Theoretical Modelling and the Scanning Tunnelling Microscope

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Curso “Introducción a la Nanotecnología”

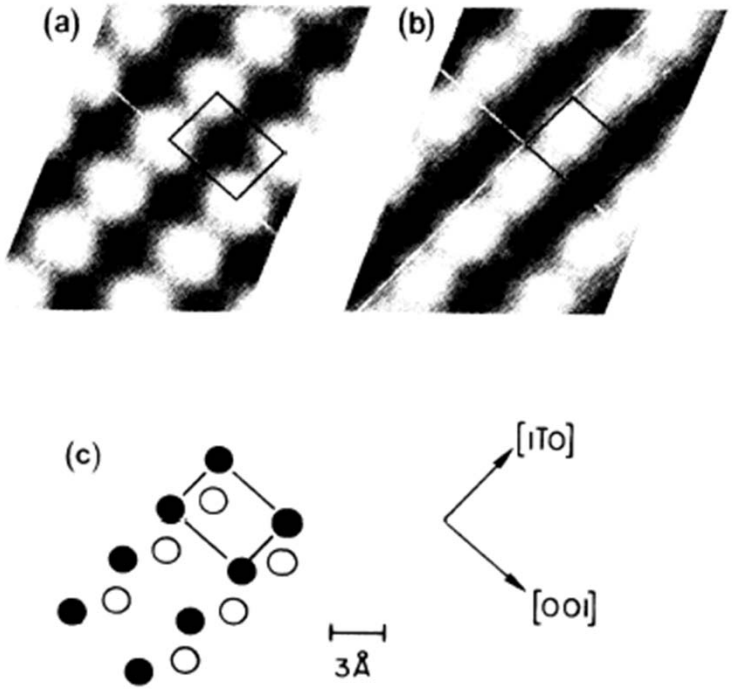
Máster de física de la materia condensada y nanotecnología

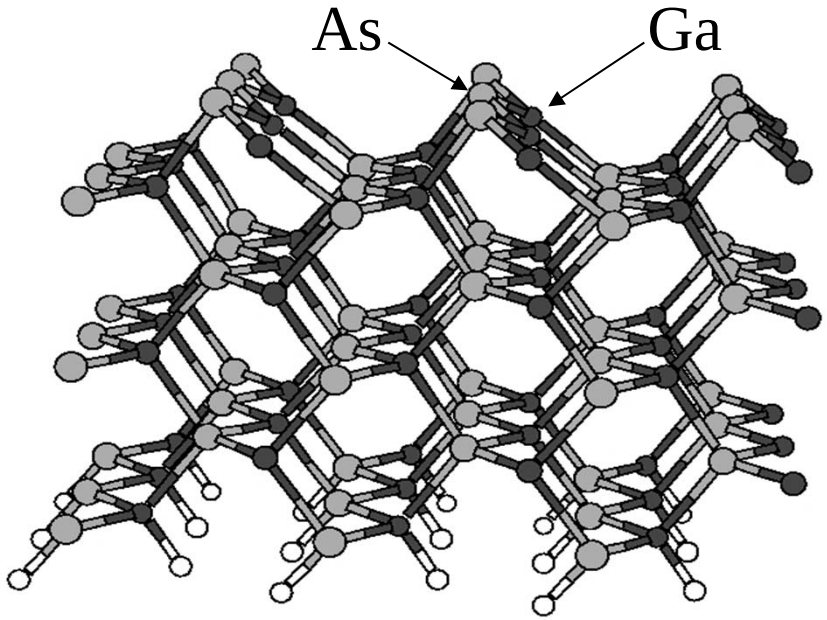
Theoretical modelling of SPM

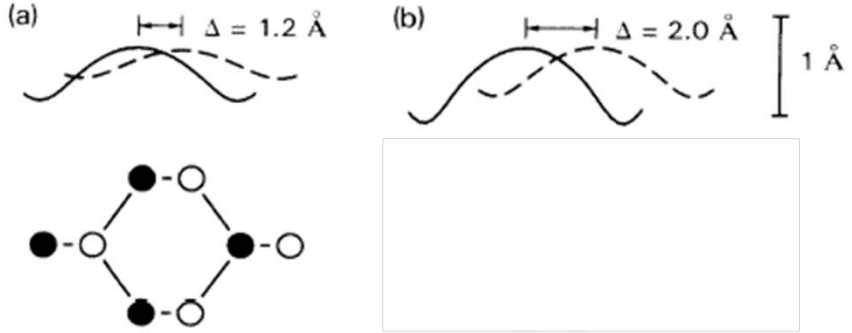
1. STM: contrast mechanisms (lecture, 20/01/13)
2. AFM: Resolution? (lecture, 30/01/13)
3. New developments (discussion based on 4 recent papers, 03/02/13)
4. STM simulations (hands-on, 06/02/13)
5. AFM simulations (hands-on, 10/02/13)

Understanding the STM contrast : GaAs (110)

STM Experiments at different polarities





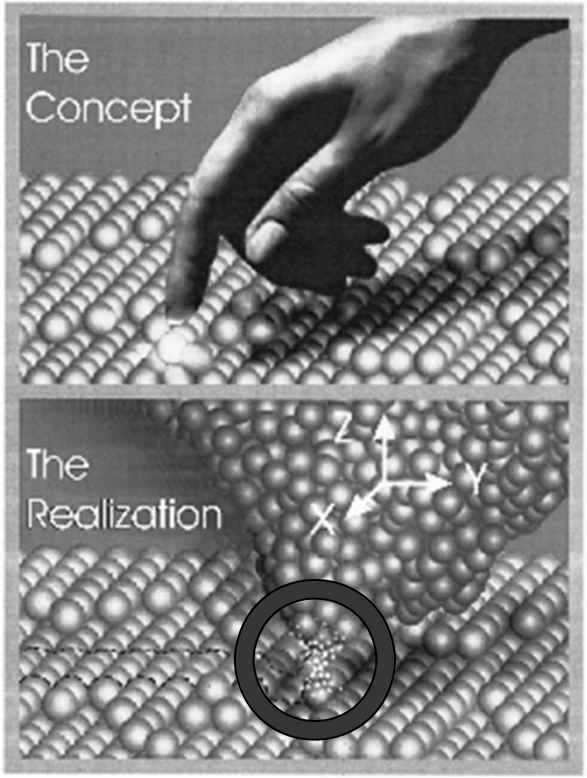


- Only one atomic specie imaged for each voltage?
- Shift between the position of the maxima?

References

- JM. Blanco, F. Flores and R. Perez. Progress in Surface Science 81, 403-443 (2006).
- W. A. Hofer. Progress in Surface Science 71, 147-183 (2003).
- C. J. Chen. “Introduction to Scanning Tunneling Microscopy”. 2nd Edition. (Oxford University Press, Oxford, 2008).
- R. Wiesendanger. “Scanning Probe Microscopy & Spectroscopy”. (Cambridge University Press, Cambridge, 1994).
- D. Bonell, Editor. “Scanning Probe Microscopy & Spectroscopy”. 2nd Edition. (Wiley-VCH, New York, 2001).

Principle of operation



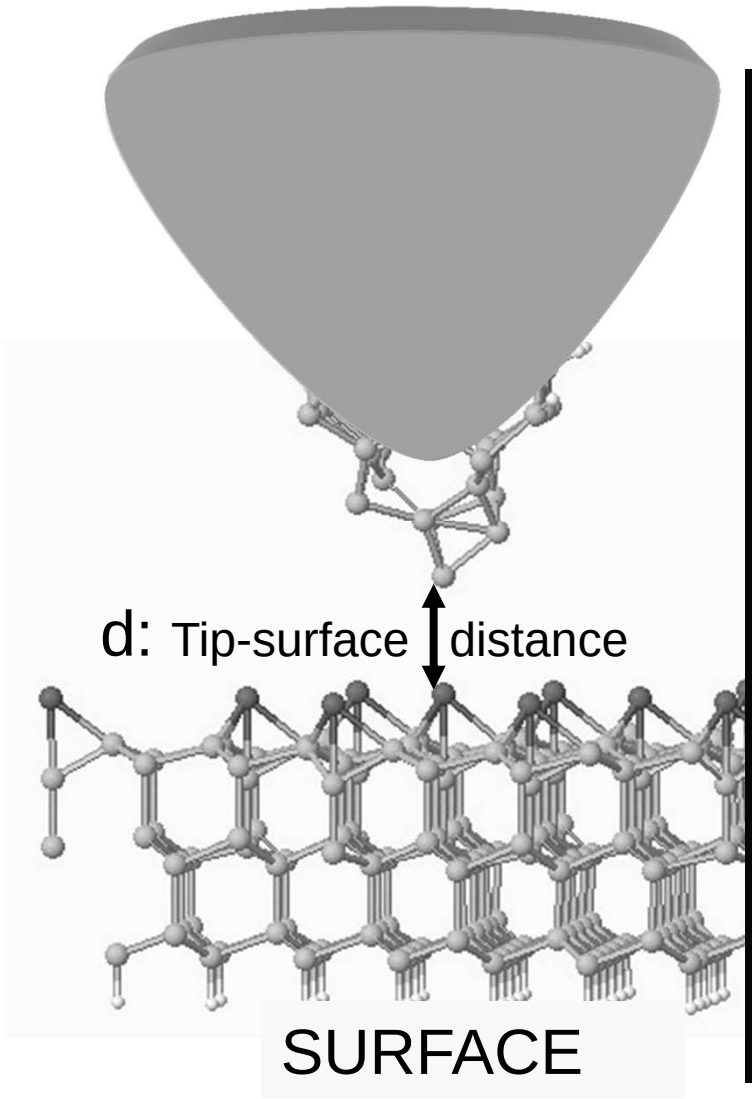
- Atomic protrusions on the tip are usually random, and with luck one atom may protrude sufficiently to dominate the tunneling geometry.
- Atomic resolution: Tunnelling probability changes an order of magnitude for every angstrom change.
- Contrast: combined effects of topography and electronic structure.

$$I(z) \propto e^{-k\sqrt{2\phi}z}$$

"It soon become apparent that it was one thing to obtain an image and quite another to understand the structure that was seen"

G.A.D. Briggs and A.J. Fisher, Surf. Sci. Rep. 33 (1999) 1-81

The problem we are facing…



STM implies describing tip, sample + tunnelling process.

Applying V ⇒ system out of equilibrium ⇒Most theoretical tools for systems in equilibrium,so...

Tip-surface distance ~ 5-10 Å ⇒ exchange-correlation and image potential effects are important (are well described by DFT??)

Conventional approaches: Sample description is usually good, while transport and tip are treated with very rough approximations... (perturbative, s-wave for the tip, no image effects) ⇒ qualitative description, but can we make it quantitative...?

Non-perturbative approaches for tunneling + first-principles description of the electronic properties of tip and sample

OUTLINE

1) Different STM approaches:

- Perturbative method: Bardeen, Tersoff-Haman, Chen
  - Bardeen: Transfer Hamiltonian + Bardeen tunnelling current
  - Tersoff – Haman approximation (T-H)
  - Chen's improvement to T-H
- Non-perturbative approaches to transport:
  - Scattering matrix
  - Landauer formalism

  (only elastic contributions)
  - Keldysh-Green function formalism

2) Combining STM and theoretical modelling: Examples

3) Recent developments & Challenges: (tip-sample interaction, electric field, spin-polarized STM)

Perturbative Methods: Bardeen , Tersoff-Haman and Chen's approach

Transfer Hamiltonian + TUNNELLING CURRENT

(J. Bardeen, PRL 6 (1961) 57)

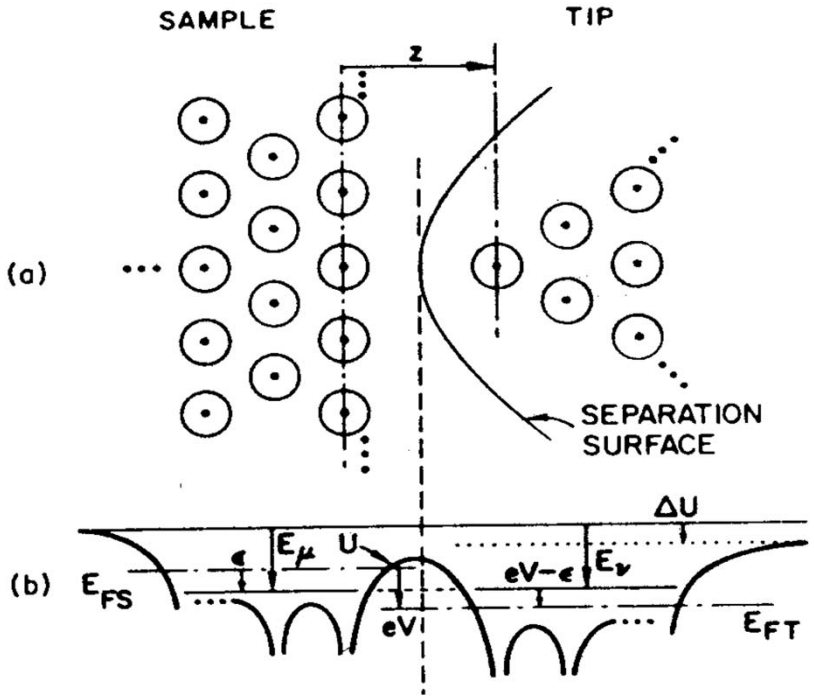
Coupled system:

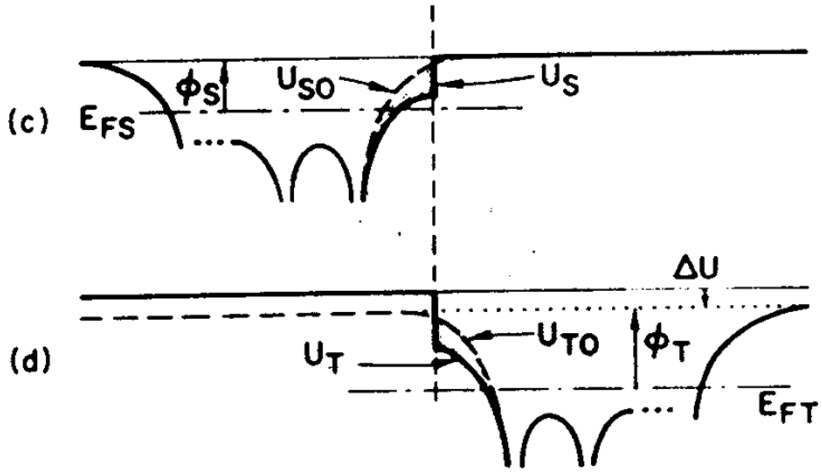
$$\hat{H} = -1/2\nabla^2 + U_T + U_S$$

Uncoupled system

$$-1/2\nabla^2 \varphi_k + U_S \varphi_k = \varepsilon_k \varphi_k$$

$$-1/2\nabla^2 \varphi_{k'} + U_T \varphi_{k'} = \varepsilon_{k'} \varphi_{k'}$$





Transfer Hamiltonian + TUNNELLING CURRENT

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Uncoupled system

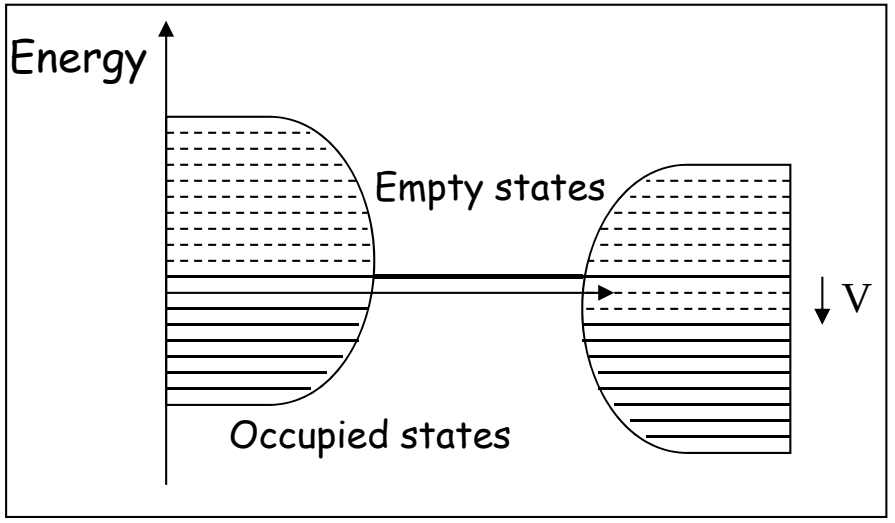
$$-1/2\nabla^2 \varphi_k + U_S \varphi_k = \varepsilon_k \varphi_k$$

$$-1/2\nabla^2 \varphi_{k'} + U_T \varphi_{k'} = \varepsilon_{k'} \varphi_{k'}$$

Current (1st order perturbation theory)

$$I_{(k \to k')} = 2\pi e/\hbar \sum_{k,occ.}^{k',empt.} \left| T_{kk'} \right|^2 \delta(\varepsilon_k - \varepsilon_{k'})$$

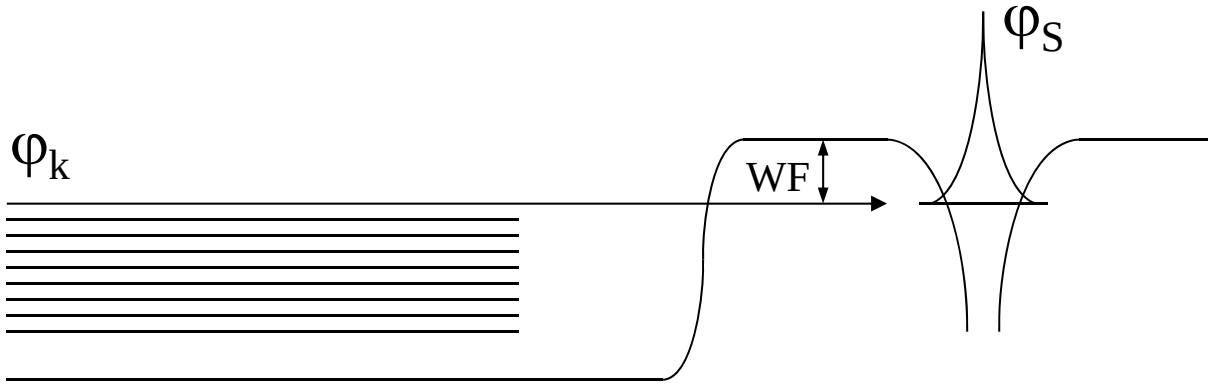
($T_{kk'}$≡tunnelling matrix element between φ_k and $\varphi_{k'}$)



Bardeen showed that under certain assumptions, $T_{kk'} = \hbar/2m \int_S d\vec{S} (\varphi_{k'} \vec{\nabla} \varphi_k - \varphi_k \vec{\nabla} \varphi_{k'})$

TERSOFF-HAMAN APPROXIMATION:

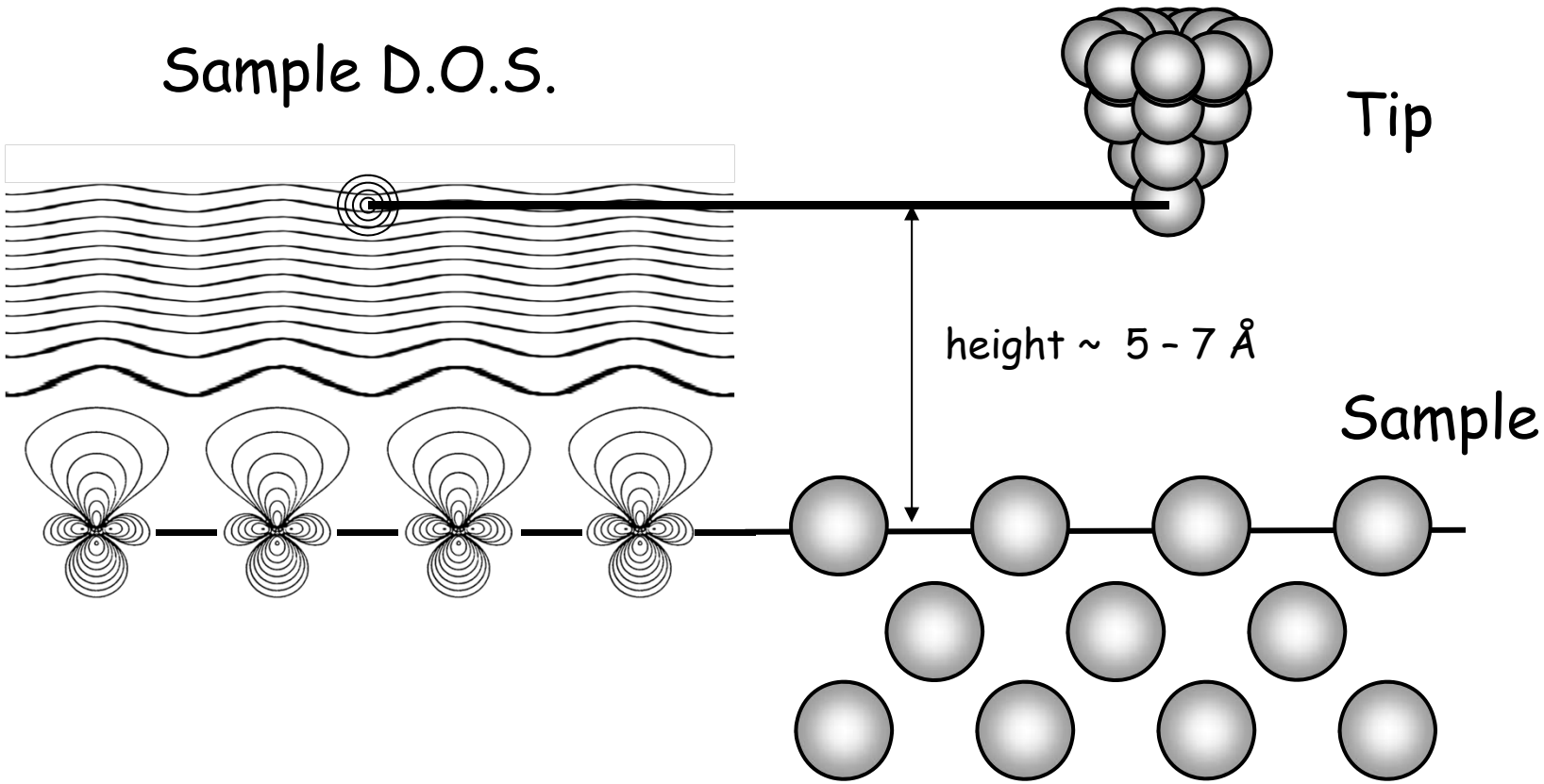
⇒ Ideal tip, with an s-like orbital in the apex



$$T_{kk'} \propto \varphi_k(\vec{r}_{tip}) \Rightarrow \left|T_{kk'}\right|^2 \propto \left|\varphi_k(\vec{r}_{tip})\right|^2 = \rho_{sample}(\vec{r}_{tip}, \varepsilon_k) \Rightarrow \frac{dI_{tunnel}}{dV} \propto \rho_{sample}(\vec{r}_{tip}, \varepsilon_k)$$

$$I_{tunnel} \propto \int_{-\infty}^{\infty} \rho_{sample}(\vec{r}_{tip}, \varepsilon)\left[f_T(\varepsilon) - f_S(\varepsilon)\right]d\varepsilon \xrightarrow{V \to 0} I_{tunnel} \propto \rho_{sample}(\vec{r}_{tip}, \varepsilon_{Fermi})$$

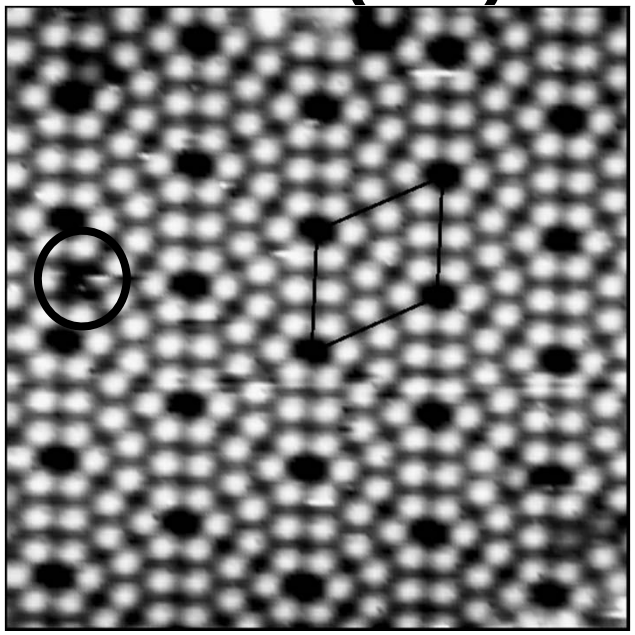
TERSOFF-HAMAN APPROXIMATION:



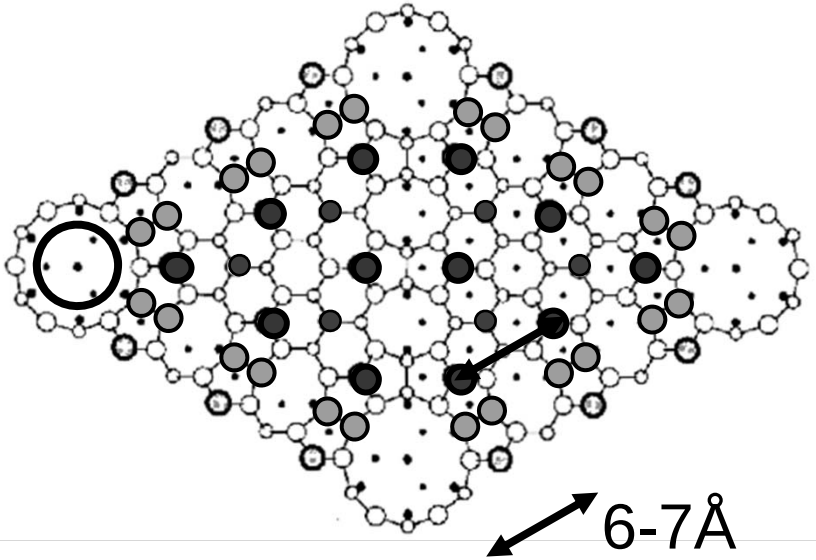
⇨ D.O.S. near the Fermi level controls the current

⇨ STM images are not topographic.

