Interpretation of STM

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XI.

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Scanning Tunnelling Microscopy

Optimist says: provides topography in a direct manner
- local - real space - probe
- atomic lateral resolution
Scanning Tunnelling Microscopy

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✔ actually, we infer on the topography from measured local DOS

✔ however, sometimes . . .
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Skeptic says: based on oversimplified theories

⇒ good for fingerprinting
✔ actually tunneling involves sensitive tails of wave functions
✔ tunnelling is a non-linear probe
✔ we are out of equilibrium! STM is a transport process
✔ tip is always treated less carefully than the sample
✔ tip - sample interactions, electronic and atomic are decisive
✔ there is no ab-initio understanding
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?? WHERE IS THE TRUTH ??
Modelling an STM

Unknown:
1. Chemical nature of STM tip
2. Relaxation of tip/surface atoms
3. Effect of tip potential on electronic surface structure
4. Influence of magnetic properties on tunnelling current/surface corrugation
5. Relative importance of the effects

Needed: extensive simulations

No simple inversion theorem to deduce surface structure from STM signal
Distance dependence of tip-sample interaction

**Tip-sample distance** \( z_0 \)

\[ z_0 > 100 \text{ Å} \]

the mutual interaction is negligible, 

strong electric field \( \rightarrow \) field emission microscopy

\[ 10 \text{ Å} < z_0 < 100 \text{ Å} \]

weak van der Waals long range interaction

\[ 3 \text{ Å} < z_0 < 10 \text{ Å} \]

attractive bounding interaction, 

electrons are moving between electrodes \( \rightarrow \) STM

\[ z_0 < 3 \text{ Å} \]

repulsive interaction is dominant, 

strong dependence on the distance, 

chemical bound biolding distance, 

tip and sample deformation \( \rightarrow \) contact mode of STM
Energy level dividing filled-empty bands is called **Fermi level**, $E_F$.

**Surface electronic structure**

Energy level of (just) free electron is **vacuum level**, $E_V$.

Energy require to move electron from $E_F$ to $E_V$ at the surface is **workfunction**, $\Phi$. 
**Work function**

\[ \Phi \] is a result of attraction between departing electron and positive image state (hole)

\[ \Phi < 2 \text{eV (alkali metals)} \rightarrow > 5 \text{eV (transition metal)} \]

**Workfunction varies between**

(i) materials

(ii) crystal faces

<table>
<thead>
<tr>
<th>Polycrystal</th>
<th>( \Phi ) (eV)</th>
<th>Single crystal</th>
<th>( \Phi ) (eV)</th>
</tr>
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<tr>
<td>Na</td>
<td>2.4</td>
<td>( W(111) )</td>
<td>4.39</td>
</tr>
<tr>
<td>Cu</td>
<td>4.4</td>
<td>( W(100) )</td>
<td>4.56</td>
</tr>
<tr>
<td>Ag</td>
<td>4.3</td>
<td>( W(110) )</td>
<td>4.68</td>
</tr>
<tr>
<td>Au</td>
<td>4.3</td>
<td>( W(112) )</td>
<td>4.69</td>
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<tr>
<td>Pt</td>
<td>5.3</td>
<td>( W(\text{poly}) )</td>
<td>4.50</td>
</tr>
</tbody>
</table>

**Workfunction is sensitive to:**

adsorbates

external electric fields

reconstruction

**Workfunction presents a barrier to electron emission.**
The tunneling effect

Solid with noninfinite walls

\[ H\Psi = E\Psi \]

\[ -\left(\frac{\hbar^2}{2m}\right)\frac{d^2\Psi}{dx^2} = E\Psi \]

\[ -\left(\frac{\hbar^2}{2m}\right)\frac{d^2\Psi}{dx^2} + V\Psi = E\Psi \]

