Interpretation of STM

František Máca

XI.

NEVF 514 Surface Physics

Winter Term 2018 - 2019

Troja, 14-th December 2018

Scanning Tunnelling Microscopy

Optimist says: *provides topography in a direct manner*

- ✔ *local - real space - probe*
- ✔ *atomic lateral resolution*

Realist says: *we learn more about the surface*

- ✔ *actually, we infer on the topography from measured local DOS*
- ✔ *however, sometimes . . .*

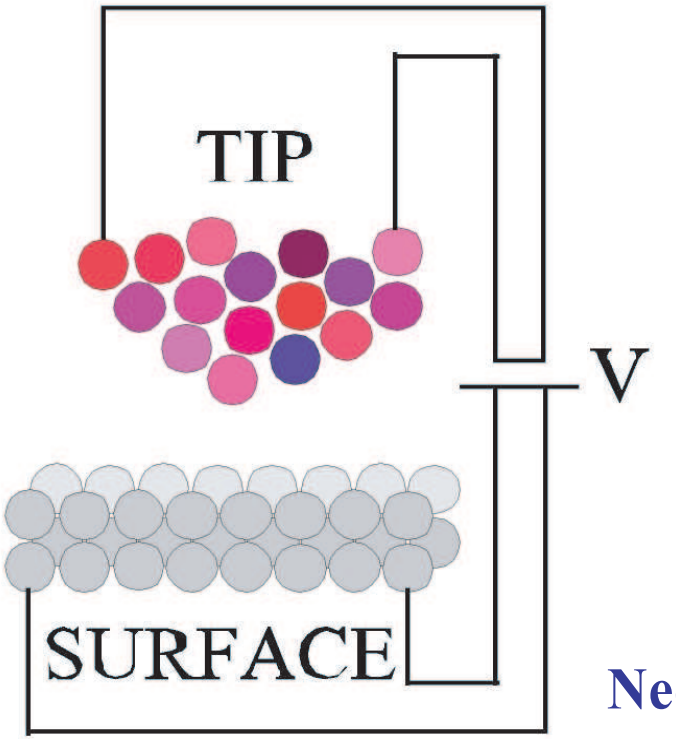
Skeptic says: *based on oversimplified theories*

$\Longrightarrow$ 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*

?? 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

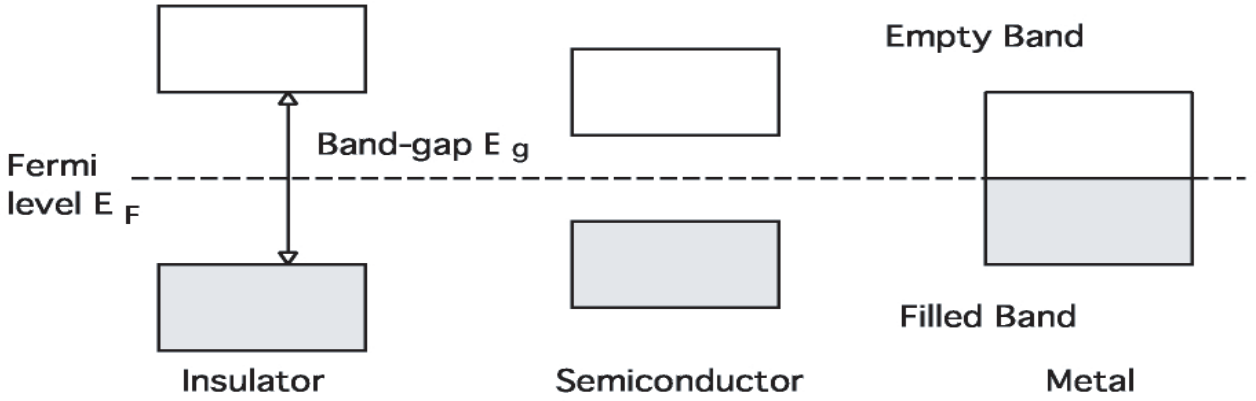
No simple inversion theorem to deduce surface structure from STM signal

Distance dependence of tip - sample interaction

tip-sample distance z_0

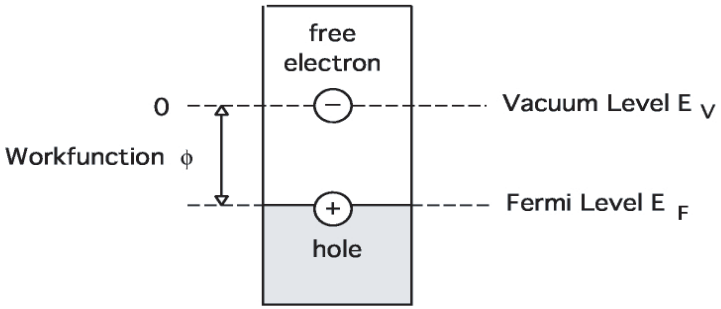
$z_0 > 100$ Å	*the mutual interaction is negligible,* *strong electric field* $\longrightarrow$ *field emission microscopy*
10 Å $< z_0 <$ 100 Å	*weak van der Waals long range interaction*
3 Å $< z_0 <$ 10 Å	*attractive bounding interaction,* *electrons are moving between electrodes* $\longrightarrow$ *STM*
$z_0 <$ 3 Å	*repulsive interaction is dominant,* *strong dependence on the distance,* *chemical bound bilding distance,* *tip and sample deformation* $\longrightarrow$ *contact mode of STM*

Electronic structure



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, Φ.

Work function

Φ *is a result of attraction between departing electron and positive image state (hole)*

Φ $<$ *2eV (alkali metals) to* $>$ *5 eV (transition metal)*

Workfunction varies between *(i) materials*
(ii) crystal faces

Polycrystal	Φ*(eV)*	*Single crystal*	Φ*(eV)*
Na	*2.4*	*W(111)*	*4.39*
Cu	*4.4*	*W(100)*	*4.56*
Ag	*4.3*	*W(110)*	*4.68*
Au	*4.3*	*W(112)*	*4.69*
Pt	*5.3*	*W(poly)*	*4.50*

Workfunction is sensitive to: *adsorbates*
external electric fields
reconstruction

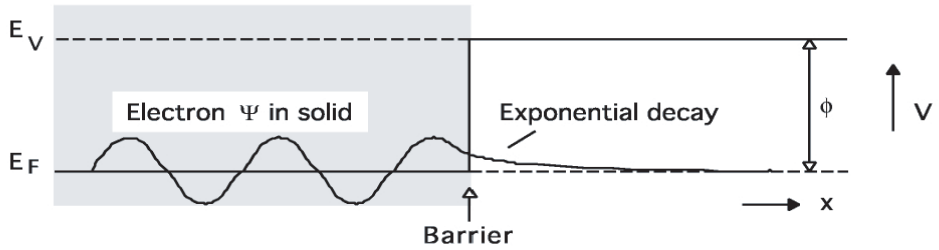
Workfunction presents a barrier to electron emission.

The tunneling effect

Solid with noninfinite walls

$$
\begin{aligned}
H\Psi &= E\Psi \\
-\left(\frac{\hbar^2}{2m}\right)\frac{d^2\Psi}{dx^2} &= E\Psi \qquad in \\
-\left(\frac{\hbar^2}{2m}\right)\frac{d^2\Psi}{dx^2} + V\Psi &= E\Psi \qquad out
\end{aligned}
$$

$$
\begin{aligned}
\Psi_{in} &= Ae^{ikx} + A'e^{-ikx}; \quad k = \frac{1}{h}\sqrt{2mE} \\
\Psi_{out} &= Be^{i\kappa x} + B'e^{-i\kappa x}; \quad \kappa = \frac{1}{h}\sqrt{2m(V-E)}
\end{aligned}
$$



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

Electron density decays exponentially away from surface

Inverse decay length $K = \frac{\sqrt{2m_e \cdot \Phi}}{\hbar} = 0.51\sqrt{\Phi}$ *for K in* Å^{-1} *and* Φ *in eV*

$K \approx$ *1-2* Å^{-1} *for a typical metal*

Two metals in contact

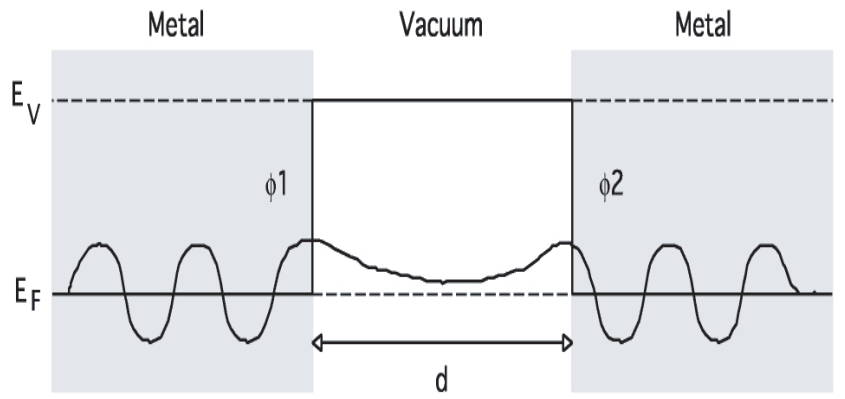
Apply potential V_{ext} to one metal to drive electrons one way:

With metal 1 negative with respect to metal 2 (as shown)

