unit cell of the overlap of surface and tip wavefunctions, as required in the Bardeen method, contains mainly the overlap at the tip apex. The integration area is usually the whole tip unit cell. This is also the default in every simulation. However, it may be necessary to check the convergency of an obtained result with respect to the integration area. In this case the area has to be explicitly specified in units of the tip lattice vectors A_1 and A_2. Note that the tip unit cell always has to be at least rectangular.

The line in the INSCAN file:

AREA = a_1 a_2

The default in every calculation is AREA = 1.0 1.0

10.2.3 BIAS

Setting the bias voltage for a topography simulation, or setting the bias voltage for evaluation of a spectrum. In the first case the bias voltage either defines the energy interval for the summation of surface charge (Tersoff-Hamann), or the shift of Fermi levels of surface and tip systems (Bardeen). In the second case also the CURRENT value has to be defined; in this case the BIAS/CURRENT couple defines the setpoint of an STS simulation, as it does in experimental spectra.

The line in the INSCAN file has the format:

BIAS = V_b

Note that negative bias ranges correspond to tunneling from filled surface states into empty tip states, positive bias ranges lead to tunneling from empty tip states into surface states.

10.2.4 CELL

The scan area depends on the symmetry of the surface (see further down) and the input CELL. For rectangular lattices the variation of the parameter CELL allows to scan across more than one unit cell. However, since the lateral resolution of the scan will be reduced, it is usually more efficient to scan across a single unit cell and to evaluate the ensuing current matrix over more than one unit cell. In this case the resolution is retained, while the ensuing constant current contours still cover a wider area.

The line in the INSCAN file:

CELL = c_1 c_2

The default in every calculation is CELL = 1.0 1.0

10.2.5 DELTA

Defines the broadening σ for the approximation of the delta functional by a Gaussian in the simulations. The difference between the energy values of surface and tip states in a scan is calculated and the probability of the transition scaled with a Gaussian distribution with halfwidth σ. This only applies to topography simulations, in spectroscopies the energy interval in the differential changes is commonly small enough (around 20mV) so that this probability is set to one.

The line in the INSCAN file:

DELTA = σ [eV]

The default value in a scan is 100meV.

10.2.6 FERROMAGNETIC

In magnetic systems the vector of magnetization will have a direction in space, which means that spin is no longer isotropic. In this case the calculation of two separate scans, one with FERROMAGNETIC, the other with ANTIFERROMAGNETIC ordering allows to simulate STM scan on magnetic systems, where the angle between surface and tip magnetization vectors is used as an input in the subsequent evaluation runs. In non-magnetic systems this parameter is ignored.

The line in the INSCAN file:

FERROMAGNETIC

The default in a scan is FERROMAGNETIC ordering of surface and tip states.

10.2.7 GRIDPOINTS

The lateral resolution in most experimental scans is in the range of 0.1 - 0.2 Å. This means that a typical unit cell of about 3 Å width, can be resolved by about thirty discrete points of a scan. A simulated scan will scale with the number of calculated points, so it is generally advisable to limit this number to the experimentally sensible. The number is defined by the intervals along the longest axis of the surface scan area. For quadratic unit cells, this leads to the same number of intervals in both directions, for oblique or hexagonal cells, the number of intervals in the shorter direction are calculated by the program.

The line in the INSCAN file:

GRIDPOINTS = N

The default is set to GRIDPOINTS = 31. Note that it is possible to do spectroscopies with only a single gridpoint. In this case the point chosen will be the point defined by the TOP position (see further down).

10.2.8 HOLLOW

The hollow position in the unit cell in units of the lattice vectors. This corresponds usually to the position of surface atoms. The input is used in spectroscopy calculations of a single point. Apart from that it only plays a role in evaluations.

The line in the INSCAN file:

HOLLOW = t_1 t_2

The default is set to HOLLOW = 0.5 0.5

10.2.9 LIMITS

Depending on the thermal environment the upper and lower limits of the bias interval are not sharp but thermally broadened. The keyword LIMITS allows to adjust the range according to thermal conditions. For room temperature scans the usual limits will be about 50meV. Note that this parameter is ignored in spectroscopy, since in this case the differential contributions from one bias interval to the next is the decisive result of a simulation.

The line in the INSCAN file has the format:

LIMITS = L_1 L_2

Note also that L_1 will be generally negative and L_2 positive.

