

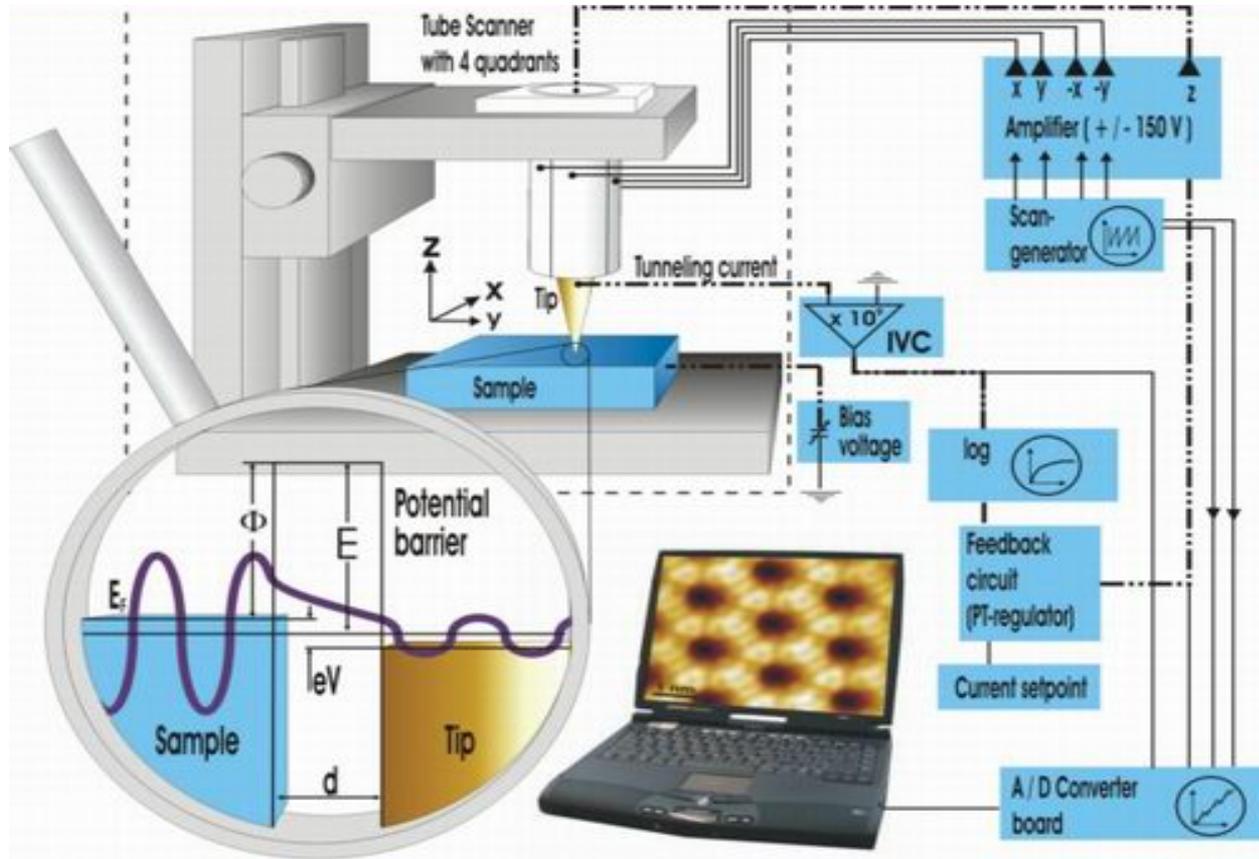


Physics at surfaces

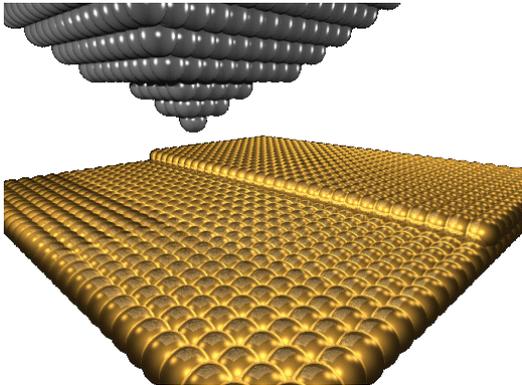
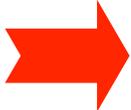
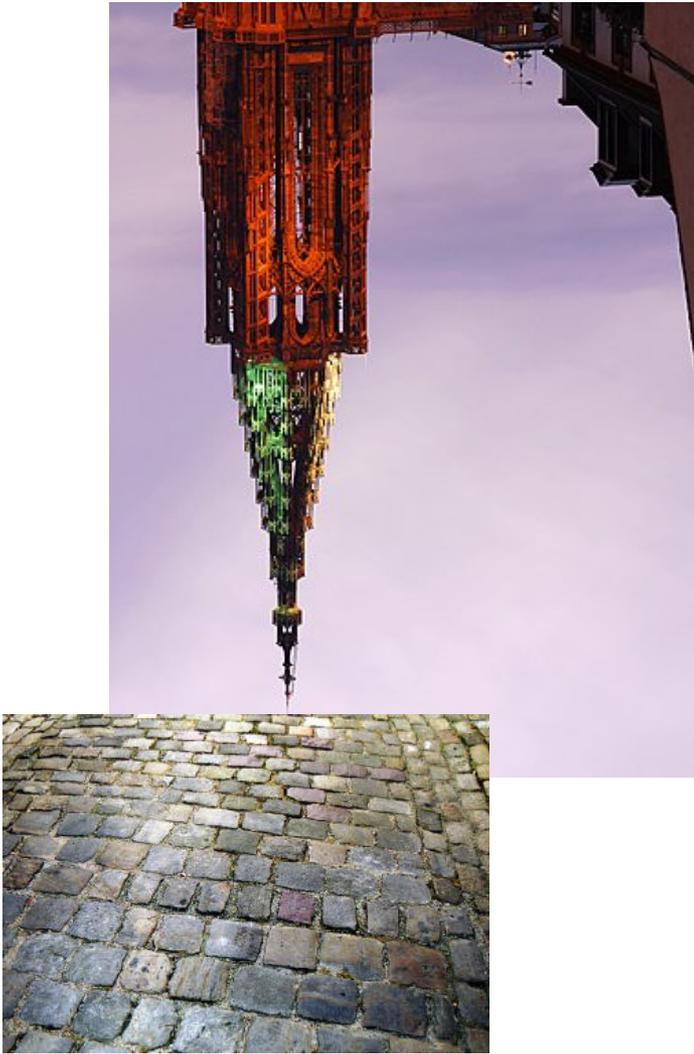
Jean-Pierre Bucher

SCANNING TUNNELING MICROSCOPY/SPECTROSCOPY

Principle of a scanning tunneling microscope

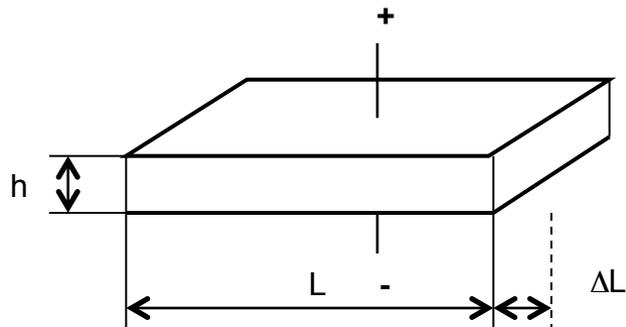


Orders of magnitude: the Strasbourg STM



Scale down : 1/ 1'000'000'000

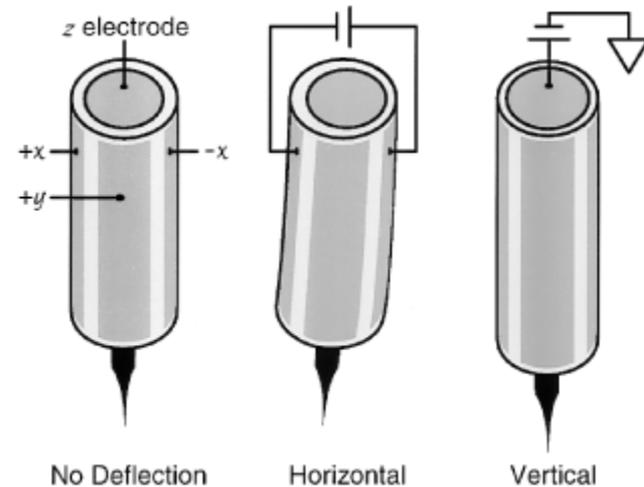
Scanning nano: the piezo-tube



$$\Delta L = d_{31} \frac{L}{h} V$$

d_{31} : piezo-electrique coefficient

PZT [Pb(Zr, Ti)O₃] tube, plated with metal on the internal and 4 external segments.



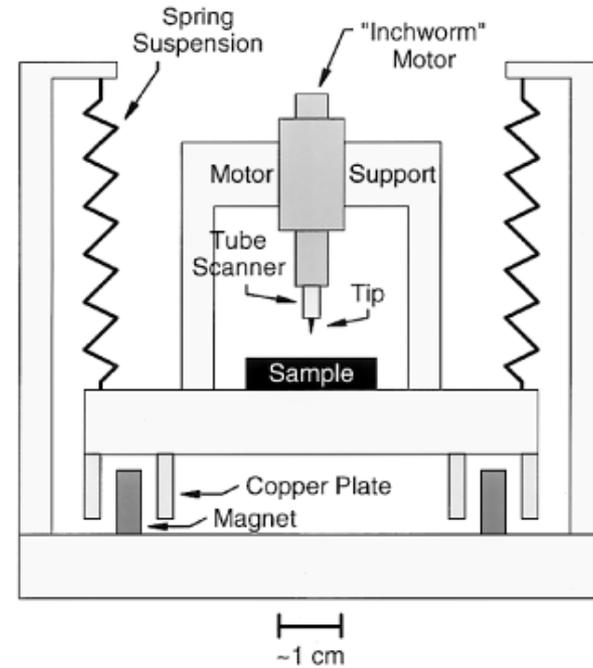
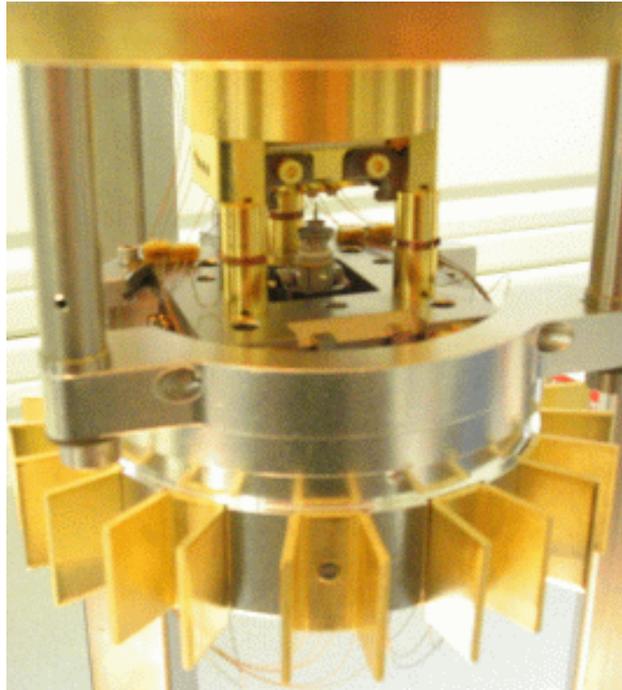
$$\Delta L = \frac{2d_{31}}{(OD - ID)} V L$$

elongation of the tube

$$\frac{\sqrt{2d_{31}}}{\pi Dh} VL^2$$

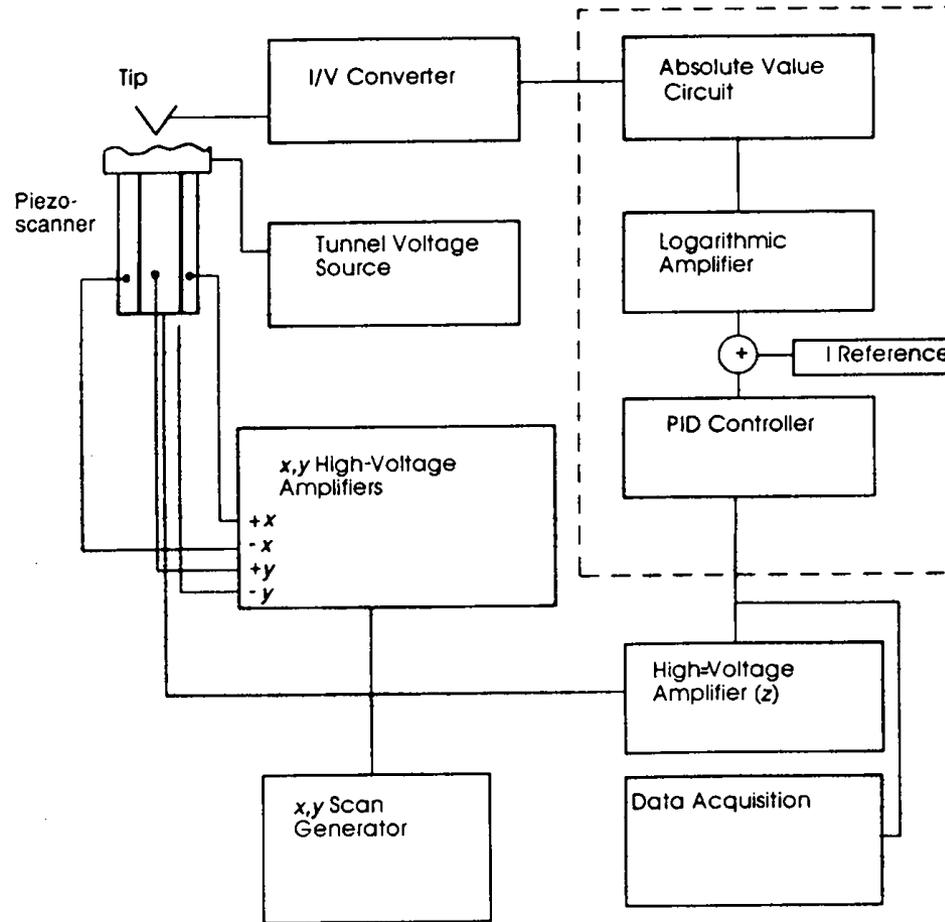
Scan range with h the wall thickness of the tube