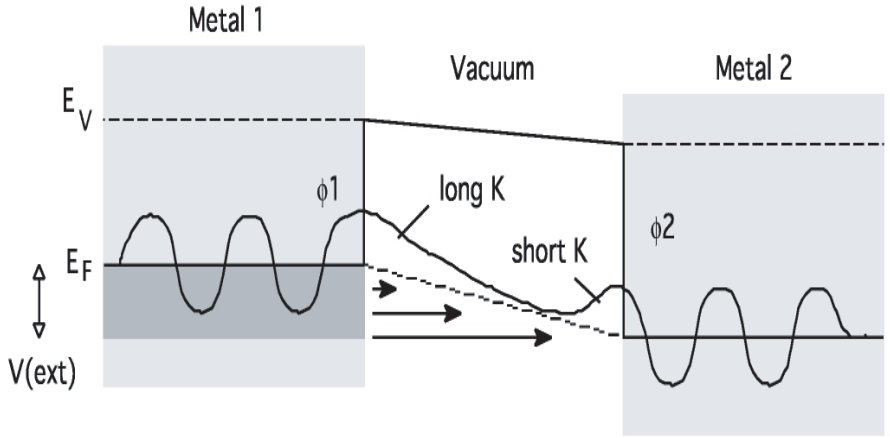
tunneling from filled states within V_{ext} of E_F in metal 1 into empty states at E_F in metal 2

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 (Φ)

(ii) thickness of barrier (d)

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

For a typical metal (K = 1 Å), current falls about an order of magnitude for an increase of 1.0 Å in d

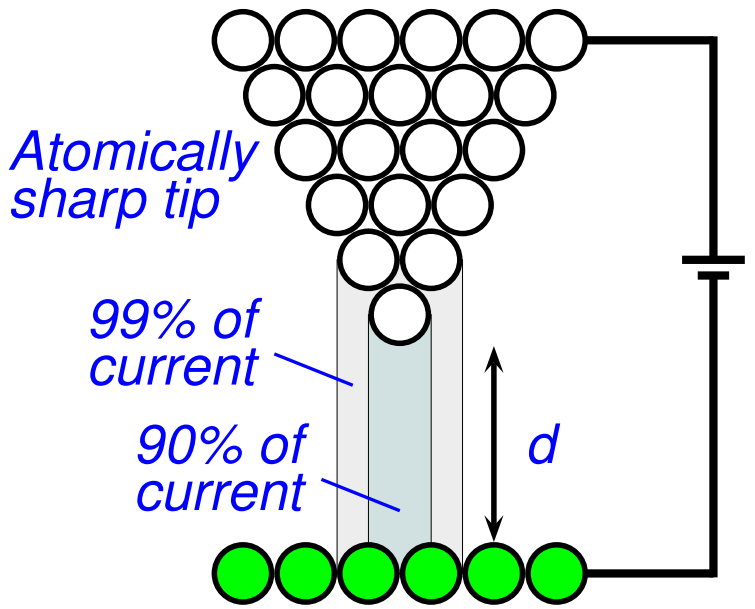
Consequence:

(1) very sensitive dependence of tunnel current on d

$\Longrightarrow$ *good vertical resolution*

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

$\Longrightarrow$ *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:

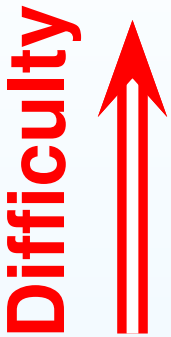
- ✔ *Landauer formula or Keldysh non-equilibrium Green's functions [1-4]*

Perturbative:

- ✔ *Transfer Hamiltonian methods [5]*
- ✔ *Methods based on the properties of the sample surface alone [6]*

[1] R. Landauer, Philos. Mag. 21 (1970) 863; M. Büttiker et. al., Phys. Rev. B 31 (1985) 6207.
[2] L. V. Keldysh, Zh. Eksp. Theor. Fiz. 47 (1964) 1515.
[3] C. Caroli et al., J. Phys. C 4 (1971) 916.
[4] T. E. Feuchtwang, Phys. Rev. B 10 (1974) 4121.
[5] J. Bardeen, Phys. Rev. Lett. 57 (1961) 6.
[6] J. Tersoff and D. R. Hamann, Phys. Rev. B 31 (1985) 805.

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*

[1] P. Jelinek et al., Phys. Rev. B **71** *(2005) 235101.*

[2] J. Cerda et al., Phys. Rev. B **56** *(1997) 15885; 15900.*

[3] H. Ness and A.J. Fisher, Phys. Rev. B **55** *(1997) 12469.*

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

Tersoff-Hamann approach

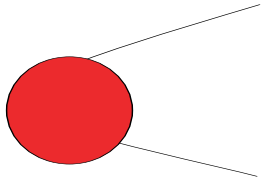
Assume, in addition to validity of perturbation theory in tip-sample interaction, that we have

- ✔ *spherical symmetric tip potential*
- ✔ *a s state on tip is the initial state for tunneling*
- ✔ *zero bias*

Asymptotic form for the wavefunctions thus

$$\psi = \sum_{G_{\text{parallel}}} a_G \exp(-\kappa_G z) \exp(i(\mathbf{k}+\mathbf{G}).\mathbf{r}_{\text{parallel}})$$

$$\chi = a \frac{\exp(-\kappa|r-r_0|)}{|r-r_0|}$$



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

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

The diferential conductance probes the density of states of the (isolated) sample, evaluated at the centre of the tip apex.

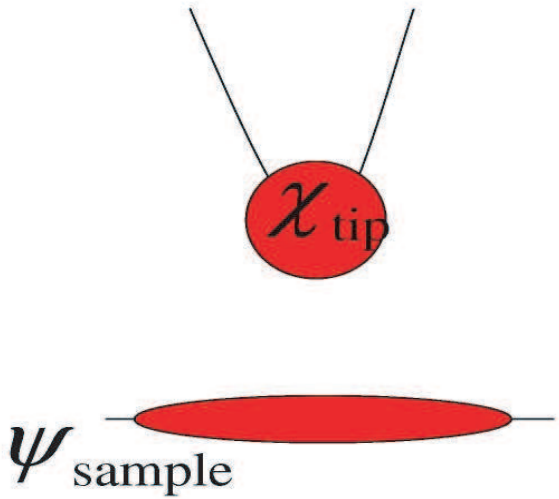
Implementing Tersoff-Hamann approach

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)*

Perturbation theory



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

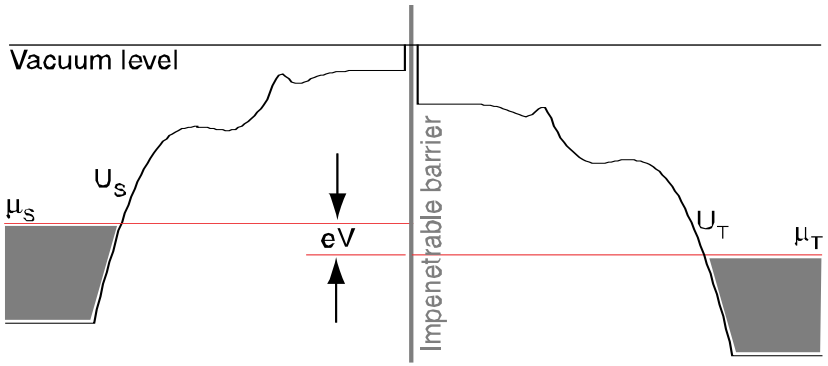
Problems:

- ✔ *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



Conditions:

$$U = U_S + U_T$$

$$U_S \cdot U_T = 0$$

(never non-zero at same point)

Result:

$$I = \frac{4\pi e}{\eta_0} \int^{eV} dE \rho_s(E_F - eV + E)\rho_T(E_F + E)|M|^2$$

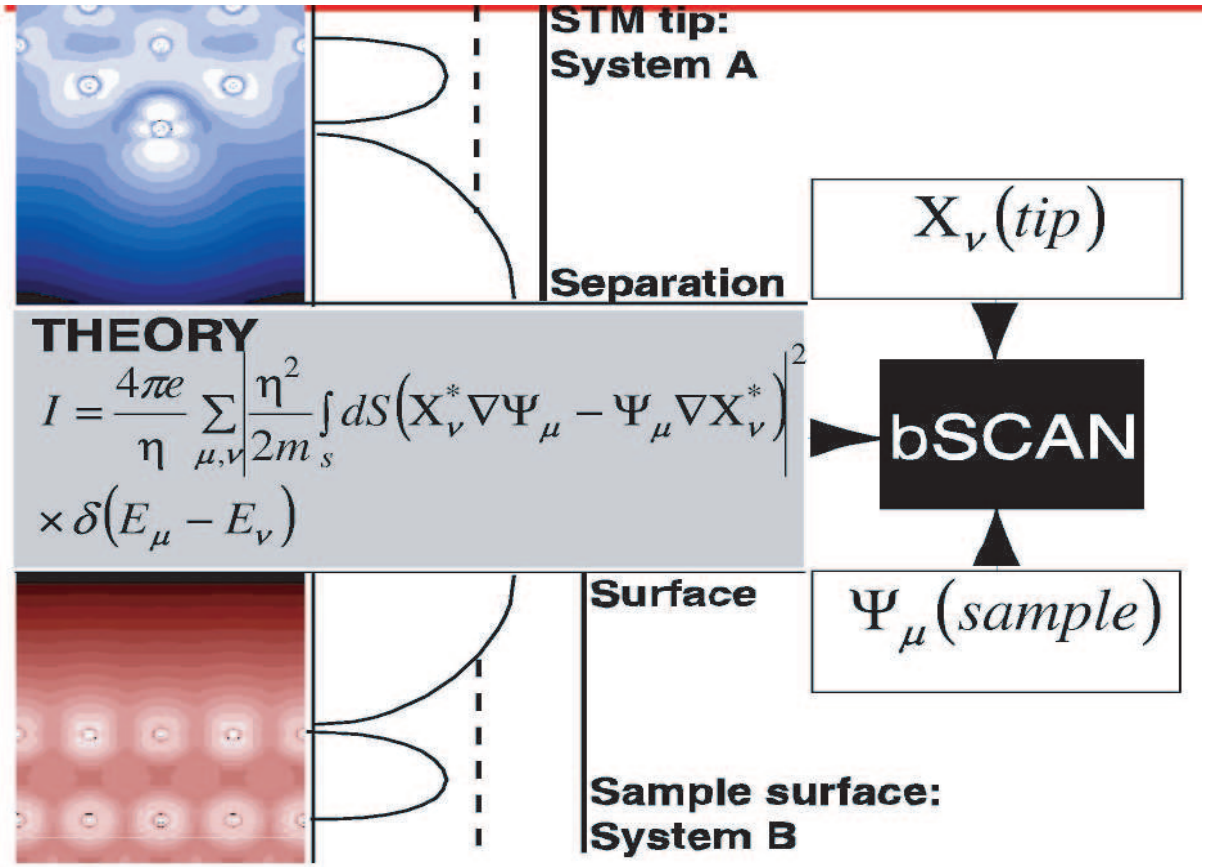
Golden rule with effective matrix element

(off-diagonal element of current density operator)

$$M = -\frac{\eta^2}{2m} \cdot \int_S dS \left(\chi_\nu^* \nabla \Psi_\mu - \Psi_\mu \nabla \chi_\nu^* \right)$$

[1] C.J. Chen, *Introduction to Scanning Tunneling Microscopy,* Oxford Univ. Press (1993)
[2] W.A. Hofer and J. Redinger, Surf. *Sci.* 447, 51 (2000)

Bardeen approach



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!

