High-resolution scanning tunneling microscopy and spectroscopy

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Scanning tunnelling microscope

How an STM works ...

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Institut f. Allgemeine Physik
TU Wien 1997-2002
STM imaging and manipulation

Cu(111)  Surface state scattering  Kanji (Atom)

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IBM Almaden
STM developments 1982 - 2002

- Terraces 1982
- Single atoms 1986
- Atomic species 1993
- Electron waves 1993
- Single Molecule Chemistry
- Reactions 1999
- Bond vibration 2001

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(Some) theoretical models

Extended Huckel theory:
coupled system, local orbitals, arbitrary offset

Keldysh formalism:
coupled system, local orbitals, no arbitrary offset

General problem in STM theory: the arbitrary offset in experimental scans and the high sensitivity of the instrument to surface electronic properties

J. Cerda et al, PRB 56, 15885 (1997)
M. Brandbyge et al, PRB 65, 165401 (2002)
- Theory
- Tip Design
- Local Spin Detection
- Single Atom Contacts
- Molecular Corrals
- Outlook
Multiple scattering technique in STM

Keldysh non-equilibrium

Landauer thermal equilibrium

Contacts from Greens functions

Dyson higher order

\[
I = \frac{e}{h} \int_{\mu_B - eV}^{\mu_B + eV} dE \text{Tr} \left[ \Sigma^< (E) G^> (E) - \Sigma^> (E) G^< (E) \right]
\]

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

\[
i \left[ G_{S(T)}^R (E) - G_{S(T)}^A (E) \right] = G_{S(T)}^R (E) \Gamma_{S(T)} (E) G_{S(T)}^A (E)
\]

\[
G_{(1)}^R = G_{(0)}^R + G_{(0)}^R V G_{(0)}^R
\]


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Greensfunctions of the interface

Zero Order Greensfunction

Surface

STM tip

Zero order current

\[ G^{R(A)}_{(0)}(r_1, r_2, E) = G^{R(A)}_S(r_1, r_2, E) + G^{R(A)}_T(r_1, r_2, E). \]

\[ G^{R(A)}_S(r_1, r_2, E) = \sum_i \frac{\psi_i(r_1)\psi^*_i(r_2)}{E - E'_i + (-)i\eta} \]

\[ G^{R(A)}_T(r_1, r_2, E) = \sum_i \frac{\chi_j(r_1)\chi^*_j(r_2)}{E - E'_j + (-)i\varepsilon} \]

\[ I_{(0)} = \frac{4\pi e}{\hbar} \sum_{ik} \left[ f(\mu_S, E'_k) - f(\mu_T, E'_i) \right] \times \]

\[ \times \left| \frac{(E'_k - E'_i)M_{ik}}{\kappa^2_i - \kappa^2_k} \right|^2 \delta(E'_i - E'_k). \]
Perturbation approach (Bardeen method)

Bardeen matrix element

\[ M_{ik} = \int dS \left[ \chi_i^*(r) \nabla \psi_k(r) - \psi_k(r) \nabla \chi_i^*(r) \right] \]

Eigenvalues \((V = 0)\)

\[ E_{i(k)}' = -\frac{\hbar^2}{2m} \kappa_{i(k)} = E_{i(k)}(V = 0) \]

Bardeen approach

\[ I_{(0)} = \frac{4\pi e}{\hbar} \sum_{ik} [f(\mu_S, E_k) - f(\mu_T, E_i)] \times \]
\[ \times \left| -\frac{\hbar^2}{2m} M_{ik} \right|^2 \delta(E_i - E_k). \]
First order transport through vacuum barrier

First order Greensfunction

Interaction energy

First order current

Current status: developed to first order

\[ G^{R(A)}_{(1)} = G^{R(A)}_{(0)} - \frac{\hbar^2}{m} \sum_{i,k} \psi_i(r_1) M_{ki}^* \chi_k^*(r_2) + \chi_i(r_1) M_{ik} \psi_k^*(r_2) \frac{f_{ik}^+(-)}{f_{ik}} \]

\[ E_{int} = -4 \left( \frac{\hbar^2}{m} \right)^2 \sum_{i,k} \frac{|M_{ki}|^2}{|E_i - E_k + eV|} \]

\[ I_{(1)} = \frac{4\pi e}{\hbar} \sum_{ik} \left[ f \left( \mu_S, E_k - \frac{eV}{2} \right) - f \left( \mu_T, E_i + \frac{eV}{2} \right) \right] \times \]

\[ \times \left( \frac{\hbar^2}{2m} - \frac{eV}{\kappa^2_k - \kappa^2_i} \right) M_{ik} \delta(E_i - E_k + eV). \]
First-principles theory of SP-STM

\[ I(\mathbf{R}) = \frac{I_F(\mathbf{R}) + I_A(\mathbf{R})}{2} \left[ 1 + \frac{I_F(\mathbf{R}) - I_A(\mathbf{R})}{I_F(\mathbf{R}) + I_A(\mathbf{R})} \cos \phi(\mathbf{R}) \right] \]

\[ \cos \phi(\mathbf{R}) = \frac{M_S(\mathbf{R})M_T(\mathbf{R})}{|M_S(\mathbf{R})| \cdot |M_T(\mathbf{R})|} \]

\[ I_{F(A)}(\mathbf{R}) = \frac{4\pi e}{\hbar} \sum_{ik} \left[ f \left( \mu_s, E_k - \frac{eV}{2} \right) - f \left( \mu_T + \frac{eV}{2} \right) \right] \]

\[ \times \left| \left( \frac{\hbar^2}{2m} - \frac{eV}{\kappa_i^2 - \kappa_k^2} \right) M_{ik,F(A)}(\mathbf{R}) \right|^2 \delta(E_i - E_k + eV) \]

\[ M_{ik,F(A)}(\mathbf{R}) = \int d\mathbf{S} \left[ \chi_{i,\uparrow}(\mathbf{r}) \nabla \psi_{k,\uparrow}(\mathbf{r}) - \psi_{k,\uparrow}(\mathbf{r}) \nabla \chi_{i,\uparrow}(\mathbf{r}) \right] \]