The low temperature UHV-STM

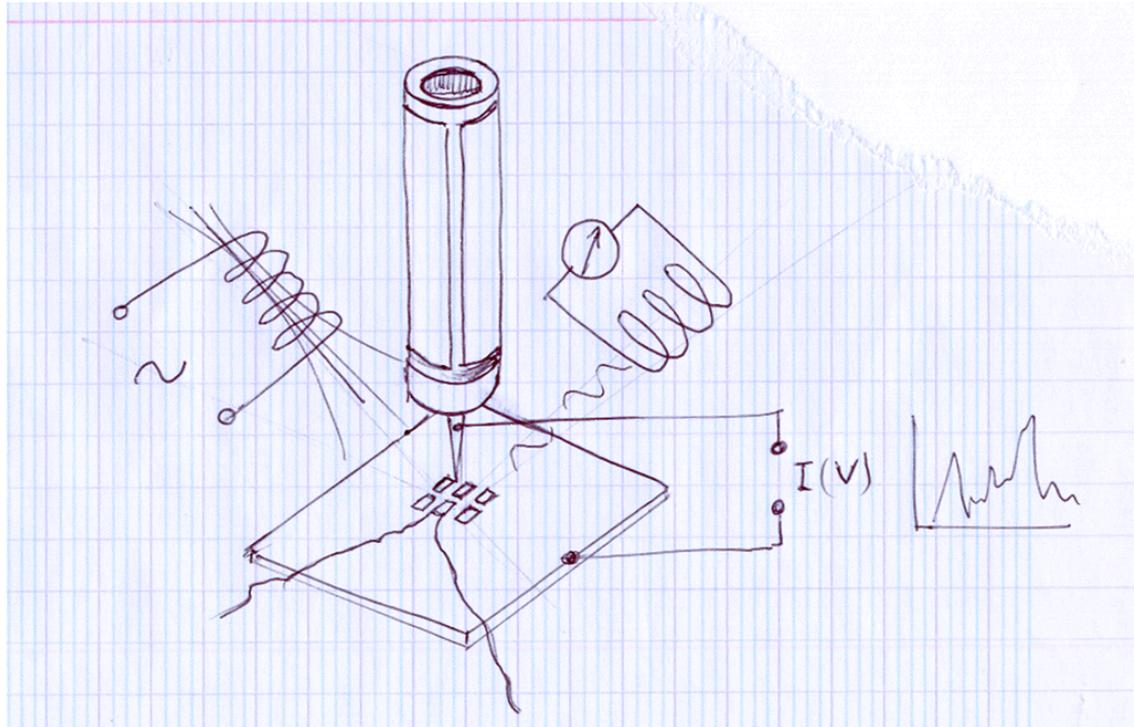


Temperature down to 2.3 K and $p=10^{-11}$ mbar

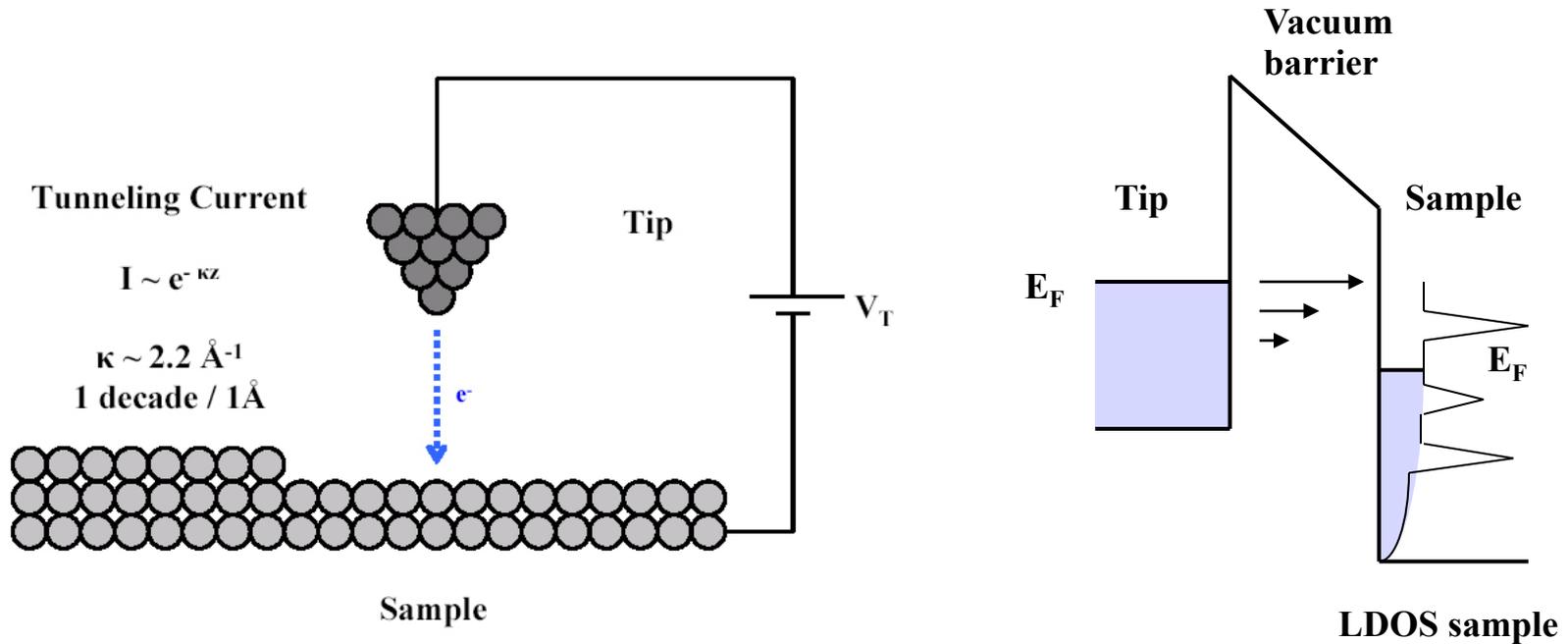
Control electronics



Scanning probe techniques



Scanning tunneling spectroscopy



$$I_T \propto e^{-\kappa z} \int_0^{eV} LDOS_{sample}(E - eV) dE$$

Scanning tunneling spectroscopy

$$I_T = \frac{4\pi e}{\hbar} \int_{-\infty}^{+\infty} [f(E - eV) - f(E)] D_S(E - eV) D_T(E) |M|^2 dE$$

f is the Fermi function :

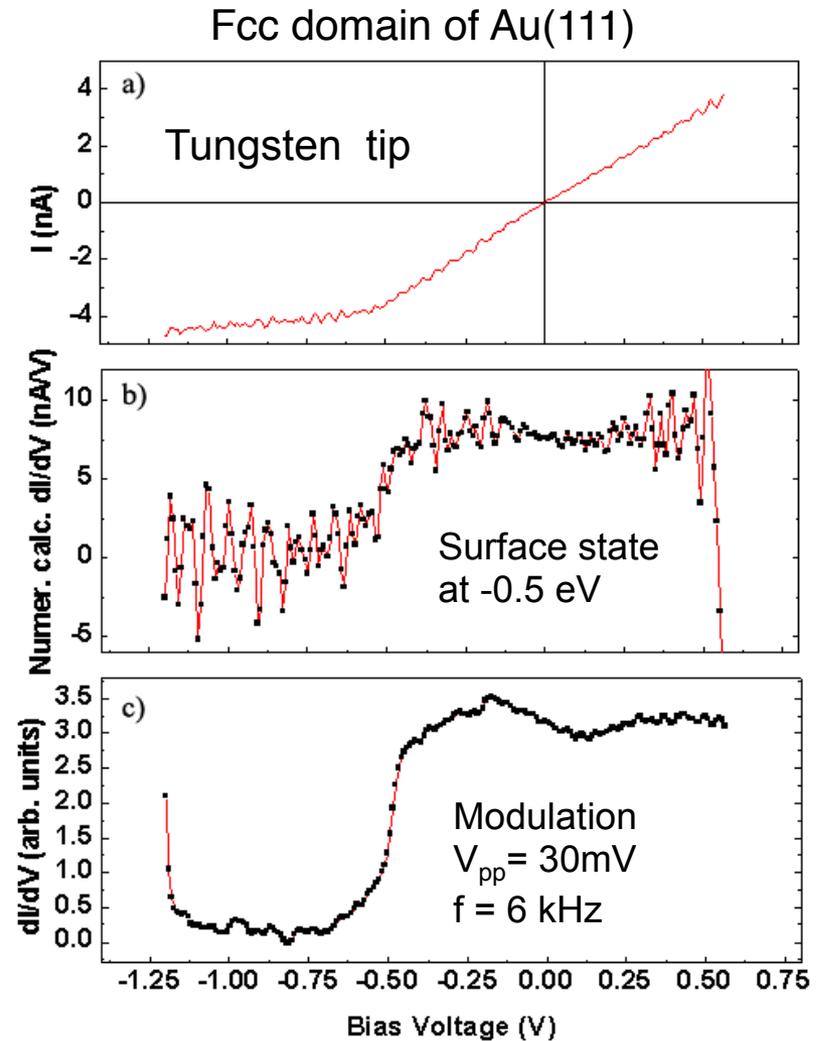
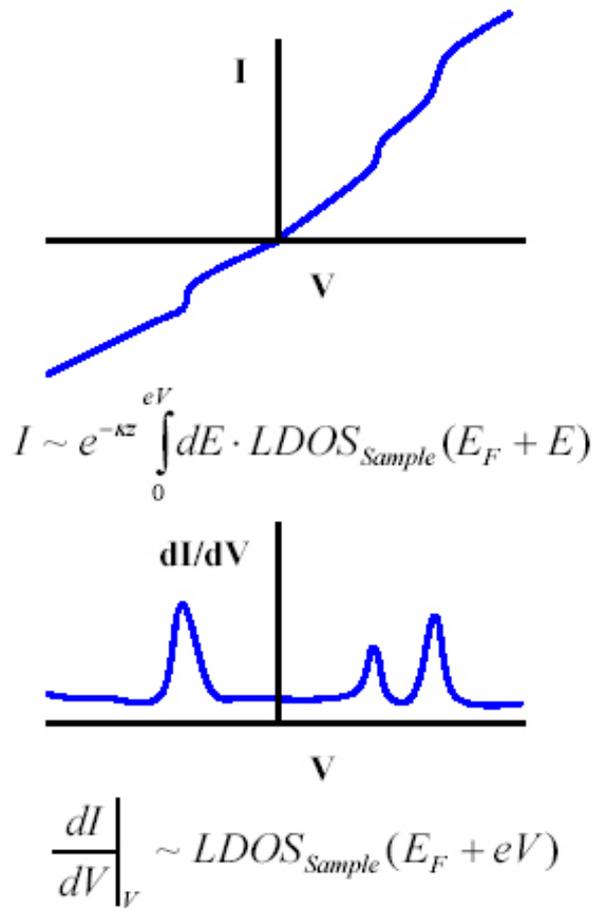
$$f(E) = \frac{1}{1 + e^{(E - E_F)/k_B T}}$$

$$M_{\mu\nu} = \frac{\hbar^2}{2m} \int (\psi_\mu^* \nabla \psi_\nu - \psi_\nu \nabla \psi_\mu^*) dS$$

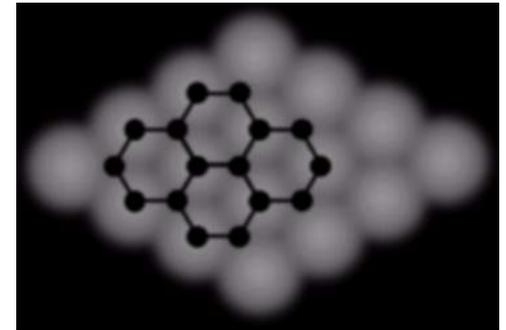
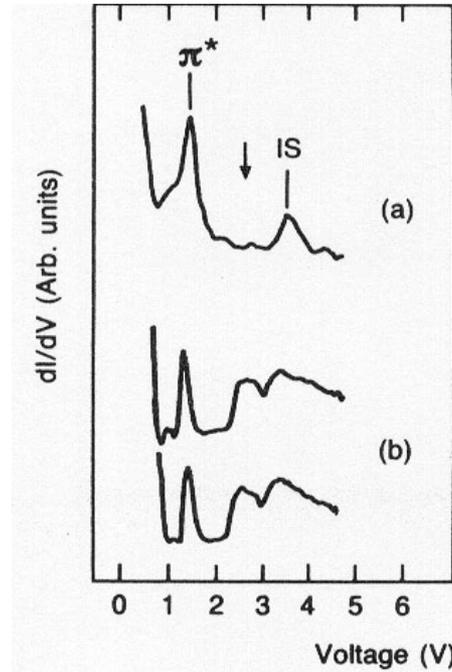
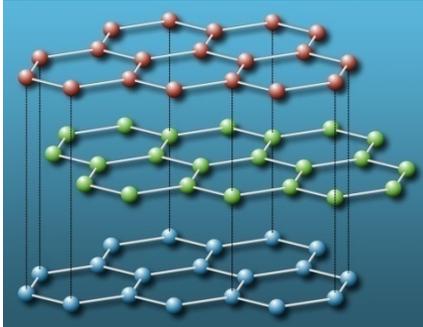
$$I_T = \frac{4\pi e}{\hbar} \int_0^{eV} D_S(E - eV) D_T(E) |M|^2 dE$$