The wave function outside the solid consists of two parts:
- the \( B \cdot e^{i\kappa x} \) part which is imaginary when \( E < V \)
- and the \( B' \cdot e^{-i\kappa x} \) part which is an exponentially decaying wave

\[ \Psi_{in} = Ae^{ikx} + A'e^{-ikx}; \quad k = \frac{1}{\hbar}\sqrt{2mE} \]

\[ \Psi_{out} = Be^{i\kappa x} + B'e^{-i\kappa x}; \quad \kappa = \frac{1}{\hbar}\sqrt{2m(V - E)} \]

Electron density decays exponentially away from surface

Inverse decay length \( K = \frac{\sqrt{2me\Phi}}{\hbar} = 0.51\sqrt{\Phi} \) for \( K \) in Å\(^{-1}\) and \( \Phi \) in eV

\( K \approx 1\text{-}2 \text{ Å}^{-1} \) for a typical metal
Two metals in contact

Apply potential $V_{ext}$ to one metal to drive electrons one way:

With metal 1 negative with respect to metal 2 (as shown)
tunneling from filled states within $V_{ext}$ of $E_F$ in metal 1 into empty states at $E_F$ in metal 2

With metal 1 positive with respect to metal 2
tunneling from filled states within $V_{ext}$ of $E_F$ in metal 2 into empty states at $E_F$ in metal 1

current flow equal in both directions!
Tunneling

Tunneling is sensitive to electronic structure:

convolution of DOS of metal A (−) and empty DOS of metal B(+) 

In addition to DOS, \( I_{tunnel} \) depends on 

(i) height of barrier (\( \Phi \))
(ii) thickness of barrier (\( d \))

\[
I_{tunnel} = A \cdot \exp(-2 \cdot K \cdot d)
\]

For a typical metal \( (K = 1 \text{ Å}^{-1}) \), current falls about an order of magnitude for an increase of 1.0 Å in \( d \)

Consequence:

(1) very sensitive dependence of tunnel current on \( d \)

\[ \Rightarrow \text{good vertical resolution} \]

(2) if one metal is sharp tip, most of \( I_{tunnel} \) will travel through apex atom

\[ \Rightarrow \text{good lateral resolution} \]
Model development

*Modeling the STM involves several stages:*

✔ establishing a realistic model of the surface from experiment and theory;

✔ establishing a realistic model of an STM tip using properties known experimentally and inferred from theory;

✔ explicitly modeling the interactions between the tip and surface;

✔ calculating the current under the influence of these interactions, and constructing a theoretical image;

✔ comparing the theoretical model with experimental images.
Current theoretical models

**Non-perturbative:**

✔ Landauer formula or Keldysh non-equilibrium Green's functions

[1-4]

**Perturbative:**

✔ Transfer Hamiltonian methods [5]

✔ Methods based on the properties of the sample surface alone [6]

Some existing numerical codes

- ✔ Codes based on the **Landauer** formula [1, 2, 3]
- ✔ Codes based on the transfer **Hamiltonian** methods [4]
- ✔ Codes based on the **Tersoff-Hamann** method

Perturbation theory

If tip and sample are weakly interacting, tip and sample states can be used as a basis for perturbation theory.

Problems:

- These states are not orthogonal, as they are eigenstates of different Hamiltonians.
- Cannot add the separate Hamiltonians to get the total, as this double counts kinetic energy.

Potential of the system is what changes when tip and sample is coupled.

What is the matrix element?
Transfer Hamiltonian model

\[ I = \frac{4\pi e}{\eta} \int_{0}^{eV} dE \rho_s(E_F - eV + E) \rho_T(E_F + E) |M|^2 \]

Conditions:

\[ U = U_S + U_T \]

\[ U_S \cdot U_T = 0 \]

(never non-zero at same point)

Golden rule with effective matrix element

(Off-diagonal element of current density operator)

\[ M = -\frac{\eta^2}{2m} \int_{S} dS \left( \chi^*_\nu \nabla \Psi_{\mu} - \Psi_{\mu} \nabla \chi^*_\nu \right) \]

**Bardeen approach**

\[
I = \frac{4\pi e}{\eta} \sum_{\mu,\nu} \frac{n^2}{2m^*} \int dS \left( X^*_\nu \nabla \Psi_\mu - \Psi_\mu \nabla X^*_\nu \right) ^2 \delta(E_\mu - E_\nu)
\]
**Tersoff-Hamann approach**