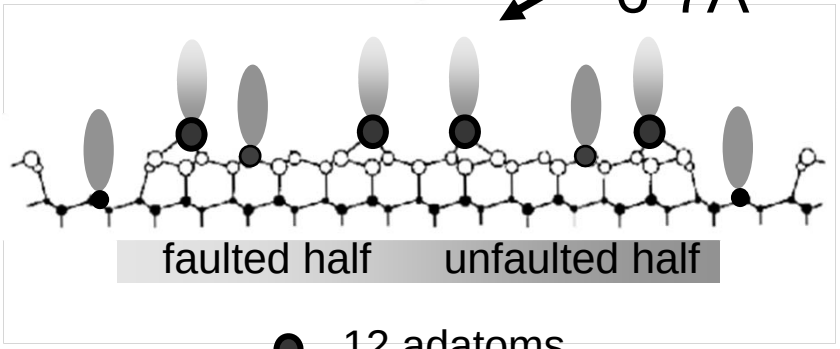
Atomic resolution on the Si(111)-7x7



100 Å



6-7Å

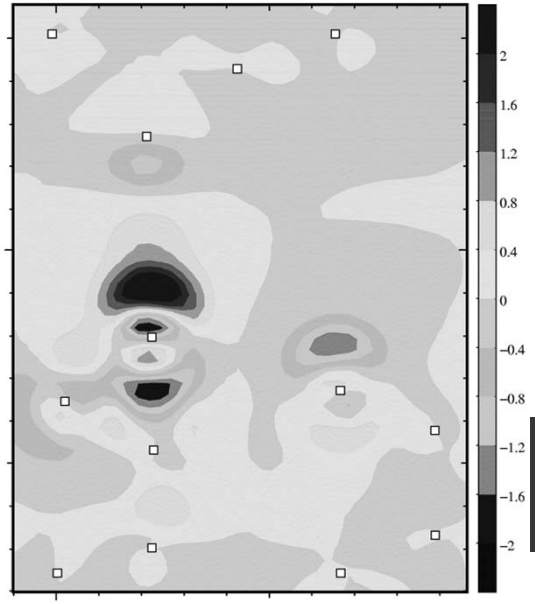


12 adatoms

6 rest atoms

corner hole

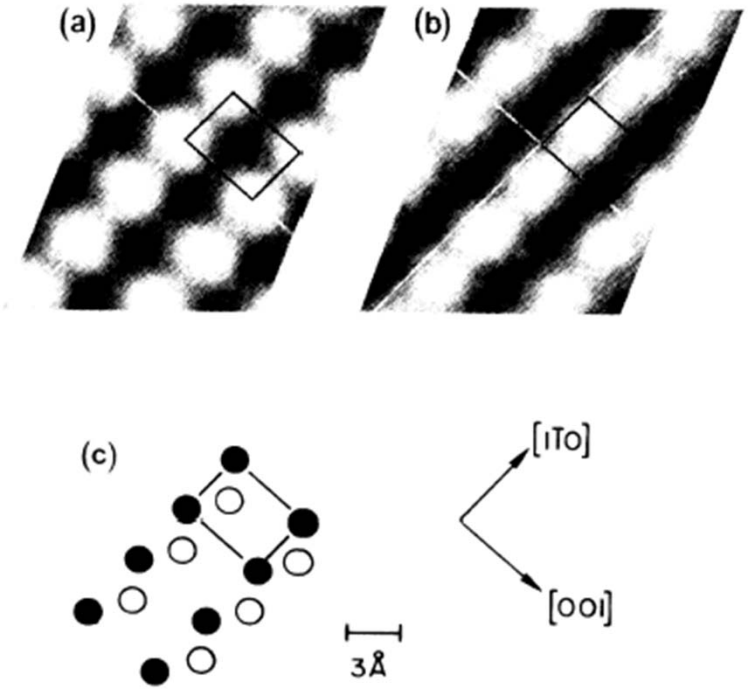
dimers

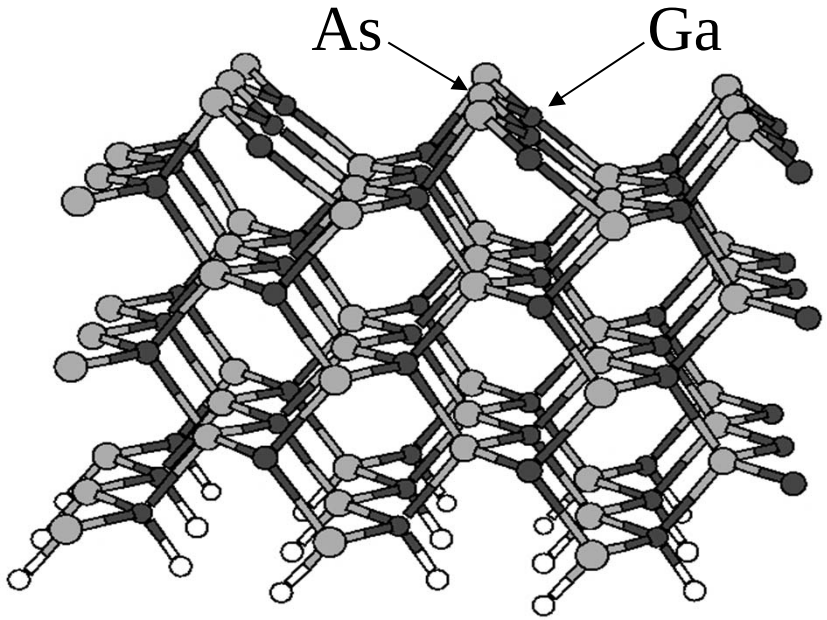


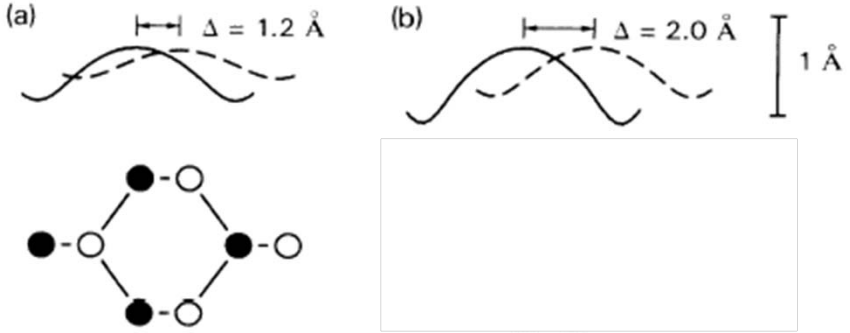
Calculated charge distribution on the states (“dangling bonds”) localized on adatom and rest atom

Understanding the bias dependence: GaAs (110)

STM Experiments

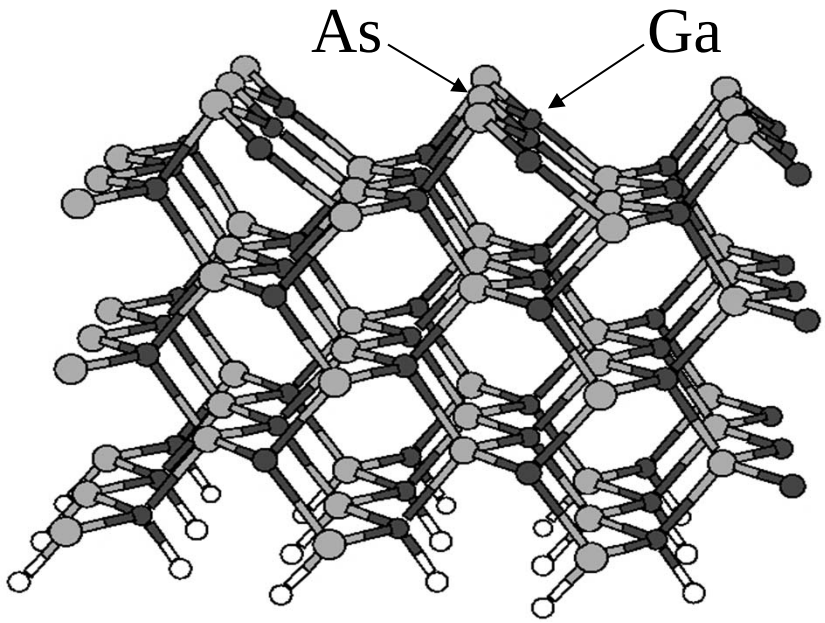


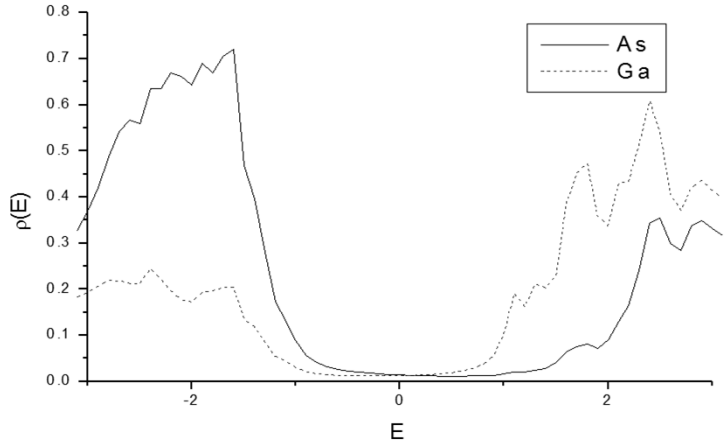


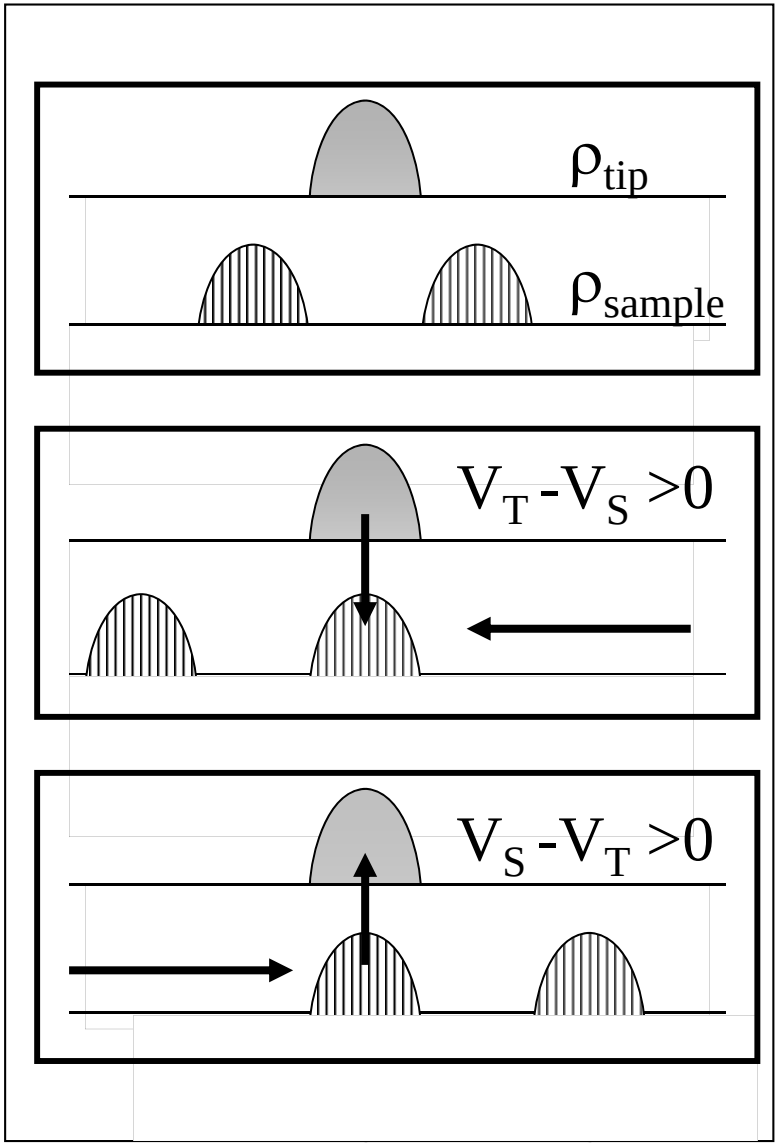


- Only one atomic specie imaged for each voltage?
- Shift between the position of the maxima?