See lecture for details

Scanning tunneling spectroscopy



STM studies on graphite

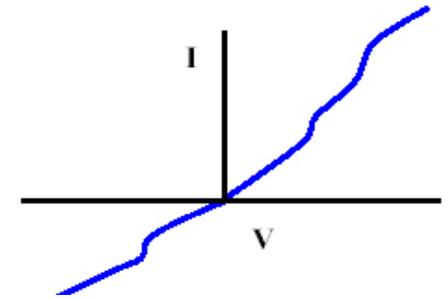
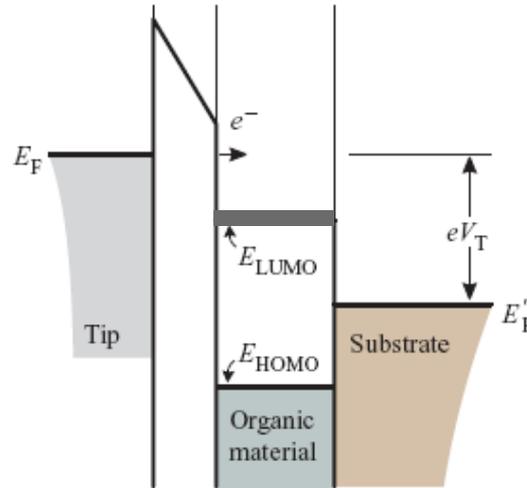
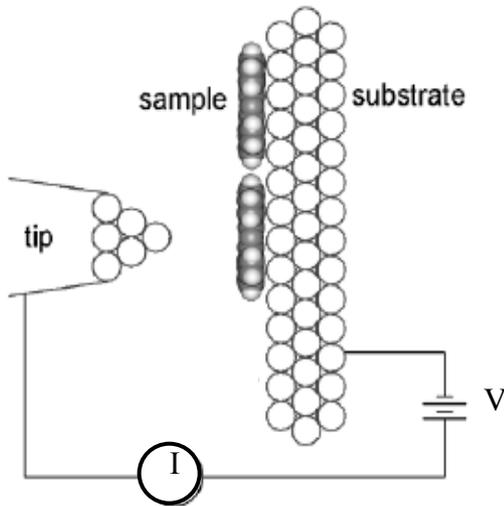


dI/dV spectra taken from two different locations of a HOPG surface [H. Fuchs, E. Tossati, Europhys. Lett. **3**, 735 (1987)].

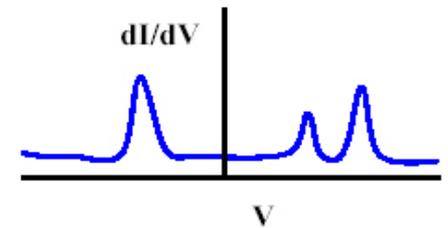
a) the first peak is attributed to a π^* -anti-bonding state of the bulk, while the second is attributed to an interlayer state.

b) These spectra show a third peak that is attributed to some impurity states that are only visible occasionally. The STM spectroscopic results are in good agreement with inverse photoemission results and with the theoretical predictions.

A matter of energy level alignment



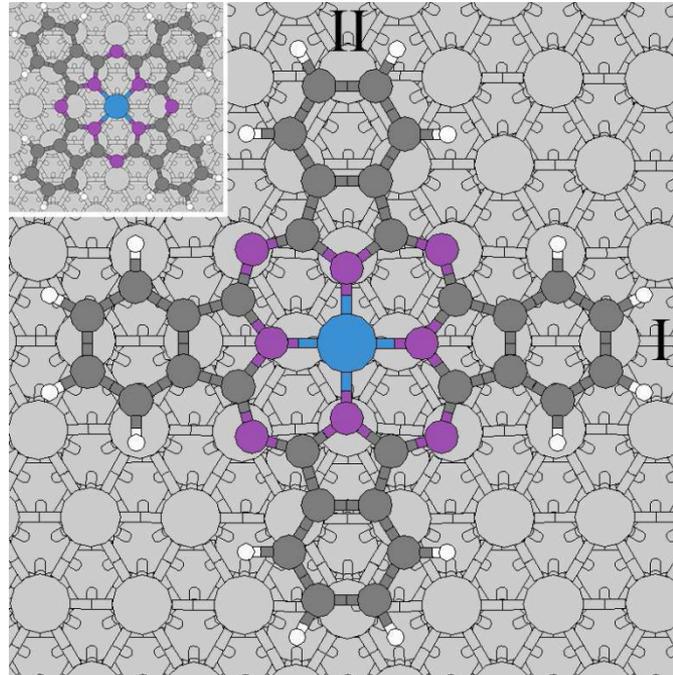
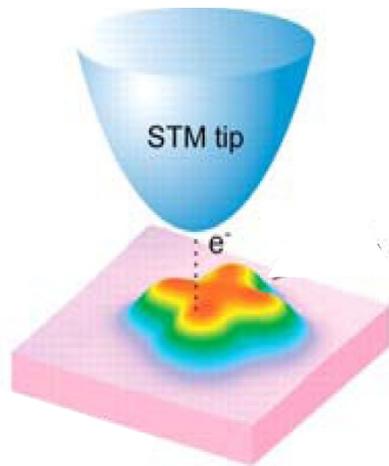
$$I \propto e^{-\kappa z} \int_0^{eV} D_S(E_F + E) dE$$



$$\frac{dI(V)}{dV} \propto D_S(E_F + eV)$$

Importance of adsorption geometry

Orbital symmetry and molecular conductance

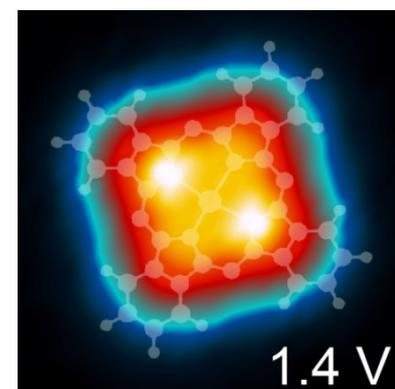
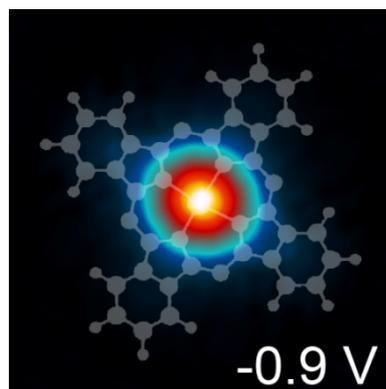


Interaction with the surface: C₄ molecule onto a fcc (111) surface :
symmetry reduction C₂

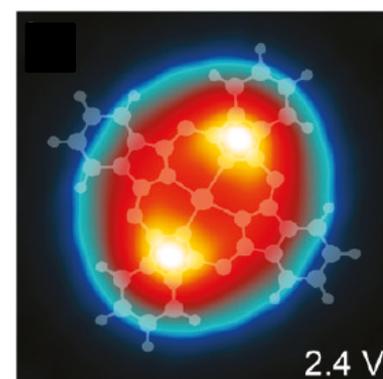
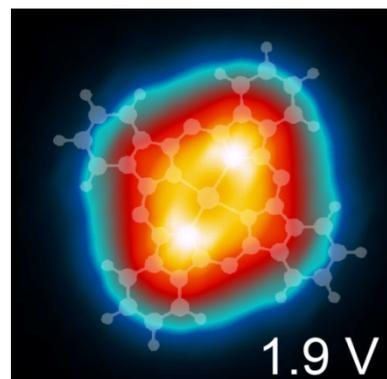
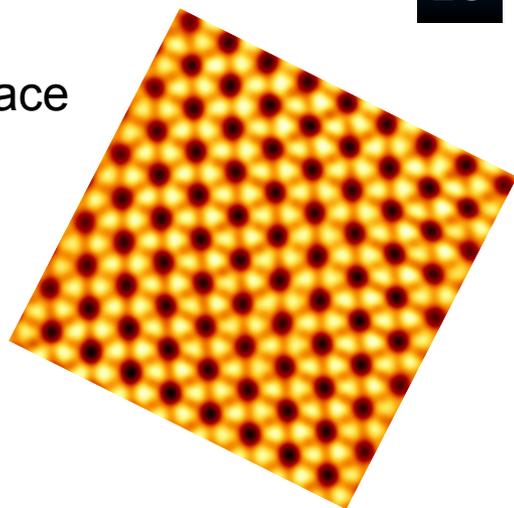
Origin of the conductance channels

CoPc on Cu(111)
Constant-height dI/dV maps

Control of adsorption
geometry : interaction
with the surface



Cu(111) surface
beside the
CoPc

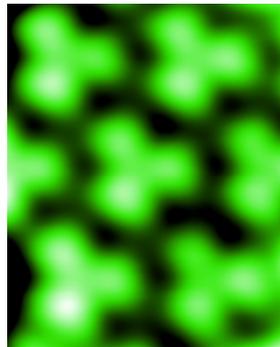
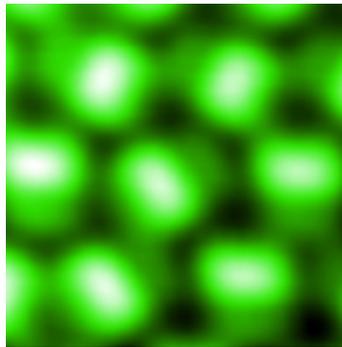


B.W. Heinrich *et al.*, J. Phys. Chem. Lett. **1**,1517 (2010).

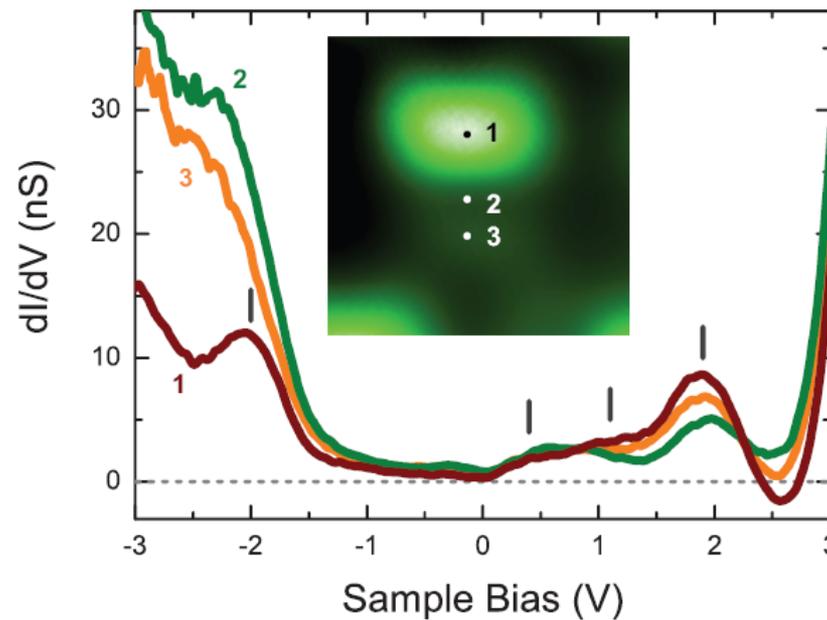
Molecular electronics: NDC of C_{60}

Cobalt

Cu(111)



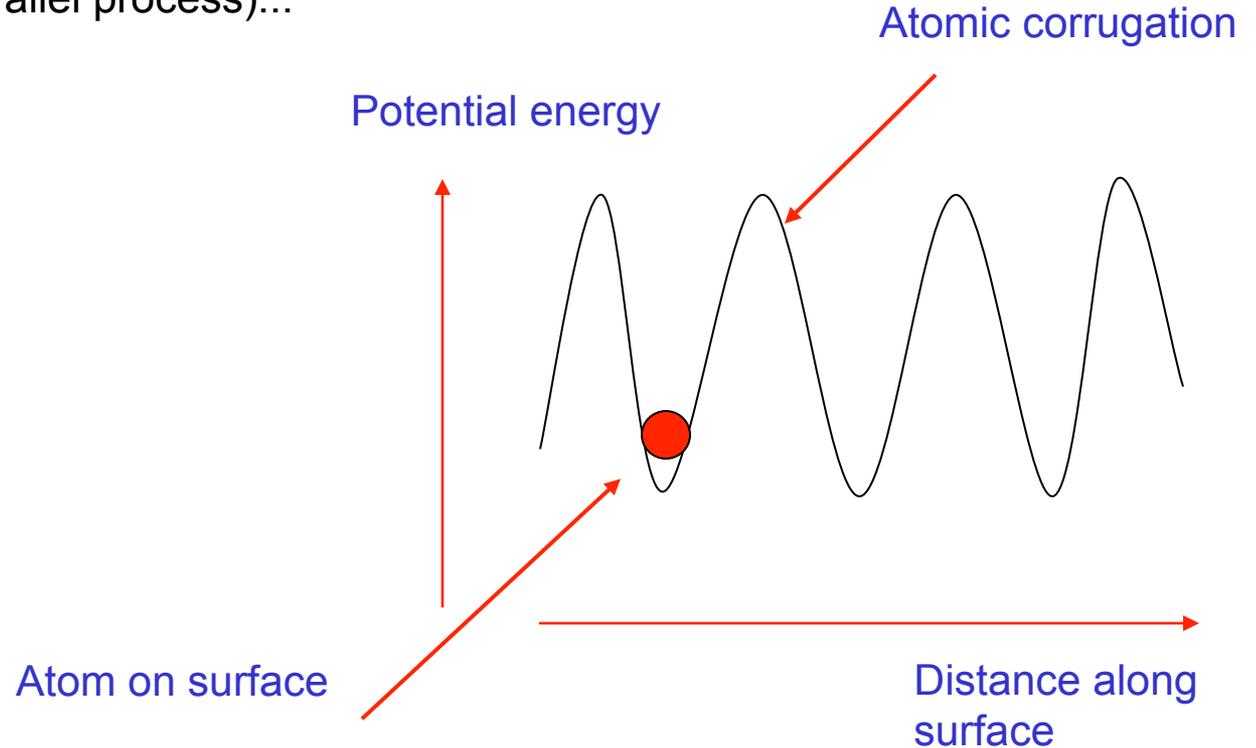
C_{60} on cobalt



B.W. Heinrich
Thesis 2011
Strasbourg

Atomic manipulation with the STM

- The presence of the tip modifies the potential energy of atoms on or near the surface
- Allows movement of individual atoms along the surface (parallel process)...