Assume, in addition to validity of perturbation theory in tip-sample interaction, that we have:
- spherical symmetric tip potential
- a s state on tip is the initial state for tunneling
- zero bias

Asymptotic form for the wavefunctions thus

\[ \psi = \sum_{G_{\parallel}} a_G \exp(-\kappa_G z) \exp(i(k + G) \cdot r_{\parallel}) \]

\[ \chi = \alpha \frac{\exp(-\kappa |r - r_0|)}{|r - r_0|} \]

\[ \frac{dI}{dV} \propto \sum_{\text{sample}} |\psi_{\text{sample}}(r_{\text{tip}})|^2 \delta(E - E_F) \]

Constant of proportionality depends sensitively on (unknown) properties of tip states!

The differential conductance probes the density of states of the (isolated) sample, evaluated at the centre of the tip apex.
Implementing Tersoff-Hamann approach

Almost any electronic structure code can be adapted to generate STM images in the T-H approximation

Need to take care that

✔ Have adequate description of wavefunction in vacuum region

✔ If a basis set code, have adequate variational freedom for wavefunction far from atoms

✔ Supposed tip-sample separations are realistic (often taken much tool close in order to match experimentally observed corrugation)
Problems perturbing

The Bardeen perturbation theory will not work when

- Tunnelling becomes strong (transmission probability of order 1, e.g. on tip-sample contact).
- More than one transmission process of comparable amplitude (e.g. in transmission through many molecular systems)

Probably OK for most tunnelling situations!
Problems perturbing

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Probably OK for most tunnelling situations!

➤ The Tersoff-Hamann approach will, in addition, be suspect

✔ If tunnelling is not dominated by tip s-states (e.g. graphite surface, transition metal tips)

✔ If we are interested in effects of the tip chemistry or geometry

✔ If we want to know the absolute tunnel current
Beyond perturbation theory

Must be solved the scattering problem for

**Tip + Adsorbate + Substrate**

**Tools:**

✔ quantum mechanical scattering theory

✔ Landauer formula (formally equivalent)

Express current in terms of transmission amplitude (t-matrix)

**Main difficulty:**

representation of the asymptotic scattering states

**One solution:** calculate conductivity instead between localized initial and final states $|i\rangle$ and $|f\rangle$ as the time-average in terms of the Green function
Landauer-Büttiker formula

In Bardeen and TH methods the wave functions, overlap matrix elements, and DOS are obtained from DFT calculations where the surface and tip are represented as finite systems.

The real system contains infinite electrodes, this is then modelled by artificially broadening the discrete energy levels to obtain a continuous DOS.

Rather than using wave functions, the transport theory can be formulated in terms of non-equilibrium Greens functions which allow for inclusion of infinite electrodes thus removing the need for artificial level broadening.

\[
I = \frac{e}{\hbar} \int d\epsilon \left[ f(\mu_S, \epsilon) - f(\mu_T, \epsilon) \right] \text{Tr} \left[ \Gamma_T(\epsilon) G^R(\epsilon) \Gamma_S(\epsilon) G^A(\epsilon) \right]
\]

- Occupation numbers, \( \mu_S \) and \( \mu_T \) denote chemical potentials of surface and tip
- \( f_S(E), f_T(E) \)
- \( \Gamma_S = i[\Sigma_S^R - \Sigma_S^A] \) represent the surface and tip contacts, which are defined by the difference between retarded and advanced selfenergies of the corresponding electrodes
- \( \Gamma_T = i[\Sigma_T^R - \Sigma_T^A] \)
- \( G^A, G^R \) Advanced and Retarded Green Functions of the vacuum barrier
Local basis formalism

Local orbital basis $\Phi_{i,\alpha} = \Phi_\mu$

$\alpha$ represents the atom $i$ and the orbital $\alpha$

There are DFT-codes like Fireball and SIESTA using that basis set.