- 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 $|i>$ *and* $|f>$ *as the time-average in terms of the Green function*

Landauer formula

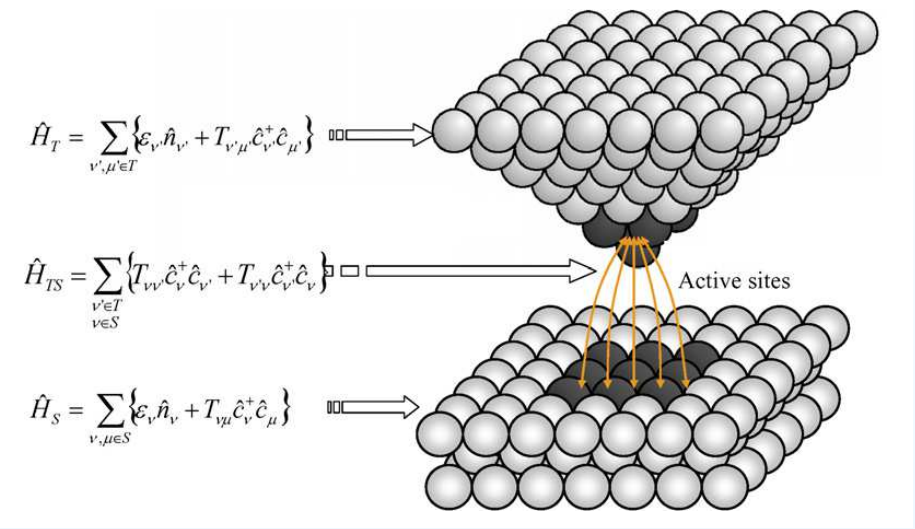
$$I = \frac{e}{h}\int d\epsilon [f_L(E) - f_R(E)] Tr[G^a \Gamma_R G^r \Gamma_L]$$

$f_L(E)$, $f_R(E)$ - *Occupation numbers*

Γ_L, Γ_R - *Embeding potentials*

G^a, G^r - *Advanced and Retarded Green Functions*

Local basis formalism



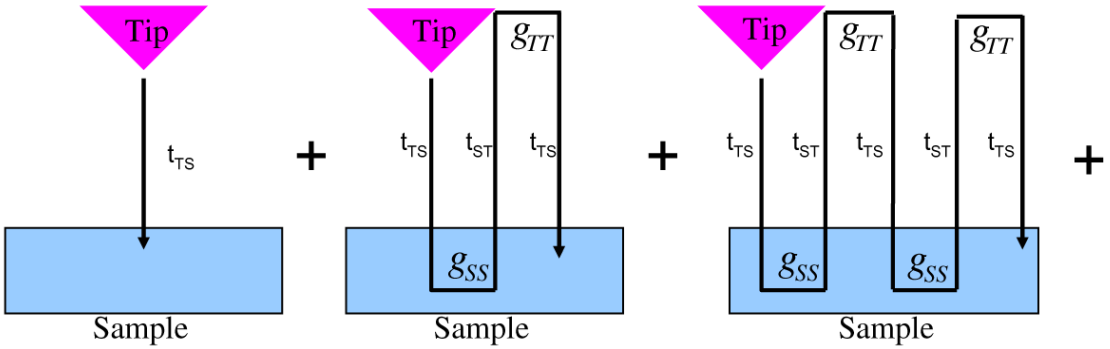
Local orbital basis $\phi_{i\alpha} = \phi_\mu$

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

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

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

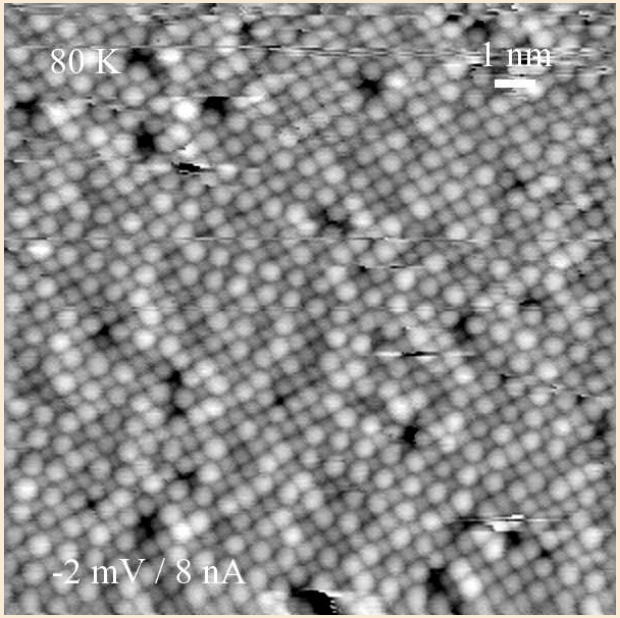
J.M. Blanco et al. / Progress in Surface Science 81 (2006) 403–443

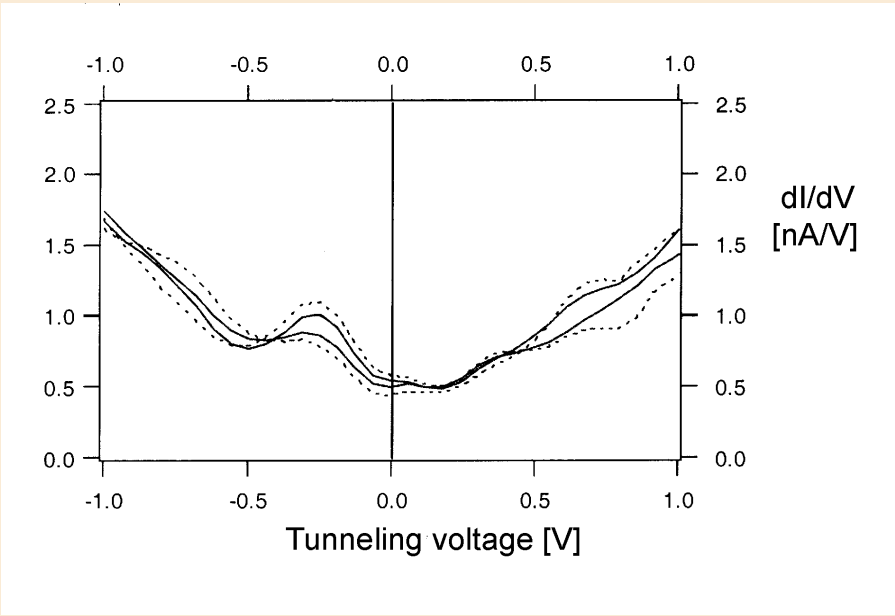


Contribution to the tunneling currents in different order of perturbation theory.