Atomic manipulation with the STM

The dipolar moment of an atom or a molecule in an electric field is:

$$\vec{p} \approx \vec{\mu} + \alpha \vec{E}$$

μ dipole moment

α polarizability

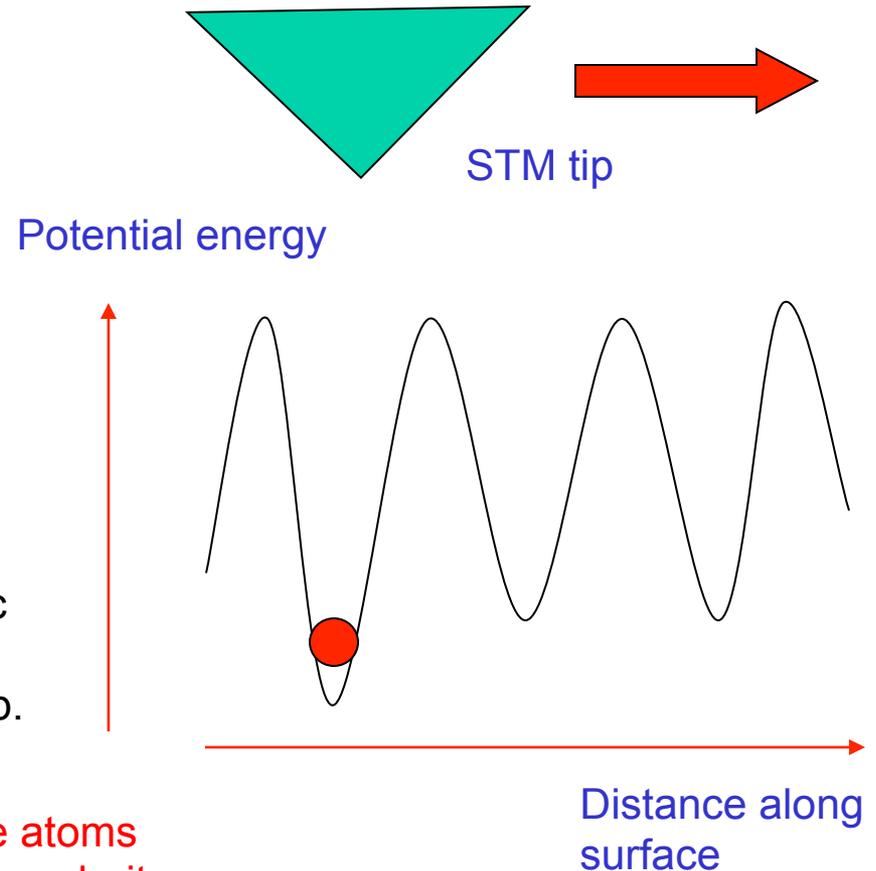
E electric field

The induced polarization energy :

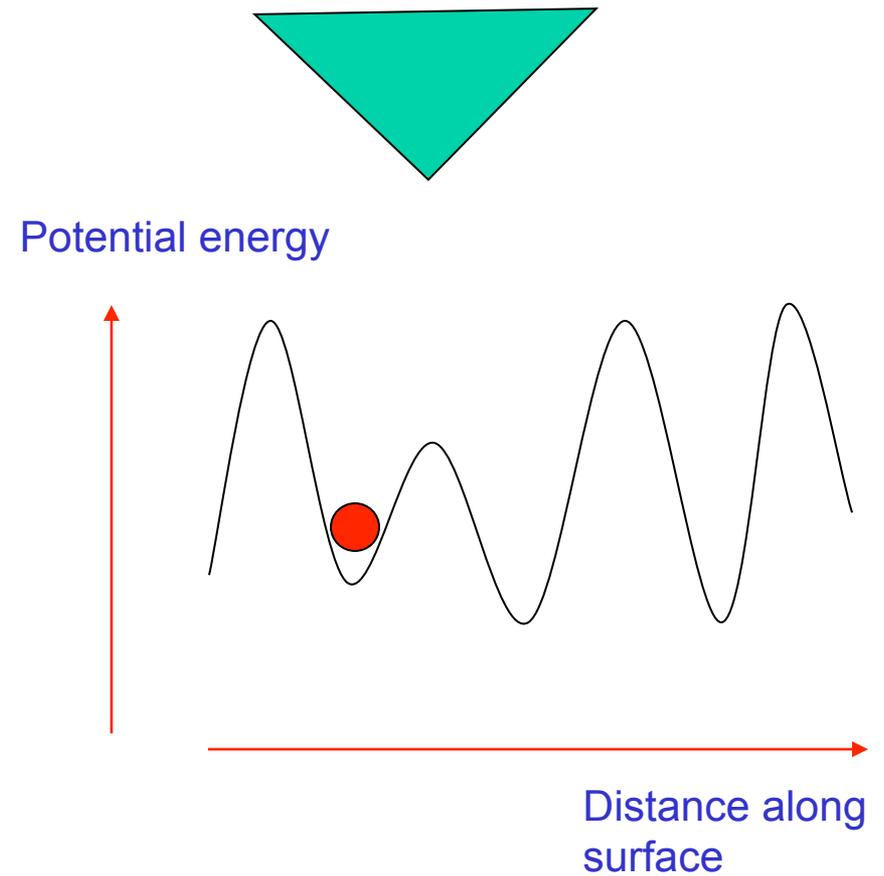
$$E_p(r) = -\vec{\mu} \cdot \vec{E}(r) - \frac{1}{2} \alpha \vec{E}^2(r)$$

When this energy is added to the periodic potential of the surface, a new potential appears that traps the object under the tip.

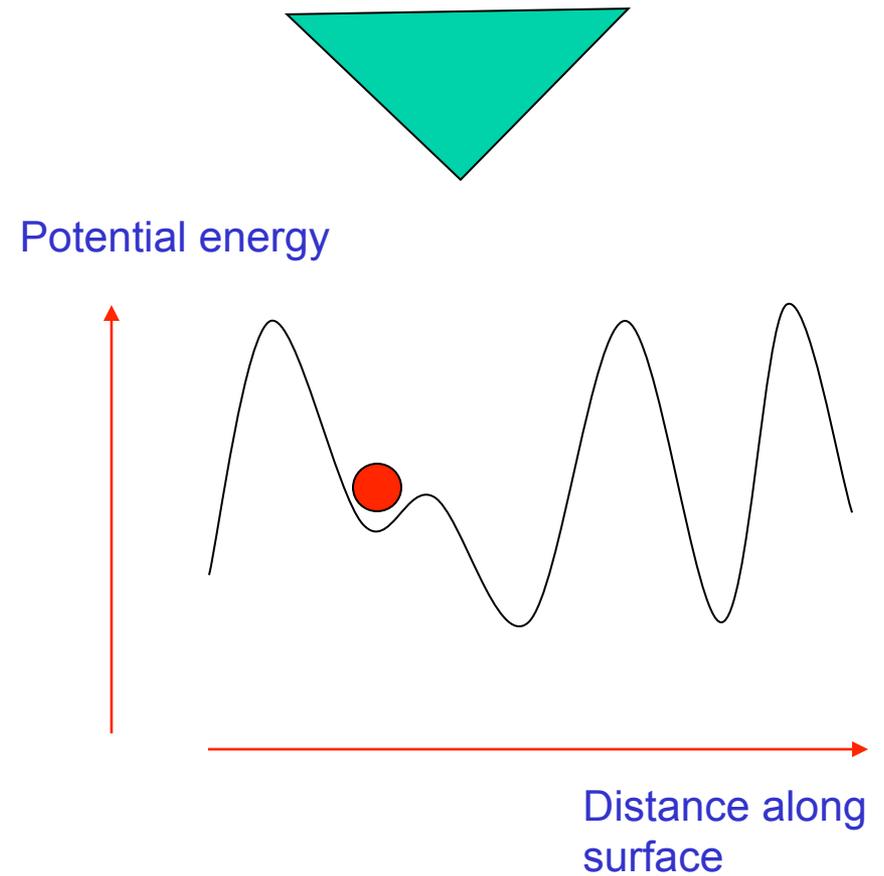
The dominant term is in E^2 for most of the atoms
→ the technique works independent of tip polarity.



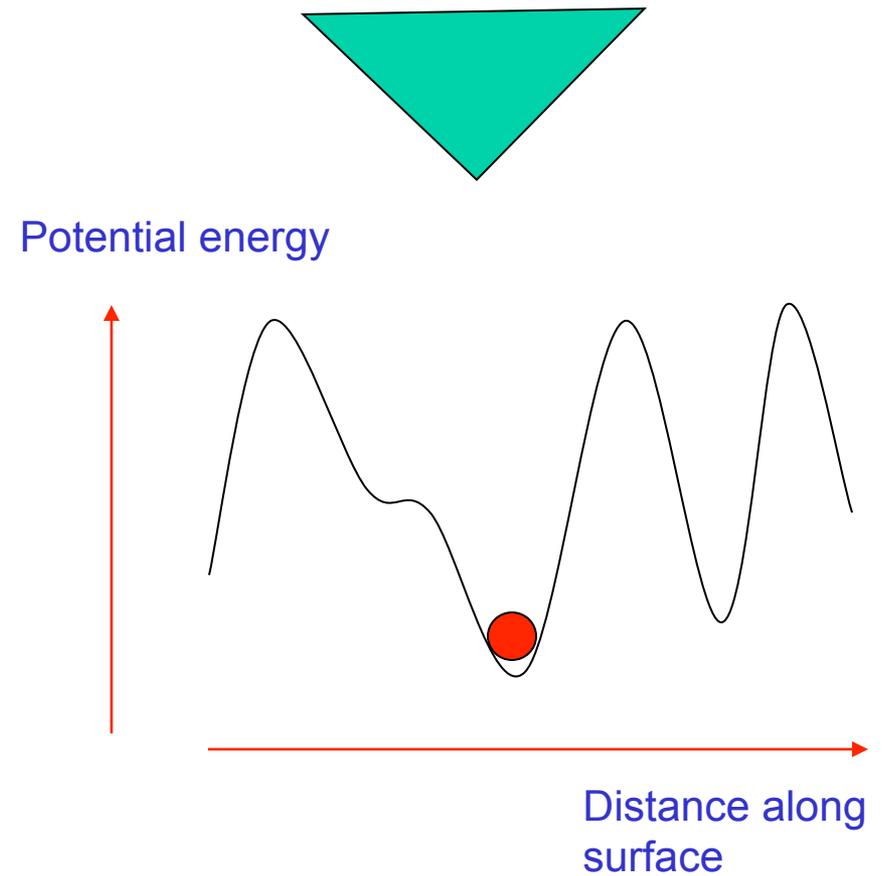
Atomic manipulation with the STM



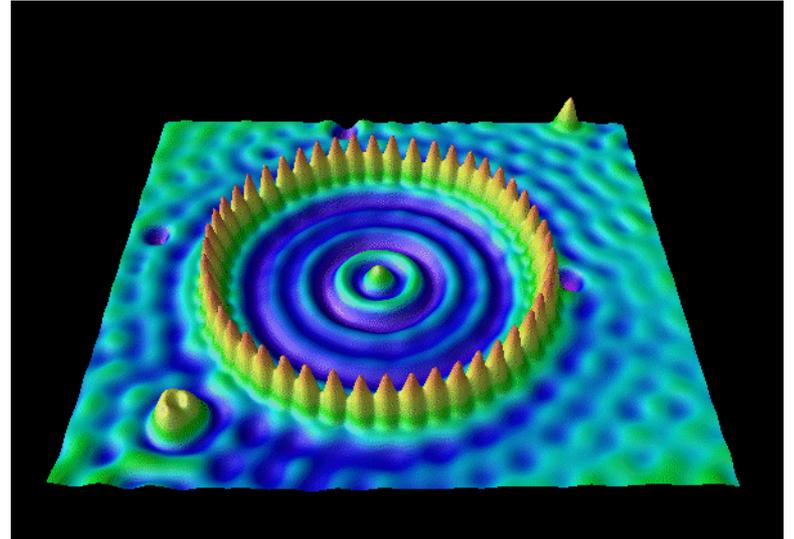
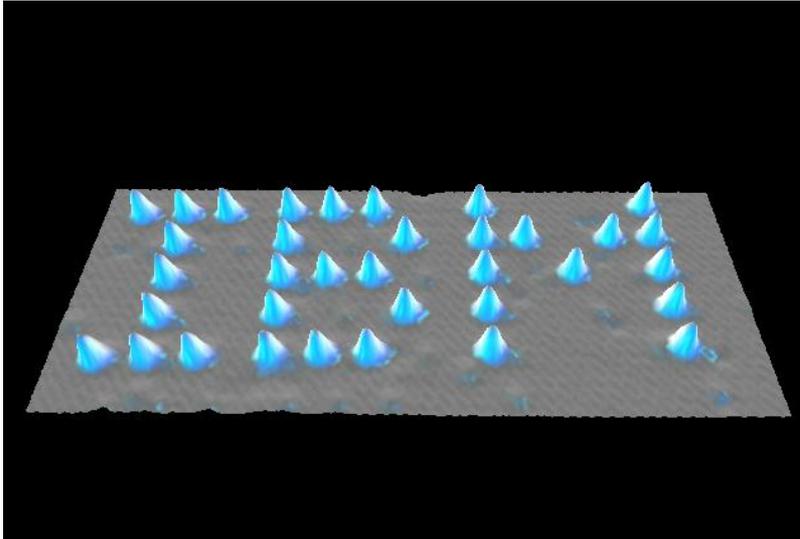
Atomic manipulation with the STM



