

Scanning probe microscopies (SPM)

SPM techniques are based in sensing interactions between a surface and a sharp tip of atomic or nanometer dimensions. Depending on the interaction chosen the technique receives specific names:

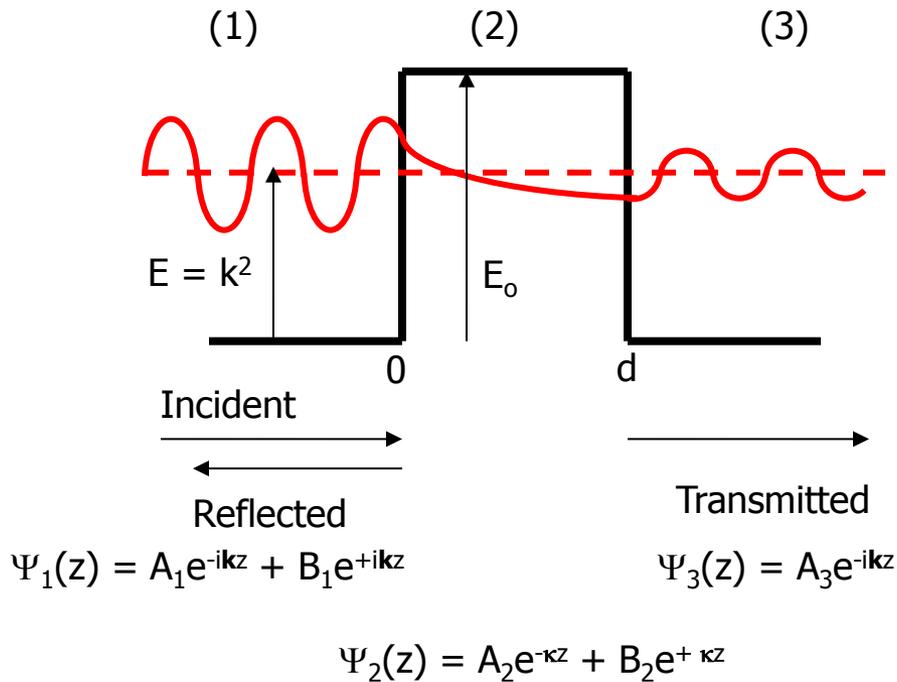
- Electron tunneling: STM
- Repulsive forces: contact AFM
- Attractive forces:
 - Electrostatic forces (EFM, SPFM, KPFM, ...)
 - Van der Waals and Chemical bonding forces
 - (NC-AFM, Dynamic Force AFM)
- Photons
 - NSOM, Tip-enhanced Raman

The tunneling process (QM review):

A simple one-dimensional model of the metallic tip (region 1), the vacuum gap (2), and the sample (3) can be solved exactly. Since the interaction potential is a constant (0 inside the tip or surface, and E_0 in the vacuum, the Schrodinger equation

$$H.\Psi(z) = E. \Psi(z), \text{ with } H = -\frac{d^2}{dz^2}, \text{ can be solved exactly in each region.}$$

The solutions are :



We define $E_0 - E = \kappa^2$

We have omitted the term $\hbar^2/2m$ in the above expressions relating the momentum k or κ to the energy E . To restore the correct expression change k^2 by $k^2 \cdot \hbar^2/2m$

Exact solution for a square 1-D barrier

$$T(E) = \frac{1}{1 + (1+k^2)/4k^2 * \sinh^2(\kappa d)}$$

For electrons tunneling from states near the Fermi level

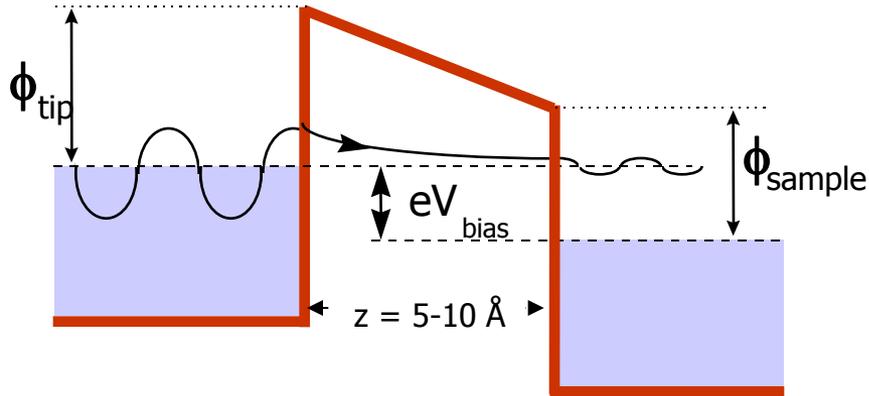
$$T(E) \sim e^{-2\kappa d} = e^{-A\sqrt{\phi} \cdot d}$$

$A \sim 1.025$ for ϕ in eV and d in Å

$\phi =$ work function of the material, which has a typical value of 4 to 5 eV for most metals and semiconductors

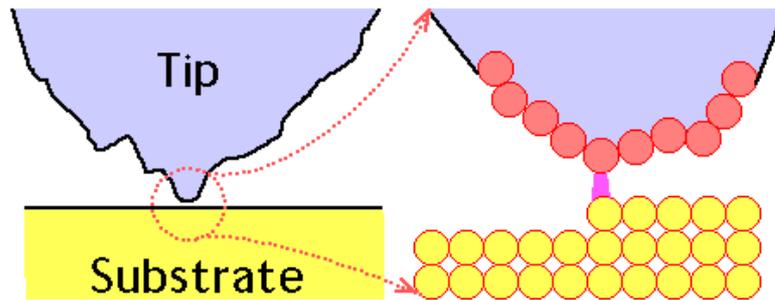
In the drawing on the left, the dashed red line represents the Fermi level. Electrons in states below the Fermi level cannot tunnel into the other electrode because the levels are full (Pauli exclusion principle)

Principle of operation of the Scanning Tunneling Microscope



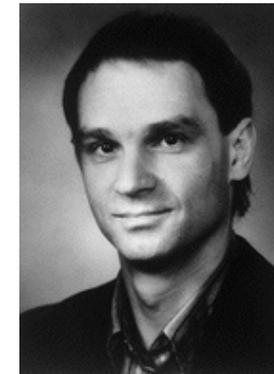
$$I \propto V \cdot N(eV) \cdot e^{-A\sqrt{\phi} \cdot z}$$

→ Z-resolution $\cong 0.1 \text{ pm}$



→ XY-resolution $\cong 100 \text{ pm}$

Nobel prize in
Physics, 1986



Gerd Binnig



Heinrich Rohrer

What determines the contrast of STM images ?

Bardeen Approximation for the current:

$$J_{fi} = (ie\hbar/2m) \cdot [\Psi_f(r) \cdot \nabla \Psi_i^*(r) - \Psi_i^*(r) \cdot \nabla \Psi_f(r)]$$

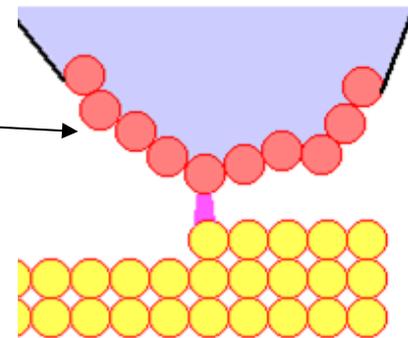
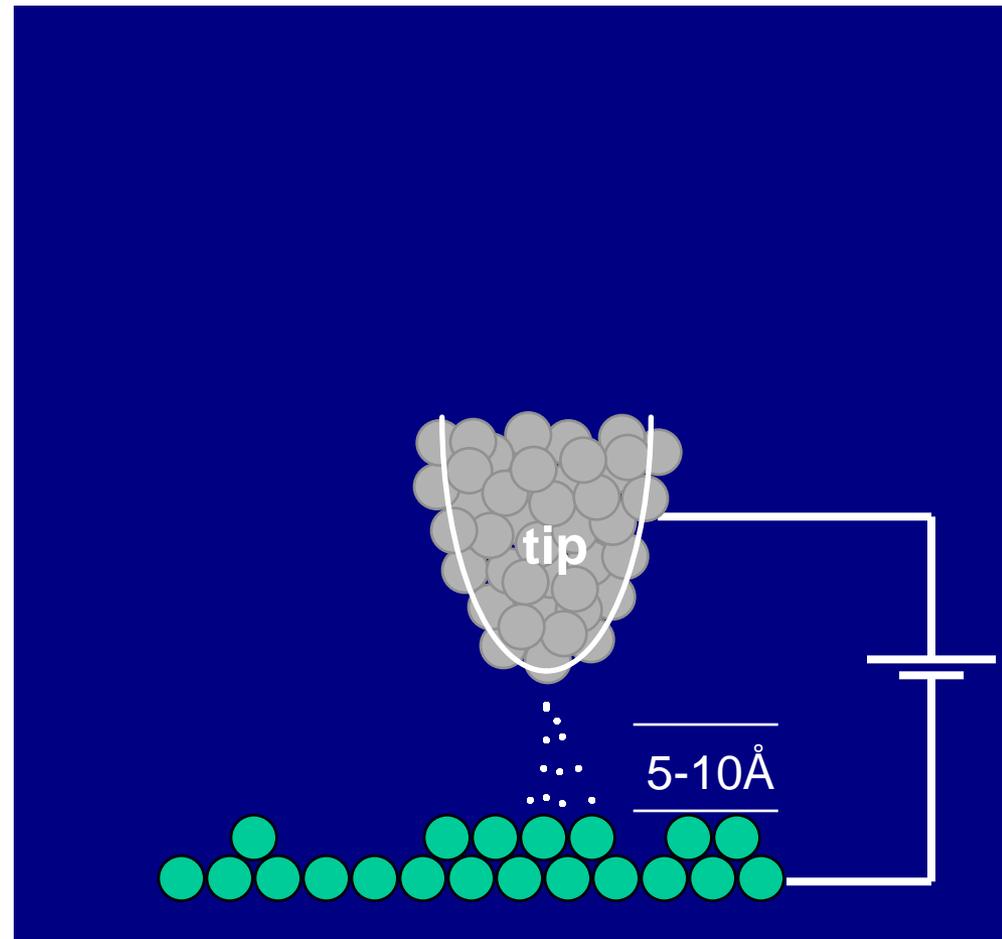
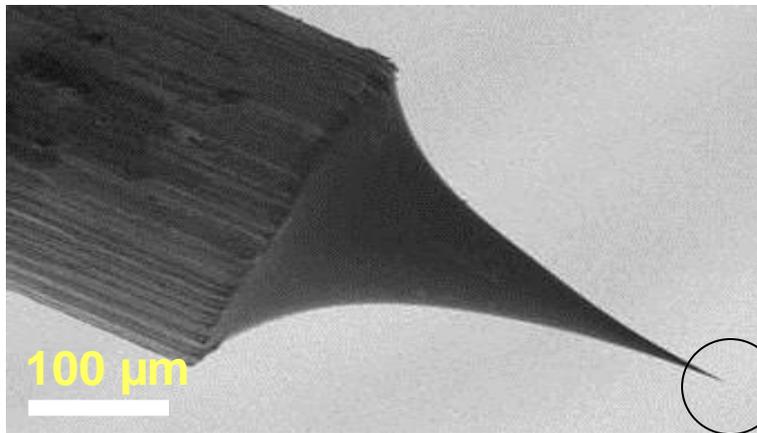
The Tersoff-Hamann theory:

$$I \propto \sum |\Psi_f(\mathbf{r}_0)|^2 \cdot \delta(E_f - E_i)$$

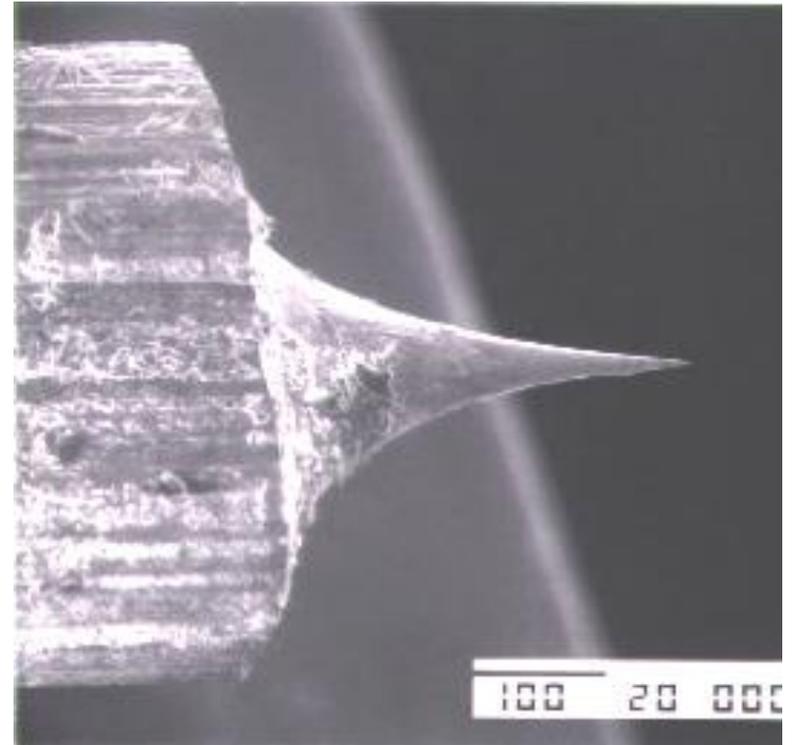
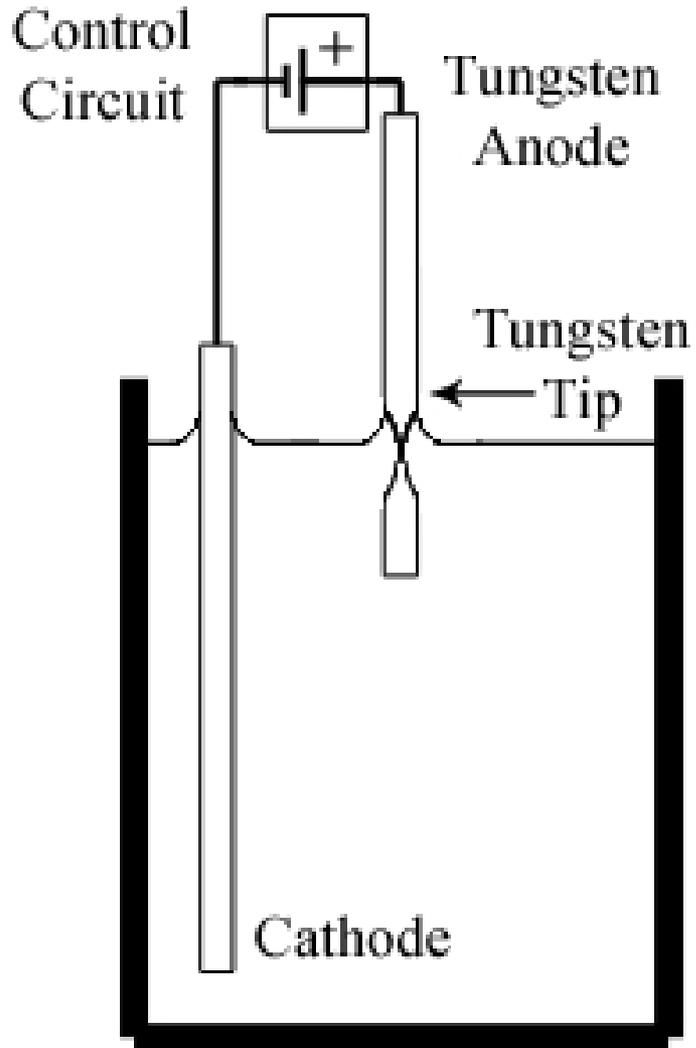
$$I = 4\pi e/h \int_0^{eV} \rho_t(E_F - eV + \varepsilon) \cdot \rho_s(E_F + \varepsilon) \cdot |M|^2 \cdot d\varepsilon$$

The Tersoff-Hamann Theory tells us that the image is a contour of the density of states of the sample at the position of the tip, assumed to be a sphere centered at \mathbf{r}_0 . In other words the images are not “pictures” of atoms by contours of electronic density at the Fermi level.