see also H. Lin at al., Front. Phys. China **5** *(2010) 369379.*

STM and STS on alloy $Ni_{0.36}Fe_{0.64}$

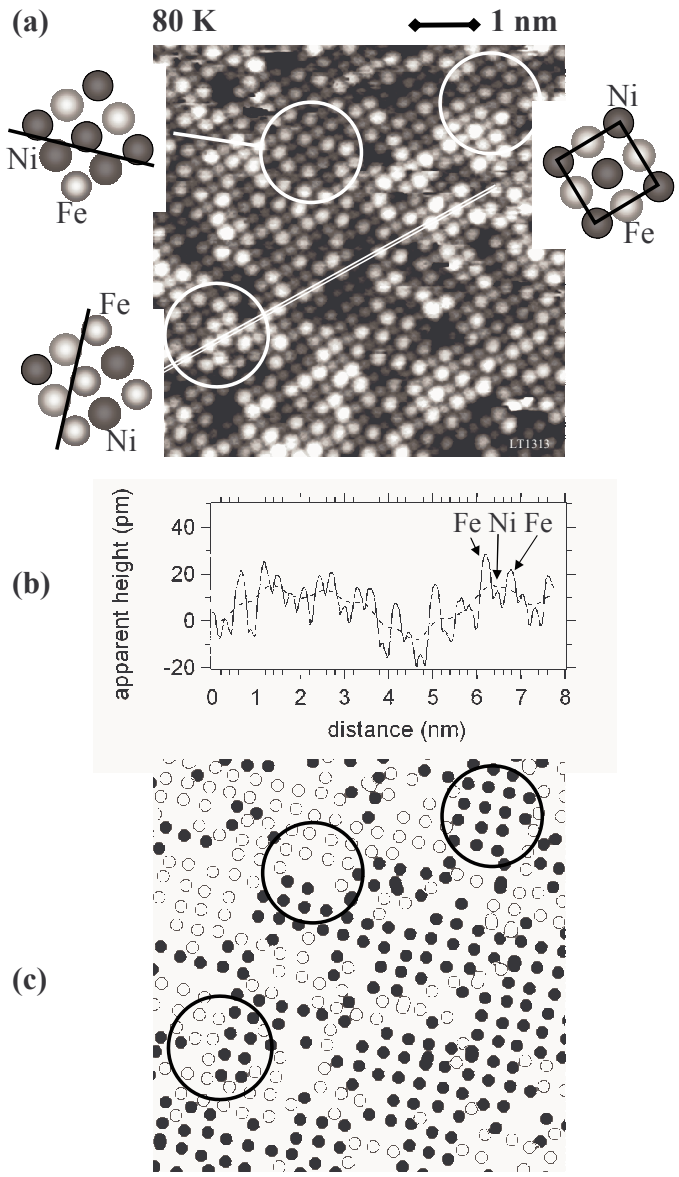




M. Ondráček, Phys. Rev. B **74** *(2006) 235437.*

- *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.*

STM image of the $Fe_{64}Ni_{36}(001)$ surface



(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.*

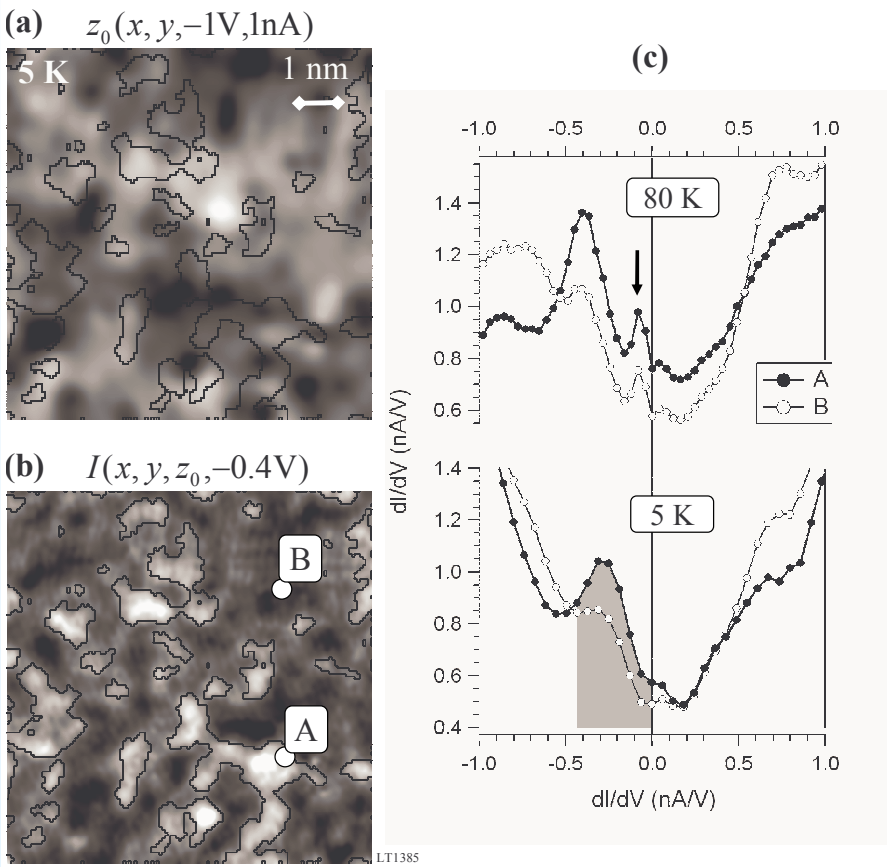
(b) *Profile of the STM image along the white line in (a). The dashed average curve indicates a long-wavelength buckling on the nanometer scale in contrast to the short-wavelength buckling distinguishing Fe and Ni atoms.*

(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 (2×2) 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.*
- ✔ *The buckling height in the top surface layer d_1 = 0.08 - 0.12 Å depends on the type of atoms in subsurface layers.*
- ✔ *We obtained an enhancement of magnetic moments for surface atoms in comparison with bulk values.*
- ✔ *The STM image of (001) invar surface reflects essentially the surface topography. The brighter spots (higher tunneling current) can be associated with Fe atoms, the darker with Ni atoms.*
- ✔ *The observed brighter and darker areas of different image contrast are related to regions of different local chemical composition in the subsurface.*

STS image of the $Fe_{64}Ni_{36}(001)$ surface



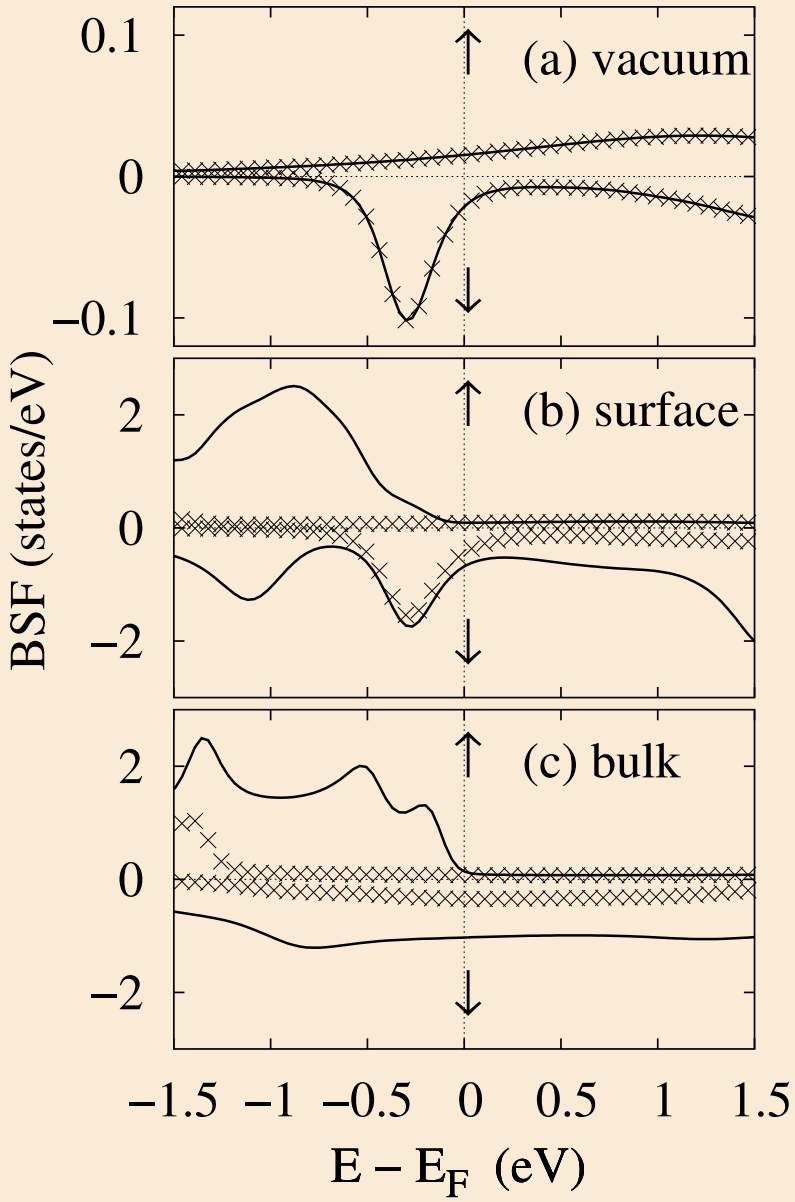
(a) *Constant current image at 5 K, 1 nA tunneling current, and -1 V sample voltage.*

(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 $Fe_{64}Ni_{36}$(001)



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

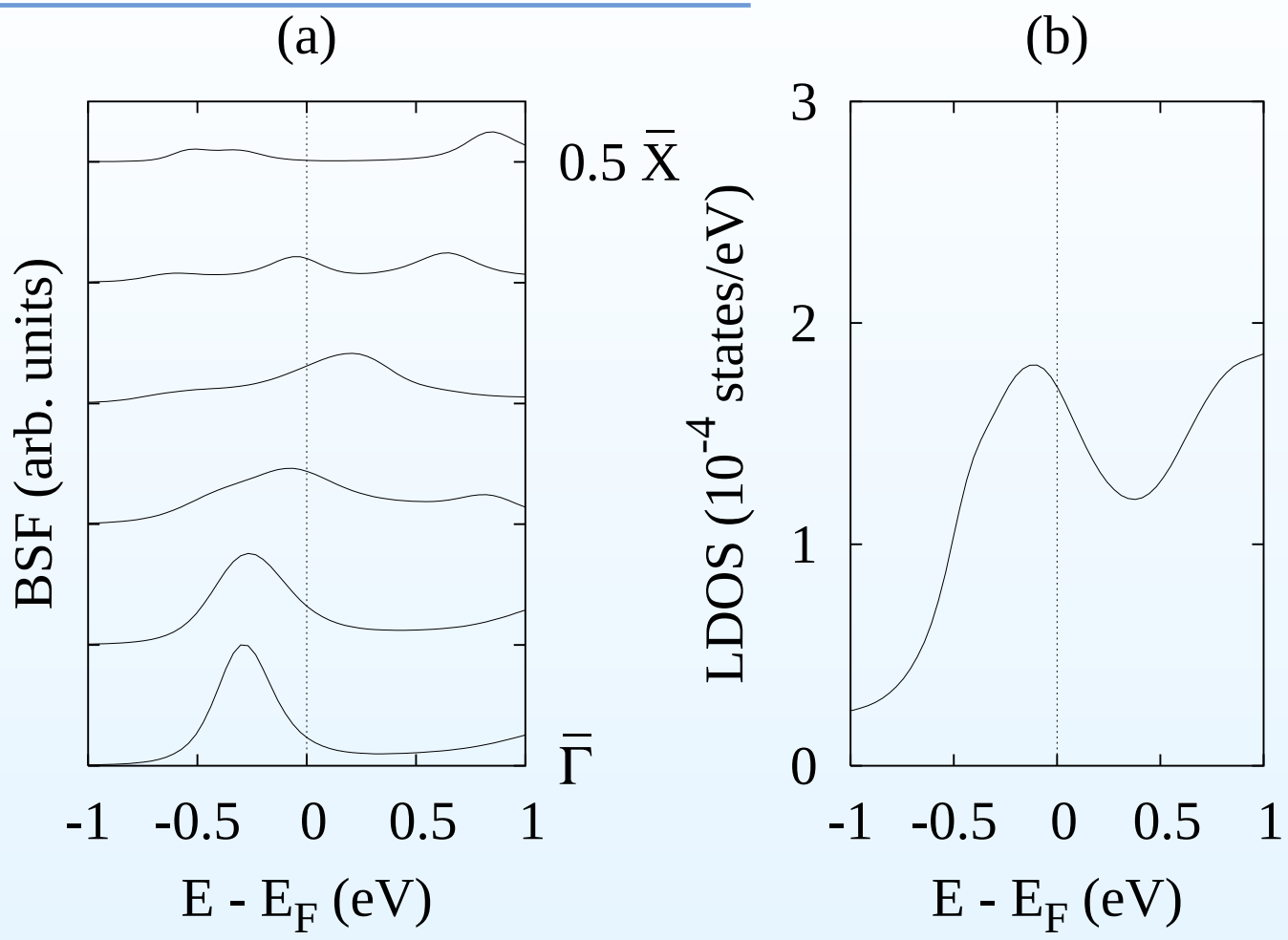
(a) *in vacuum 3.6 Å above the surface,*