Atomic manipulation with the STM



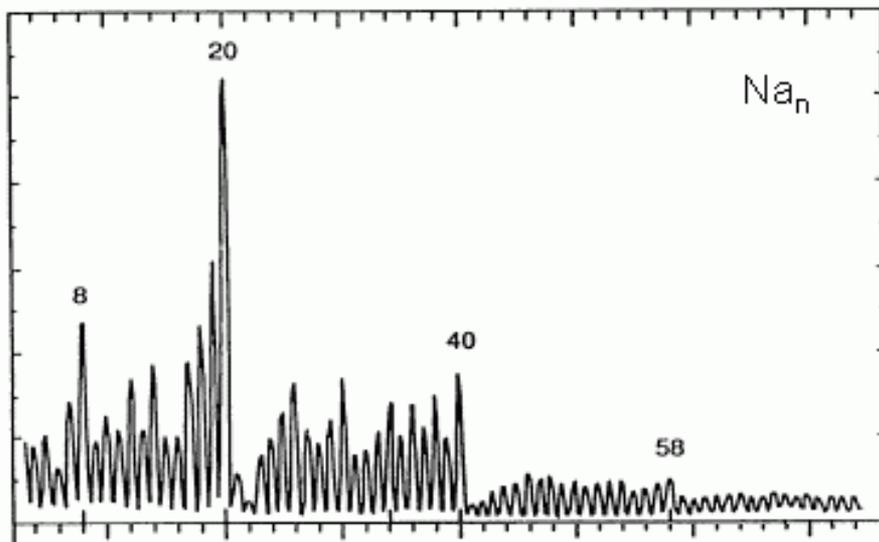
Atomic manipulation: quantum confinement



- Individual Xe atoms manipulated by the parallel process at $T=4\text{K}$. STM tip moves `up' over atoms, showing that electrons tunnel more easily through them than through vacuum
- Fe atoms on the perimeter of a circle on $\text{Cu}(111)$: confinement of surface electrons within the quantum corral. Don Eigler et al (IBM Almaden)

ELECTRONIC PROPERTIES: TWO LIMITS

Electronic shell structure of Na clusters



W.D.Knight et al. Phys.Rev.Lett. 52, 2141 (1984)

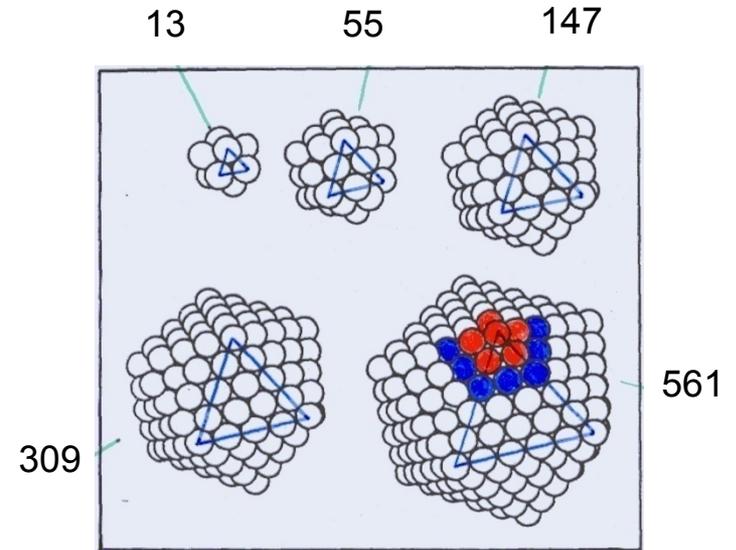
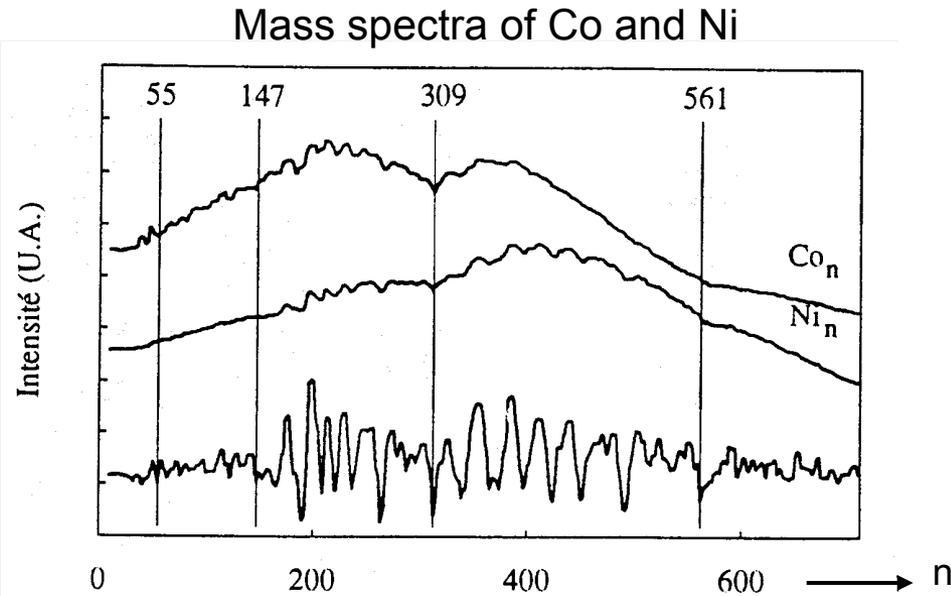
The configurations of the most stable clusters are those that fill an electronic shell :

- Na_8 : $1s^2 1p^6$
- Na_{20} : $1s^2 1p^6 1d^{10} 2s^2$
- Na_{40} : $1s^2 1p^6 1d^{10} 2s^2 1f^{14} 2p^6$
- Na_{58} : $1s^2 1p^6 1d^{10} 2s^2 1f^{14} 2p^6 1g^{18}$

The maxima satisfy the free electron model: one considers a spherical potential where the solutions of the Schrödinger equation for the electrons are given by the angular momenta (as in the atoms). The degenerate states, with the same angular momentum l , but with the different magnetic quantum numbers m ($m = -l, \dots, l$) form one shell.

Electronic shell structure, see also J.L. Martins, R. Car, J. Buttet, Surf. Sci. **106**, 265 (1981)

Atomic shell structure of Co and Ni clusters



M. Pellarin et al. Chem. Phys. Lett. **217**, 349 (1994)

The most stable clusters are those icosahedral clusters that fill an atomic shell :

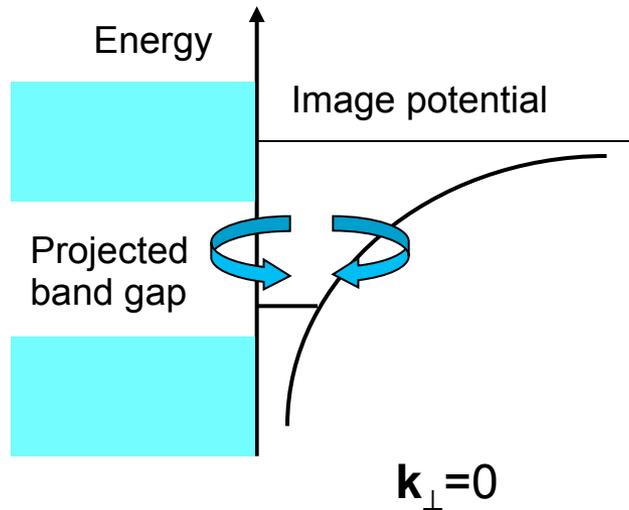
$$N = 1 + \sum_{p=1}^n (10p^2 + 2)$$

2D ELECTRONIC STRUCTURE

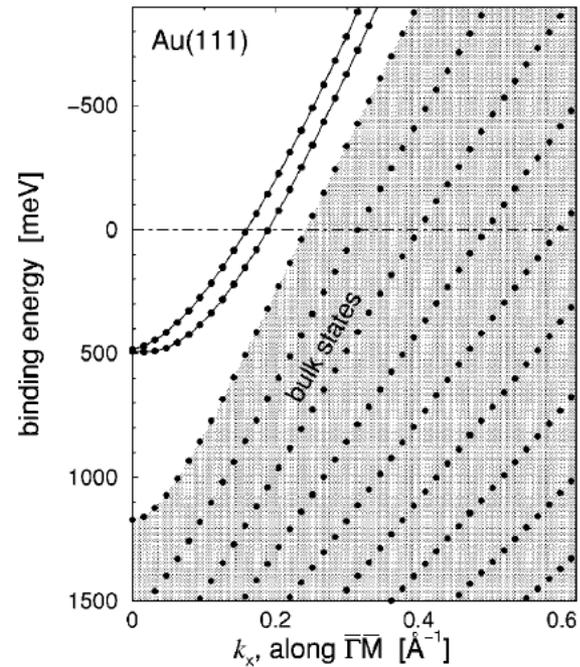
The origin of surface states

The Fermi surface of Cu, Ag and Au has a gap in the states along the $\langle 111 \rangle$ direction

Electrons at the surface cannot enter the surface nor leave to the vacuum



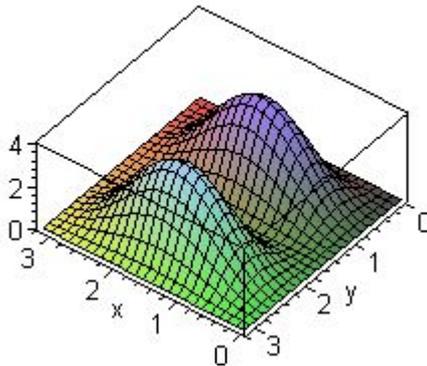
This leads to 2D surface states



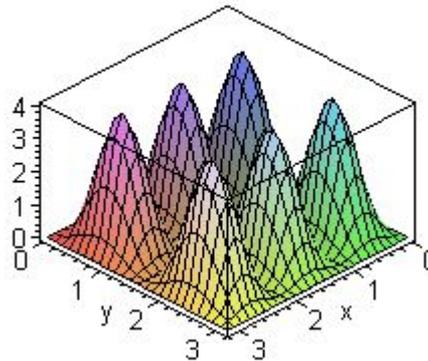
Nicolay et al. Phys. Rev. B **65** (2001)

Confinement of a 2D electron gas

probability density, $j=1, k=2$



probability density, $j=3, k=2$



Probability densities for various stationary states of a particle confined to a finite interval in two dimensions

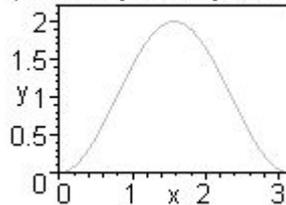
$$E_n = \frac{\pi^2 \hbar^2 n^2}{2ma^2}$$

$$n^2 = n_x^2 + n_y^2$$

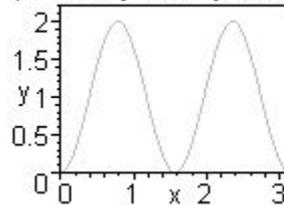
Solutions of 2D Schrödinger equation :

$$-\frac{\hbar^2}{2m} \left(\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} \right) + E_p(x, y)\psi = E\psi$$

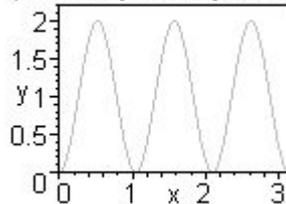
probability density, $n=1$



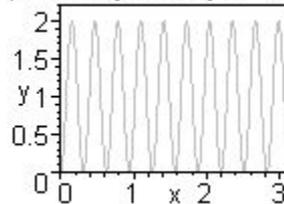
probability density, $n=2$



probability density, $n=3$



probability density, $n=10$



Probability densities for various stationary states of a particle confined to a finite interval in one dimension

DOS for a 2D electron gas

For a 2D gas in a square of side "a" : $E = \frac{h^2}{8ma^2} (n_1^2 + n_2^2)$; $n_1, n_2 > 0$

$n^2 = n_1^2 + n_2^2$ orbital state (new variable)