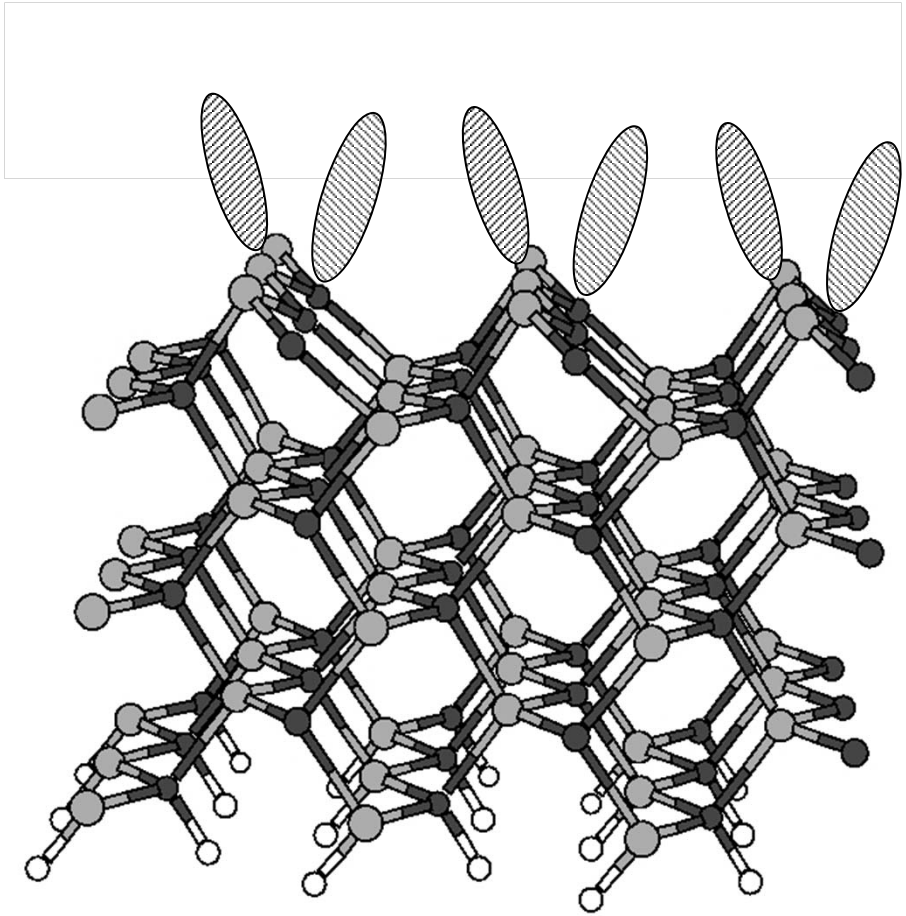
GaAs (110): Understanding the bias dependece



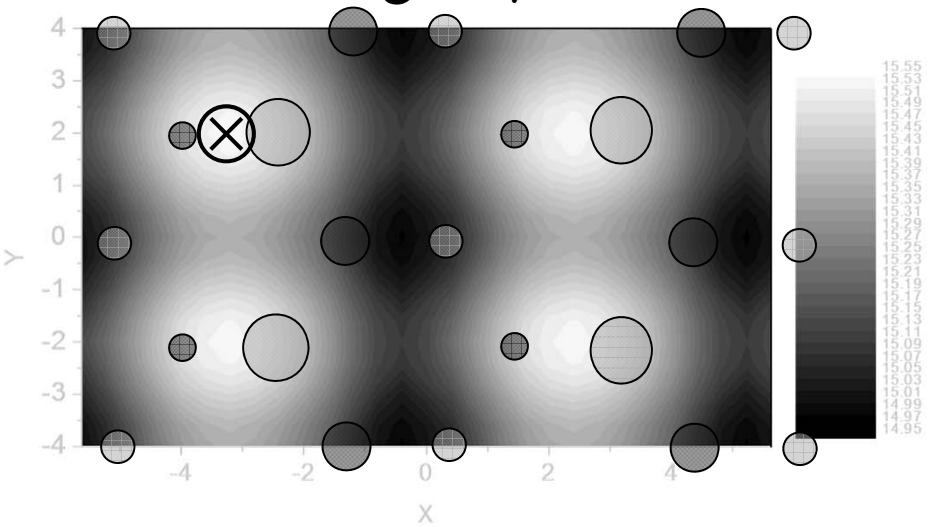




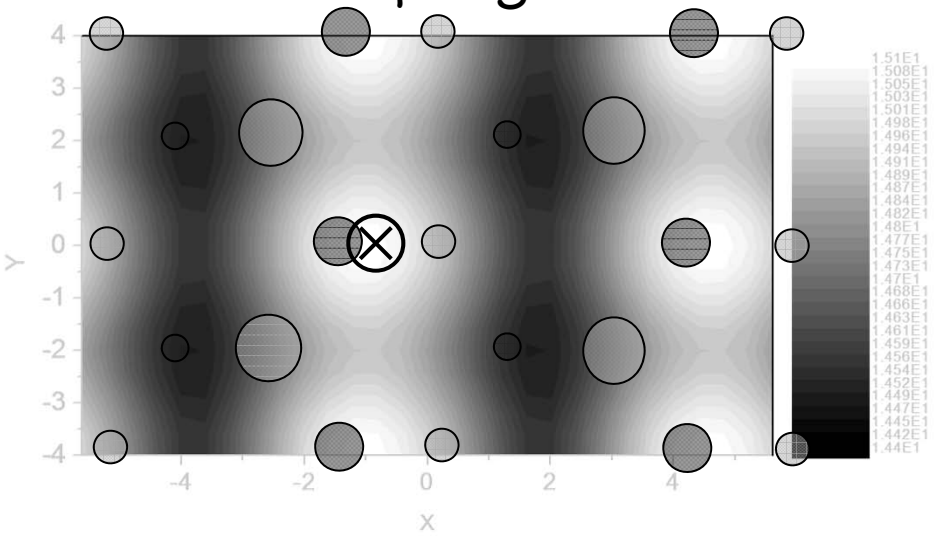
GaAs (110): Theoretical STM images

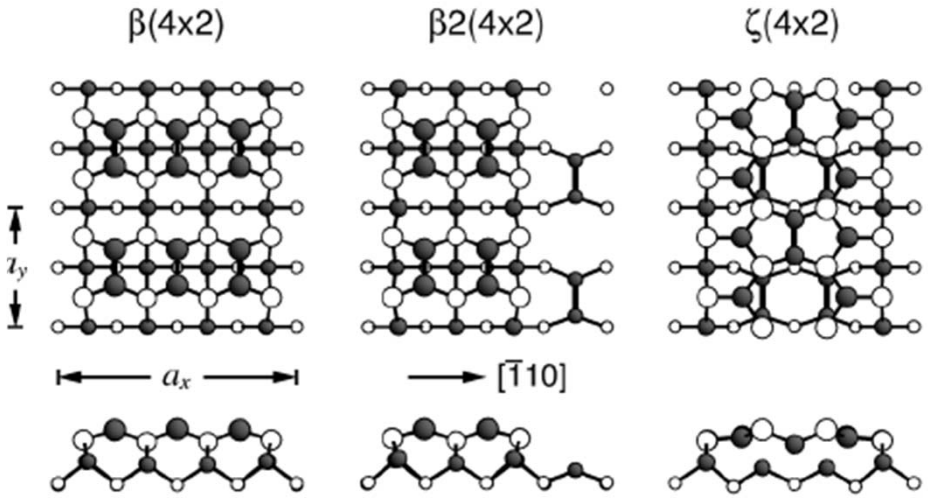


$V_S - V_T > 0$

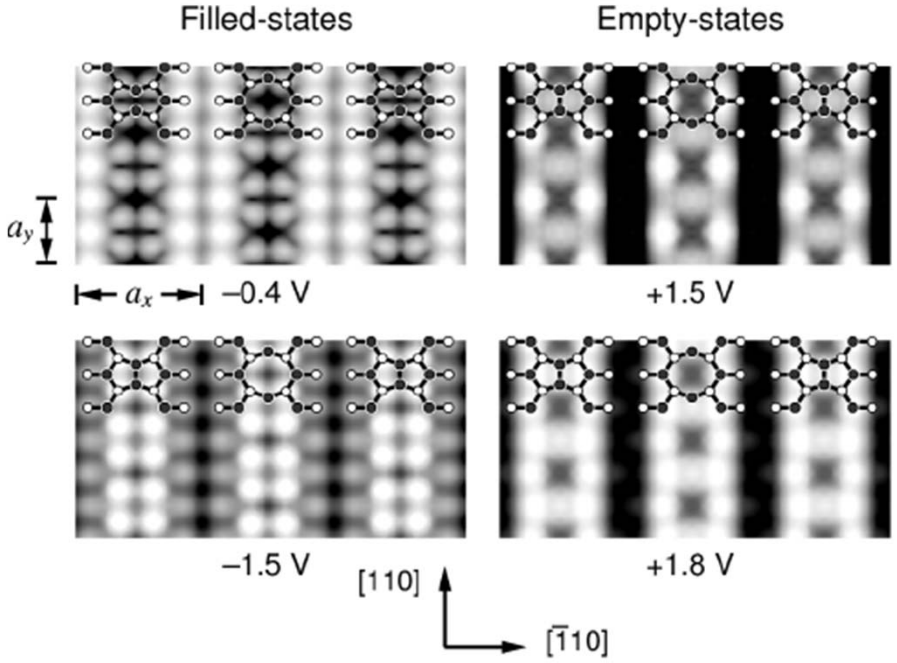


$V_T - V_S > 0$





First principles calculations of ρ_{sample} + T-H approach for tunneling



A typical application of Tersoff-Hamann Approach

(S-H. Lee et al, PRL 85 (2000) 3890)

Novel surface geometry for GaAs(100) under low As pressure

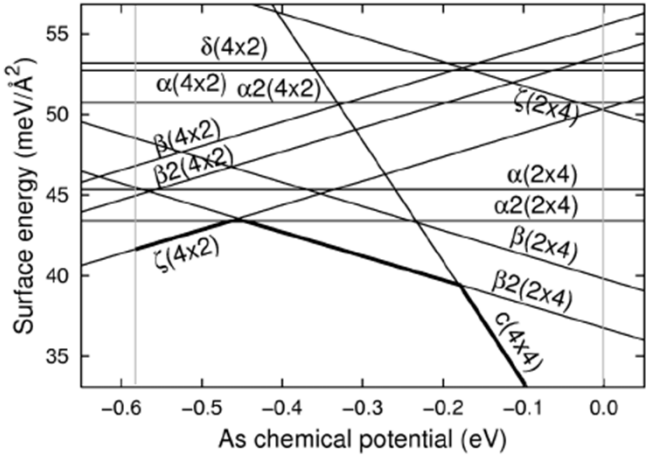


FIG. 3. Simulated STM images of the $c(8 \times 2)$ ζ structure of GaAs(001) for different bias voltages, V_b, which are given with respect to the valence band maximum, E_{VB}. The images map the height of constant electron density $[n(\vec{r}) = 5 \times 10^{-6}$ bohr$^{-3}]$ for the electron density integrated over an energy range between E_{VB} and $E_{VB} + eV_b$. The constant density surface is at 3–4 Å above the atomic surface and has a height corrugation of ~1.5 Å. Full dots mark positions of Ga atoms and open dots mark As atoms.

CHEN's IMPROVEMENT TO TERSOFF-HAMAN

(C.J. Chen, PRL 65 (1990) 448 ; PRB 42 (1990) 8841; PRL 69 (1992) 1656)

T-H reproduces qualitatively large period surface reconstructions + adsorbates on metals

But CANNOT reproduce:
- Lateral atomic resolution in closed-packed metal surfaces
- Large atomic corrugations
- Inverted contrast images

⇒ Directional p or d-like orbitals at the tip apex needed

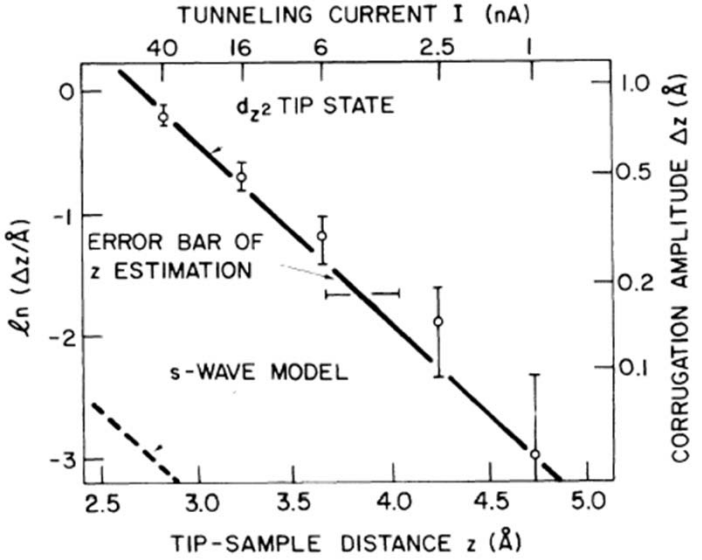
For a p-like orbital

$$T_{kk'} \propto \frac{d\varphi_k(\vec{r}_{tip})}{dx_i}$$

For a d-like orbital

$$T_{kk'} \propto \frac{d^2\varphi_k(\vec{r}_{tip})}{dx_i\,dxj}$$

$$T_{kk'} \propto \frac{d^2\varphi_k(\vec{r}_{tip})}{dz^2} - \frac{2}{3}W\,\varphi_k(\vec{r}_{tip})$$



PROBLEMS WITH B — T-H — CHEN APPROACH:

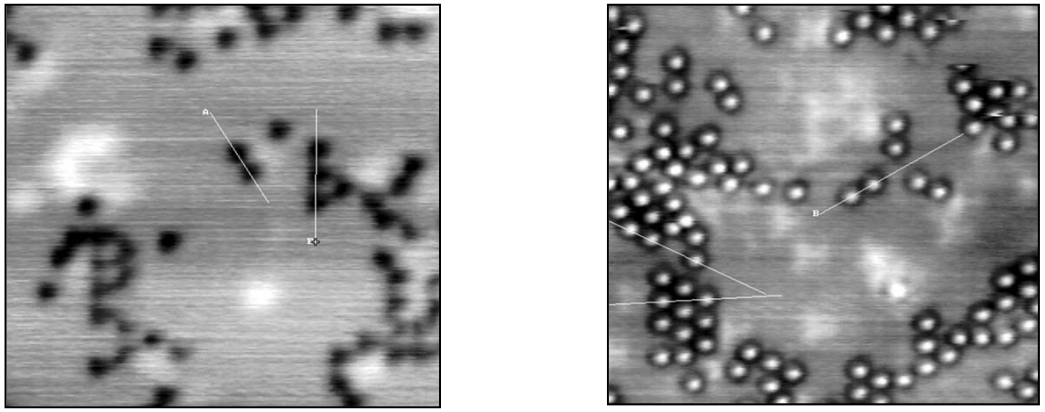
1) Gives just the 1st order perturbation term

2) Small T-S distances: $T_{kk'}$ don't include the effect of tip-sample chemical interaction.