How it works

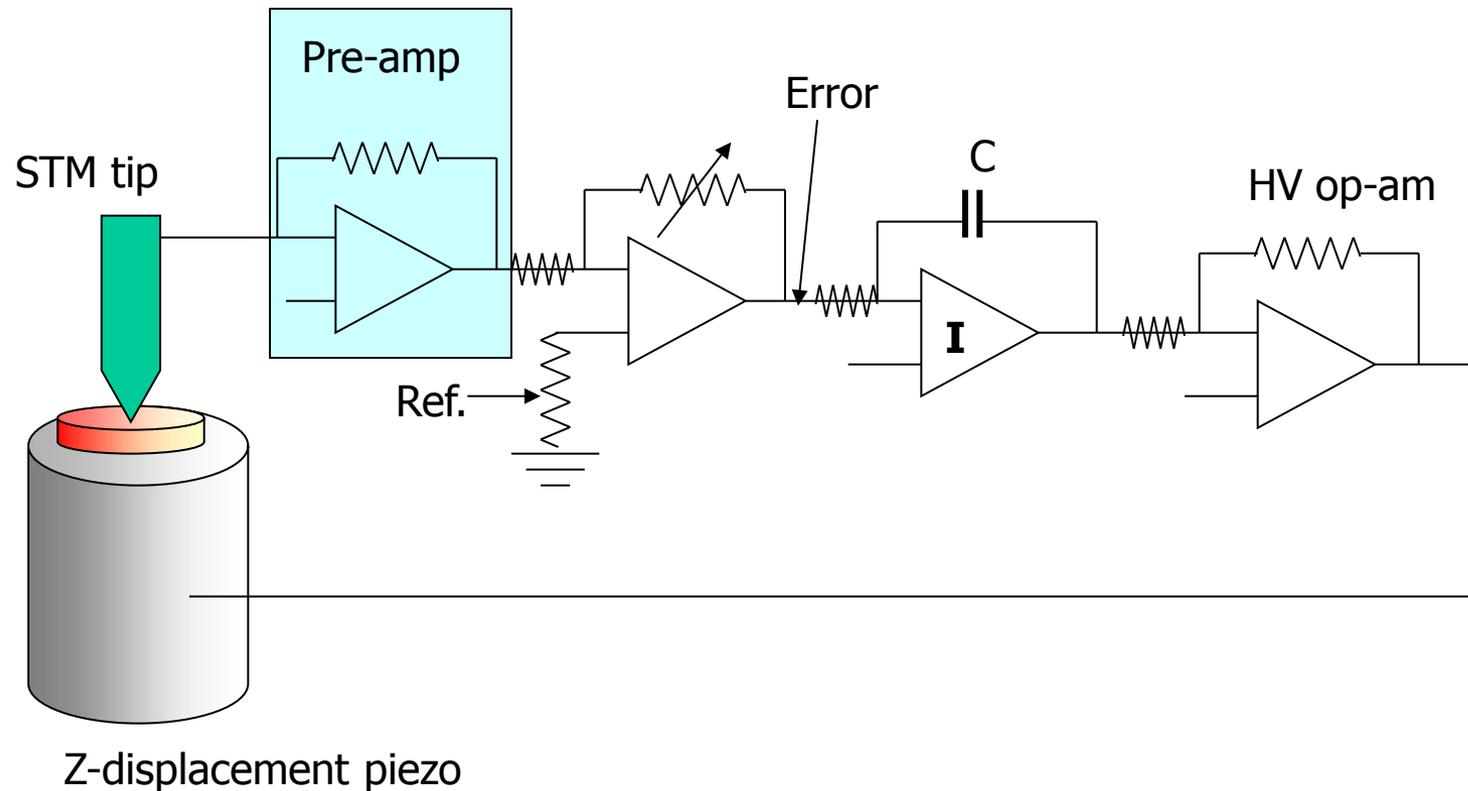


Tip fabrication

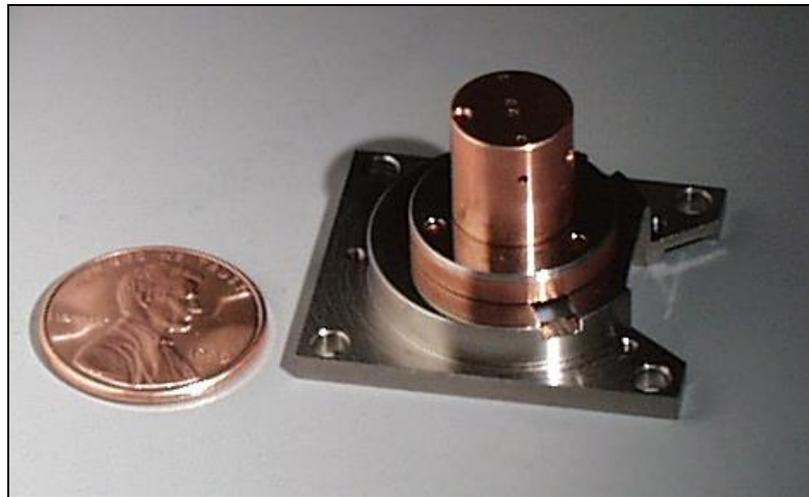
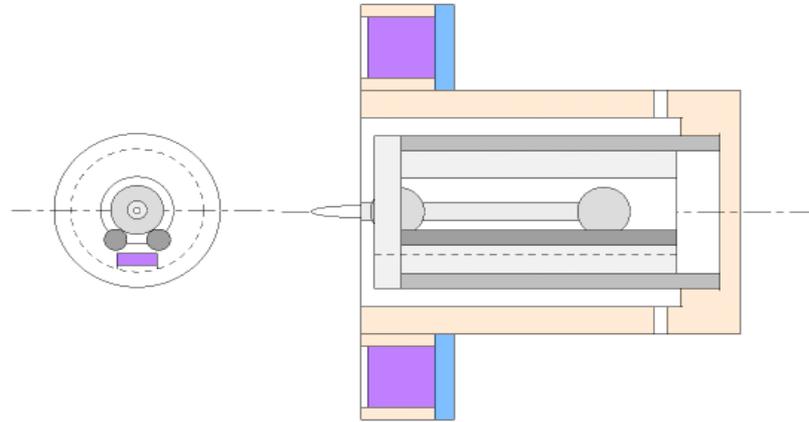
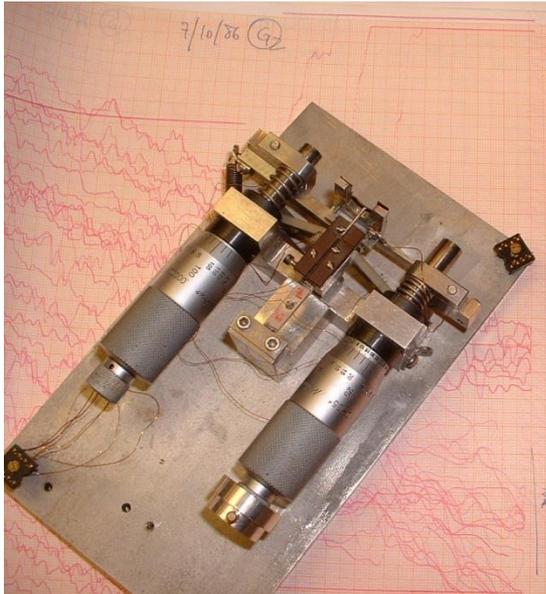


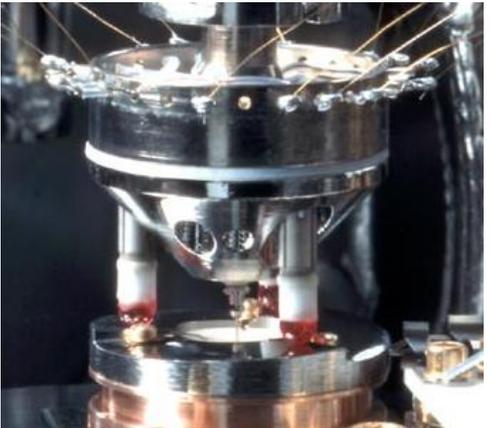
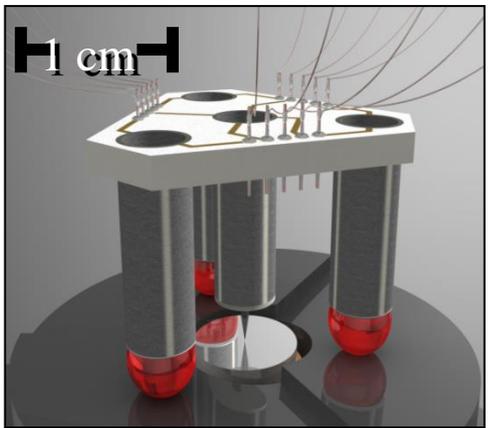
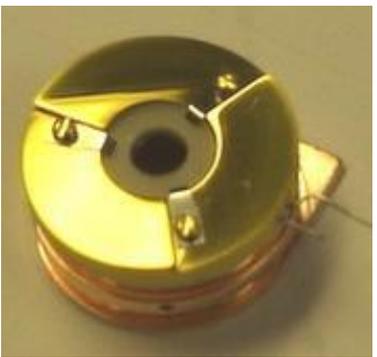
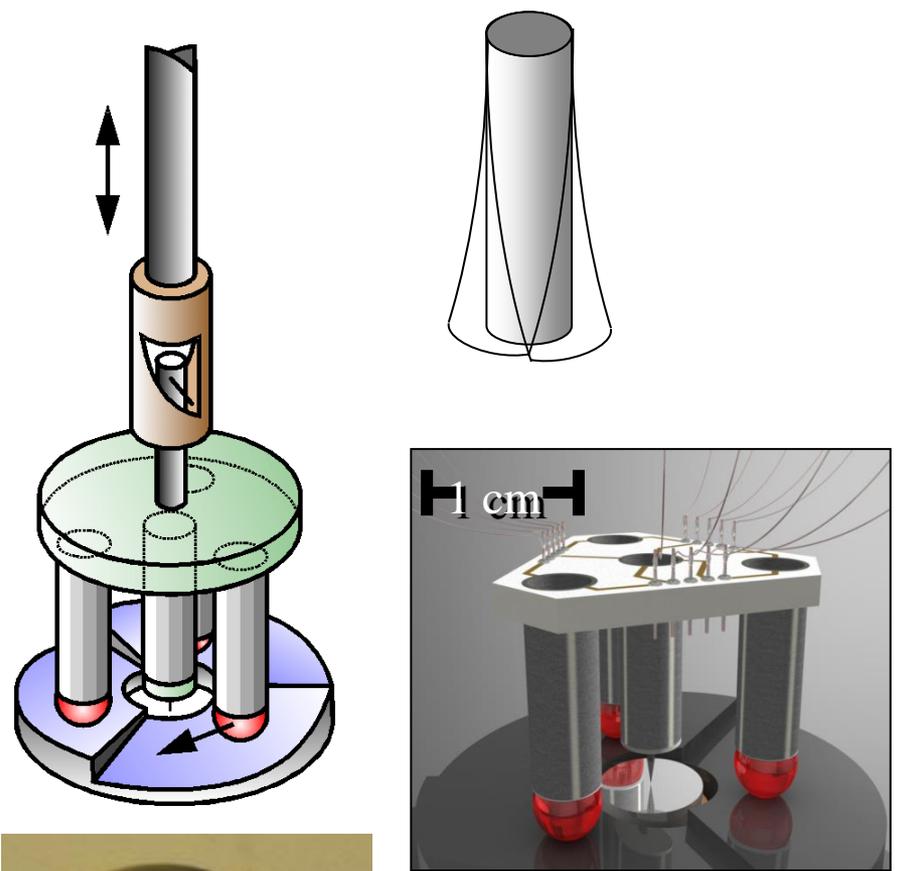
The STM technique

