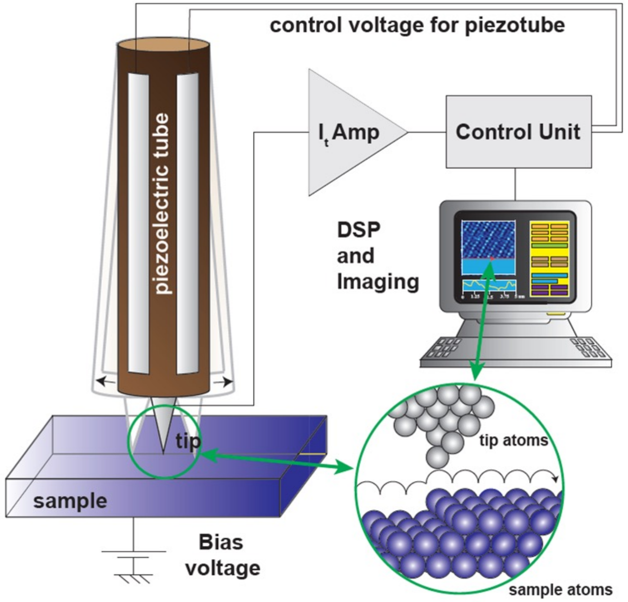
STM: a multitask tool for nanoscience



Atomically resolved

Topography → shape

Spectroscopy → electronic properties

- electronics
- spintronics
- chemistry

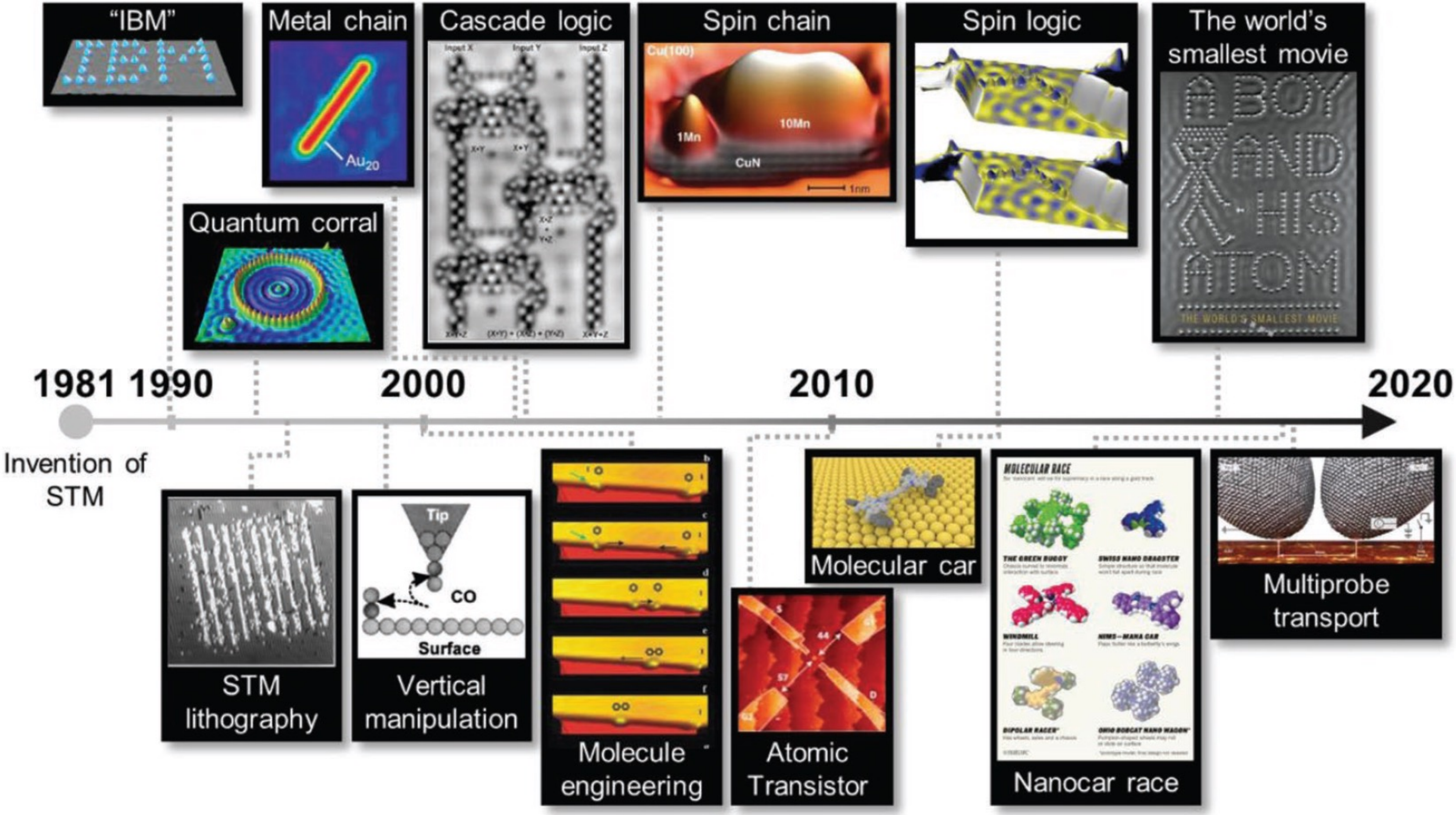
Manipulation →

- atom-by-atom assembly
- defect creation
- charging
- dissociation

....