Geometry for the local basis formalism. Active sites are shown (in black).

\[ \hat{H}_i = \sum_{\nu,\mu \epsilon S} \{ t_{i\nu} c^*_i \hat{n}_\nu + T_{i\mu} c^*_\nu \hat{n}_\mu \} \]

\[ \hat{H}_{\text{TS}} = \sum_{\nu,\mu \epsilon S} \{ t_{\nu\mu} c^*_\nu \hat{n}_\mu + T_{\nu\mu} c^*_\mu \hat{n}_\nu \} \]

\[ \hat{H}_s = \sum_{\nu,\mu \epsilon S} \{ t_{s\nu} c^*_s \hat{n}_\nu + T_{s\mu} c^*_\nu \hat{n}_\mu \} \]

\[ J. M. Blanco et al. / Progress in Surface Science 81 (2006) 403–443 \]

Tip

$g_{IT}$

Sample

Tip

$g_{ST}$

Sample

Tip

$g_{IT}$

Sample

Tip

$g_{ST}$

Sample

Tip

$g_{IT}$

Sample


Contribution to the tunneling currents in different order of perturbation theory.
Tip

LDOS and integrated DOS of selected magnetic and nonmagnetic STM tip models.

The tip is mimicked by a W(100) surface with single 3d and 4d impurities.

Hofer, Redinger and Podloucky, PRB 64 (2001) 125108.
The STM image shows the atomic resolution.
Darker and brighter atom-like spots are observed.
Brighter and darker area of different image contrast can be distinguished.
A pronounced peak at $\approx 0.25$ eV below $E_F$ found in STS.

(a) STM image (\(U_s = -2\) mV, \(I = 8\) nA). The three details highlight a \(c(2 \times 2)\)-ordered area (unit cell marked) and both a short Ni-rich and a short Fe-rich anti-phase domain boundary segment.

(b) Profile of the STM image along the white line in (a). The dashed average curve indicates a long-wavelength buckling on the nanometer scale in contrast to the short-wavelength buckling distinguishing Fe and Ni atoms.

(c) Map of automatically detected Fe atom locations (corrugation maxima) in the STM image omitting the Ni atoms, with each of the Fe atoms assigned to one of the two \((2 \times 2)\) anti-phase sublattices.
STM image reflects surface geometry

✔ In all simulations we obtain an identical picture for the surface relaxation: the top surface NiFe ordered monolayer is buckled with Fe pushed outwards and Ni inwards.
**STS image of the (001) surface**

(a) $z_0(x, y, -1V, 1nA)$

5 K

1 nm

(b) $I(x, y, z_0, -0.4V)$

(b) Constant current image at 5 K, 1 nA tunneling current, and -1 V sample voltage.

(b) Corresponding current map at -0.4 V, showing the intensity of a surface resonance below the Fermi-level (shaded area in 5 K spectrum to the right).

(c) $dI/dV(V)$ spectra at 5 K corresponding to the images at left and of a separately prepared sample at 80 K. Shown are spectra near extremal points of the surface resonance intensity, both for maximum (A) and minimum (B) intensity.

The small peak at -0.1 V in the 80 K spectra is a tip-related state (arrow). The contour lines in (a) and (b) encompass the relatively small surface fraction that shows spectra which are more similar (smaller root mean square deviation) to spectrum A than to spectrum B.
**Bloch spectral function for the (001)**

Solid lines: Layer- and spin-resolved Bloch spectral functions at $\bar{\Gamma}$ for Fe/Fe$_{0.64}$Ni$_{0.36}$

(a) in vacuum 3.6 Å above the surface,

(b) in the top surface layer,

(c) in a layer deep in the bulk.

Crosses denote the $A_1$-symmetry component of the BSF.
Dispersion of the surface resonance

(a) Minority-spin BSF in vacuum 5.4 Å above the Fe/Fe$_{0.64}$Ni$_{0.36}$ surface plotted for different $k_\parallel$-vectors along the path from $k_\parallel = \bar{\Gamma}$ (bottom) to $k_\parallel = 0.5 \bar{X}$ (top).