Electronic feedback:

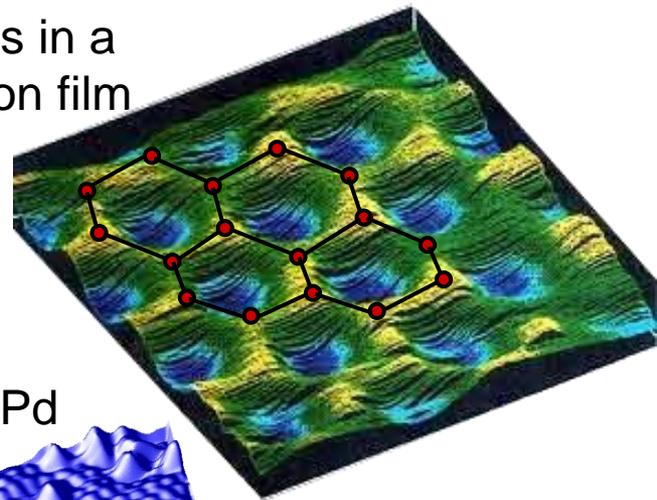


The Instruments

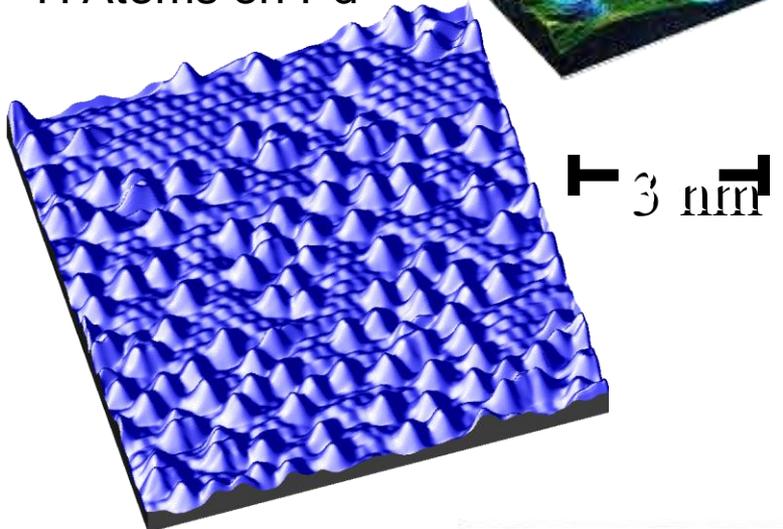




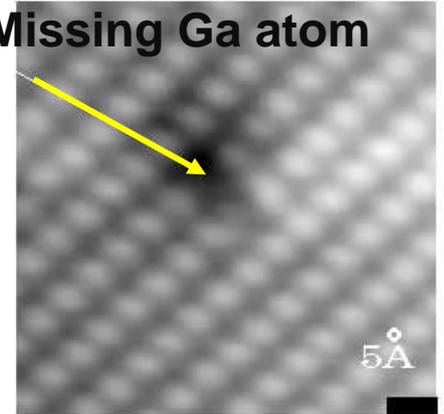
Chemical bonds in a Graphitic Carbon film



H Atoms on Pd



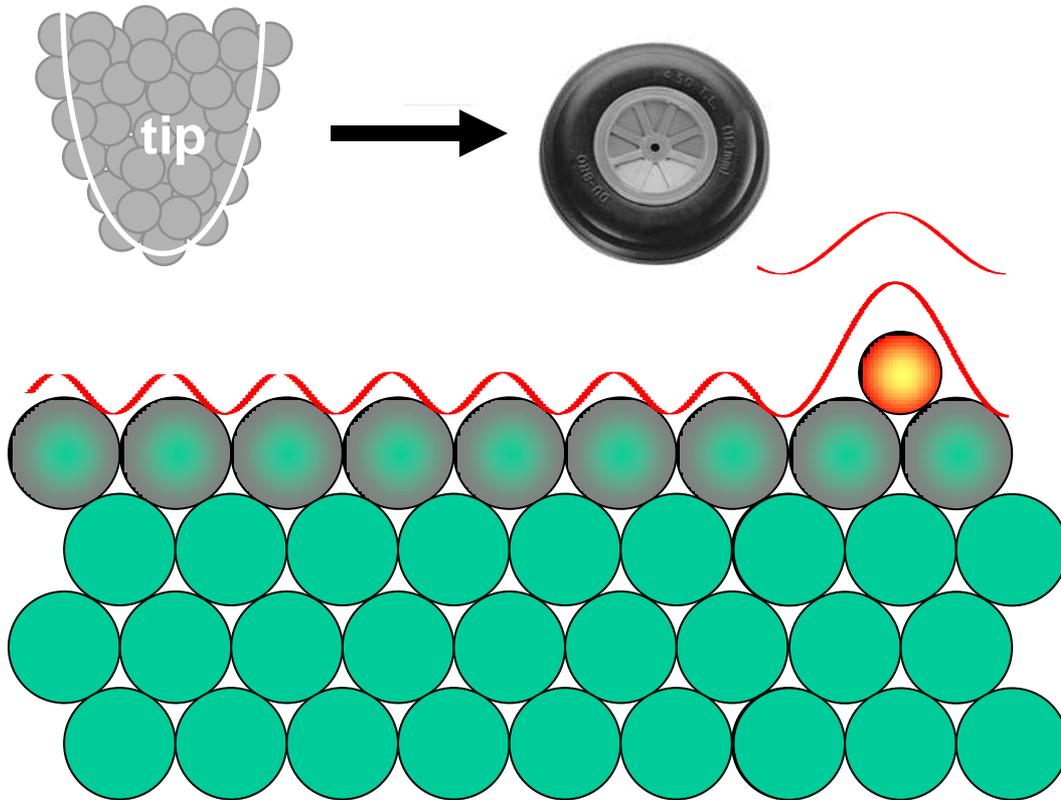
Missing Ga atom



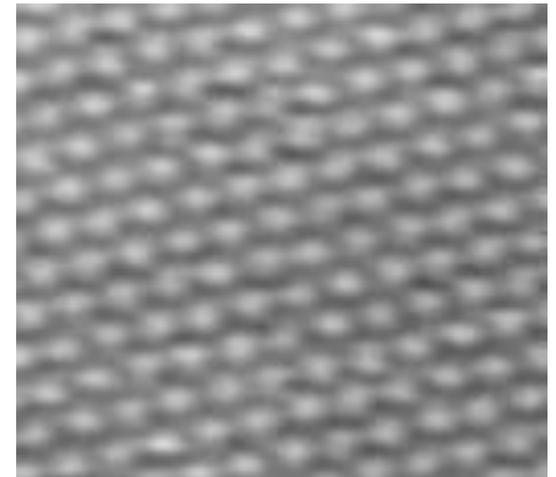
How big are the atoms in the STM images ??