(b) *in the top surface layer,*

(c) *in a layer deep in the bulk.*

Crosses denote the A_1-symmetry component of the BSF.

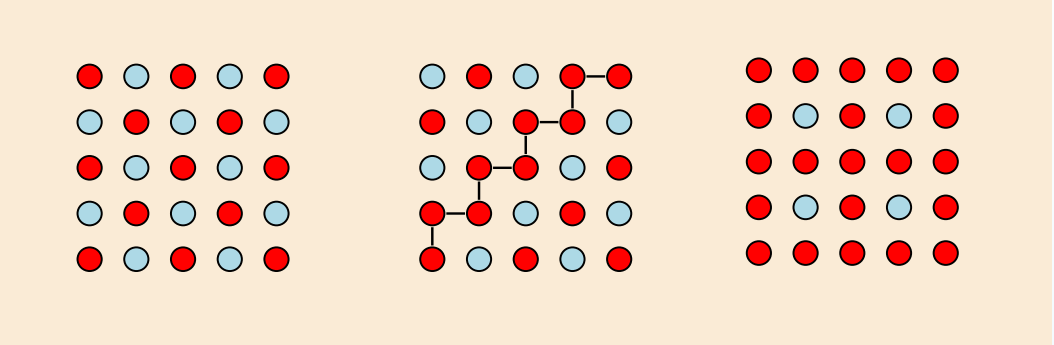
Dispersion of the surface resonance



(a) *Minority-spin BSF in vacuum 5.4 Å above the* $\mathbf{Fe}/\mathbf{Fe_{0.64}Ni_{0.36}}$ *surface plotted for different* $\mathbf{k}_{||}$*-vectors along the path from* $\mathbf{k}_{||} = \bar{\mathbf{\Gamma}}$ *(bottom) to* $\mathbf{k}_{||} = \mathbf{0.5}\,\bar{\mathbf{X}}$ *(top).*

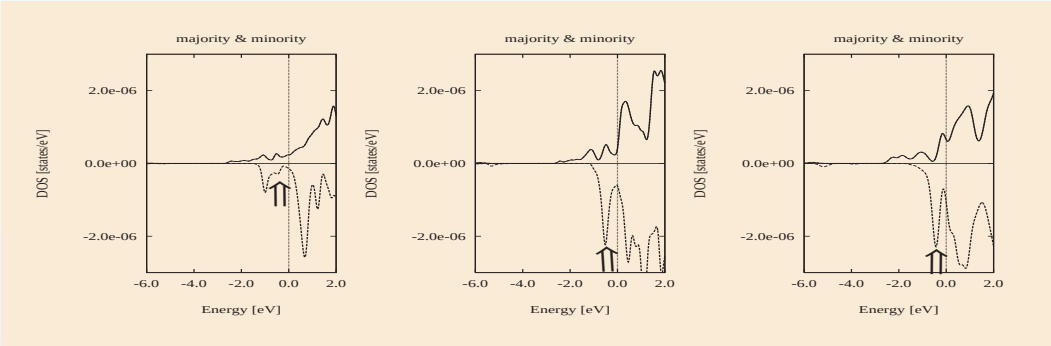
(b) *Local density of states in vacuum 5.4 Å above the* $\mathbf{Fe}/\mathbf{Fe_{0.64}Ni_{0.36}}$ *surface.*

Surface resonance and Iron coverage I



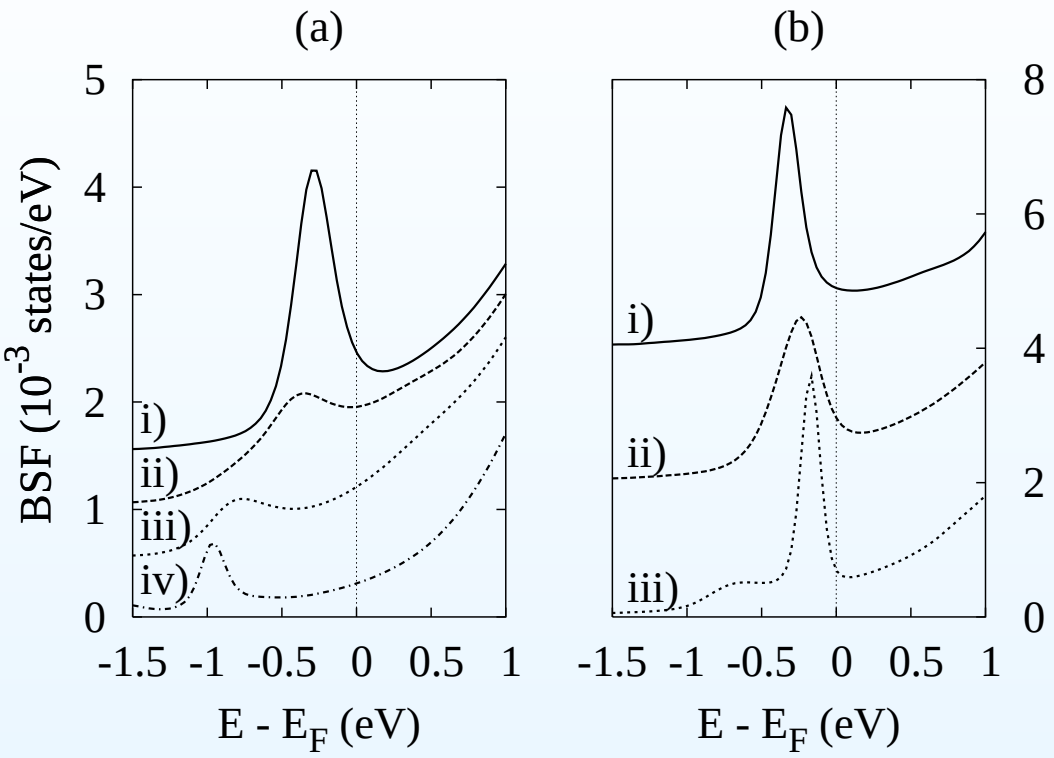
Models of the top surface layer with 50%, 33% and 25% of Ni used in our simulations.

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) $\mathbf{Fe}$, *ii)* $\mathbf{Fe_{0.75}Ni_{0.25}}$, *iii)* $\mathbf{Fe_{0.50}Ni_{0.50}}$, *and iv)* $\mathbf{Ni}$.

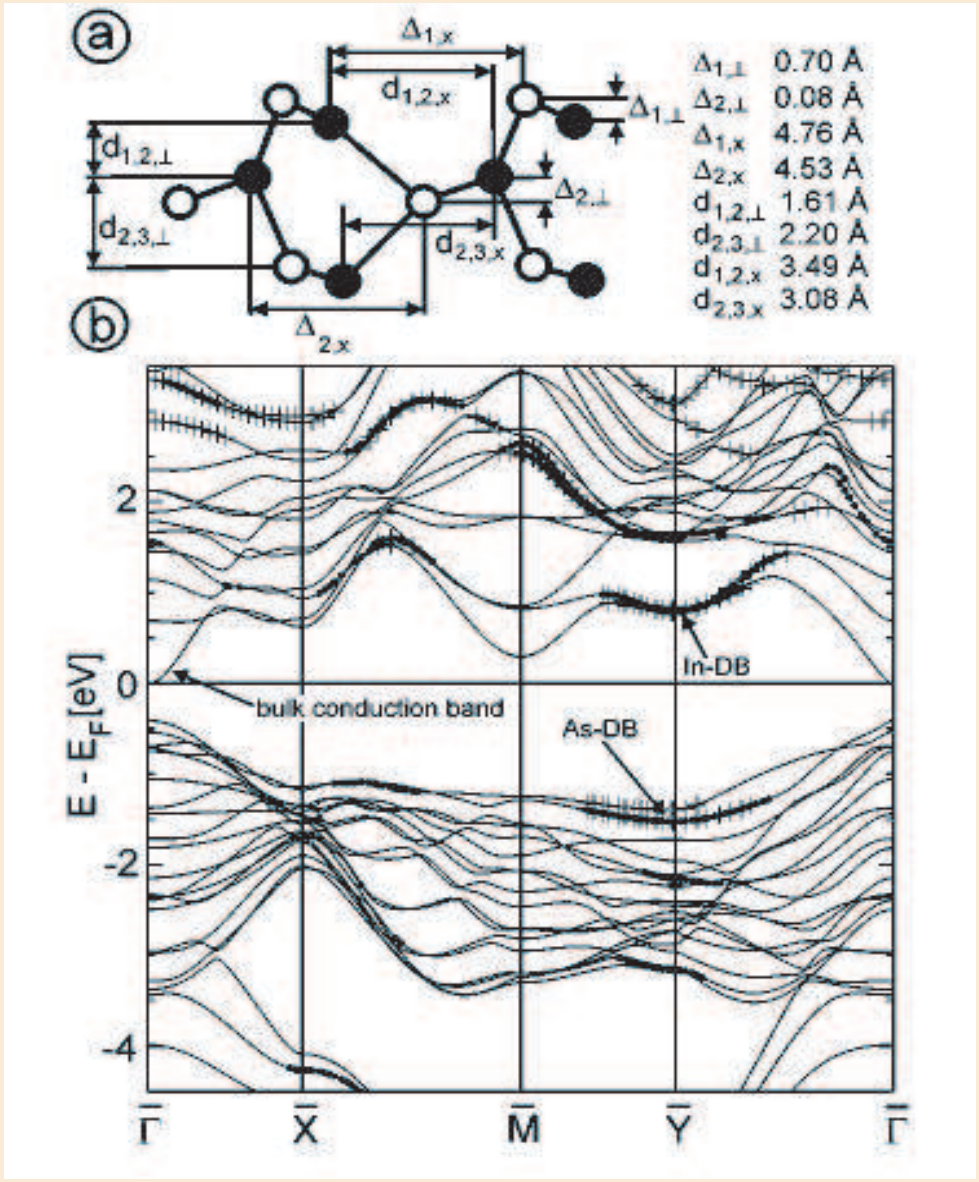
(b) *The subsurface layer composition is changed: i)* $\mathbf{Fe/Fe/Fe_{0.64}Ni_{0.36}}$,