3) Long T-S distances : $T_{kk'}$ smaller than actual values due to long range atomic potentials.

4) T-H: At typical tip-sample distances, $\rho_{\mathbf{sample}}(r_{tip}, \varepsilon)$ can't be used.

5) T-H: Neglects the dependence on the tip structure



Atomic oxygen on Pd(111) imaged with two diffent tips (M. Salmeron group)

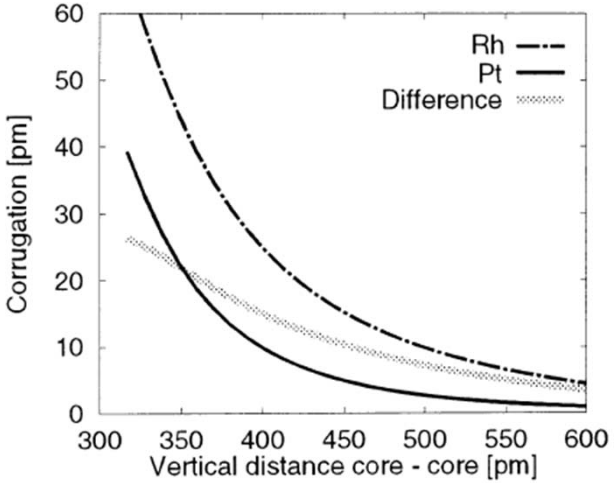
6) Chen: Not easy to combine different tip-orbital symmetries to get real image.

Approaches based on Bardeen's tunneling currents and First Principles calculations

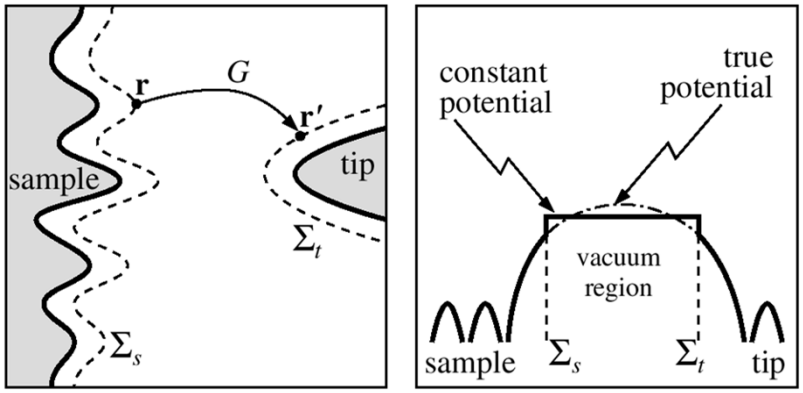
$$M_{ts} = -\frac{\hbar^2}{2m}\int_{\Sigma}[\varphi_t^*(\mathbf{r})\nabla\varphi_s(\mathbf{r}) - \varphi_s(\mathbf{r})\nabla\varphi_t^*(\mathbf{r})]d^2\hat{\mathbf{r}}$$

W. Hofer & J. Redinger Surf. Sci. **447,** 51 (2000)
W. Hofer et al RMP **75,** 1287 (2003)

FLAPW calculations for isolated tip & sample + Numerical evaluation of the Bardeen integral over a plane located at the medium distance



O. Paz et al PRL **94,** 056103 (2005)



Propagating the sample wfn's with the vaccuum Green's function G

$$\begin{aligned} M_{ts}(\mathbf{R}) &= -\frac{\hbar^2}{2m}\int[\mathbf{B}_t^*(\mathbf{r}'-\mathbf{R})\cdot\nabla\varphi_s(\mathbf{r}') \\ &\quad - \varphi_s(\mathbf{r}')A_t^*(\mathbf{r}'-\mathbf{R})]d^3\mathbf{r}' \\ &= \frac{\hbar^2}{2m}\int[\tilde{A}_t^*(\mathbf{k}) - i\mathbf{k}\cdot\tilde{\mathbf{B}}_t^*(\mathbf{k})]\tilde{g}(\mathbf{k})[\tilde{A}_s(\mathbf{k}) \\ &\quad + i\mathbf{k}\cdot\tilde{\mathbf{B}}_s(\mathbf{k})]e^{i\mathbf{k}\cdot\mathbf{R}}d^3\mathbf{k}. \end{aligned}$$

Non-perturbative approaches to electronic transport: Calculating the STM current

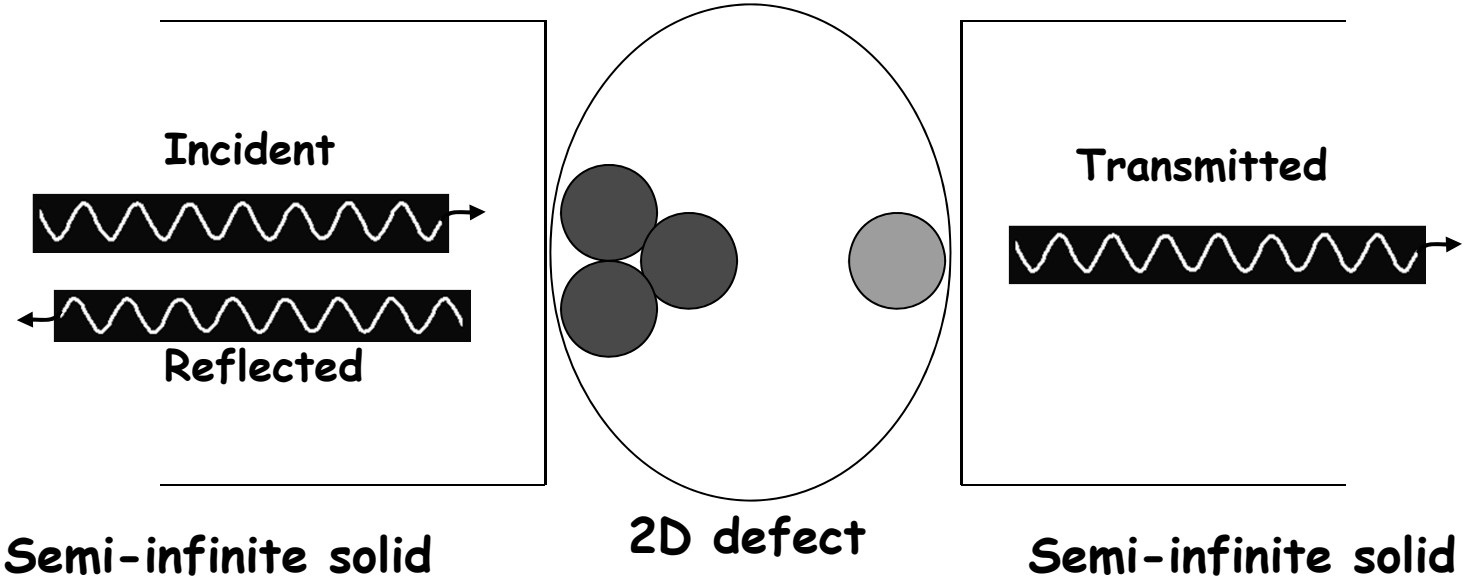
MULTIPLE SCATTERING formalism

(P. Sautet, Chem. Rev. 97 (1997) 1097; SS 374 (1997) 406; J. Cerdá et al, PRB 56 (1997) 15885)

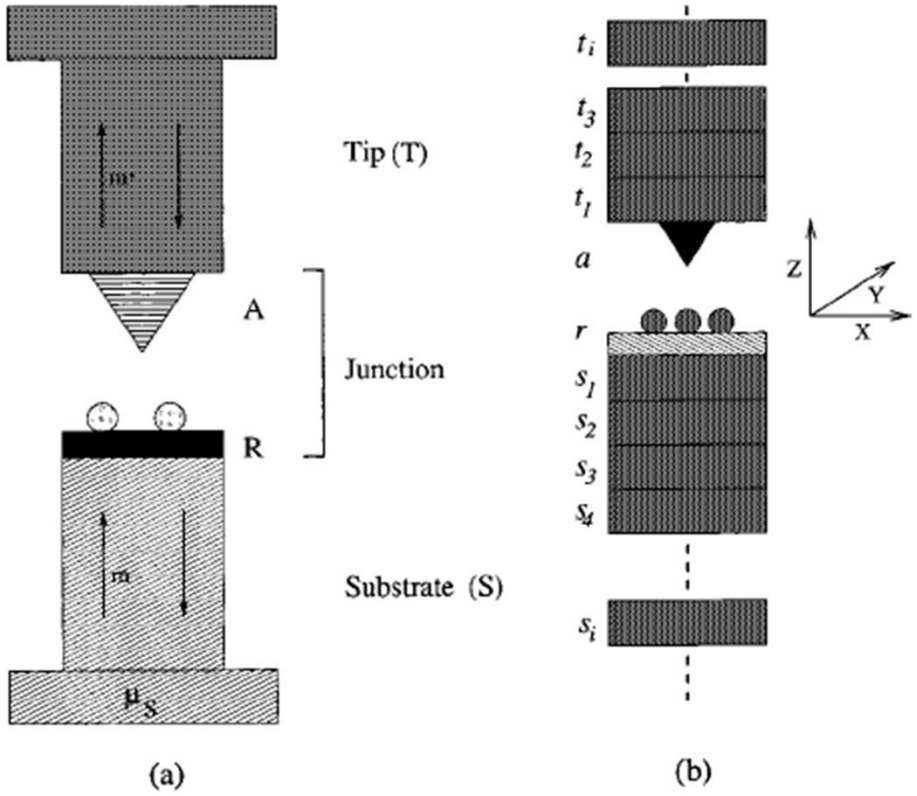
1) Electron tunnelling viewed as a scattering process.

2) Tunnel gap treated as a 2-dimensional defect.

3) Scattering matrix contains the probability amplitudes for conduction electrons.



MULTIPLE SCATTERING formalism



$$I(V)=\frac{e}{\pi\hbar}\int_0^{-eV} T^{\pm}(E+\mu_T)dE.$$

$$T^{\pm}(E)=\sum_{m,m'} T^{\pm}_{mm'}(E),$$

$$T_{mm'}(E)=|\mathsf{S}_{mm'}(E)|^2\frac{V_m}{V_{m'}},$$

Calculating $S_{mm'}(E)$?

- ESQC: transfer matrix tech. (both sides have to be identical, only zero bias).
- Surface Green's function matching (finite bias, more robust computationally)

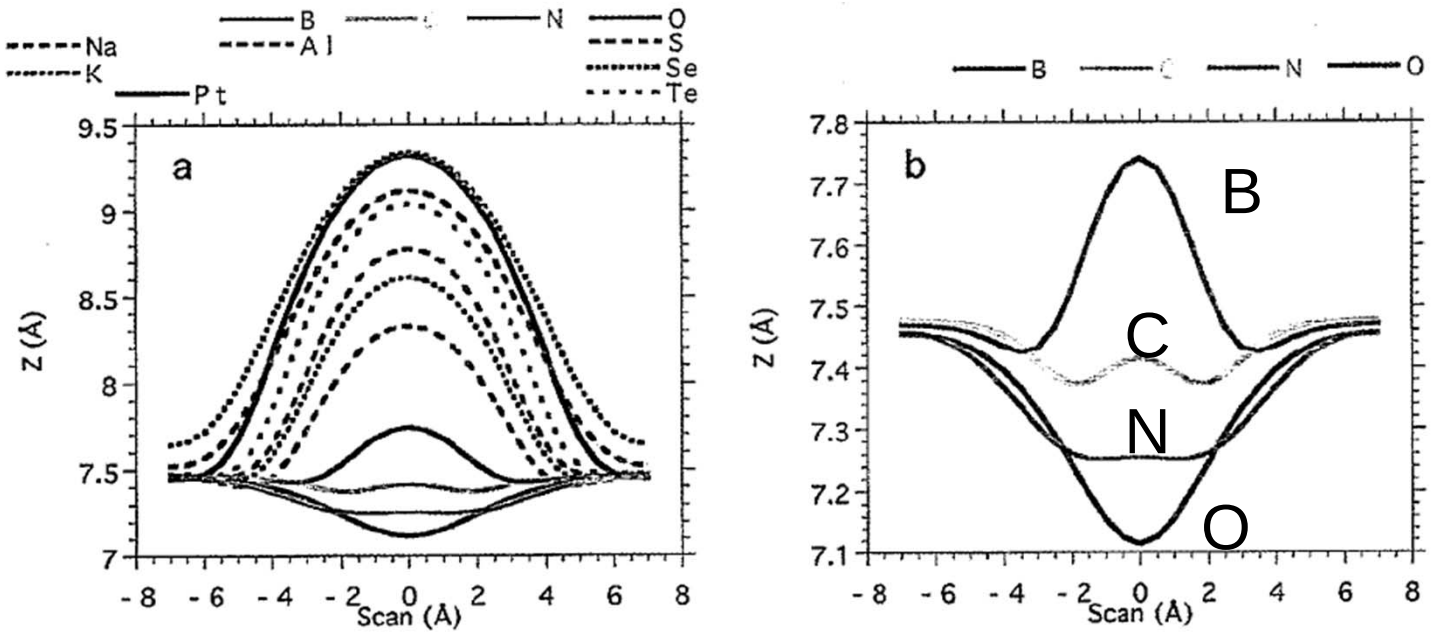
$$\mathsf{S}(E)=\mathsf{T}_{sr}\mathsf{G}_{ra}\mathsf{T}_{at} \quad \text{if } V<0,$$

$$\mathsf{S}(E)=\mathsf{T}_{ta}\mathsf{G}_{ar}\mathsf{T}_{rs} \quad \text{if } V>0.$$