10.2.10 NKELDYSH

The NKELDYSH switch controls whether the scattering approach is used for calculating the tunneling current, see section on Scattering method. It is highly recommended to use the zero or first order scattering method for all cases dealing with non-zero bias, in order to handle the bias dependency correctly.

NKELDYSH = n

where n means the following:

- n = -1 (the default) is the standard Bardeen approach
- n = 0 is the zero order scattering approach
- n = 1 is the first order scattering approach

10.2.11 NSPECTRUM

In spectroscopy runs the bias range is divided in a number of intervals, the differential changes are computed separately for every interval. It is recommended that the energy resolution is about 20-50mV. This is sufficient for tunneling spectroscopy in the ambient regime, down to about 150 Kelvin. For very low temperature spectra the surface bandstructure cannot be resolved with sufficient resolution (required are about 1meV), in this case interpolation routines for the bandstructure have to be developed. This part of spectroscopy is currently under development.

The line in the INSCAN file:

NSPECTRUM = N

The default is set to NSPECTRUM = 11. It should be noted that a lower resolution does not necessarily increase the speed of the calculation, since transitions are calculated within every interval. A larger energy interval thus will increase the number of transitions which have to be calculated.

10.2.12 PIVOT

The keyword is part of a group of three keywords, specifying the scan area. The PIVOT point is the lower left point of every scan. Its default is PIVOT = -0.5 -0.5, so that the zero point of the surface unit cell is in the middle of the scan. Note that the units given in PIVOT are units of the lattice vectors A_1 and A_2 of the surface.

The line in the INSCAN file:
PIVOT = p_1 p_2
The default in every calculation is PIVOT = -0.5 -0.5

10.2.13 TOP

The on-top position in the unit cell in units of the lattice vectors. This corresponds usually to the position of surface atoms. The input is used in spectroscopy calculations of a single point. Apart from that it only plays a role in evaluations.

The line in the INSCAN file:
TOP = t_1 t_2
The default is set to TOP = 0.0 0.0

10.2.14 ZVACUUM

The vacuum boundary is compulsory to be given for every evaluations in units of Å as
ZVACUUM = z
The default value is
ZVACUUM = 0.0
which, in turn, results an error message. It should be noted that using wavefunctions from VASP it is the first value after the STM command in the INCAR file.

10.3 EVALUATION

bSKAN provides a variety of methods to analyze the data gained in STM/STS simulations. Generally, it was sought to provide an interface to standard and open source visualization software. The OpenDX program, which can be downloaded free of charge from www.opendx.org is compatible with most of the output.

The most important command line for an evaluation is

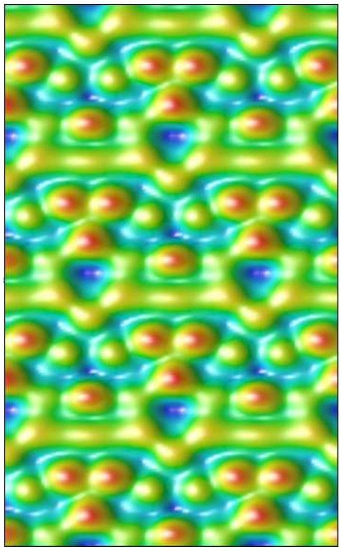

Figure 10.1: Constant current contour on Si(111) (7 × 7), measured with a clean tungsten tip. The contour value: 2V, 100pA.

10.3.1 CURRENT

In this case a line can either be:
CURRENT = I_{val}
or
CURRENT = 0.0

In the first case the evaluation routines search for a current value, which at the defined **BIAS** will match I_{val}. Since the current range in the simulation depends on the z-range, it is not guaranteed that I_{val} is part of the result. In this case the program stops with an errormessage, typically:
CURRENT VALUE NOT FOUND

In this case a line in the **OUTSCAN** file should specify the minimum and maximum current value in the simulation. Note that closed current contours exist only for a limited range of values, so that even though the program writes a file **PLOTCON**, the contour may contain holes. The values in the file are the x, y, and z values of a given I_{val} contour. They can easily be plotted with standard utilities, e.g. gnuplot.

In the second case, if $I_{val} = 0.0$, the whole three dimensional current map will be written to a file **CURRENT**, which contains the current in three nested loops.