(b) Local density of states in vacuum 5.4 Å above the Fe/Fe$_{0.64}$Ni$_{0.36}$ surface.
Surface resonance and Iron coverage I

Models of the top surface layer with 50%, 33% and 25% of Ni used in our simulations.

**LDOS**

Spin-resolved local density of states 7.5 Å above the surface for systems with 50%, 33% and 25% of Ni in the top surface layer. The arrow shows on the surface resonance peak.
Surface resonance and Iron coverage II

*Bloch spectral functions in vacuum 5.4 Å above the surface.*

(a) The top surface layer composition is changed:

i) Fe, ii) Fe$_{0.75}$Ni$_{0.25}$, iii) Fe$_{0.50}$Ni$_{0.50}$, and iv) Ni.

(b) The subsurface layer composition is changed: i) Fe/Fe/Fe$_{0.64}$Ni$_{0.36}$,

ii) Fe/Fe$_{0.50}$Ni$_{0.50}$/Fe$_{0.64}$Ni$_{0.36}$, and iii) Fe/Ni/Fe$_{0.64}$Ni$_{0.36}$.
Surface resonance observed in STS

- We found a surface resonance laying approximately 0.3 eV below the Fermi level, $E_F$, in the minority-spin component of the LDOS.

- This surface resonant state was detected in the vicinity of the $\Gamma$ point. This result agrees well with the general expectation that tunneling microscopy can probe only states with the lowest decay in the vacuum.

- The surface resonance can be ascribed to the peak observed at 0.25 eV below $E_F$ in STS experiment.

- The resonance peak is pronounced in systems with iron-rich surface composition.

- The accurate energy position of the surface resonance is in our simulations slightly dependent on the chemical composition of the thin film model. The reason is the sensitivity of $E_F$ to this quantity.
(a) Relaxation of the InAs(110) surface with indicated atomic distances (black dots, In; white dots, As). The calculated values of the relaxed distances are listed on the right.

(b) InAs(110) band structure. Large symbols mark states that lie more than 80% in the upper two layers, pluses (+) mark states with more than 15% probability in the vacuum.

The states corresponding to the dangling bonds of the In and As atoms as well as the bulk conduction band at $\Gamma$ are marked.

InAs(110) - LDOS

Local density of states spatially integrated over MT regions. Black lines correspond to MT's directly at the surface and gray lines to atoms in the middle of the slab.

(a) As-MT's,

(b) In-MT's.

(a)-(c) Calculated topography images 5 Å above the surface taken at energies as indicated, with $E_F$ at the CBM.

(d1)-(i1) Calculated LDOS at 5 Å above the surface with marked energies given with respect to the CBM.

(d2)-(i2) Measured $dI/dV$ images taken at voltages as indicated, $I=1500$ pA, $V_{mod}=20-40$ mV.

Tip - sample interaction on carbon structures

Total force (black) between the tip and the different carbon structures.

Tips of different chemical reactivity are used: a) Si-, Si-O-tip, b) W-tip, c) W-, Si-tip. Force maxima on the hollow site.

Ondráček et al., PRL 106 (2011) 176101.
**Tip - sample interaction on carbon structures**

Total force (black) between the Si-tip and the carbon nanotube. Open/solid symbols correspond to the top/hollow site. The vdW part and the shortrange part of the interaction are shown. Force maxima on the hollow site.

Constant-height STM images on (0001) graphite for different W tip-surface distances (bias = -300 mV). Maxima on top or hollow sites. Results of perturbative approach and multiple scattering approach are shown.

Ondráček et al., PRL 106 (2011) 176101.
Conclusion

✔ Scanning Tunnelling Microscopy is the unique local - real space - probe with atomic resolution.

✔ The cutting edge in theory is now an exact description of current.

✔ The general problem of all STM simulations:
   the inability to treat satisfactorily the real structure of the tip

✔ The theoretical analysis based on realistic simulations is
   unavoidable to interpret the images and spectra of complex
   systems correct.
References