General approach for arbitrary magnetic structures including the properties of the STM tip

Spin-polarized current

Angle between surface and tip magnetization

Ferromagnetic/Anti-ferromagn. current

Tunnelling matrix element

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Theoretical procedures

STM tip model

DFT (VASP)

Bias voltage

DFT (VASP)

__Current contours__

\[ \chi \]

\[ \Psi \]

The importance of efficient programming:

- Typical STM simulation:
  - No of k-points: 36
  - No of G-vectors: 100
  - No of gridpoints: > 1000
  - No of integrations: \(36^2 \times 100^2 \times 1000 = 10^{10}\)

Required: highly efficient parallel code with minimum operations in the integration kernel.
Development time: about three years
Required: large computer arrays
Typical requirement for simulations

- Group of eight PostDocs/PhD students
  - Typical job profile: 8CPU/24-48hours
  - Typical number of jobs: 2/person
  - Typical CPU-hours/year: > 500000
  - Typical data storage: > 50Gb/person

- Data sharing:
  - Visual program output: OpenDX
  - Numbers: text files
  - Inputs: text files
Relation to the NW-Grid: the future

Required:
- Data transfer to experimental collaborators
- Data storage of calculated structures
- Data sharing with theoretical collaborators

A grid environment is potentially the most suitable Way to organise cross-institutional collaborations.

Caveats:
- not yet developed in our research area
- Needs to operate across national boundaries
- Theory
- Tip Design
- Local Spin Detection
- Single Adatom Contacts
- Molecular Corrals
- Outlook
Perylene molecules on Ag(110)

Adsorption site

STM experiments and simulations

With a clean STM tip the scans show the molecular states
Functional STM tip

Perylene molecule adsorbed on a tungsten tip

A functional tip shows the states of the clean silver surface

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PRL 96, 156102 (2006)
Tip design: revealing subsurface atoms

Si(111) 7x7 Silicon tip Charge density New tip X

Two dangling bonds Resolved by STM ‘Infinitely sharp’ Even sharper: rest atoms resolved

Tip design: spectroscopy tips

Problem: tungsten tips distort the electronic surface structure

The prediction:

- The same tip is suitable for topography – high contrast- and spectroscopy – minimum distortion of the surface structure.
Co-islands on Pt(111): magnetic contrast

Tunnel Magneto Resistance: 50% \( \text{Model} \) \( \frac{\text{M}}{\text{L}} \) \( \text{L} \)

Tunnel Magneto Resistance: 850% \( \text{Model} \) \( \frac{\text{M}}{\text{L}} \) \( \text{L} \)

APL 87, 162514 (2005).
The reason? Adsorbates

Cr tip with Cr apex
\(dz = 0.45\) Angstrom

Cr tip with H at surface
\(dz = 0.00\) Angstrom

Cr tip with Co apex
\(dz = 0.18\) Angstrom

Cr tip with O at surface
\(dz = 0.00\) Angstrom

Cr tip with O at apex
\(dz = 0.88\) Angstrom

Standard tip

Non-magnetic tip

High-contrast tip

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PRL, submitted
Stability of giant magnetic contrast

Giant magnetic contrast stable over wide bias range
- Theory
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Magnetic semiconductors: Mn-doped GaAs

Mn atoms in low concentration form regular pattern on GaAs

-2V As

Polarized tip

+2V Ga

Polarized tip

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Localization of Mn states

GaAs  GaMnAs

(a) As  Ga  Mn

GaAs(110)  GaMnAs(110)

Mn states in the bandgap

Simulated/measured spectra

Mn states do not couple to lattice
Magnetic contrast of Mn-states measured with spin-polarized tip

SP-STS potentially suitable to detect the spin-state of Mn atoms (caveat: magnetic anisotropy energy very low)
Nanopatterning with polar molecules

The principle: take a halogenated molecule, adsorb it on a surface, and by a voltage pulse of 2-4V detach the halogen.
Patterning of silicon surfaces

Proof of principle:

The molecular arrangement can be used to pattern the surface.

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But somehow ... we were sidetracked.

Why is this atom fuzzy?

Chlorododecane $\text{ClC}_12\text{H}_{25} @ \text{Si}(111)$

$V = -1.5\text{V}, I = 0.2\text{nA}$
Type I corral

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Simulation of type I corral

Adsorption energy: ~ -1.5 eV/molecule

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Surface Dipoles

Interactions at the surface lead to charge redistribution and a shift of the DOS in the range of one eV.
STM simulations

The corralled atom appears lower by 0.4 Angstrom, in line with experiment.
Switching currents: type II corral

Chlorododecanes adsorb in pairs on Si(111) and create a corral-like molecular structure.

JACS 128, 16791 (2006)
Nanotechnology 18, 044012 (2007)
Switch driven by conformation changes

DOS shifted by 1 eV:
Induced surface dipole
Outlook

- Multiple scattering through an interface
- STM induced photon emission
- Design of tips for optimum performance
Thank you for your attention