

Project of collaboration Lyngby-Liverpool. Stay of Dr. Lin at Technical University of Denmark: Development of an STM simulation code based on Green's functions

Haiping Lin

June 17, 2009

1 Purpose of the visit

Recent STM experiments have shown that the modification of localized surface states of semiconductors can be achieved by dopant atoms, which are often buried deeply beneath the surface [1, 2, 3]. Since semiconductor surfaces are regarded as important templates for a wide range of applications in nano-scale devices, a thorough understanding how dopant influence the electronic structure at the atomic level will play a crucial role in designing and fabricating microscopic electronic devices in future. To date, however, the theoretical interpretations of STM images of doped semiconductor surfaces has been missing due to the lack of knowledge of tunnelling mechanism at the interfaces and inside the leads (surface and tip). Through this collaboration, we are aiming at a scheme for calculating coherent electron transport in a complete STM imaging processes (substrate-interface-vacuum-interface-tip).

The project is based on the density functional theory calculations implemented in the GPAW package [4]. In the first step, the electronic structures of surface, tip, surface bulk and tip bulk are characterized from accurate DFT calculations. The resulted wave functions (Bloch states) can then be represented by maximally-localized Wannier functions. The localized basis functions together with the obtained effective potentials can then be employed to construct the Green's functions (g_{TT} and g_{SS}) of the semi-infinite surface and tip systems.

We assume that the Green's functions of tip and surface does not change during the STM imaging process. Thus, for each tip-surface configuration, in the combined system, the tip-surface coupling (V_{TS} and V_{ST}) can be calculated by

$$V_{TS} = \langle \phi_i | V_{eff} + \nabla^2 | \phi_j \rangle \quad (1)$$

where $V_{eff} = V_S + V_T$ while ϕ_i and ϕ_j are the localized basis functions of tip and surface respectively.

$$V_{ST} = V_{TS}^\dagger \quad (2)$$

The current value is then given by:

$$I = \int d\omega (f_S - f_T) \text{Tr}[V_{ST}\alpha_{TT}(\omega)V_{TS}\alpha_{SS}(\omega)], \quad (3)$$

where

$$\alpha_{TT} = g_{TT} - g_{TT}^\dagger \text{ and } \alpha_{SS} = g_{SS} - g_{SS}^\dagger. \quad (4)$$

2 Description of the work carried out during the visit

2.1 Implementation of Hamiltonian calculations within GPAW framework

The formula used to calculate the Green's function of a semi-infinite lead (surface or tip) is given by

$$(z\mathbf{S} - \mathbf{H})\mathbf{G}^r(\epsilon) = \mathbf{I}. \quad (5)$$

where \mathbf{H} and \mathbf{S} are the Hamiltonian matrix and overlap matrix of the system respectively. \mathbf{I} is the identity matrix and $z = \epsilon + i\eta$, with η being a positive infinitesimal. However, the \mathbf{H} and \mathbf{S} cannot be obtained directly because this kind of system cannot be calculated with DFT. As shown in Fig. 1(a), a typical surface slab used in DFT calculations is composed of several layers of atoms and a large vacuum in z direction. This supercell is periodically repeated in three dimensions. If the surface slab is thick enough, the electronic properties

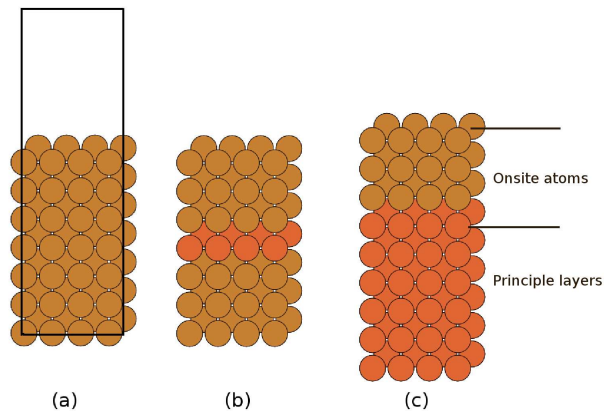


Figure 1: (a) A typical surface slab can be calculated with DFT, (b) the electronic properties of the high-lighted atoms (a principal layer) in the slab should be the same as those of the bulk atoms, (c) the semi-infinite system can be constructed by following the on-site atoms with infinite number of principal layers.

of the atoms in the center area, as highlighted in Fig. 1(b), should be the same

as those of bulk atoms. This periodic layer is called a principal layer of the semi-infinite system. In this project, the semi-infinite lead is represented by a group of on-site atoms and an infinite number of principal layers, see Fig. 1(c), where the on-site part should include at least one principal layer. In addition, the thickness of the principal layers should be large enough so that they interact only with the closest neighbours. The Hamiltonian of the semi-infinite system can then be represented as:

$$\mathbf{H} = \begin{pmatrix} \mathbf{H}_0 & \mathbf{V}_{10}^\dagger & 0 & 0 & \dots \\ \mathbf{V}_{10} & \mathbf{H}_1 & \mathbf{V}_{11}^\dagger & 0 & 0 \\ 0 & \mathbf{V}_{11} & \mathbf{H}_1 & \mathbf{V}_{11}^\dagger & 0 \\ 0 & 0 & \mathbf{V}_{11} & \mathbf{H}_1 & \mathbf{V}_{11}^\dagger \\ \vdots & 0 & 0 & \mathbf{V}_{11} & \ddots \end{pmatrix}. \quad (6)$$