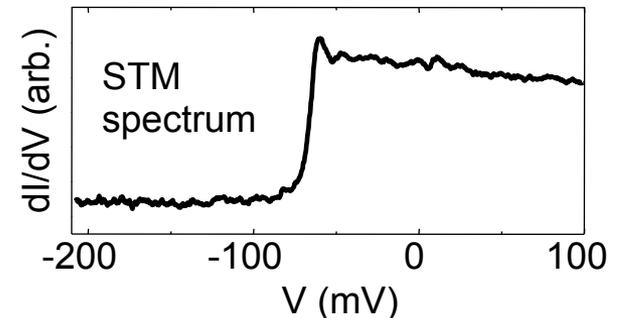
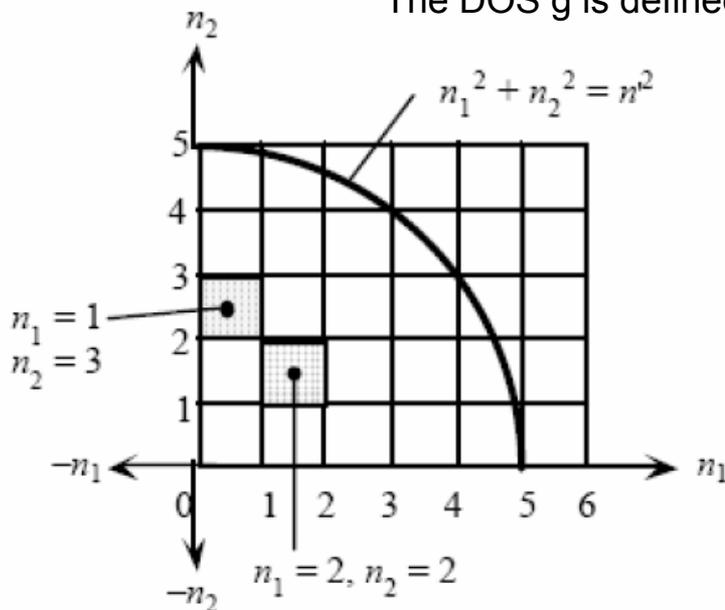
How many states with $E < E'$? E' such that $n < n'$: $n' = \sqrt{\frac{8a^2 m E'}{h^2}}$

Area of the quarter arc is the total number of states for $E < E'$: $S = 2\left(\frac{1}{4} \pi n'^2\right) = \frac{4\pi a^2 m E'}{h^2}$

The DOS g is defined as the number of states per unit area per unit energy:

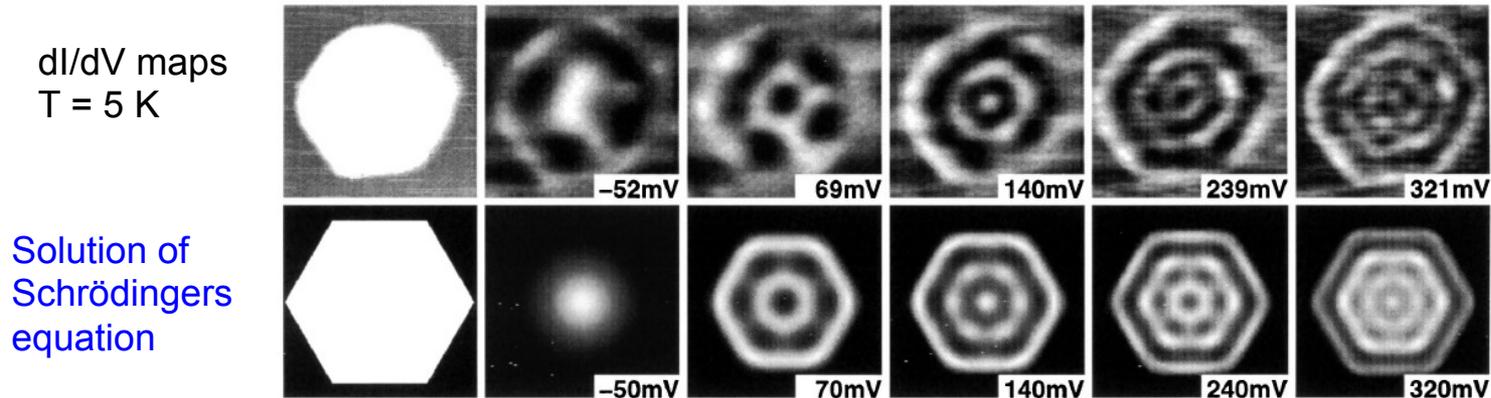
$$g = \frac{1}{a^2} \frac{dS}{dE'} = \frac{4\pi m}{h^2} \quad \text{The DOS is constant !}$$

Surface state
of Ag(111)



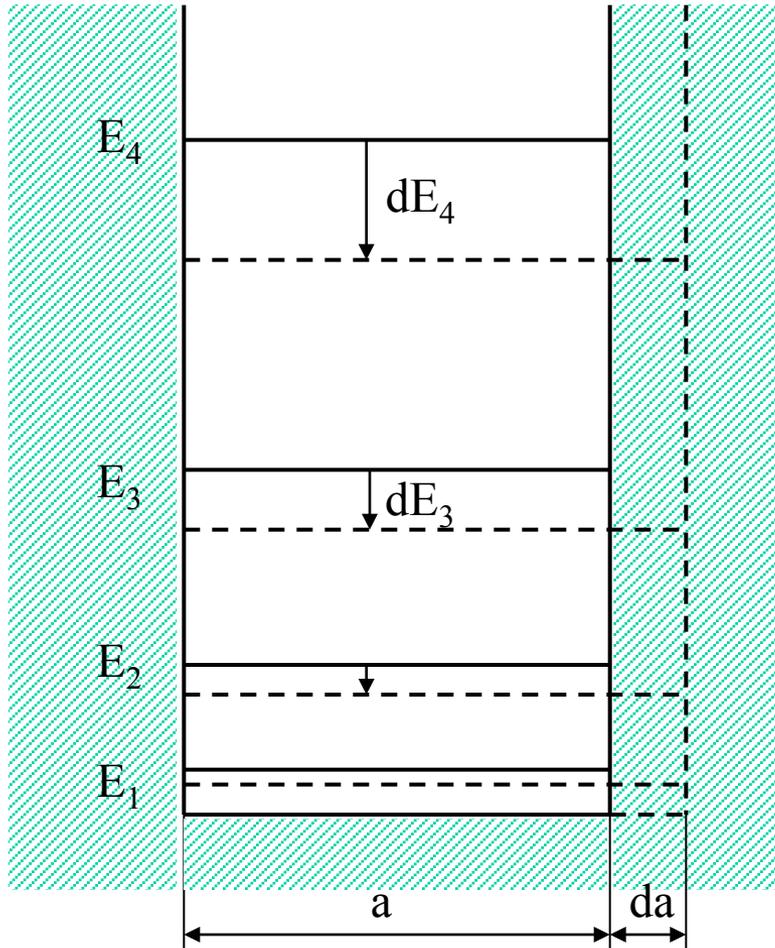
Quantum confinement of surface states in clusters

Ag islands on Ag(111)



- 1) The higher the energy of an electron, the more nodes can be introduced in a given geometry, since the wave length of a standing wave decreases.
- 2) Following a particular mode, for example the fundamental one and increasing the size of the clusters, one decreases the energy of that mode.

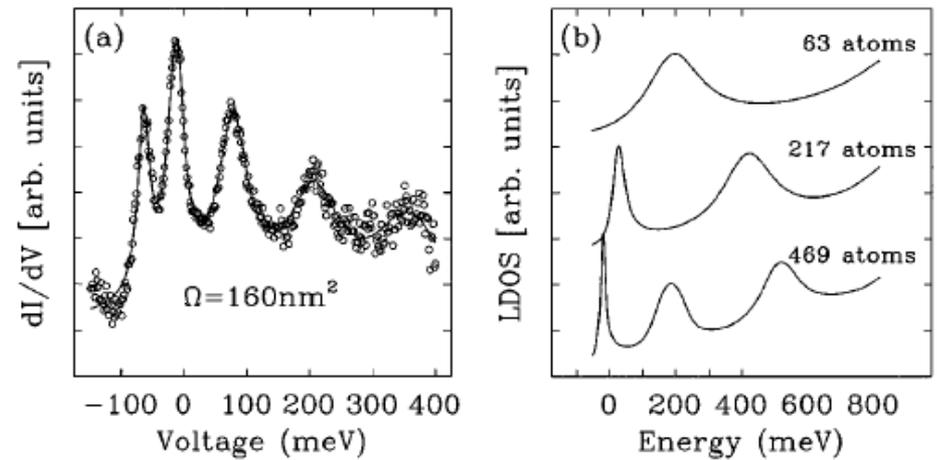
Change the size of the box



$$E_n = \frac{\pi^2 \hbar^2 n^2}{2ma^2}$$

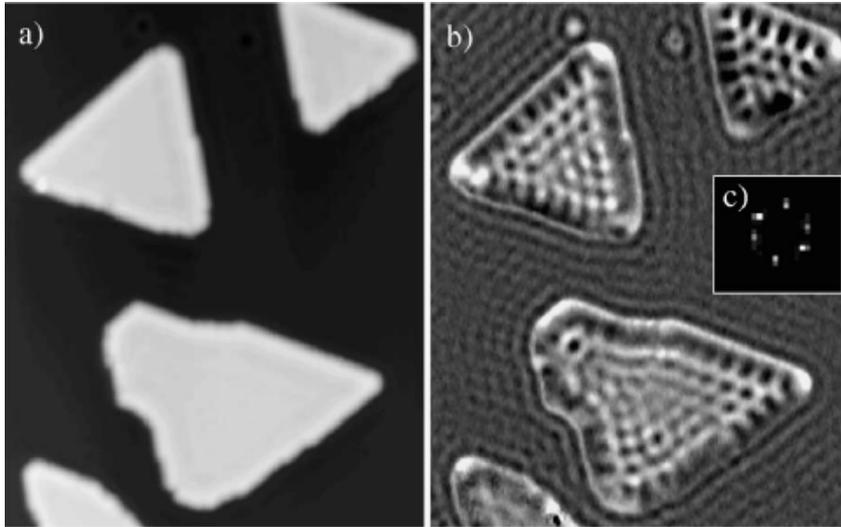
$$n^2 = n_x^2 + n_y^2$$

Energy levels shift to lower energies

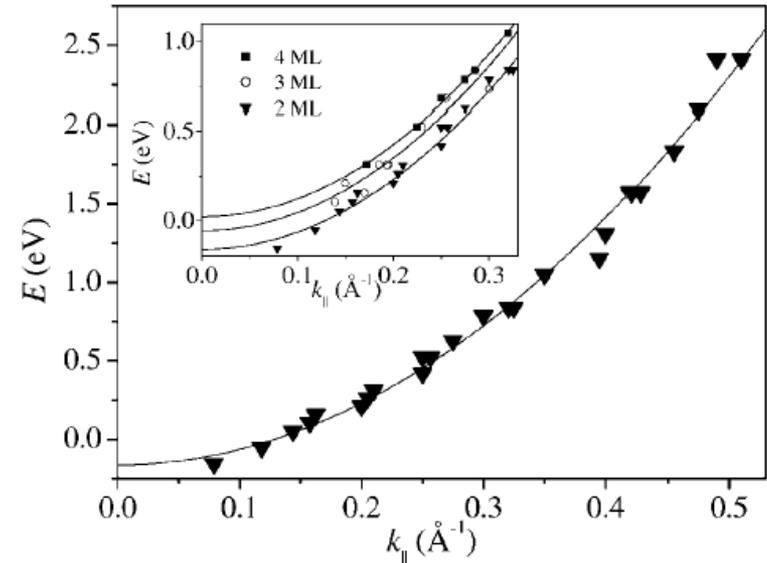


Ag islands on Ag(111)

Surface states in Co islands



- (a) Topographic image and (b) dI/dV maps of Co islands on Cu(111). Bright contrasts correspond to large LDOS. $U=0.5\text{V}$, $I=1.8\text{ nA}$. Images $32\text{ nm} \times 41\text{ nm}$.
- (c) Fourier transform of the standing wave pattern of the cobalt islands [Phys. Rev. Lett. **90**, 236801 (2003)].



Dispersion relation of the electronic states determined from the standing waves of Co islands. The continuous line corresponds to the parabolic fit.

The data points are perfectly reproduced by the parabolic dispersion relation

$$E(k_{\parallel}) = E_0 + \hbar^2 k_{\parallel}^2 / 2m^* \quad \text{with } E_0 = -0.16\text{ eV, effective mass } m^* = 0.38 m_e.$$

THE TIGHT BINDING APPROACH

The Tight Binding model

Solve the Schrödinger equation : $\mathbf{H}\psi_n = E_n \psi_n$

$$\mathbf{H} = T + \sum_{i=1}^N V(\vec{r} - \vec{R}_i) \quad \text{or} \quad \mathbf{H} = T + \sum_i V_i \quad \text{with} \quad T = \frac{\vec{p}^2}{2m_e}$$

Looking for solutions that are combinations of atomic orbitals $\Phi(\vec{r} - \vec{R}_i)$
of energy close to E_n

$$|\psi_n\rangle = \sum_i a_i(E_n) |i\rangle; \quad \langle i | j \rangle = \delta_{ij}$$

$$\rightarrow (T + \sum_j V_j) \sum_i a_i |i\rangle = E_n \sum_i a_i |i\rangle$$

$$T \sum_j a_j |j\rangle + \sum_i V_i a_i |i\rangle + \sum_{i \neq j} V_j a_i |i\rangle = E_n \sum_i a_i |i\rangle$$

Since $|i\rangle$ is an atomic eigenstate we get : $(T + V_i) |i\rangle = E_0^i |i\rangle$

The Tight Binding model (cont)

actually one introduces a pseudopotential $V_i(\vec{r} - \vec{R}_i)$ in order to account for the perturbation of the atomic potential by the other atoms in the crystal:

$$\sum_j E_0^i a_i |i\rangle + \sum_{\substack{i,j \\ i \neq j}} V_j a_i |i\rangle = E_n \sum_i a_i |i\rangle$$

Multiplying by $\langle k |$

$$E_0^k a_k + \sum_{\substack{j \\ j \neq k}} a_k \langle k | V_j | k \rangle + \sum_{\substack{i \\ i \neq j}} a_i \langle k | V_k | i \rangle + \sum_{\substack{i,j \\ i \neq j \\ i \neq k \\ k \neq j}} a_i \langle k | V_j | i \rangle = E_n a_k$$

with: $\beta_{k,i} = \langle k | V_k | i \rangle$; $\alpha_k = \langle k | \sum_{j \neq k} V_j | k \rangle$

Schrödinger: $(E_0^k - E_n) a_k + \alpha_k a_k + \sum_{\substack{i \\ i \neq j}} \beta_{k,i} a_i = 0$

$$a_k (E_0^k - E_n + \alpha_k) + \sum_{\substack{i \\ i \neq k}} \beta_{k,i} a_i = 0$$

The Tight Binding model (cont)

- ◆ The $\beta_{k,i}$ represent the coupling between atoms. In terms of perturbation theory, they express the separation between the eigenstates of the energy. They determine the band width.
- ◆ The α_k express the perturbation of the atomic potentials by the crystal field; they determine the shift of the band with respect to the atomic level.