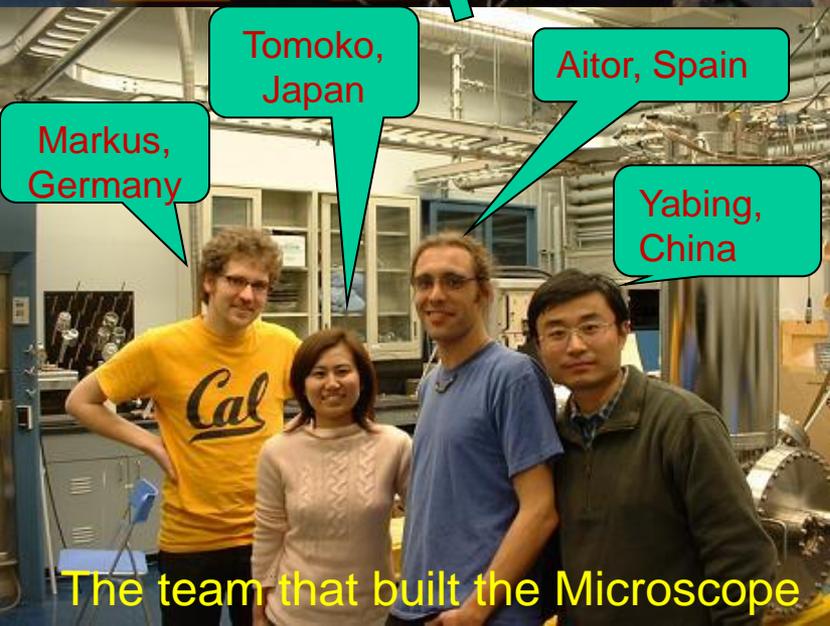
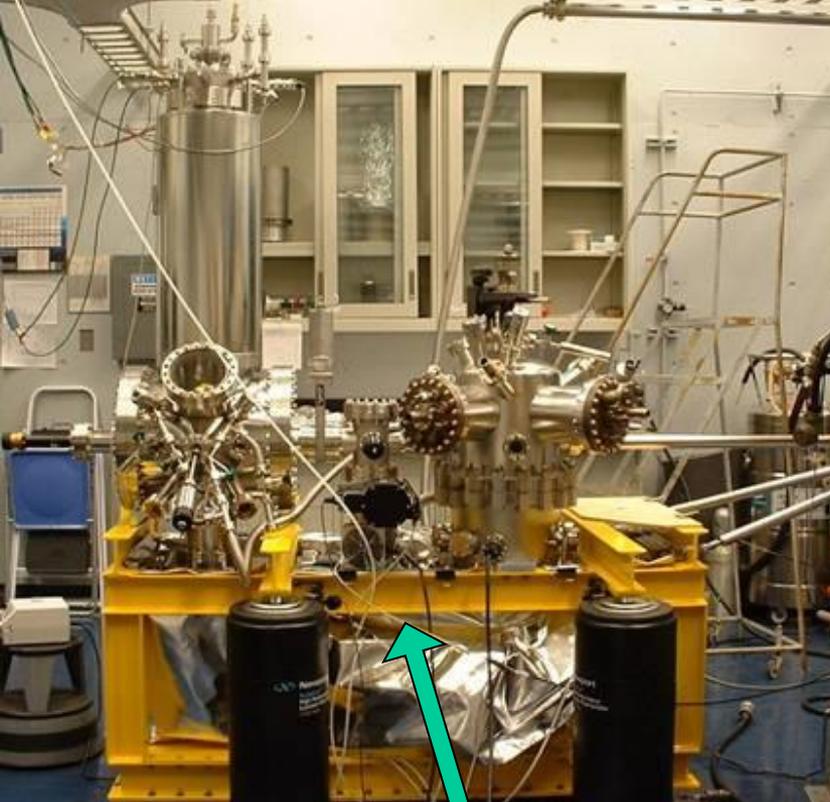
Example:

Palladium atoms at the surface



Surface atomic profile
Tip cruising altitude ~ 500 pm
 $\Delta z = 2$ pm



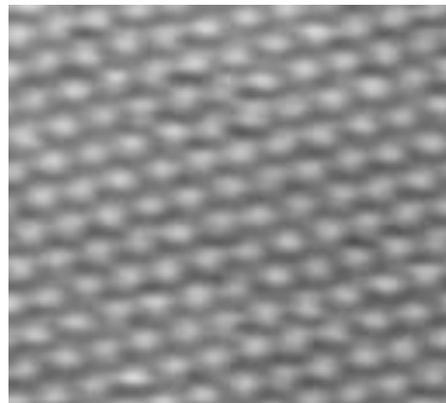
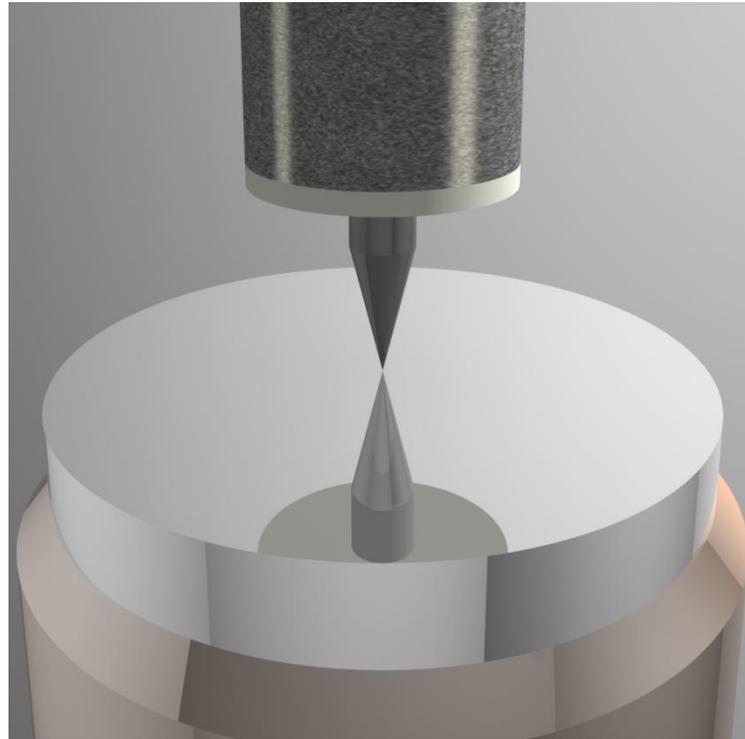
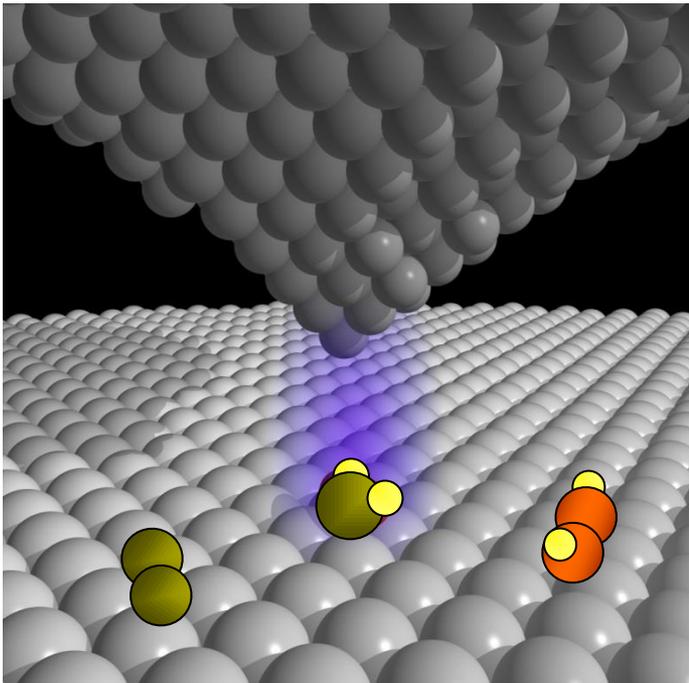


The team that built the Microscope

Tomoko fills the Cryostat with liquid Helium

Scanning Tunneling Microscopy

Molecules on metals:
H₂O, CO, H₂, ...
on Pd, Ru, Pt, ...

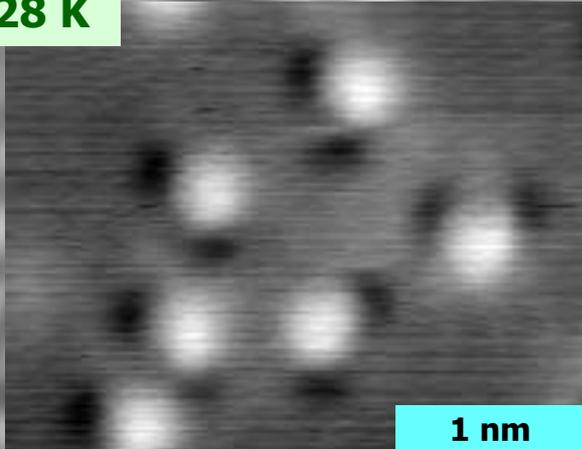


Pd(111) surface
Tip height ~ 500 pm
Corrugation $\Delta z = 2$ pm

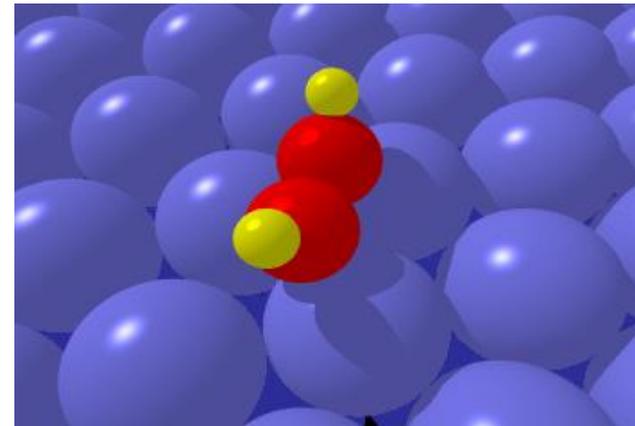
What determines the image contrast ?