The evaluation routine produces a file which looks exactly like the CHGCAR files in VASP, with the only differences (i) the z-extension of the lattice, which is now the z-range of the simulation; (ii) the z-values of the atoms, which are now generally negative, since the atoms are below the vacuum boundary. This file can now either be directly visualized by OpenDX, or the atomic positions and the current values are combined into three separate OpenDX script files, with a utility programmed by David Bowler at UCL. In any case the resulting image looks like (for +2V/50pA on Si(111)) the image shown in Fig. 10.1.

10.3.2 CORRUGATION

It is generally advisable to compute the full current map and to determine the difference in apparent height for different points on the surface from the plot routines e.g. OpenDx. However, in simple cases, e.g. on flat metal surfaces, the corrugation can also be calculated from the difference in apparent height of two specific points. These points are defined as the TOP and the HOLLOW position, given in direct lattice coordinates. Here it has to be taken care that both points are actually part of the surface grid. If they are not, then the nearest points to the defined ones will be computed by the program automatically. The input for a corrugation calculation is:

CORRUGATION = T
TOP = x_T y_T
HOLLOW = x_H y_H

The output file, PLOTCOR contains apart from the current values at top and hollow position also the apparent barrier height, defined as the 0.95 the logarithmic derivative of the current for both positions.

10.3.3 MERGE

For magnetic systems the program calculates the current and spectra depending on the angle between the surface and tip magnetization vectors. In this case two separate calculations need to be performed: one with ferromagnetic ordering,

FERROMAGNETIC

and one with antiferromagnetic ordering for the electron transition from surface to tip. The two current or spectrum maps need to be renamed: the CURMAT from a ferromagnetic calculation becomes CURFM, the CURMAT from the antiferromagnetic calculation becomes CURAFM. For spectral maps the corresponding names are CURSFM and CURSAFM. After the two maps have been calculated, they can be merged by

MERGE = T
PHI = ϕ

This creates a new CURMAT or CURSPEC file containing the maps for the chosen angle ϕ. This file can then be evaluated in the usual manner

10.3.4 PLOTS

Even though it is generally better to obtain the full current map it is sometimes necessary to look at the current values at horizontal planes above the surface. In this case the necessary input is:

PLOTS = N
FPLOT = FILE
ZPLOT = z_1 z_2 ... z_N

The program then creates N files, the filenames are $FILE.001$ to $FILE.N$, containing the current values in a horizontal plane, specified by the values ZPLOT.

Chapter 11

Spectroscopy evaluations

A full three dimensional map of all the differential contributions $dI(x, y, z, eV)/dV$ is probably the most complete information about a surface electronic structure one can have. From version 3.6 bSKAN is able to compute such a map and to extract the data in a variety of different manners. From a practical point of view the information, which can be compared to experimental data is usually:

1. A $I(V)$ or a $dI(v)/dV$ *graph* either as a statistical average over a surface region, or at a specific point of the surface.

2. A two dimensional $I(V)$ or a $dI(V)/dV$ *map* over a certain region of the surface; every gridpoint at the surface given by its unique values.

Experimentally, spectra are always taken at a certain *setpoint*. This is a combination of four values: I, V, X, and Y. The I, V values in this case determine the vertical distance Z. After the setpoint is determined, experimenters switch off the feedback loop and perform a spectrum $I(V)$. In certain cases the bias voltage is oscillated with low frequency and amplitdues of about 20mV. The $dI(V)/dV$ value is then directly determined by lock-in techniques from the variation of the current signal.

The three main inputs in an evaluation of a spectrum are the three lines:

BIAS = V_{bias}

CURRENT = I

TOP = x_t y_t

The file CURSPEC, which is created after the differential spectrum has been completed and written to CURDSPEC is then searched for the three input values. If the combination is not part of the calculation the program stops with an error message. Otherwise, it performs different tasks, depending on whether a statistical evaluation is required or not. If the input also contains the line:

STATISTICAL = T

then the whole current and differential current maps are read. The z-value of the evaluation is then determined depending on the I, V combination in the input. And the output written to PLTSTAT contains the statistical average of $I(V)$ and $dI(V)/dV$ values over a two dimensional plane.