Perfect tool to investigate the nanoworld

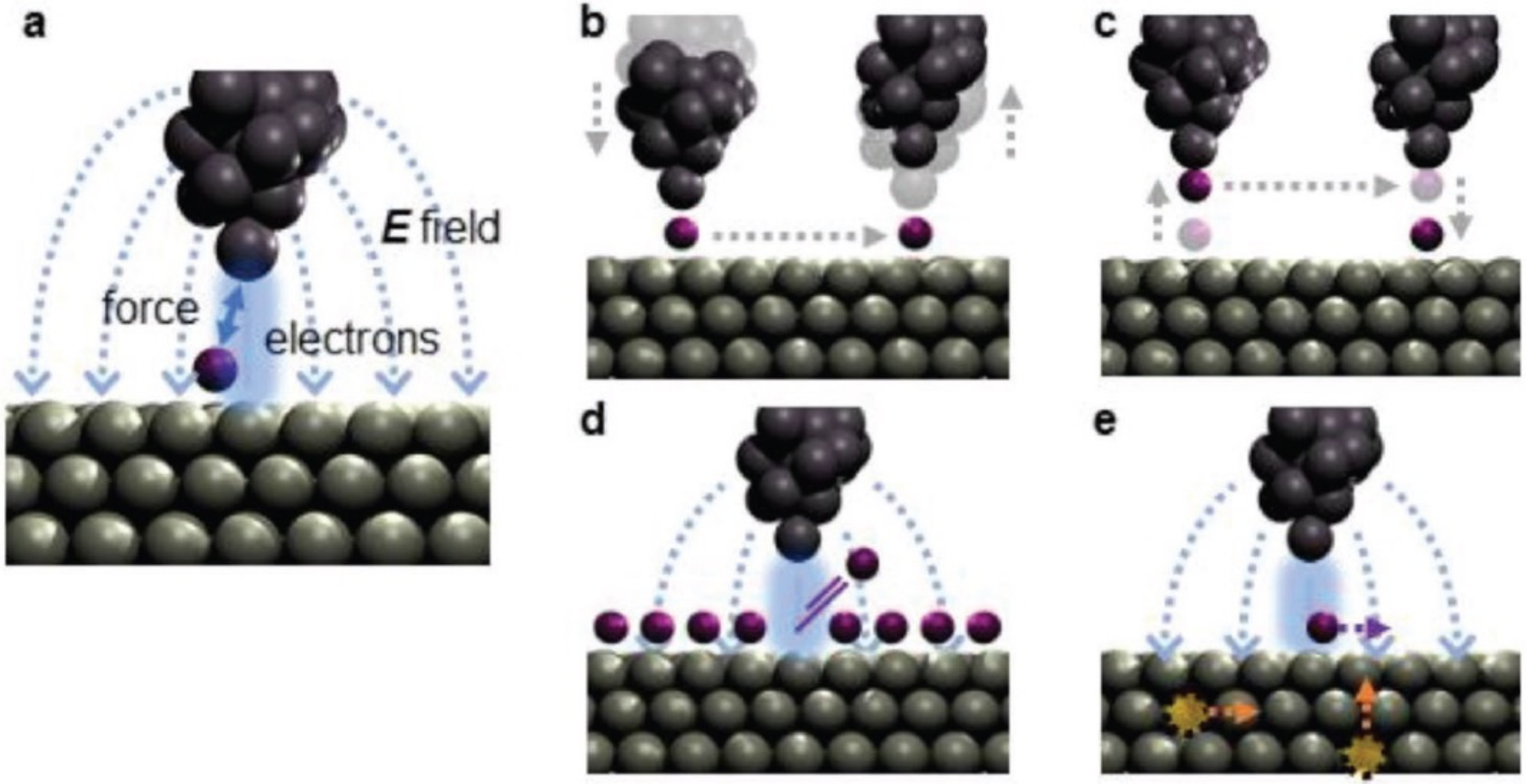
Atomic-scale manipulation



Ko et al., Adv. Funct. Mater. **29**, 1903770 (2019)

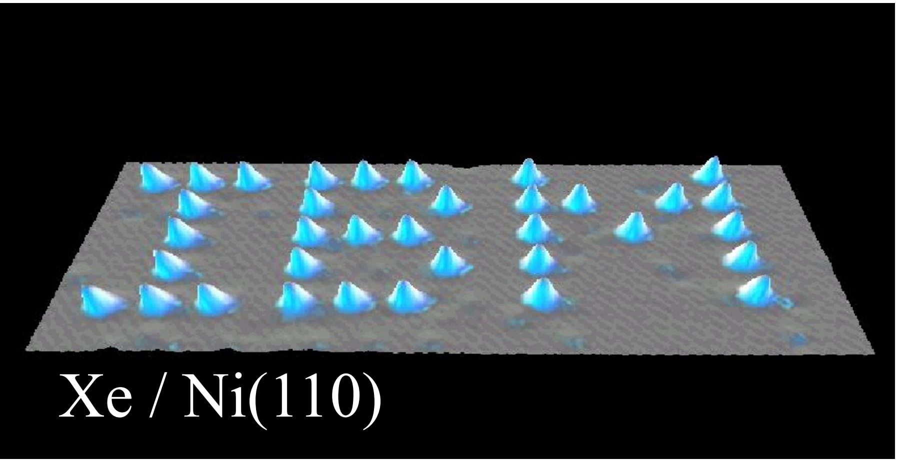
Atomic-scale manipulation

lateral manipulation   vertical manipulation



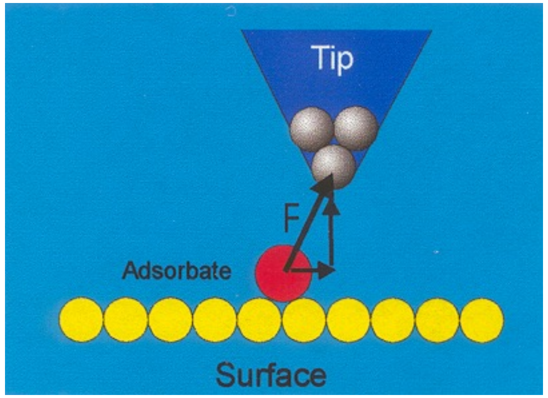
Ko et al., Adv. Funct. Mater. **29**, 1903770 (2019)