MULTIPLE SCATTERING formalism: Applications

A theoretical approach to adsorbate identification

(P. Sautet, SS 374 (1997) 406)



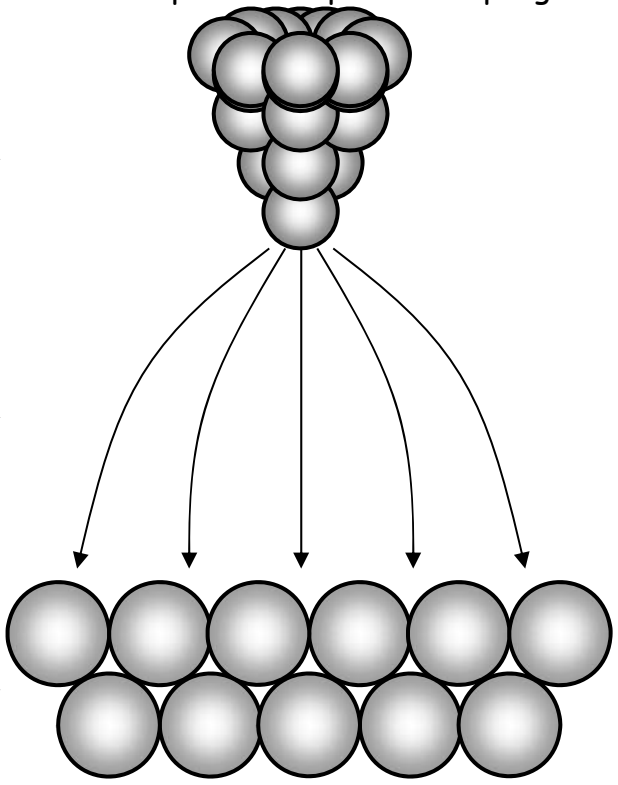
KELDYSH-GREEN'S FUNCTION METHOD

- Non-equilibrium diagramatic technique.
- Formalism equivalent to the other non-perturbative approaches in the elastic tunneling and for the limit of zero bias
- BUT also appropriate for finite bias, inelastic and correlation effects!!!.
- Naturally formulated in a local orbital basis (using atomic-like orbitals).
- It can be efficiently linked with first-principles local basis codes (Fireball, Siesta) to calculate the effective hamiltonians ($H = H_{sample} + H_{tip} + H_{coupling}$).

$$\hat{H}_T = \sum_{\alpha\beta} \left\{ \varepsilon_\alpha \hat{n}_\alpha + T_{\alpha\beta} \hat{c}_\alpha^+ \hat{c}_\beta \right\}$$

$$\hat{H}_P = \sum_{i\alpha} \left\{ T_{i\alpha} \hat{c}_i^+ \hat{c}_\alpha + T_{\alpha\, i} \hat{c}_\alpha^+ \hat{c}_i \right\}$$

$$\hat{H}_S = \sum_{i} \left\{ \varepsilon_i \hat{n}_i + T_{ij} \hat{c}_i^+ \hat{c}_j \right\}$$



KELDYSH-GREEN'S FUNCTION METHOD

(N. Mingo et al, PRB 54 (1996) 2225; L. Jurczyszyn et al, SS 482 (2001)1350)

1) Lowest order in $T_{i\alpha}$

$$I_{tunnel} = 4\pi e/\hbar \int_{-\infty}^{+\infty} Trace\left\{\hat{T}_{TS}\hat{\rho}_{SS}\hat{T}_{ST}\hat{\rho}_{TT}\right\}\left[f_T(\varepsilon) - f_S(\varepsilon)\right]d\varepsilon$$

$\rho_{ss}(\varepsilon)$, $\rho_{tt}(\varepsilon)$ = D.O.S. matrices for the sample and the tip.

T_{st}, T_{ts} = hopping matrices between the tip and the sample.

$f_S(\varepsilon)$,$f_T(\varepsilon)$ = Fermi distribution functions for the sample and the tip.

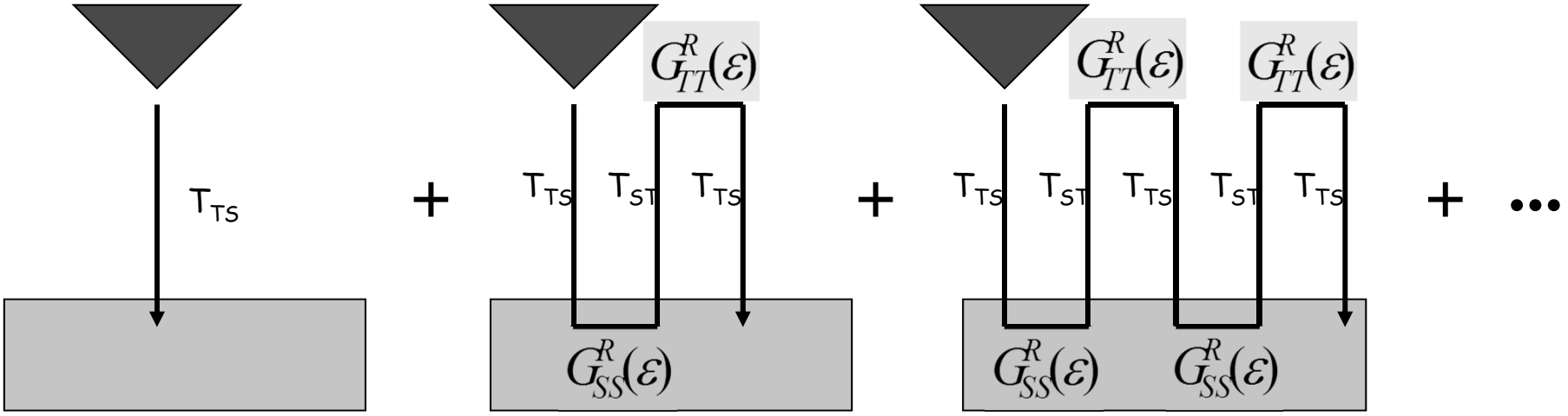
KELDYSH-GREEN'S FUNCTION METHOD

(N. Mingo et al, PRB 54 (1996) 2225; L. Jurczyszyn et al, SS 482 (2001)1350)

2) Exact solution to all orders in the tip-sample hoppings

$$I_{tunnel} = 4\pi e/\hbar \int_{-\infty}^{+\infty} Trace\left\{\hat{T}_{TS}^{eff}\,\hat{\rho}_{SS}\hat{T}_{ST}^{eff}\,\hat{\rho}_{TT}\right\}\left[f_T(\varepsilon) - f_S(\varepsilon)\right]d\varepsilon$$

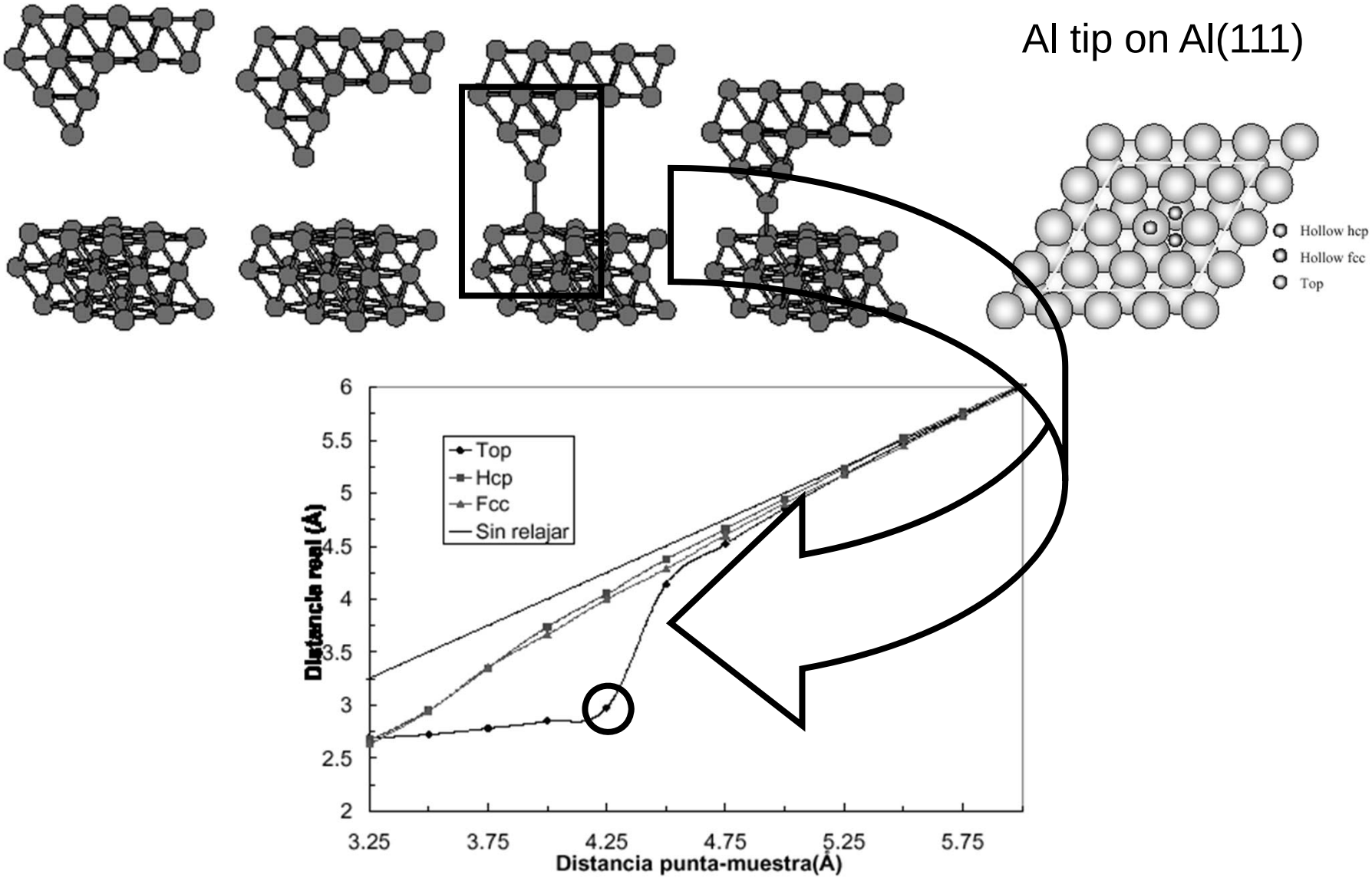
$$\hat{T}_{TS}^{eff} = \left\{1 - \hat{G}_{SS}^{R}\,\hat{T}_{ST}\,\hat{G}_{TT}^{R}\,\hat{T}_{TS}\right\}^{-1}\hat{T}_{TS} = \hat{T}_{TS} + \hat{T}_{TS}\hat{G}_{SS}^{R}\hat{T}_{ST}\hat{G}_{TT}^{R}\hat{T}_{TS} + ...$$



2) Combining STM and theoretical modelling:

- STM currents: from tunneling to the contact regime
- Conflicting images: Role of tip and imaging conditions

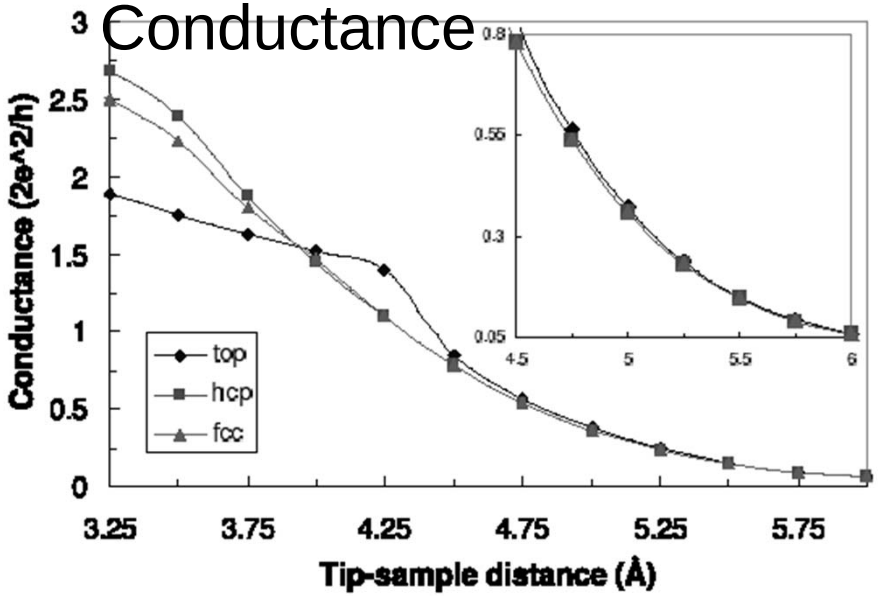
From tunneling to the contact regime…

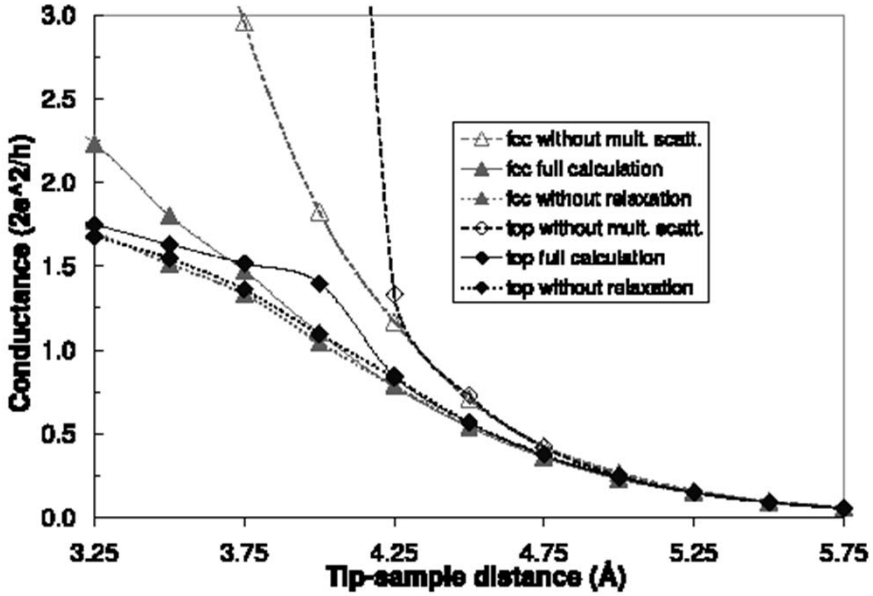


J.M. Blanco et al, PRB 70, 085405 (2004)