The default in evaluations is STATISTICAL = F, in this case the program writes the separate two dimensional maps to separate files. Here, the convention is that the dI/dV maps are written to files

PLTS.xxx

where xxx is the bias index. The integrated differential currents are written to files

PLTI.xxx

The integrated files are somewhat different than the files one could obtain by performing a straightforward topography simulation. This is due to the approximations used in differential spectroscopy. However, the difference should in general be minor.

In addition, the program writes in both cases a file PLOTSPC, which contains the graph for the spectrum at the TOP position.

Chapter 12

WAVEFUNCTIONS

The format of the wavefunction files used in bSKAN is roughly: (i) a header giving the scale, the lattice vectors, the number of spins, k-points, maximum eigenvalues, G-vectors, and z-gridpoints; (ii) for each k-point the position (reciprocal lattice) and the weight, as well as the number of bands and G-vectors; (iii) the complex amplitudes for each Fourier component at the z-gridpoints in the vacuum. The first few lines of a typical WAVSAMPLE (WAVTIP) file are shown in Table 13.4.

The first line is a comment, the next three lines define the surface lattice. Line one and two give the lattice vectors in the surface plane, line three has only one element, defining the distance between the first z gridpoint of the amplitudes and the core of the surface atoms. The next three lines define the electronic structure of the system: Fermi level, the number of spins, k-points, z-values, G-vectors (reciprocal lattice vector for the 2dim expansion of the wavefunctions), and eigenvalues. Then for every k-point the file contains first the coordinates (in reciprocal space), and the weight of the k-point. Then for every eigenstate at this point the expansion in reciprocal lattice vectors with their complex and z dependent amplitudes.

Chapter 13

Geometry files

The geometry files ASAMPLE and ATIP contain the atomic positions of the surface and the tip, respectively in the same format as the **CONTCAR** file in VASP simulations (cms.mpi.univie.ac.at/vasp/). The first line is a comment line. The following four lines define the three dimensional repeated unit cell in the calculation. The next line defines the number of atoms of each species followed by a line irrelevant for bSKAN, and the final line before the atomic positions in direct coordinates is:

```
Direct
```

It is important to note that cartesian coordinates do not work. It is also important that the scale (the second line of the file) is equal to unity.

The header of an ASAMPLE (ATIP) file thus looks roughly like:

```
THIS LINE IS A COMMENT LINE
    1.000000000000000
13.5340237999999990 0.0000000000000000 0.0000000000000000
0.0000000000000000 9.5700000000000002 0.0000000000000000
0.0000000000000000 0.0000000000000000 25.0000000000000000
90 2 2
Selective dynamics
Direct
0.1666666666642058 0.0000000000000000 0.0000000000000000 F F F
0.5000000000000000 0.0000000000000000 0.0000000000000000 F F F
0.8333333333357941 0.0000000000000000 0.0000000000000000 F F F
```

Bibliography

[1] W. Hofer and J. Redinger, Surf. Sci. 447, 51 (2000).

[2] W. A. Hofer, Progs. Surf. Sci. 71, 147 (2003).

[3] W. A. Hofer and A. J. Fisher, Surf. Sci. Lett. 515, L487 (2002).

[4] W. A. Hofer and A. Garcia-Lekue, Phys. Rev. B 71, 085401 (2005).

[5] K. Palotas and W. A. Hofer, J. Phys: Condens. Mat. 17, 2705 (2005).

[6] G. Binnig and H. Rohrer, Helv. Phys. Acta 55, 726 (1982).

[7] G. Binnig, H. Rohrer, C. Gerber, and E. Weibel, Appl. Phys. Lett. 40, 178 (1982).

[8] G. Binnig, H. Rohrer, C. Gerber, and E. Weibel, Phys. Rev. Lett. 49, 57 (1982).

[9] M. Büttiker, Y. Imry, R. Landauer, and S. Pinhas, Phys. Rev. B 31, 6207 (1985).

[10] J. Tersoff and D. R. Hamann, Phys. Rev. Lett. 50, 1998 (1985).

[11] J. Tersoff and D. R. Hamann, Phys. Rev. B 31, 805 (1985).

[12] J. C. Chen, Phys. Rev. Lett. 65, 448 (1990).

[13] J. C. Chen, Phys. Rev. B 42, 8841 (1990).

[14] P. Sautet and C. Joachim, Chem. Phys. Lett. 185, 23 (1991).