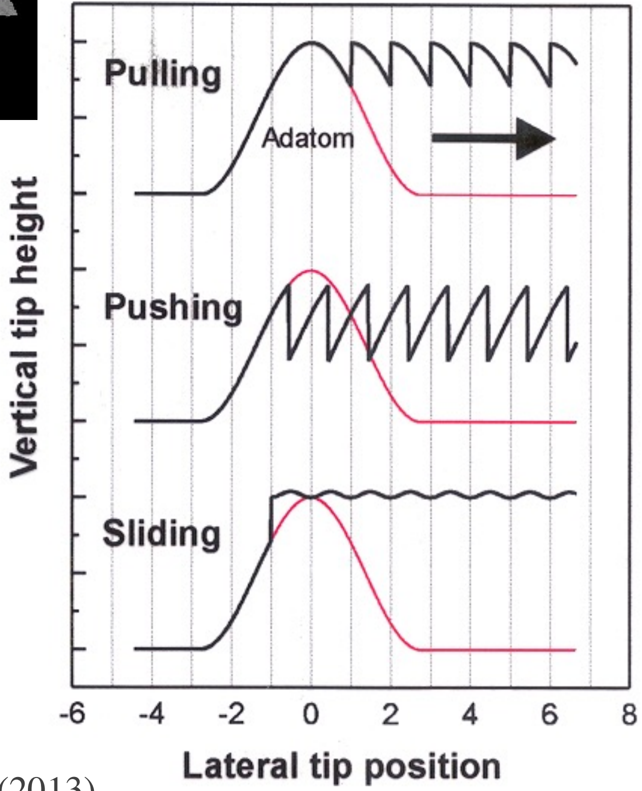
Lateral manipulation



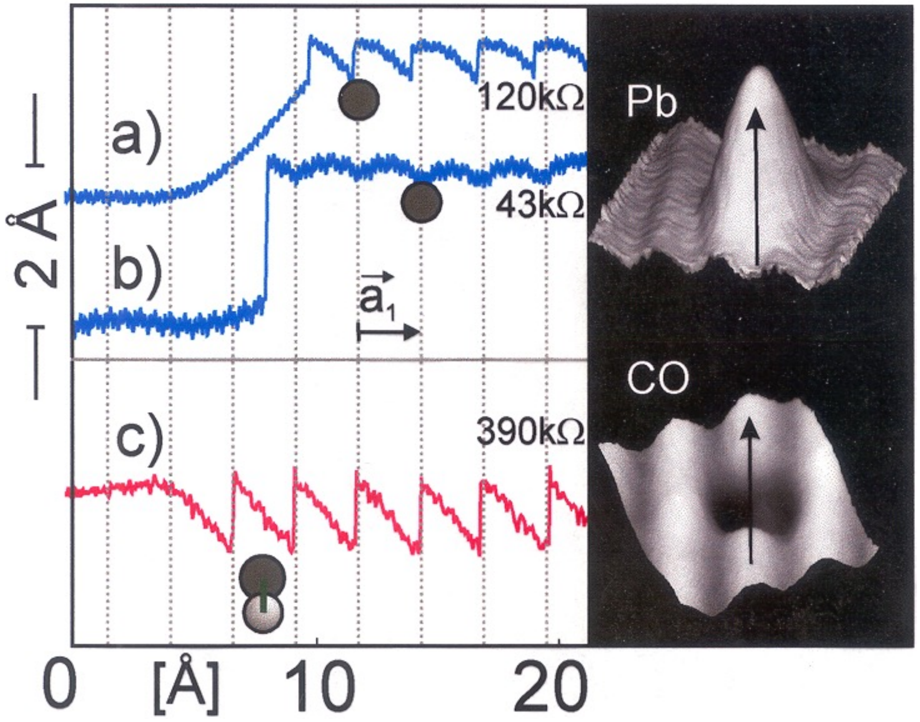
D. Eigler & E. Schweizer,
Nature **344**, 524 (1990)

Model:





Experiment:



The tip is approached close to the adsorbate by reducing the tunneling resistance and then, at constant tunneling current, moves parallel to the surface, with the atom following the tip.
The steps in the tip height clearly indicate a discontinuous movement of the atom, meaning the atom is jumping from one adsorption site to the next.