From tunneling to the contact regime…

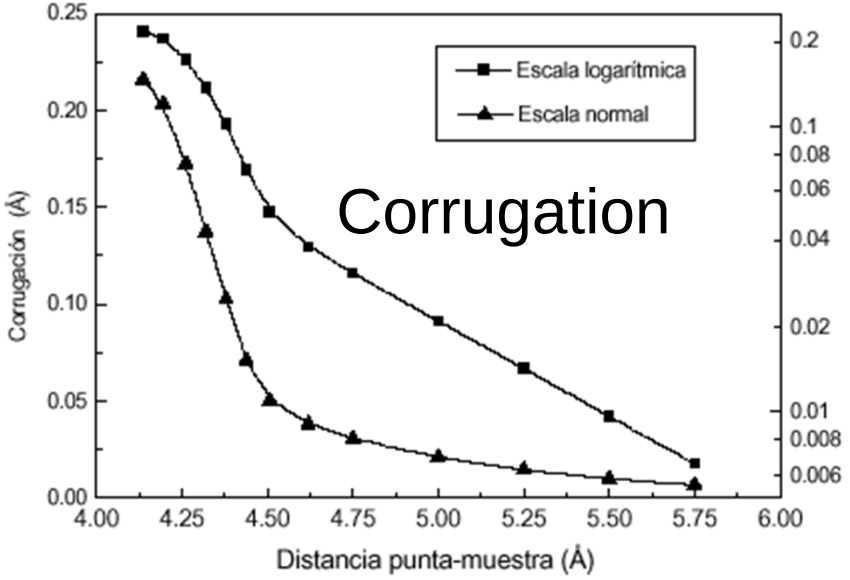
Conductance





Al tip on Al(111)

Keldysh-Green´s function formalism



Corrugation

Corrugation: combined effects of atomic relaxation & current saturation !!!

J.M. Blanco et al, PRB 70, 085405 (2004)

Comparison of different transport formalisms

Landauer formalism

$$G = \frac{dI}{dV} = \frac{2e^2}{h} \operatorname{Im} Tr[\hat{t}(E_F)\hat{t}^{+}(E_F)]$$

Keldish-Green's function formalism

$$G = \frac{dI}{dV} = \frac{4\pi e^2}{\hbar} \operatorname{Im} Tr[\hat{T}_{TS}\hat{\rho}_{SS}(E_F)\hat{D}^{r}_{SS}(E_F)\hat{T}_{ST}\hat{\rho}_{TT}(E_F)\hat{D}^{a}_{TT}(E_F)]$$

$$G = \frac{dI}{dV} = \frac{2e^2}{h} 4\pi^2 \operatorname{Im} Tr[\hat{t}(E_F)\hat{t}^{+}(E_F)]$$

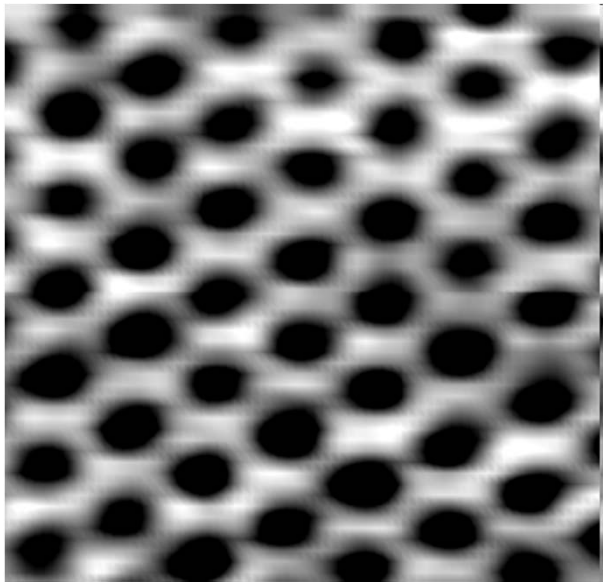
$$\hat{t} = \hat{\rho}^{1/2}{}_{SS}(E_F)\hat{D}^{r}_{SS}(E_F)\hat{T}_{ST}\hat{\rho}^{1/2}{}_{TT}(E_F)$$

Conflicting experiments: O(2x2) / Pd(111)

Motivation

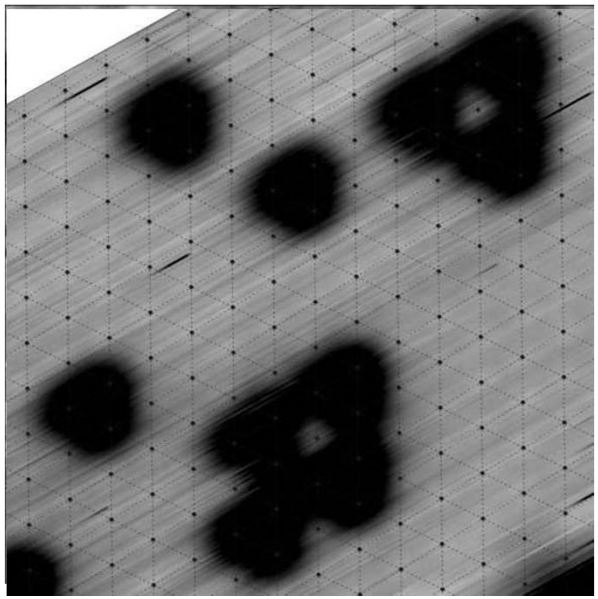
- Directly related with catalysis of gases over surfaces.
- Discrepancies between different experimental images of O/Pd(111).

Oxigen with circular shape.



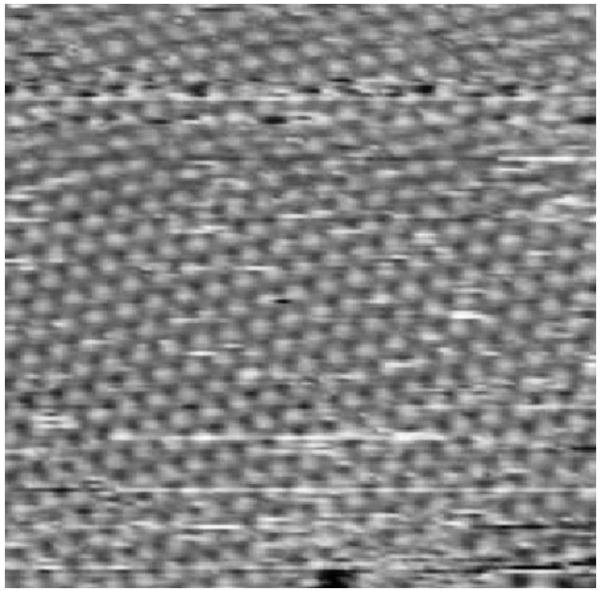
V = -1.4
J. Méndez et al., Berlin

Oxigen with triangular shape



V ~ 0
M. Salmeron et al., Berkeley

Inverse contrast



V = 0.29 V
J. Méndez et al., Berlin

...that cannot be explained with approximations like Tersoff-Hamann.

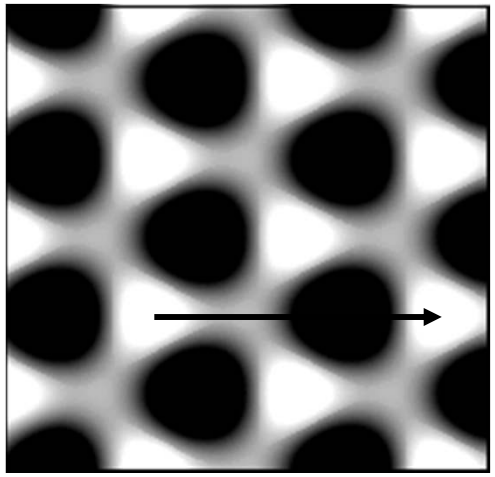
J.M.Blanco et al., PRB 71, 113402 (2005)

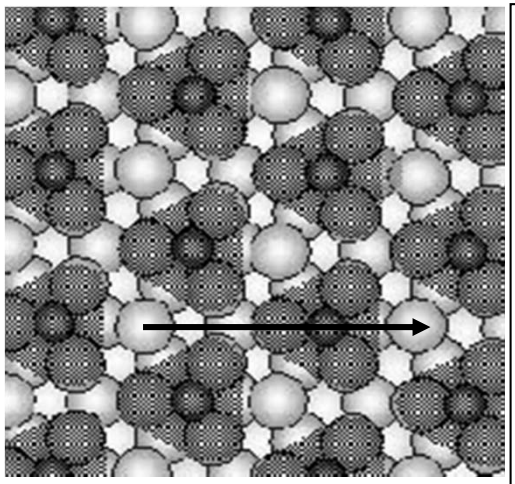
Theoretical simulations

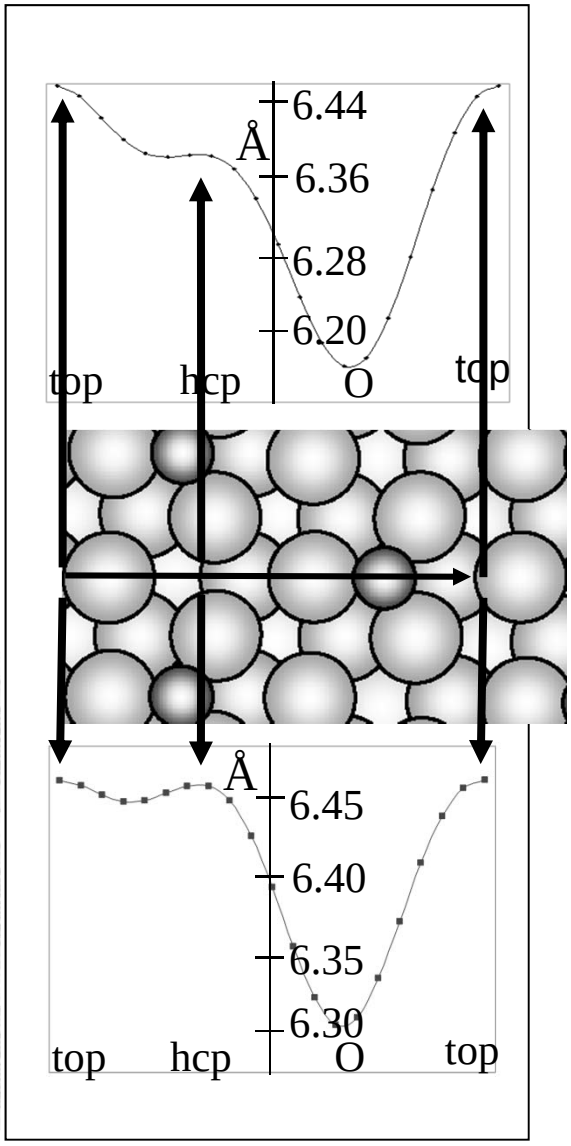
Pt tip:

d=6.46 (top)

V=-0.030 V



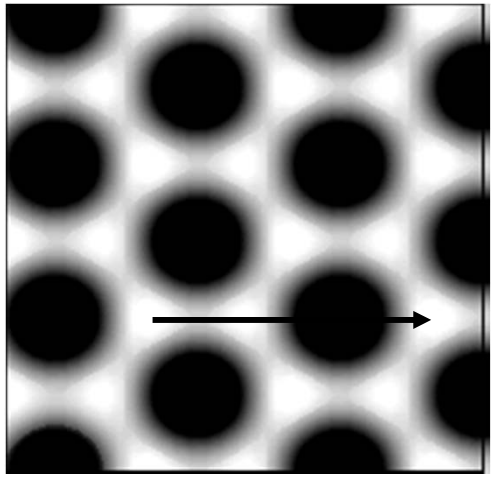


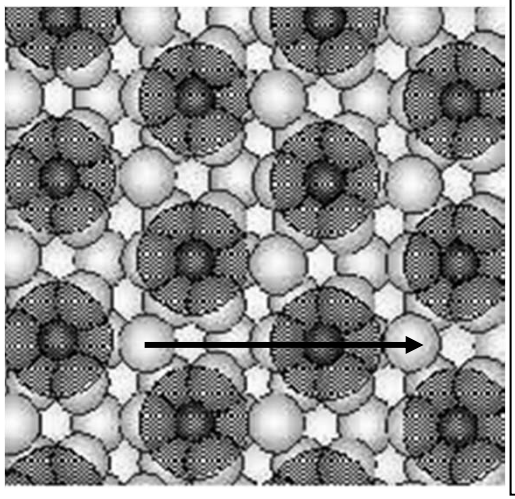


W tip

d=6.46 (top)