[15] G. Binnig, N. Garcia, H. Rohrer, J. M. Soler, and F. Flores, Phys. Rev. B 30, 4816 (1984).

[16] F. Tersoff, P. L. de Andres, F. J. Garcia-Vidal, L. Jurczyszyn, N. Mingo, and R. Perez, Progs. Surf. Sci. 48, 27 (1995).

[17] J. Bardeen, Phys. Rev. Lett. 6, 57 (1961).

Table 13.1: INPUT FILES

FILE	FUNCTION	FORMAT	ESSENTIAL
INSCAN	all the input parameters	ASCII	YES
WAVSAMPLE	Kohn-Sham states of surface	ASCII	YES
WAVTIP	Kohn-Sham states of model tip	ASCII	NO
ASAMPLE	atomic position of surface atoms	ASCII	YES
ATIP	atomic positions of tip atoms	ASCII	NO
INEIGENVAL	list of eigenvalues excluded	ASCII	NO
INFORCE	list of parameters for FORCE calculation	ASCII	NO
CURFM	current map of ferromagnetic topography	ASCII	NO
CURAFM	current map of antiferromagnetic topography	ASCII	NO
CURSFM	current map of ferromagnetic spectrum	ASCII	NO
CURSAFM	current map of antiferromagnetic spectrum	ASCII	NO

Table 13.2: OUTPUT FILES

FILE	FUNCTION	FORMAT	ESSENTIAL
OUTSCAN	all the output information	ASCII	YES
CURMAT	current matrix of a topographic simulation	BINARY	YES
CURSPEC	current spectrum and matrix of spectroscopy simulation	BINARY	YES
CURSAVE	current spectrum or matrix in ASCII format	ASCII	YES
TRANSLOG	log file for transitions in spectrum simulations	ASCII	NO
PLOTCON	contour plot of topography simulation	ASCII	NO
PLOTCOR	corrugation plot of topography simulation	ASCII	NO
PLOTSPC	I/V spectrum of surface	ASCII	NO
CURRENT	current matrix in OpenDX format	ASCII	NO
README	error messages after input error	ASCII	NO

Table 13.3: KEYWORDS

KEYWORD	FUNCTION
ANTiferromagnetic	ordering of surface and tip states
AREa	of integration in unit cells of the tip
BIAs	voltage in a topography
CELls	of the surface in the dimension of the image
CORrugation	of the surface electronic structure
CURrent	value in the simulated 3D images of the surface
DELta	functional mimicked by a Gaussian for tunneling transitions
FERromagnetic	ordering of surface and tip states
FORce	chemical interactions between surface and tip
FPLot	name of the plot files in the output of horizontal plots
GRIdpoints	of 2-dim surface structure
HOLlow	position on the surface
LIMits	in the energy range due to thermal broadening
MERge	used for magnetic systems
NKEldysh	controls the usage of scattering method
NUMerical	evaluation (Bardeen integration)
NSPectrum	number of energy gridpoints in a spectrum
PHI	angle between magnetization of surface and tip
PIVot	point of the surface image
PLOts	number of parallel surface plots
STAtistical	evaluation of spectra over all surface gridpoints
STErsoff	Tersoff-Hamann model of tunneling spectra
SPEctroscopy	Bardeen model of tunneling spectra
TERsoff Hamann	model of tunneling topographies
TOP	position on the surface
WAVe	decay characteristics of a single surface state
ZPLot	z-gridpoint for the output of parallel plots
ZVAcuum	vacuum boundary of the surface in z direction

Table 13.4: WAVFUNCTION FORMAT

ASCII characters
Scale for VASP output: 0.0468651
5.4159547 0.0000000 0.0000000
0.0000000 5.4159547 0.0000000
0.0000000 0.0000000 1.9458969
fermi-energy: 0.0873040
ispin: 2 k-points: 10 z-values: 101 G-vectors: 16 max-eigenval 37
k-point 1 bands 33 G-vectors 13
k-point 0.0625000000 0.0625000000 0.0625000000
eigenenergy 0.0453091754 occupancy 0.0625000000
G-vector: 0 0
(-0.40120E-02, 0.55003E-02)
(-0.40098E-02, 0.54972E-02)
(-0.39832E-02, 0.54609E-02)
(-0.39363E-02, 0.53965E-02)
(-0.38726E-02, 0.53092E-02)
(-0.37954E-02, 0.52033E-02)