G. Meyer *et al.,* Applied Physics A **68**, 125 (1999)

K. Morgenstern et al., Phys. Status Solidi B **250**, 1671 (2013)

Building 1D chains

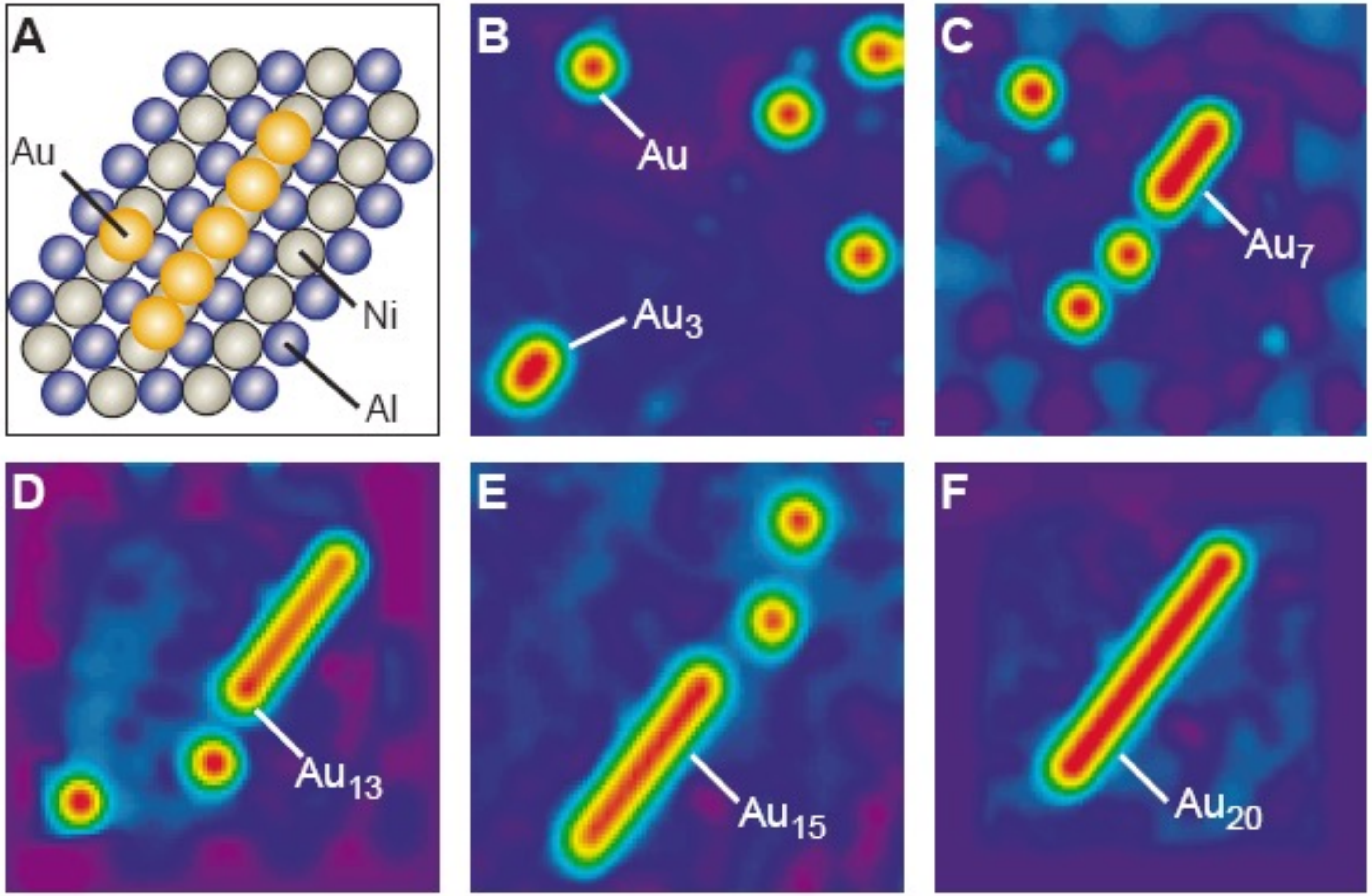
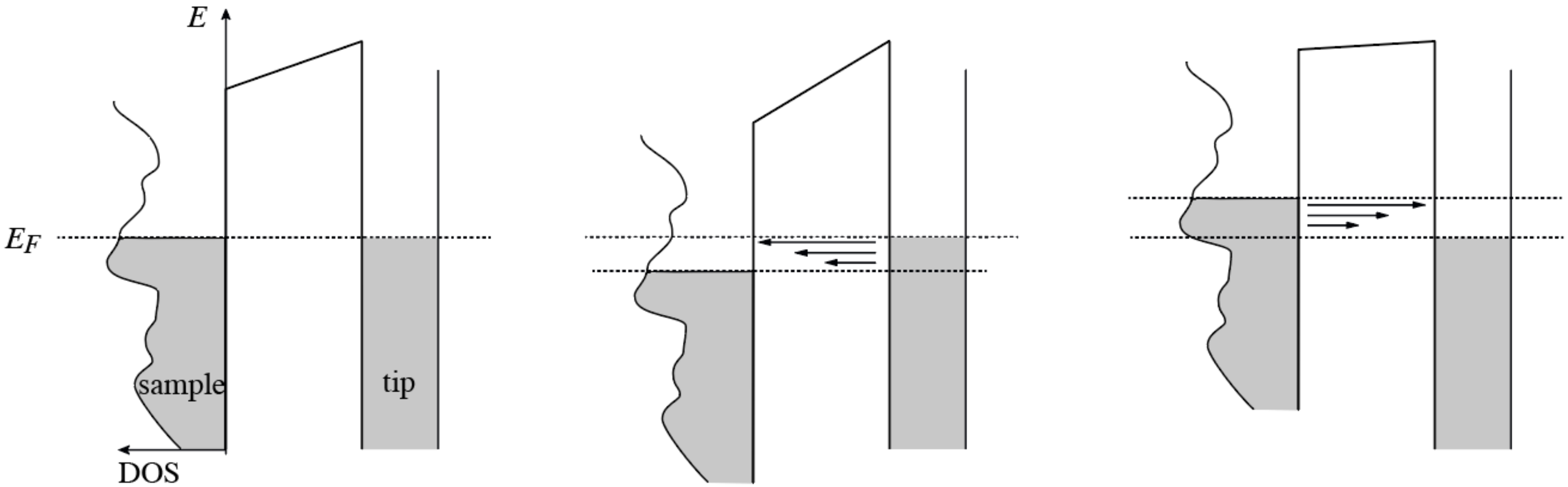