ii) $\mathbf{Fe/Fe_{0.50}Ni_{0.50}/Fe_{0.64}Ni_{0.36}}$, *and iii)* $\mathbf{Fe/Ni/Fe_{0.64}Ni_{0.36}}$.

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 Γ 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.*

InAs(110) - STM and surface electronic structure



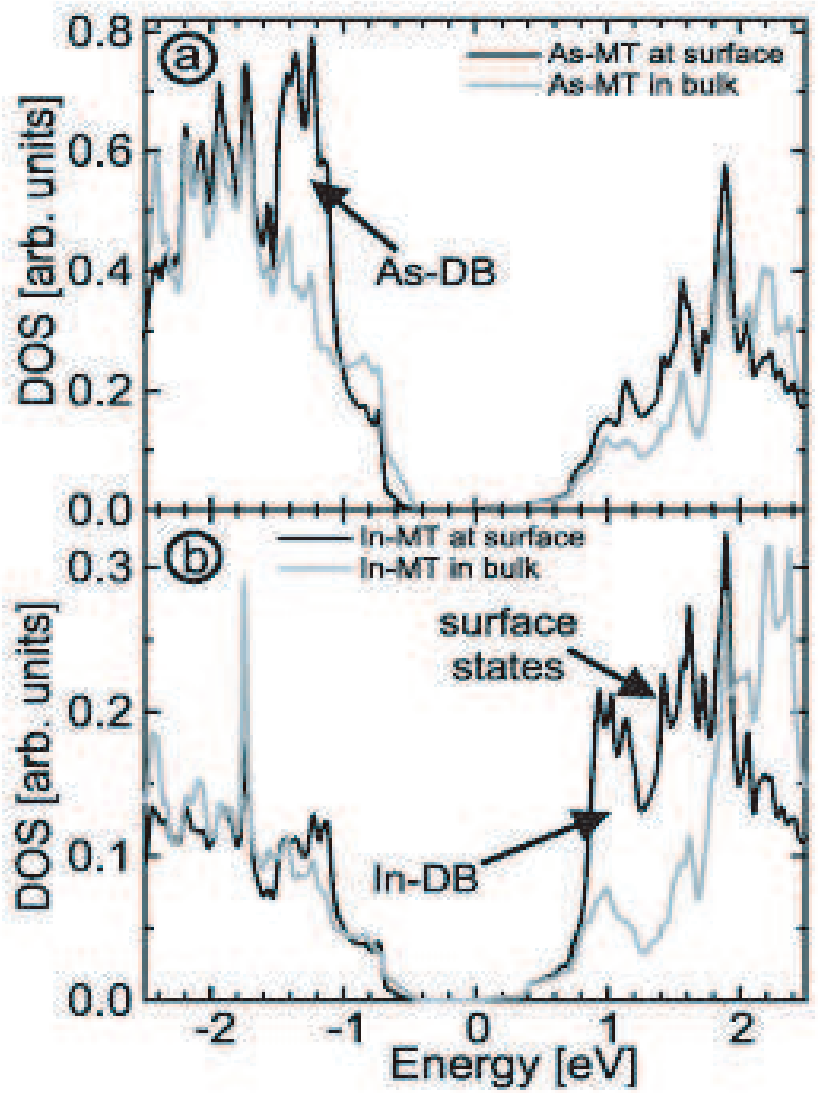
(a) Relaxation of the InAs(110) surface with indicated atomic distances (black dots, In; white dots, As). The calculated values of the relaxed distances are listed on the right.

(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 Γ are marked.

[1] J. Klijn at al. PRB **68** *(2003) 205327.*

InAs(110) - LDOS



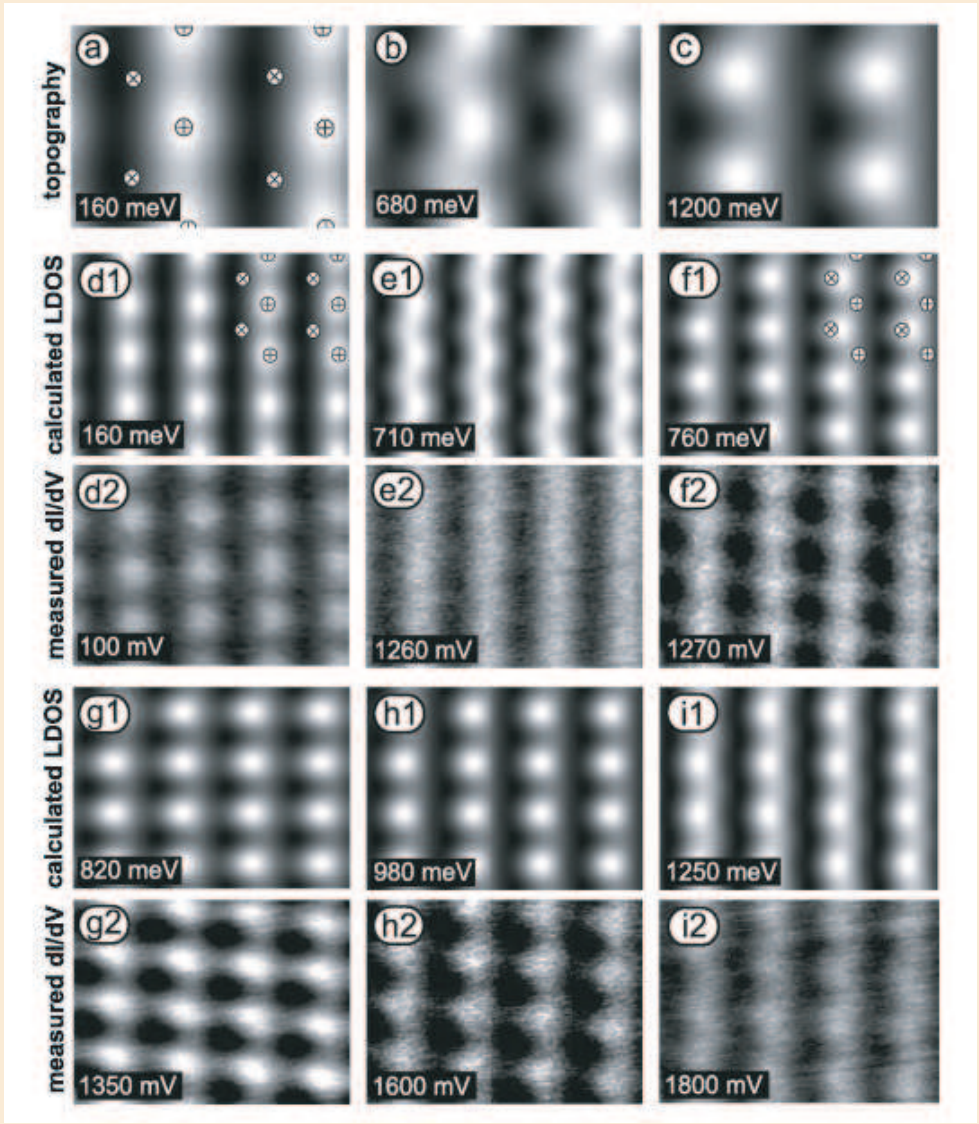
Local density of states spatially integrated over MT regions. Black lines correspond to MT's directly at the surface and gray lines to atoms in the middle of the slab.

(a) As-MT's,

(b) In-MT's.