Here, \mathbf{H}_0 and \mathbf{H}_1 refer to the Hamiltonian matrix of the on-site atoms and principal layer atoms respectively. \mathbf{V}_{10} and \mathbf{V}_{11} represent the interactions between a principal layer and on-site atoms and between two principal layers. The Green's function of the coupled system can then be expressed as

$$\mathbf{G}^r(\epsilon) = (z\mathbf{S}_0 - \mathbf{H}_0 - \Sigma^r(\epsilon))^{-1}, \quad (7)$$

the matrix Σ^r is the self energy which incorporates the coupling of principal layers to the on-site part of the system.

$$\Sigma^r(\epsilon) = (z\mathbf{S}_{0\alpha} - \mathbf{H}_{0\alpha})\mathbf{g}_\alpha^r(\epsilon)(z\mathbf{S}_{0\alpha}^\dagger - \mathbf{H}_{0\alpha}^\dagger) \quad (8)$$

Here, $\mathbf{S}_{0\alpha}$ and $\mathbf{H}_{0\alpha}$ are the coupling of Hamiltonian and overlap matrix and $\mathbf{g}_\alpha^r(\epsilon)$ is the Green's function of the principal layers.

$$\mathbf{g}_\alpha^r(\epsilon) = (z\mathbf{S}_\alpha - \mathbf{H}_\alpha)^{-1} \quad (9)$$

As can be seen, the calculation of Hamiltonian and overlap matrix is of great importance to the current calculation Eq. (3). Although the mathematical formula is quite simple, in practice, the bottle-neck arise from the memory and efficiency requirements. In this project, instead of projecting basis functions onto the original unit cell (as shown in Fig. 1(a)), we save the localized functions in small boxes, the length of which are typically 6-8 Angstroms. Each box has two labels: corner coordinate and index number. In this case, as shown in Fig 2, much memory can be saved reading the basis functions. Of more importance, the integration of the basisfunctions over all grid points can be performed only between the small grid boxes, this improves the calculation efficiency dramatically. In the code, the Hamiltonian and overlap matrix can be calculated for any selected atoms of a system. Once H_0 , H_1 , S_0 , S_1 , V_{10} , V_{11} are known (see Eq. (6)), the Green's function of a semi-infinite lead can be evaluated from an utility implemented in GPAW.

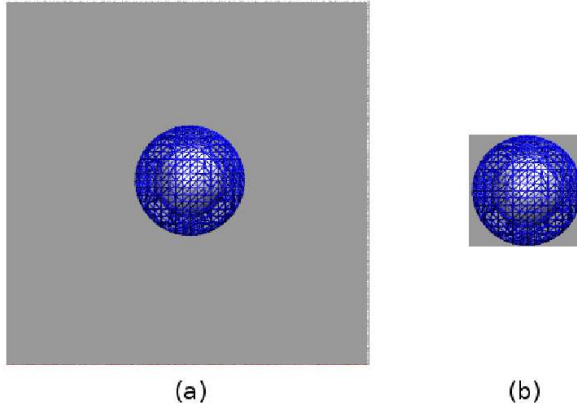


Figure 2: (a) A basis function is projected on the large grid, memory is wasted for remembering zeros (b) the localized basis functions are saved in a small grid box, outside of the box the basis function has only zero values. Each box knows its corner coordinate and index number

2.2 Calculation of V_{TS} and V_{ST}

When the tip and surface are close to each other, the Hamiltonian matrix of the combined system is represented as below:

$$\mathbf{H} = \begin{pmatrix} \mathbf{H}_{T\alpha} & \mathbf{V}_{T\alpha 0} & 0 & 0 \\ \mathbf{V}_{T0\alpha} & \mathbf{H}_T & \mathbf{V}_{TS} & 0 \\ 0 & \mathbf{V}_{ST} & \mathbf{H}_S & \mathbf{V}_{S0\alpha} \\ 0 & 0 & \mathbf{V}_{S\alpha 0} & \mathbf{H}_{S\alpha} \end{pmatrix}. \quad (10)$$

where, α denotes to the principal layers of semi-infinite systems.