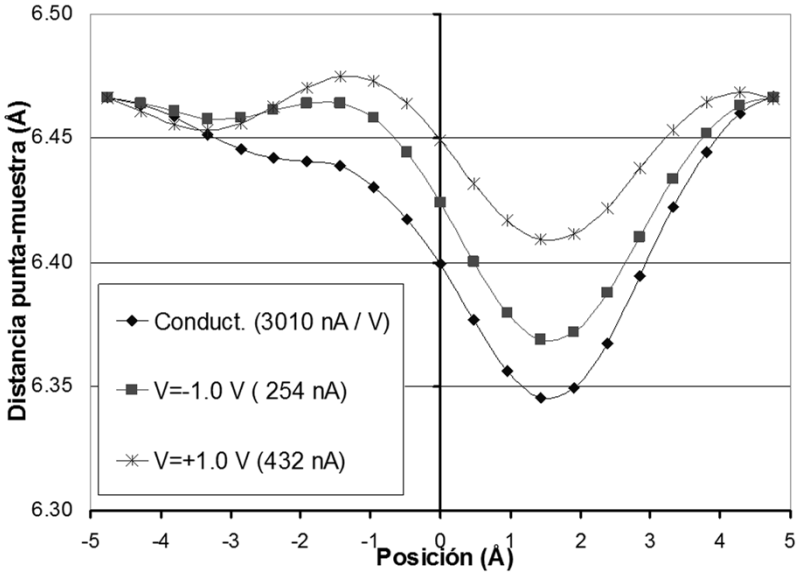
V=-1.4 V



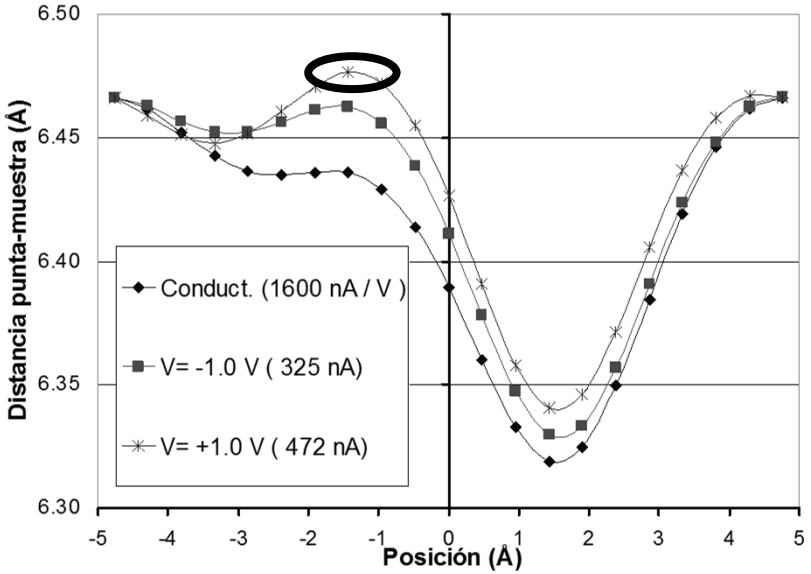


¿Different composition or different voltage?

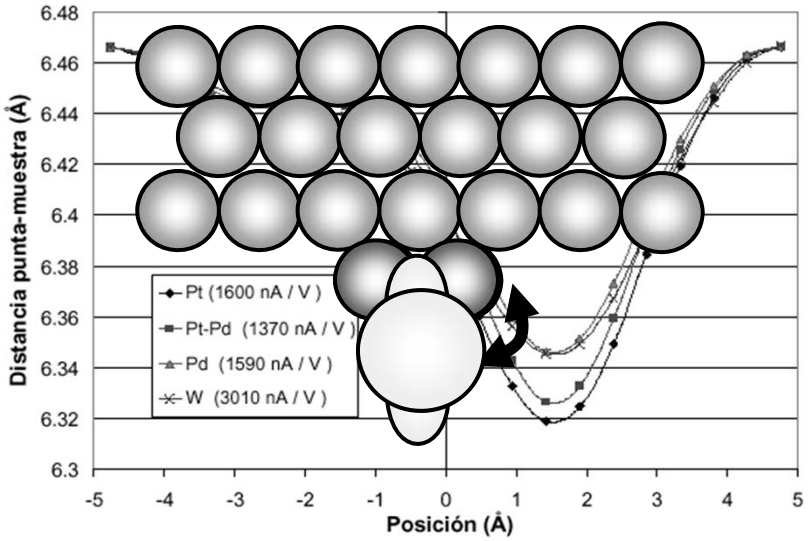
Pt tip:



W tip:

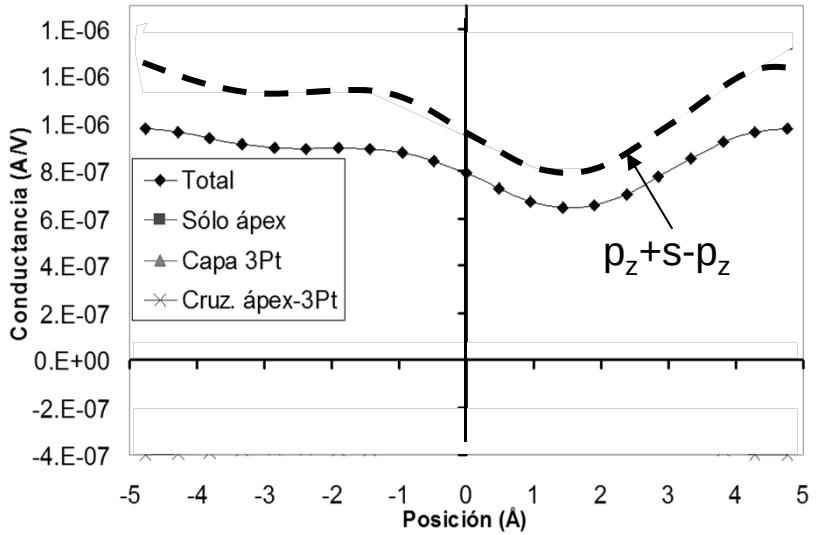


Corrug. for different tips:



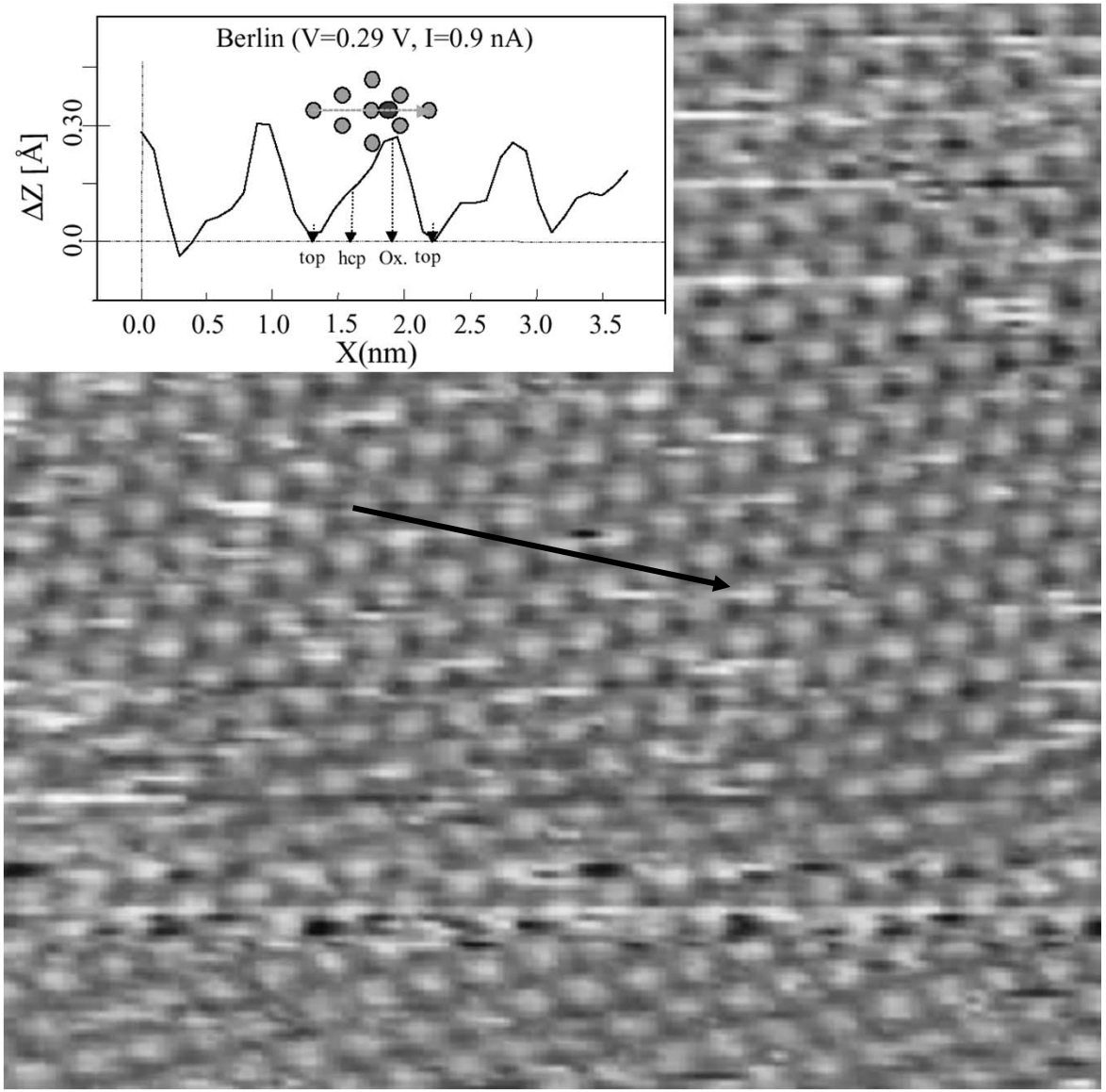
Corrug. for different geometries:

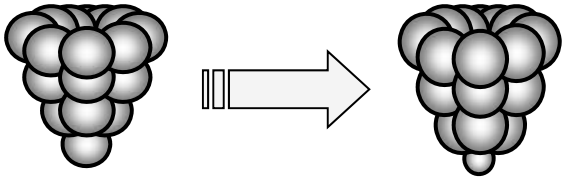
Analysis in tip orbitals



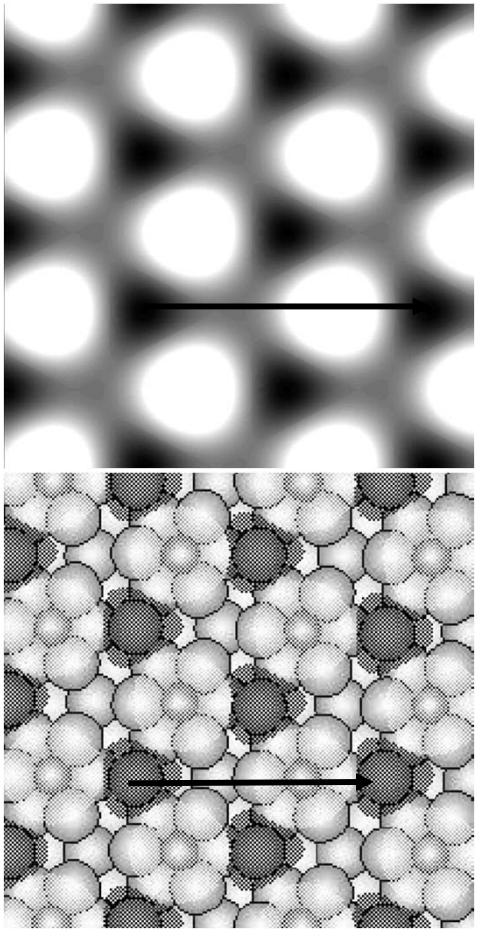
Contrast inversion:

Sometimes, images have inverted contrast**:**





Oxigen contaminated tip :



CONCLUSIONS

1) A proper theoretical treatment of the STM has to describe not only the properties of the tip and the sample, but also should include a good description of the tunnelling process.

2) Perturbative methods of calculating STM images (in particular Tersoff-Hamman approx.) can in some cases give an approximate qualitative behavior, but don't take into account effects that can be crucial to understand the experiments.

3) Keldysh-Green´s function formalism, exact to all orders of the coupling, provides a clear picture of the physics involved and offers great flexibility in its application. (+ it can handle inelastic and correlation effects)

$$I_{tunnel} = 4\pi e/\hbar \int_{-\infty}^{+\infty} Trace\left\{\hat{T}_{TS}^{eff}\ \hat{\rho}_{SS}\hat{T}_{ST}^{eff}\ \hat{\rho}_{TT}\right\}\left[f_T(\varepsilon) - f_S(\varepsilon)\right]d\varepsilon$$

4) More effort is needed in the characterization (both experimental and theoretically) of the tips and their properties.