[1] J. Klijn at al. PRB **68** *(2003) 205327.*

InAs(110) - STM



· *cca 500 meV shift due to the tip-induced band bending*

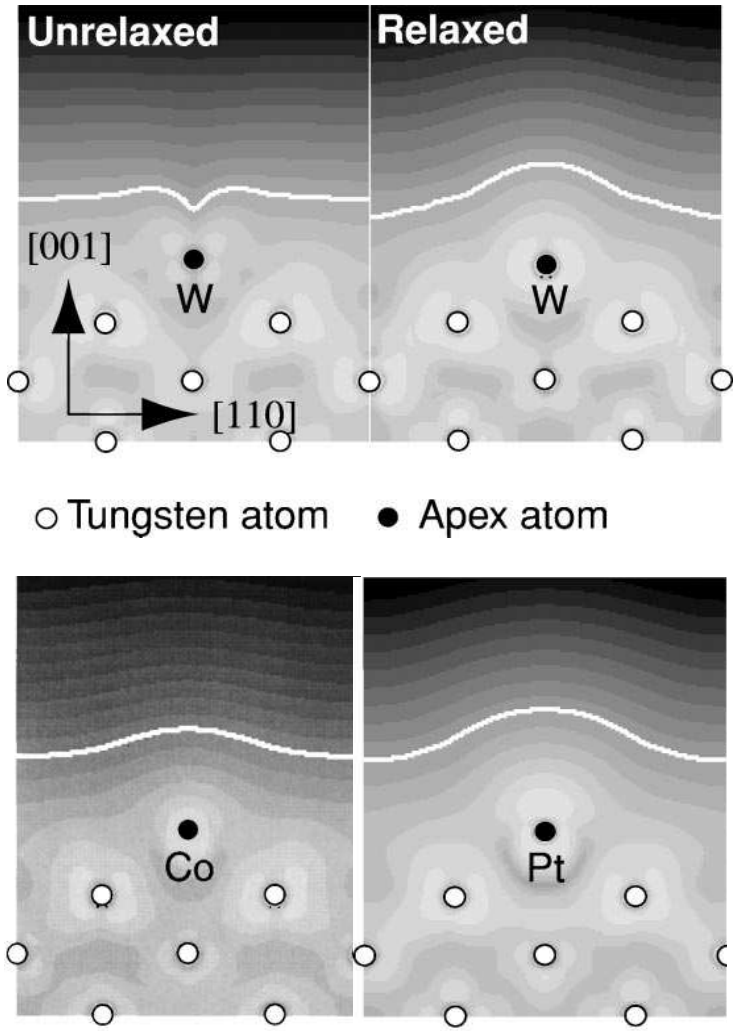
(a)-(c) Calculated topography images 5 Å above the surface taken at energies as indicated, with E_F *at the CBM.*

(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.*

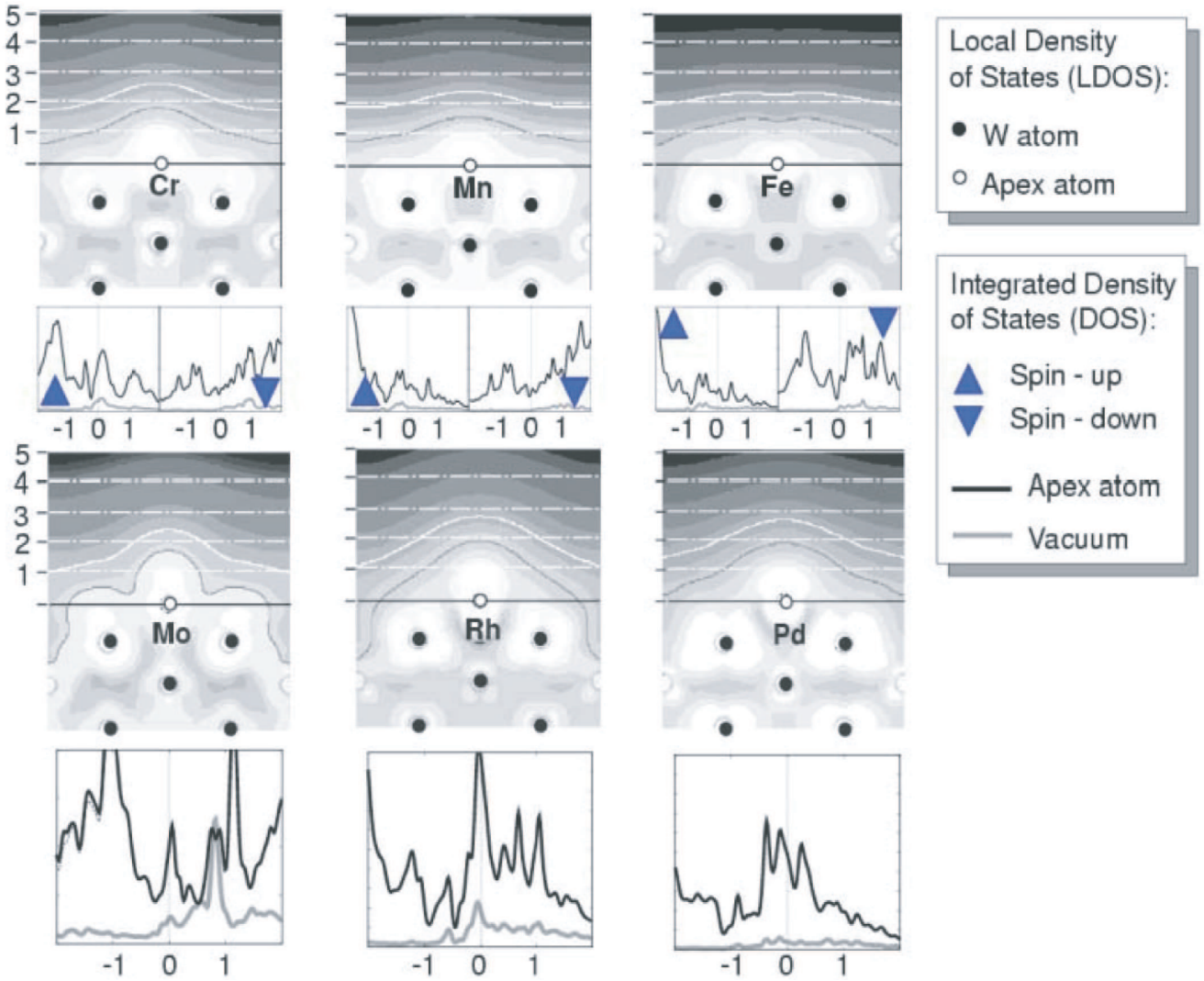
[1] J. Klijn at al. PRB **68** *(2003) 205327.*

Tip



W.A. Hofer, J. Redinger, Surf. Sci. 447 (2000) 51.

Tip

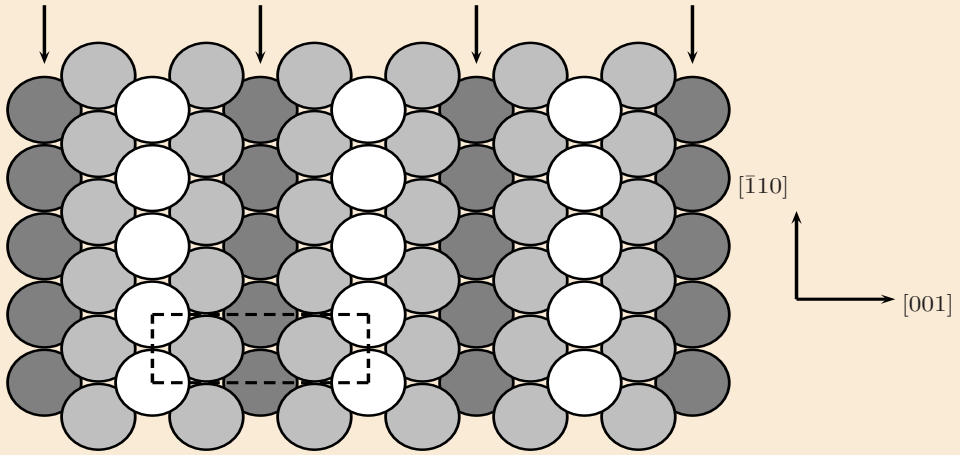


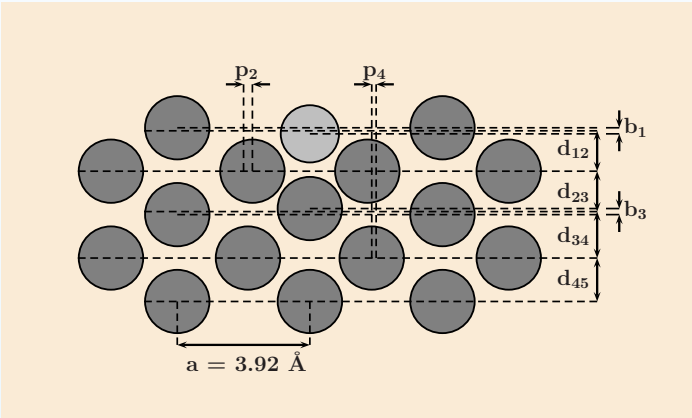
LDOS and integrated DOS of selected magnetic and nonmagnetic STM tip models.

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

Hofer, Redinger and Podloucky, PRB 64 (2001) 125108.