C₂H₂ on Pd(111)

28 K



- 3 equivalent orientations

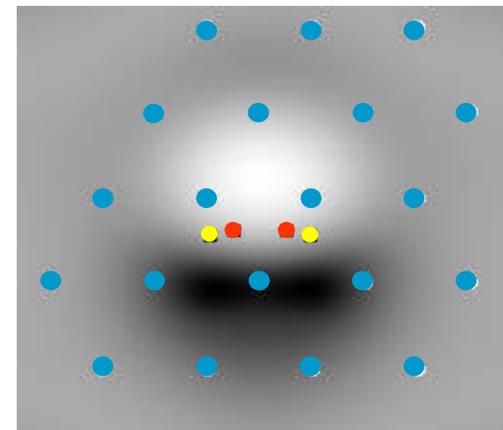
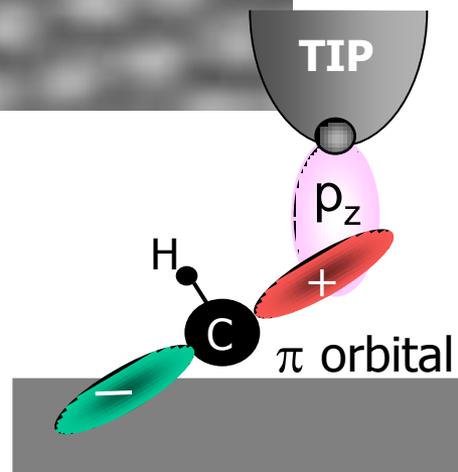


● C atom

● H atom

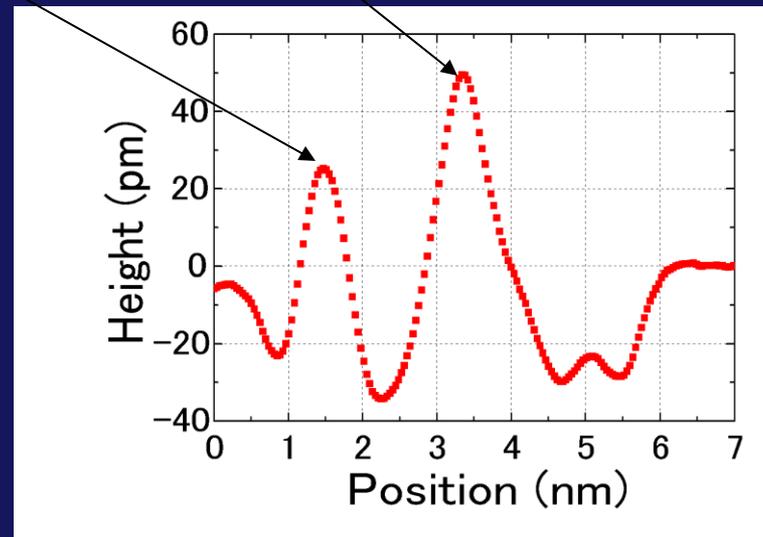
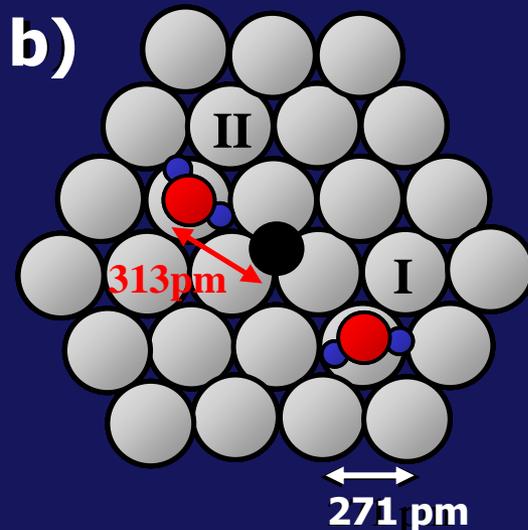
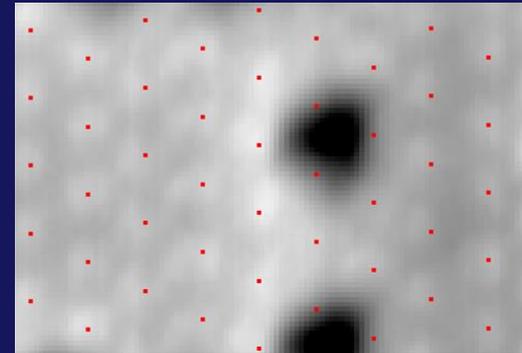
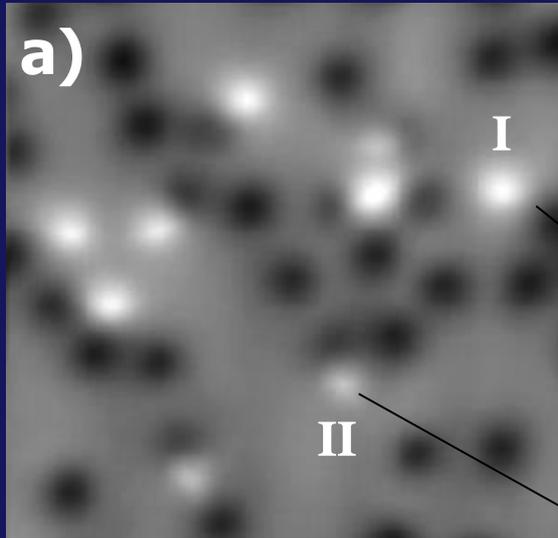
DFT-GGA Calculated Geometry

The images reflect the structure of the molecular orbitals participating in the tunneling current. In this case it is the pi orbital of the molecule



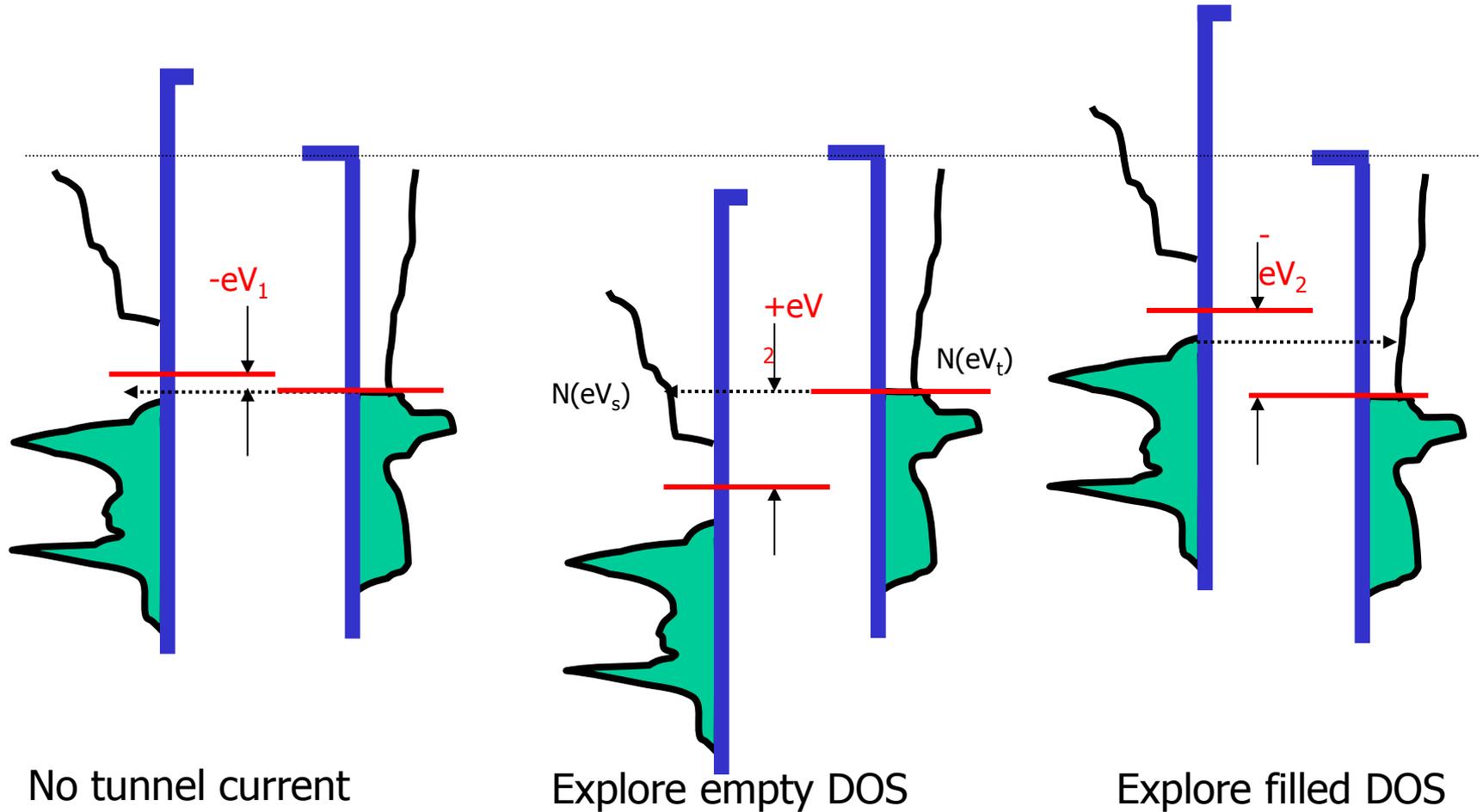
ESQC Calculated Image

Water adsorption on Ru(0001) (with a few atoms of C) $T = 6\text{ K}$



Another unique capability of STM:
atomic scale electronic structure
(I-V spectroscopy)