In this project, we assume that when the two leads (tip and surface) are moved close to each other, their Hamiltonian matrices remain unchanged and so do the Green's functions. As the tip move above the surface, for each tip-surface configuration, the coupling of the systems, i.e. \mathbf{V}_{TS} and \mathbf{V}_{ST} need to be evaluated. In the first step, the basis functions are read from DFT calculations and then stored in the small grids as shown in Fig. 2. In order to take into account the periodic conditions in the imaging process, the surface basis functions which are at the edge of the unit cell are periodically repeated. Since the basisfunctions are quite localized, only a part of the basis functions of the two leads have non-zero contribution to \mathbf{V}_{TS} and \mathbf{V}_{ST} . In this code, the calculations are only performed if the surface basis function are close enough to the tip and vice versa. Secondly, for each given tip-surface configuration, the corner coordinates of the small grid boxes containing tip basis functions are shifted so that they have the same origin point as the surface basis functions. Up to this stage, the matrix \mathbf{V}_{TS} can be calculated using Eq. (1). However, one needs to consider that the Fermi energy of a tip is usually not equal to the Fermi level of a surface. A rigid shift of the effective potential is required to align the Fermi levels.

2.3 Calculation of current

When the calculations of Green's functions and \mathbf{V}_{TS} have been done, the implementation of transport calculation is rather straightforward, see Eq. (3).

3 Description of the main results obtained

Through this collaboration, a basic version of STM simulation code has been implemented in the GPAW package. To perform an STM simulation, one needs to calculate the isolated tip, surface system and their principal layers in advance. The calculation of Green's functions of semi-infinite leads are carried out automatically. The user then need to indicate the bias voltage as well as the area of the STM scanning. Form our estimation, the current calculation of each tip-surface configuration can be finished within one second. This speed is as good or better than the other STM simulation methods.

The code is written for any localized basis functions, not only Wannier functions but also LCAO basis functions. For testing purpose, we use an Al nano wire as the STM tip and an Al chain as the surface. Fig. 3 shows the simulated

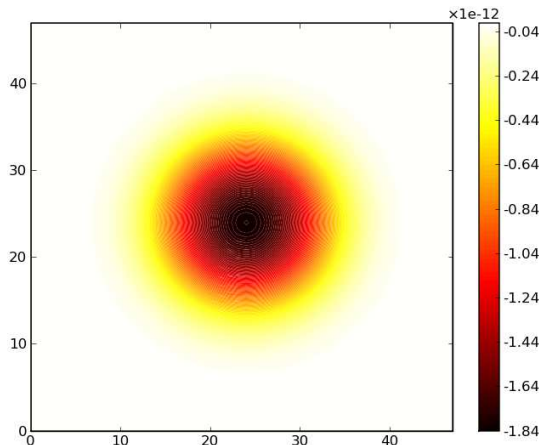


Figure 3: STM simulation of an Al nano wire scans another Al nano wire. $V_{bias} = 1.0$ V

image of this model system. It is quite clear that the one peak feature in Fig. 3 consistent with the structures of an Al chain. We then take a step further to perform the STM simulations of a realistic system, Al tip on a Cu(110) surface. The atomic structure of the surface as well as the simulated images are shown in Fig. 4. As can be seen, the simulated image fits well to the surface configurations. Although a few more complicated tests need to be done in the future, by now we are confident that this STM code is able to produce correct STM images for simple modle systems. In the next step, some clean and doped semiconductor surfaces are going to be investigated.

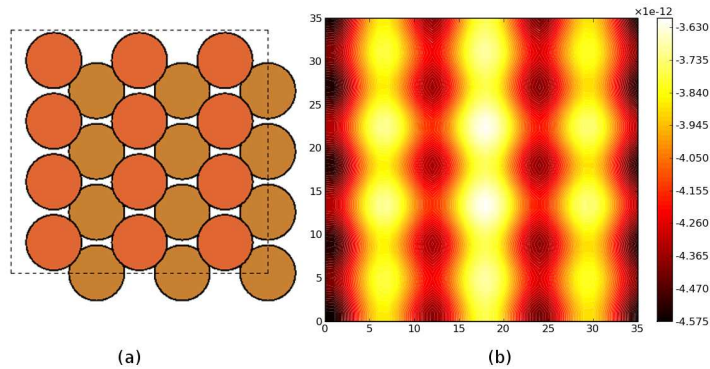


Figure 4: (a) The atomic configuration of a Cu110 surface slab (b) the simulated image with constant height mode. $V_{bias} = -1V$

4 Projected publications/articles resulting or to result from the STSM

Since at the present stage, the implementation of the STM simulation code within GPAW can be considered finished and the computational approach working, the investigation of semiconductor surfaces with charged defects are going to be published. In addition, to our best knowledge, such a theoretical description of the STM imaging process has not implemented in any solid state plane wave simulation package. Consequently, documentation of our implementation could be of interest for the computational Solid State Physics community.

References

- [1] I. Vaquira, J. W. Rabalais, J. Wolfgang and P. Nordlander, Surf. Sci. Lett. **489**, L561-L567 (2001)
- [2] G. W. Brown, H. Grube, M. E. Hawley, S. R. Schofield, N. J. Curson, M. Y. Simmons and R. G. Clark, J. Appl. Phys., **92** No.2 820-824 (2002)
- [3] L. Oberbeck, N. J. Curson, T. Hallam, M. Y. Simmons, R. G. Clark, Thin Solid Films, **464-465**, 23-27 (2004)
- [4] J. J. Mortensen, L. B. Hansen, and K. W. Jacobsen, Phys. Rev. B, **71**, 035109 (2005)