Deposition of Co on the Pt(110) surface - low coverage



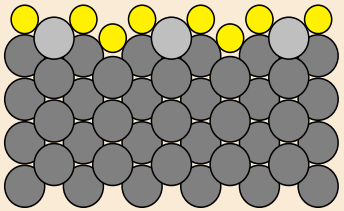


Deposited Co fills the missing rows of $p(1 \times 2)$ *Pt(110).*

1.5 ML of Co on the Pt(110) surface

System I

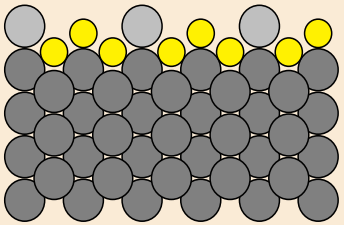
Co



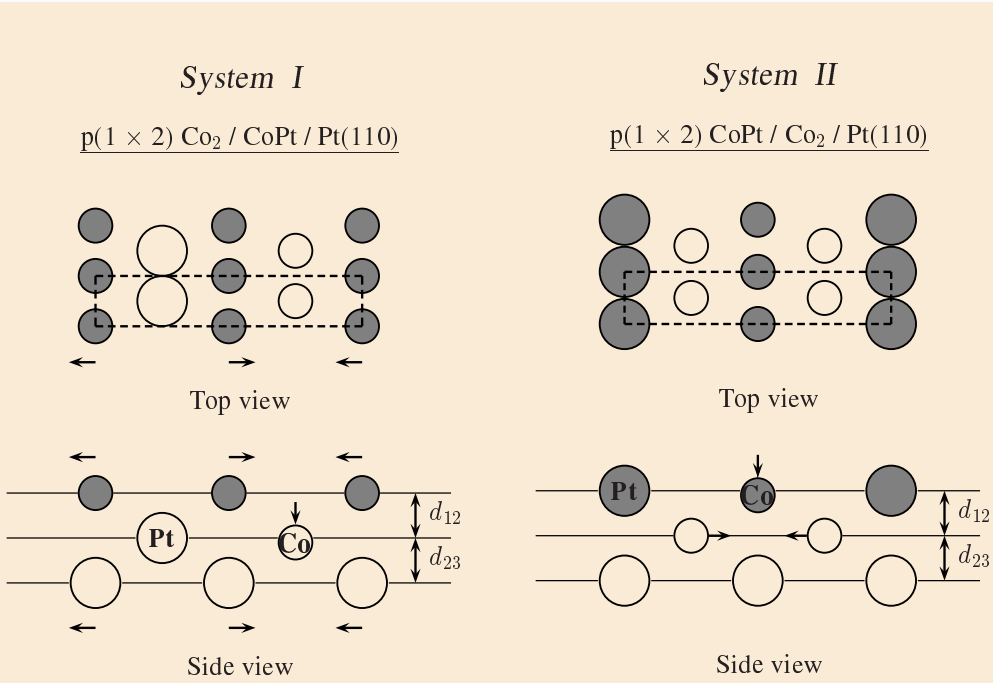
$p(1 \times 2)\mathbf{Co_2/CoPt/Pt(110)}$

System II

Pt



$p(1 \times 2)\mathbf{CoPt/Co_2/Pt(110)}$



Two models of geometry for the coverage 1.5 ML of Co on $p(1 \times 2)$Pt(110).

0.5ML and 1.5ML Co on Pt(110)

Experiment: M. Schmid, P. Varga, TU-Wien

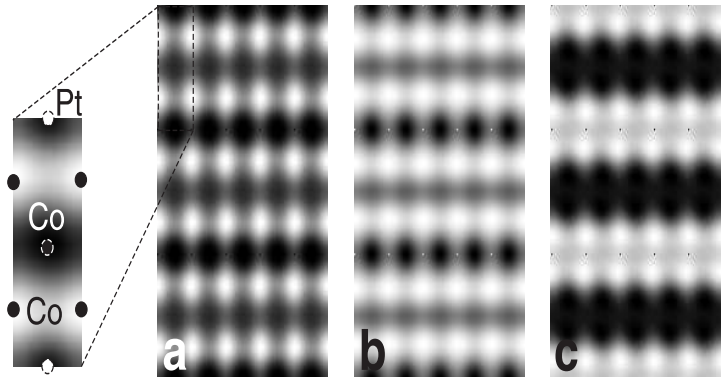


Fig. 2. Calculated contrast STM images for system with Co ML on top. Constant current images for very small bias voltage $U = -10$ mV and tunnel current $I = 1$ nA are shown for three different tips: (a) W, (b) Pt, (c) Co. Full contrast means that the full grey-scale range was used for the bitmap image.

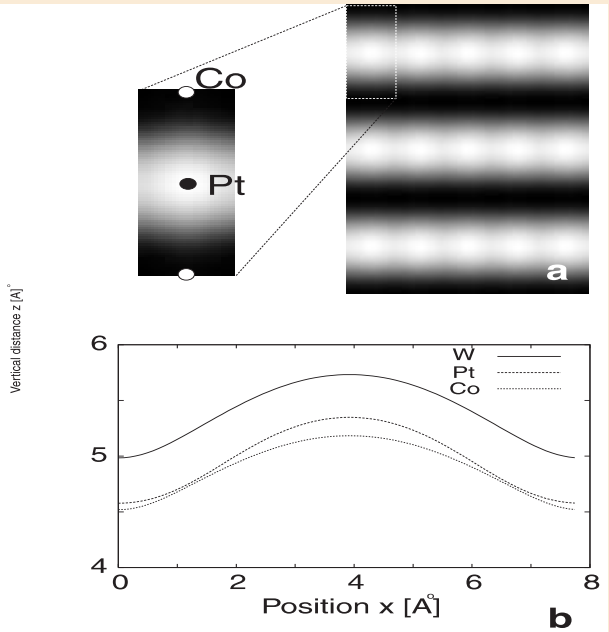
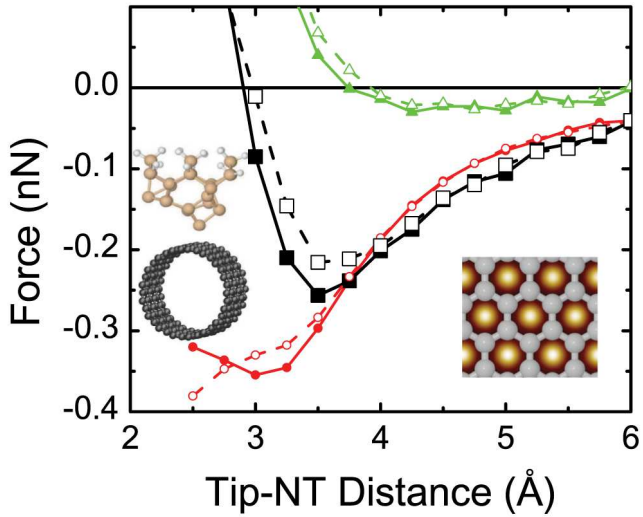
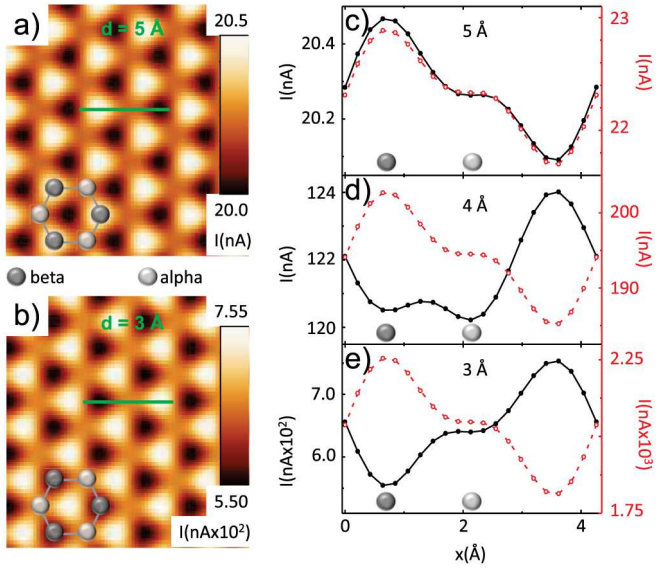


Fig. 3. (a) Simulated contrast STM image for system with CoPt ML on top (Pt terminated tip, $U = -10$ mV, $I = 0.1$ nA). (b) Corrugation amplitudes along the line in the direction [0 0 1] perpendicular to a Pt row and above the Pt ($x = 3.92$) and Co atoms ($x = 0, 7.84$) for different terminated tips.

STM image simulations in Bardeen model: *F. Máca at al., Surf. Sci.* **482-485** *(2001) 844.*

Tip - sample interaction on carbon structures



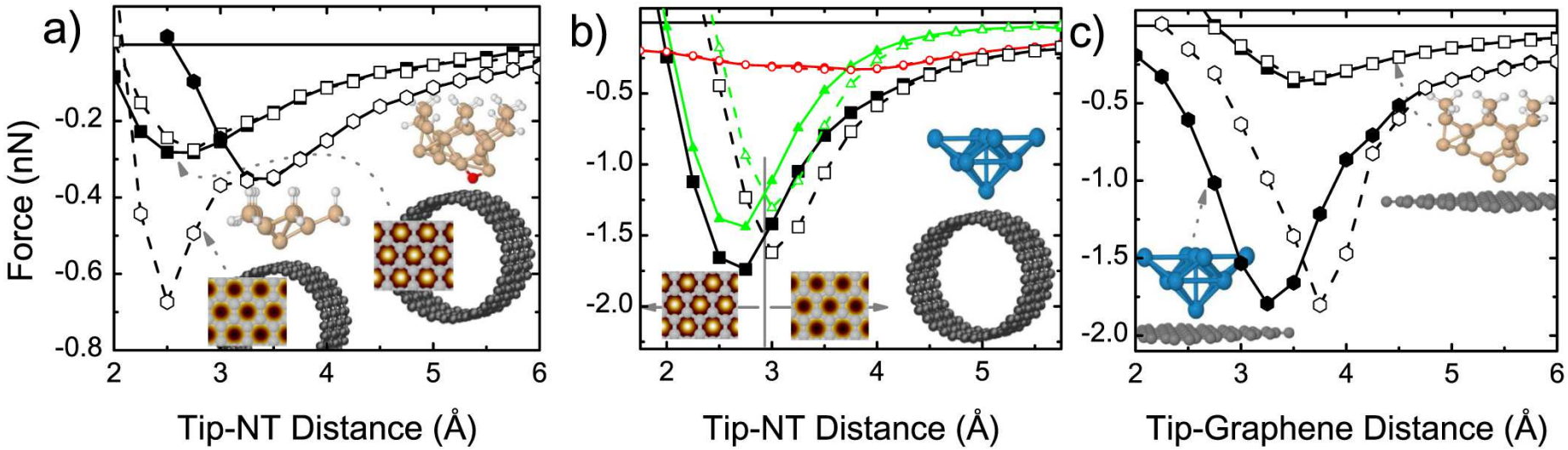


Total force (black) between the Si-tip and the carbon nanotube. Open/solid symbols correspond to the top/hollow site. The vdW part and the short-range part of the interaction are shown. Force maxima on the hollow site.

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

Constant-height STM images on (0001) grafite 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.

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.

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.*