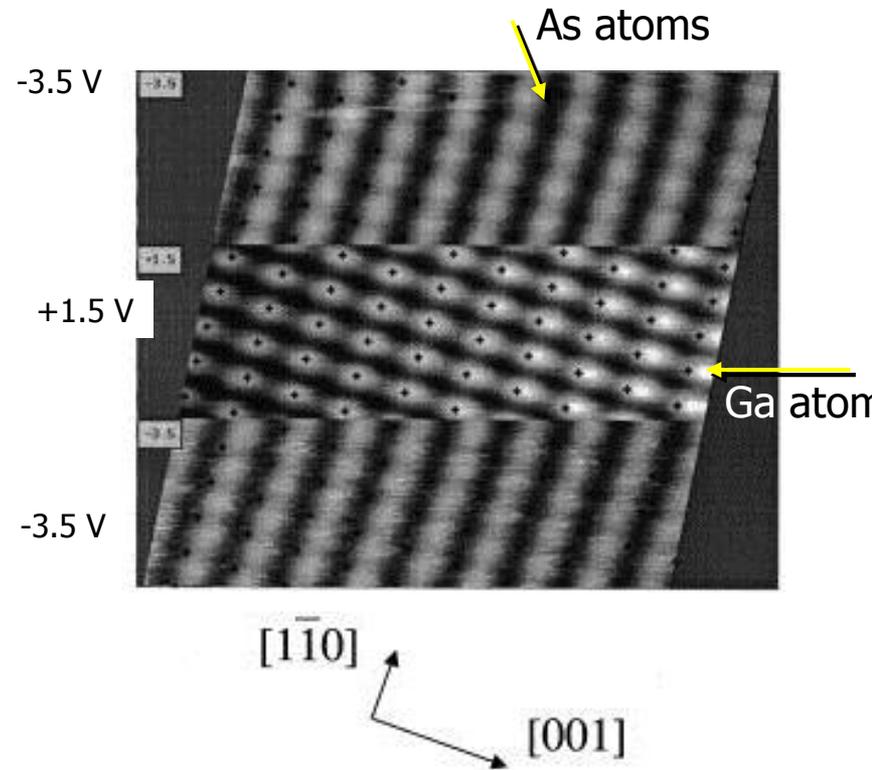
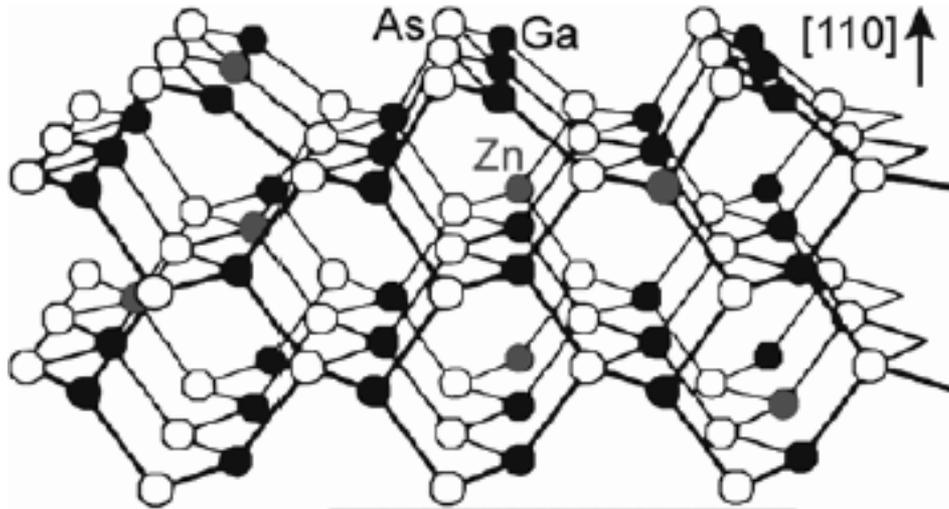
Electronic spectroscopy with the STM



$$I_{\text{tunnel}} \propto \int N(eV_t) \times f(eV_t) \times N(eV_s) \times [1-f(eV_s)] \times T(\phi + eV) \times dV$$

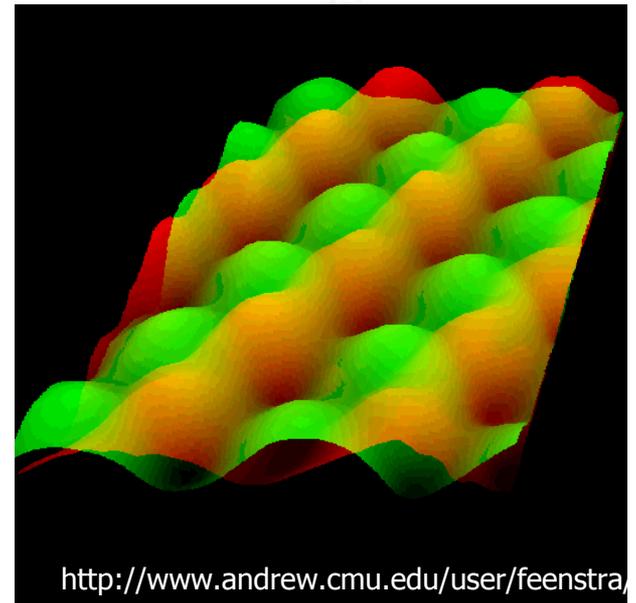
Spectroscopy in STM images

N-type GaAs(110)



At negative sample bias (top and bottom third of the image), electrons tunnel out of the As atoms, because the full As orbitals make the valence band. The bias has to be larger than the band gap, which for GaAs is 1.4 eV.

At positive sample bias electrons tunnel from the tip to empty orbitals (conduction band), which are made of Ga orbitals



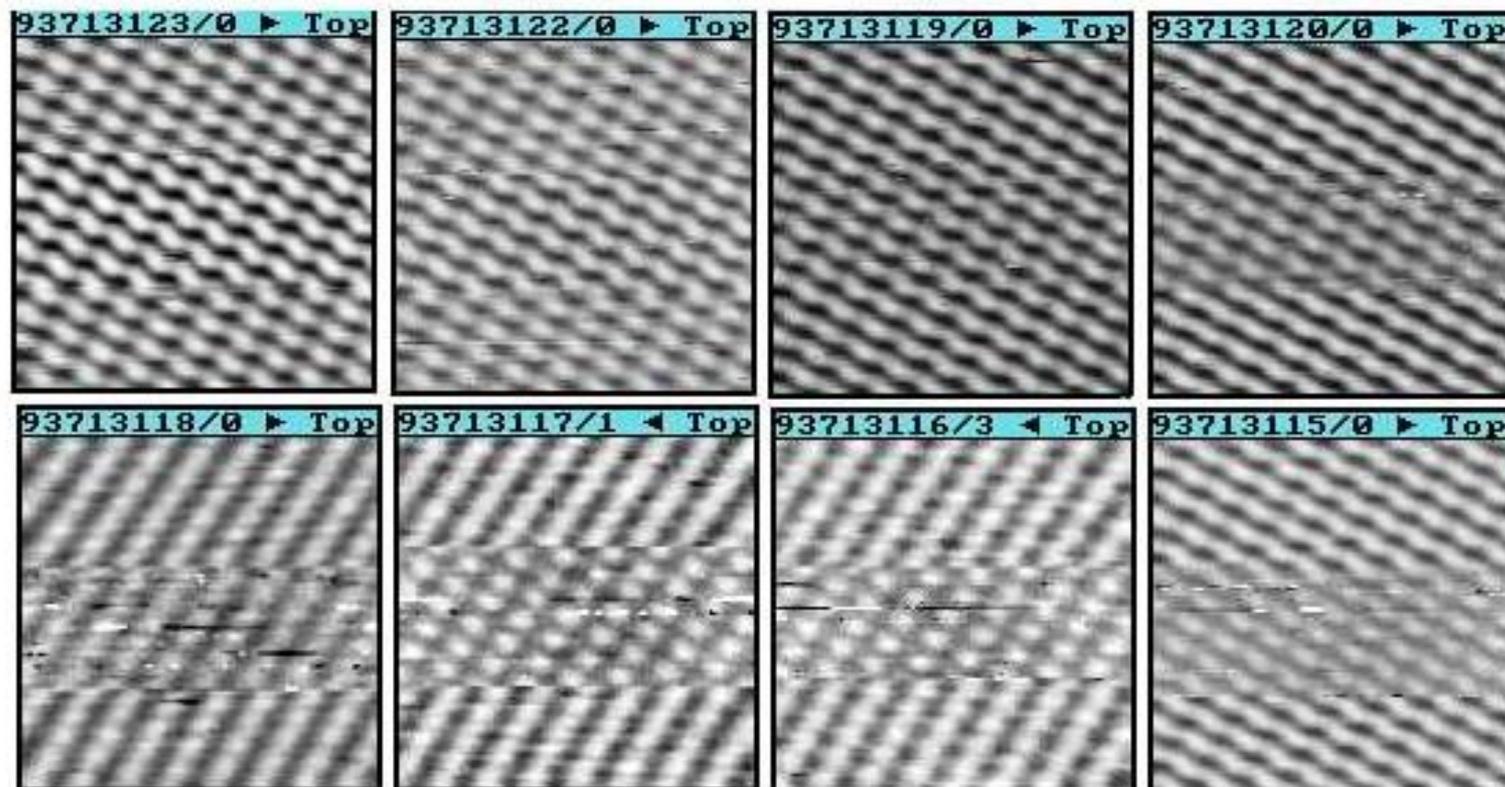
n+ GaAs Sample bias (V)