Local density of states (LDOS):

$$n_i(E) = \sum_{n=1}^N a_i^* a_i \delta(E - E_n); \quad a_i = a_i(E_n)$$

Equivalently:

$$n(\vec{r}, E) = \sum_{n=1}^N \langle \vec{r} | n \rangle \langle n | \vec{r} \rangle \delta(E - E_n)$$

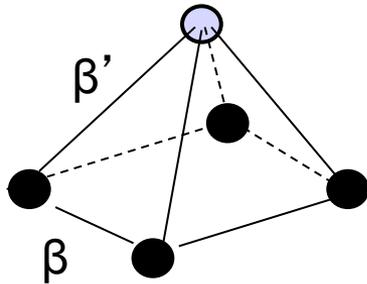
$$H\psi_n = E_n \psi_n \quad n = 1, \dots, N$$

Total density of states (DOS):

$$n(E) = \frac{1}{N} \sum_{n=1}^N \delta(E - E_n)$$

Where $|n\rangle$ are the eigenvectors of the hamiltonian and E_n are the corresponding eigenvalues.

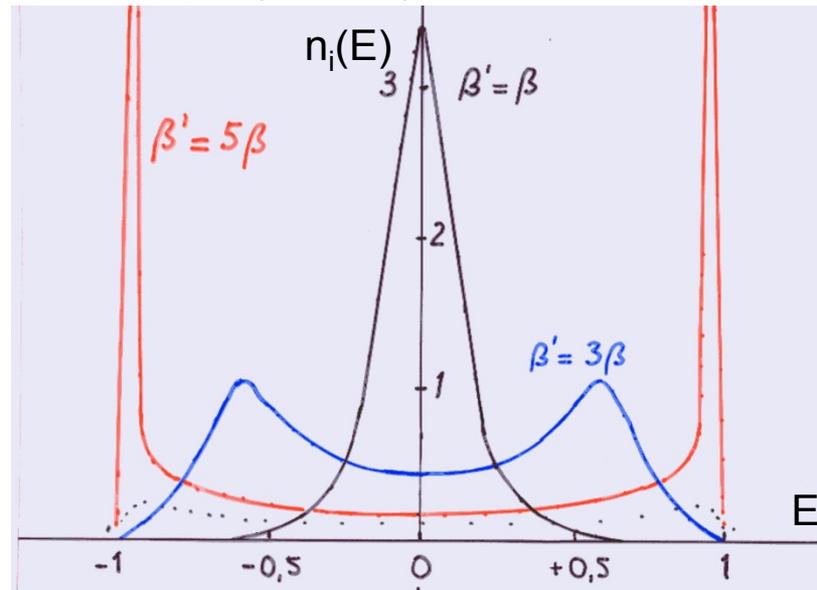
Adsorption on a cubic crystal (100)



Narrow
s-band substrate

β' : coupling between adsorbate and substrate atoms

β : coupling among substrate atoms



$E_a = E_0$

E_a energy of an
atomic state

$\beta' \leq \beta$ **weak coupling** : emergence of a bound level with atomic character, i.e. localized on the adatom

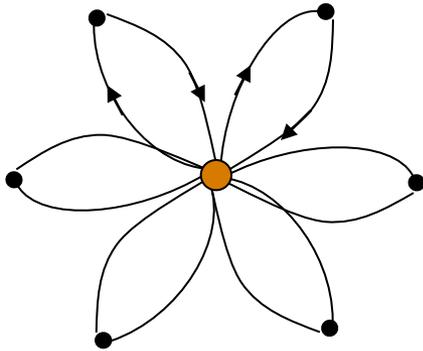
$\beta' \gg \beta$ **strong coupling** : the adatom and its first neighbors form a weakly bound molecule to the rest of the substrate \rightarrow appearance of bound states and anti-bound states of the molecule on the surface.

Moments of the DOS

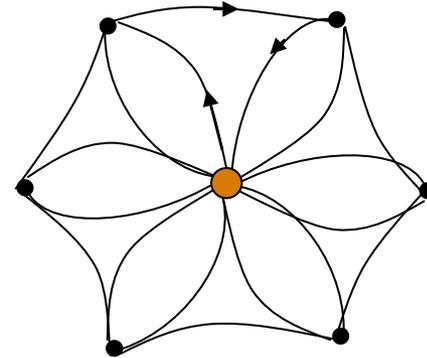
The p'th moment of the DOS

$$\mu_p = \frac{1}{N} \int E^p n(E) dE = \frac{1}{N} \sum_{i,j,k,\dots} \langle i|H|j\rangle \langle j|H|k\rangle \langle k|H|\dots|H|i\rangle$$

← p terms



$$z = 6$$



$$\mu_{2,i} = \int E^2 n(E) dE = z \beta^2$$

Related to the band width

$$\mu_{3,i} = \int E^3 n(E) dE$$

Related to the band assymetry

μ_1 Related to the center of gravity of the band

The rectangular d-band approximation

The DOS of a d-band is calculated as:

$$n(E) = \frac{1}{5N} \sum_i \sum_{n,\lambda} |\langle i\lambda | n \rangle|^2 \delta(E - E_n)$$

$|n\rangle$ Eigenstate of H with eigenvalue E_n
 $|i\lambda\rangle$ Atomic orbital with degeneracy λ

The cohesive energy (d-band):

$$E_{coh} = 10 \int_{-\infty}^{E_F} E n(E) dE$$

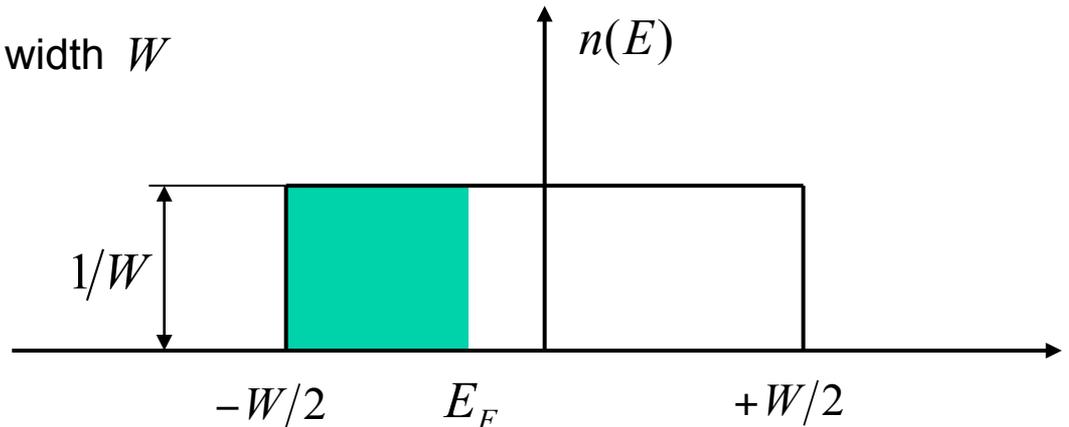
Total number of d-electrons:

$$N_d = 10 \int_{-\infty}^{E_F} n(E) dE$$

The rectangular d-band of width W

$$E_F = \frac{W}{10} (N_d - 5)$$

$$E_{coh} = \frac{W}{20} N_d (N_d - 10)$$

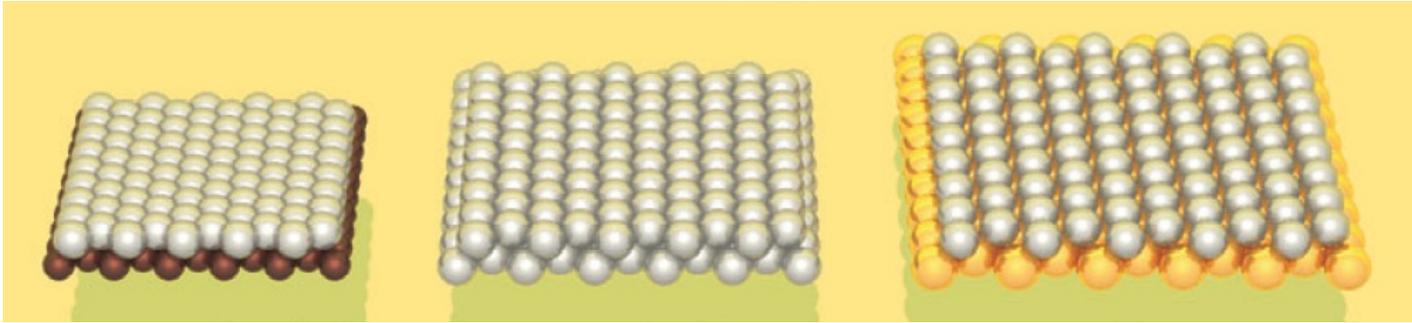


$$E_{coh} \leq 0$$

attractive

$$\mu_2 = \frac{1}{W} \int_{-W/2}^{+W/2} E^2 dE = \frac{W^2}{12} = z \beta^2 \rightarrow W \propto \sqrt{z}$$

Strain and d-band shift

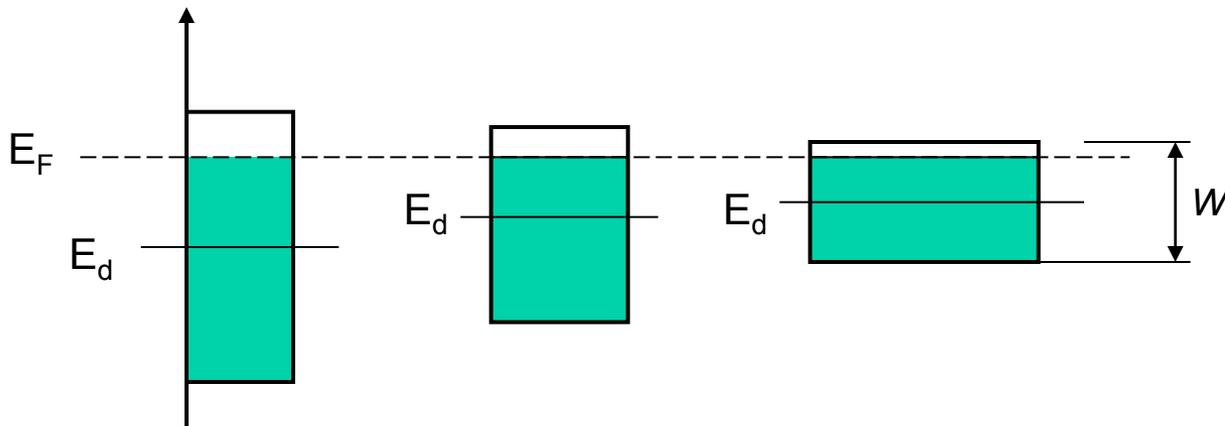


Compressive strain

massive Co

tensile strain

Friedel model → band width : $W(r) = 2\sqrt{3z} |\beta(r)|$ transfer integral: $\beta(r) = \beta_0 e^{-qr}$



Total number of d-electrons: $N_d = 10 \int_{-\infty}^{E_F} n(E) dE = const$

Chemisorption: a simple model

A variety of **experimental techniques** (FIM, STM, LEED, AUGER, XRA, XPS, UPS, EELS, IR...) allow us to derive **systematic trends** for the evolution of physical quantities

1) The bond length increases with the coordination number “z” of the adsorbate:

	Ni(111)	Ni(100)
z	3	4
O-Ni	1.88 Å	1.98 Å
S-Ni	2.02 Å	2.19 Å

- 2) The most stable adsorption site is usually the one with the largest coordination number available on the surface (for an exception, see H on W(100)).
- 3) Only small variation of the binding energy with the crystallographic plane of the surface are observed.
- 4) Systematic trends of the binding energy:
- For 5d adatoms, on W and Ir, one obtains a parabolic variation (maximum in the middle of the series).
 - For a given adsorbate, N, O, H, F, ... the binding energy along a transition series shows a systematic decrease from V to Cu, Nb to Ag and Ta to Au.
- 5) Activation energies for surface diffusion (see for ex. 5d adatom on W) show the same type of behavior than the corresponding binding energies.