0.76

1.01

1.50

1.76

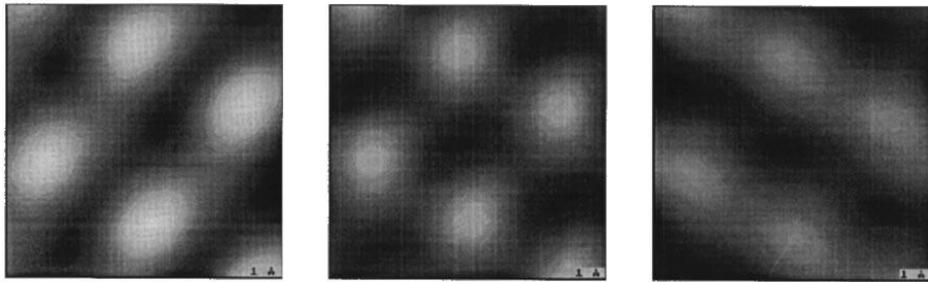
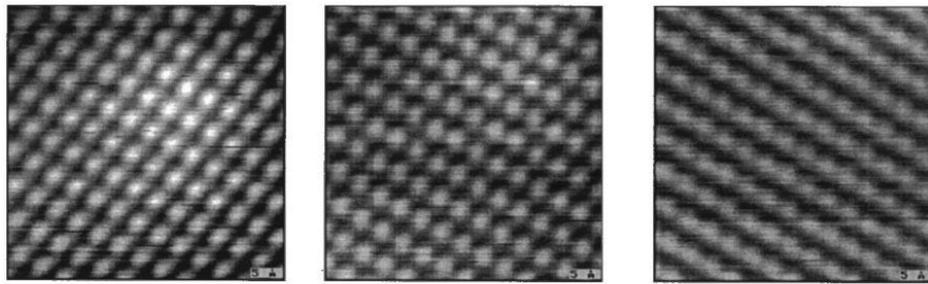


3.00

2.76

2.51

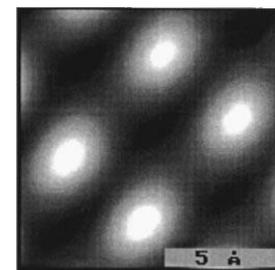
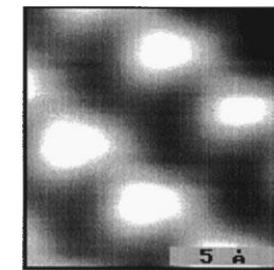
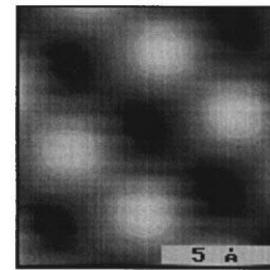
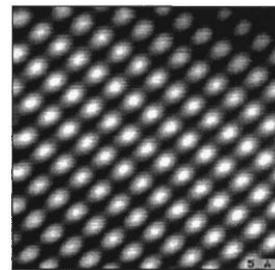
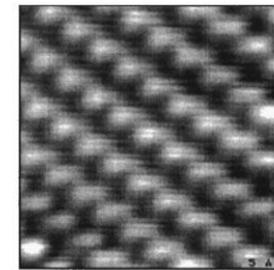
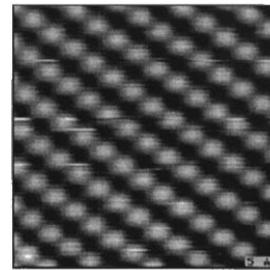
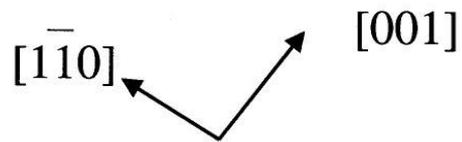
2.01



0.5 V
a)

0.7 V
b)

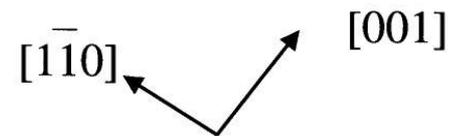
1.1 V
c)



-2.5 V
a)

-1.9 V
b)

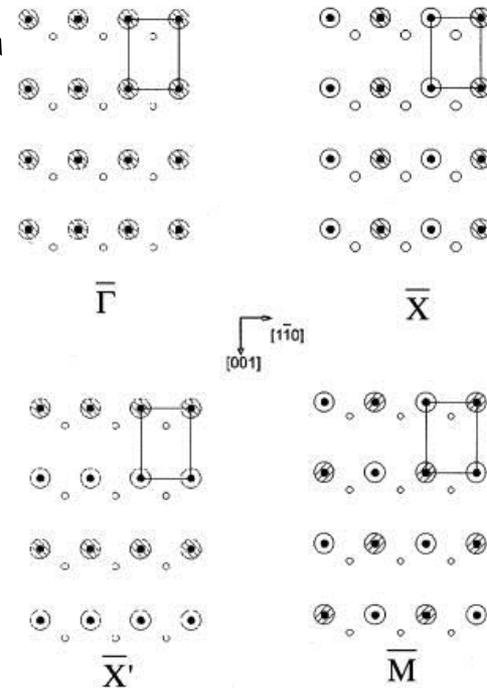
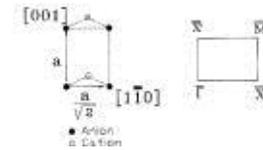
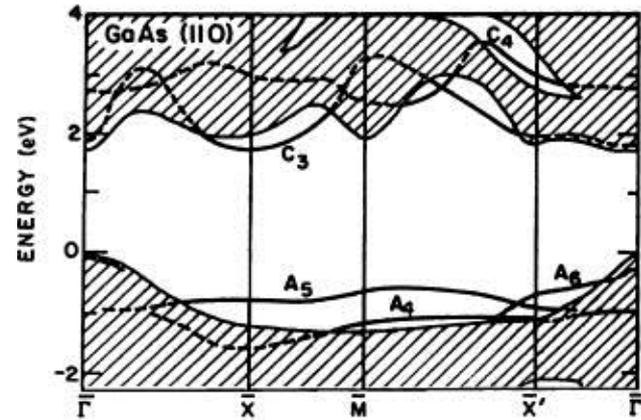
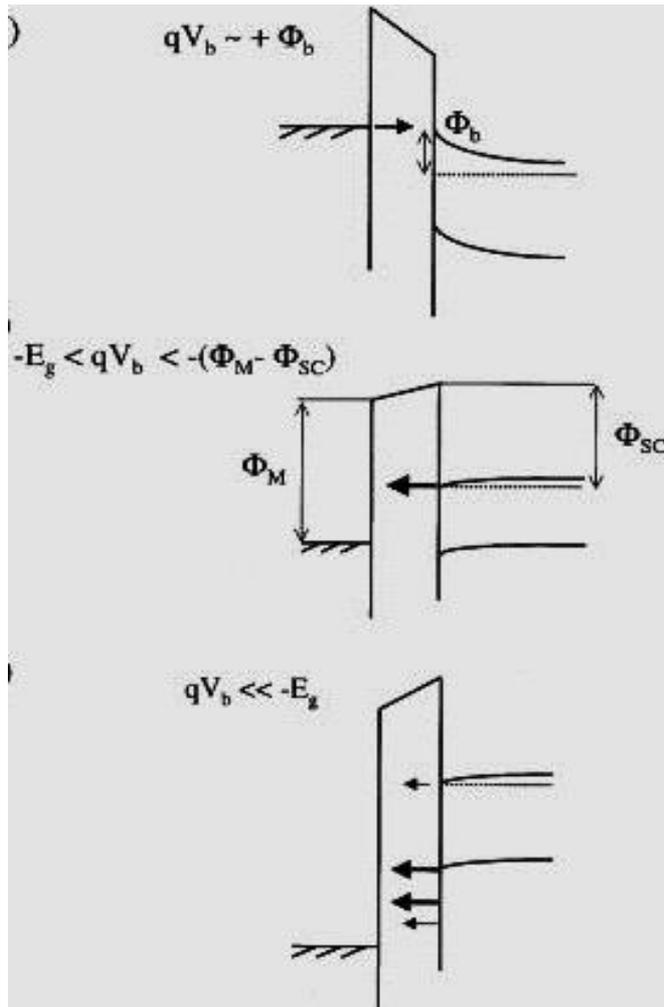
-1.4 V
c)



Interpretation of GaAs(110) scanning tunneling microscopy image contrast by the symmetry of the surface Bloch wave functions

N.D. Jäger, E.R. Weber and M. Salmeron.

J. Vac. Sci. Technol. B 19, (2) 511 (2001)



$$\Psi_k(\mathbf{r}) = \sum_j \phi_a(\mathbf{r} - \mathbf{r}_j) \cdot e^{i\mathbf{k}(\mathbf{r} - \mathbf{r}_j)}$$

Cross-Sectional STM Image of $\text{In}_{0.2}\text{Ga}_{0.8}\text{As}/\text{GaAs}$ Multiple Quantum Wells

-Atomic Resolution Image of Indium and Gallium Atoms, Interfaces