See also M.C. Desjonquères, D. Spanjaard “Concepts in Surface Physics” (Springer)

Chemisorption a simple model (the weak coupling limit)

The binding energy of the adatom can be written: $E_B = E_{rep} + E_{band}$

$$E_{band} = \frac{W_a}{2L_a} N_a (N_a - L_a) \quad \begin{array}{l} N_a \text{ is the number of electrons in the valence band of the adsorbate,} \\ L_a \text{ is its degeneracy.} \end{array}$$

$$E_{rep} = zA e^{-pR} \quad A, p = \text{constant};$$

$$\text{Taking } \mu_{2a} = z\beta_a^2 = z\beta_{0a}^2 e^{-qR}$$

$$\Rightarrow E_B(R) = zA e^{-pR} - \sqrt{z} B e^{-qR}$$

The equilibrium distance is obtained for : $\left. \frac{\partial E_B}{\partial R} \right|_{R=R_0} = 0$

$$\Rightarrow R_0 = \frac{1}{2(p-q)} \log z + \frac{1}{(p-q)} \log \frac{pA}{qB}$$

Thus R_0 increases with z

In order to get an energy minimum: $\left. \frac{\partial^2 E_B}{\partial R^2} \right|_{R=R_0} > 0$

and $p(p-q)zAe^{-pR_0} > 0$ Thus $p > q$

Chemisorption a simple model (cont)

If R_0 is substituted into $E_B(R)$ we get the binding energy at equilibrium :

$$E_B(R_0) = \left(\frac{q}{p} - 1\right)B \left(\frac{pA}{qB}\right)^{\frac{-q}{p-q}} z^{\frac{p-2q}{2(p-q)}}$$

therefore $E_B(R_0) \propto z^\alpha$ $\alpha = \frac{p-2q}{2(p-q)}$

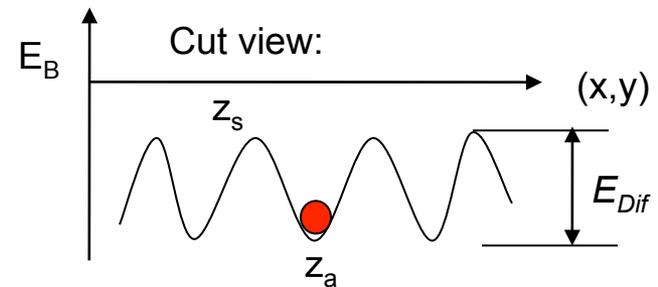
For real systems $p > 2q$, and **the binding energy increases with z** , therefore :

The stable position corresponds to the site with the largest coordination number available on the surface

p/q values from experimental data are comprised between 2 and 4 and $0 < \alpha < 0.33$

Activation energy for surface diffusion:

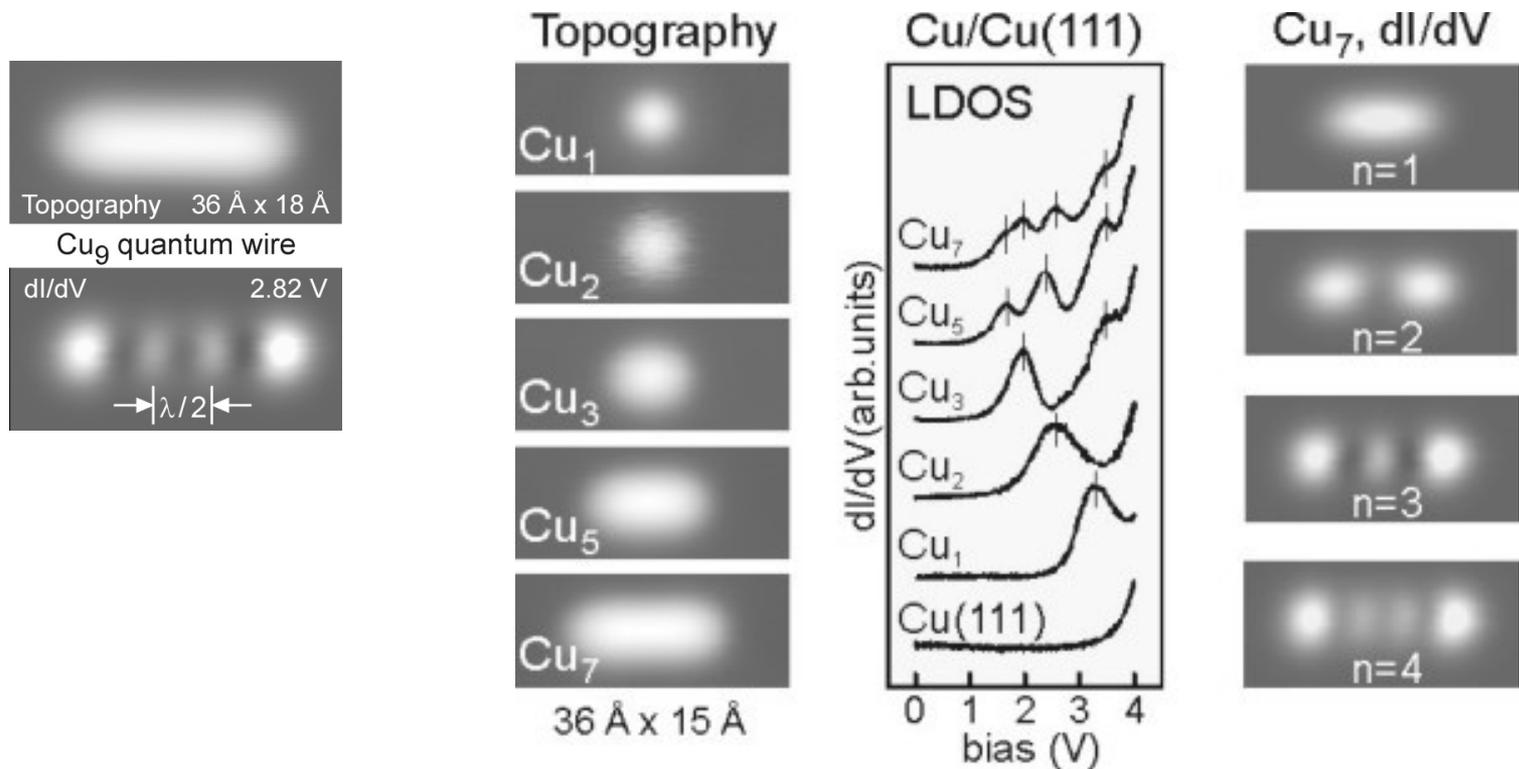
$$E_{Dif} = E_B(z_s) - E_B(z_a) = \left[1 - \left(\frac{z_s}{z_a}\right)^\alpha\right] |E_B(z_a)|$$



Same trend than the binding energy

z_s corresponds to the the saddle point.

The monatomic Cu chain on a surface

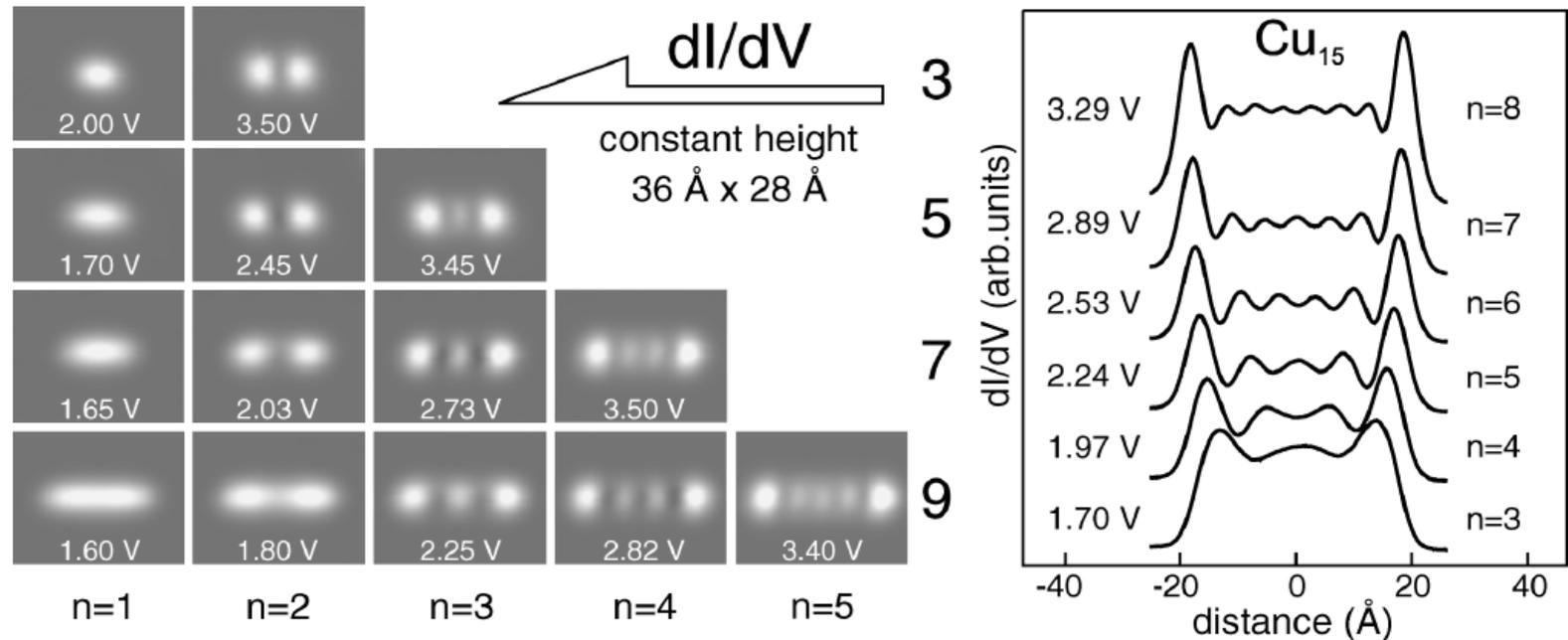


S. Fölsch et al., Phys. Rev. Lett. **92**, 56803 (2004)

Spectroscopy of quantum wires

Starting with a single Cu adatom on Cu(111), monatomic Cu chains can be successively assembled by means of lateral manipulation (left panel). Spectroscopy measurements reveal that these Cu chains represent 1D quantum wells as evident from a series of chain-localized bound states (center panel). The square of the wavefunction of the respective eigenstates (cf. for example dI/dV maps of a Cu_7 chain, right panel) reveal clear quantum wire behavior.

The monatomic Cu chain on a surface

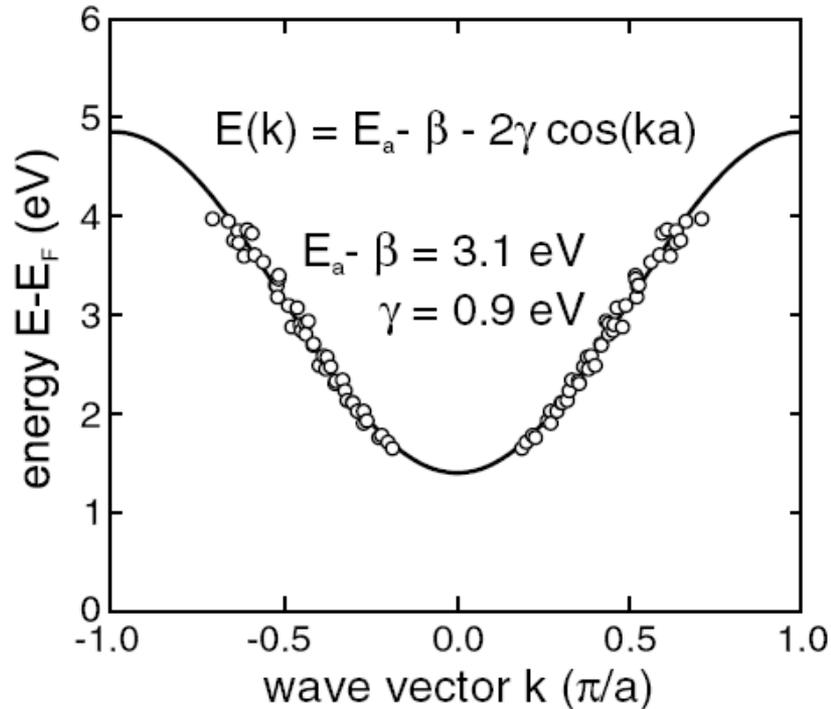


Left panel: dI/dV maps measured at constant tip height showing the square wave function of the chain-localized states (tunneling parameters prior to opening the feedback loop: 1 nA, 1V). Rows from top to bottom correspond to chains of three, five, seven, and nine atoms while columns include eigenstates of fixed order n (n , number of lobes).

Right panel: dI/dV contours measured along a Cu_{15} chain for orders $n=3$ to $n=8$ taken at the same initial tunneling parameters as the dI/dV maps (left).

Dispersion described by a 1D Tight Binding Model

The dispersion relation is fully described within a 1D tight binding approach



Linear combination of atomic orbitals:

$$\psi = \sum_n e^{ikR_n} \Phi(x - R_n) = \sum_n e^{ikna} \Phi(x - na)$$

$\Phi(x - na)$: atomic wave function of an electron in its stationary state, and $n = 1, 2, 3, \dots, N$

The average energy of an electron described by the wave function ψ is:

$$E = \frac{\int \psi^* H \psi dx}{\int \psi^* \psi dx}$$

where
$$H = -\frac{\hbar^2}{2m_e} \frac{d^2}{dx^2} + E_p(x)$$

and $E_p(x)$ is the periodic potential energy of an electron in the lattice

$$E(k) = E_a - \beta - 2\gamma \cos ka$$

where E_a is the energy of an atomic state associated with the wave function $\Phi(x - na)$