Fig. 1. (**A**) Structure model of a Au$_5$ chain and a Au atom on NiAl(110). (**B** to **F**) STM topographic images showing intermediate stages of building a Au$_{20}$ chain. Single Au atoms were manipulated with the STM tip and attached on both sides to the chain (image sizes 95 Å by 95 Å, V_{sample} = 2.1 V, I = 1 nA).

Nilius et al., Science **297**, 1853 (2002).

STS: Scanning Tunneling Spectroscopy



$k_BT \ll eV$

Focussing on the sample DOS ρ_s
Assuming ρ_t constant
Assuming $|M|^2$ constant

For positive sample bias, electrons tunnel from tip to sample, the current is proportional to the integral of the unoccupied sample states between E_F and $E_F + eV$

For negative sample bias, electrons tunnel from the sample to the tip, the current is proportional to the integral of the occupied sample states between $E_F - |eV|$ and E_F

Taking $E_F = 0$ V as reference:

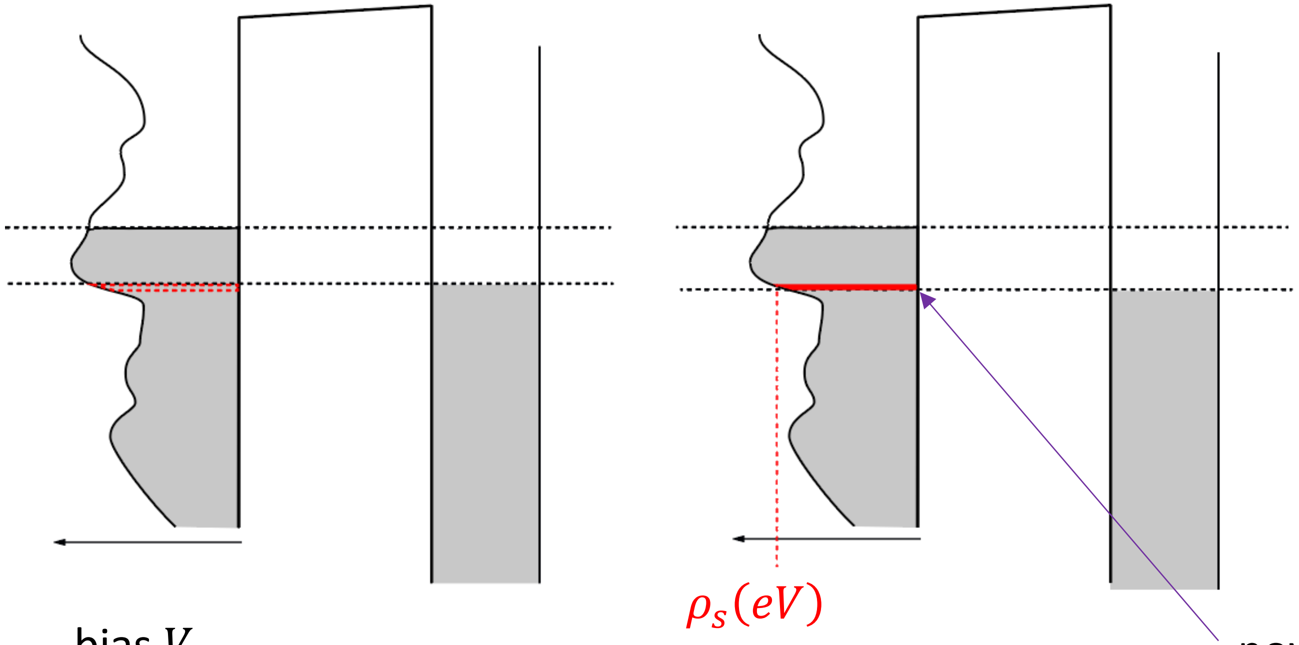
$$I \propto \int_0^{eV} \rho_s(\varepsilon)\,\rho_t(E_F)|M|^2 d\varepsilon \propto \int_0^{eV} \rho_s(\varepsilon)\,d\varepsilon$$

$$I \propto \int_{-|eV|}^{0} \rho_s(\varepsilon)\,\rho_t(E_F)|M|^2 d\varepsilon \propto \int_{-|eV|}^{0} \rho_s(\varepsilon)\,d\varepsilon$$

STS: Scanning Tunneling Spectroscopy

$$\frac{dI}{dV} \propto \frac{d}{dV}\ \rho_t \int_0^{eV} \rho_s(\varepsilon)\, d\varepsilon \rightarrow \qquad \frac{dI}{dV} \propto \rho_t\ \rho_s(eV)$$

The variation of the tunneling current upon a variation dV of the applied bias is proportional to DOS at the energy corresponding to the bias voltage V (with $E_F = 0$ eV as reference)



$\rho_s(eV)$

bias V

bias $V + dV$

now also these
states contribute to
the current

STS: Scanning Tunneling Spectroscopy

$$\frac{dI}{dV} \propto \rho_t \ \ \rho_s \ (eV)$$

Experimentally:
acquisition technique: small ac-modulation voltage added to V bias, lock-in acquisition, provides directly dI/dV

- dI/dV point spectra: typically with the feedback loop open (constant distance), acquired as a function of the tunneling bias V

- dI/dV mapping → LDOS variation in space

assumptions/conditions:
the density of states of the tip is fairly constant in the chosen voltage range;
small modulation voltages

Electronic properties of nano-objects

Atoms

- Discrete energy levels
- Electrons localized at the atom site

Bulk

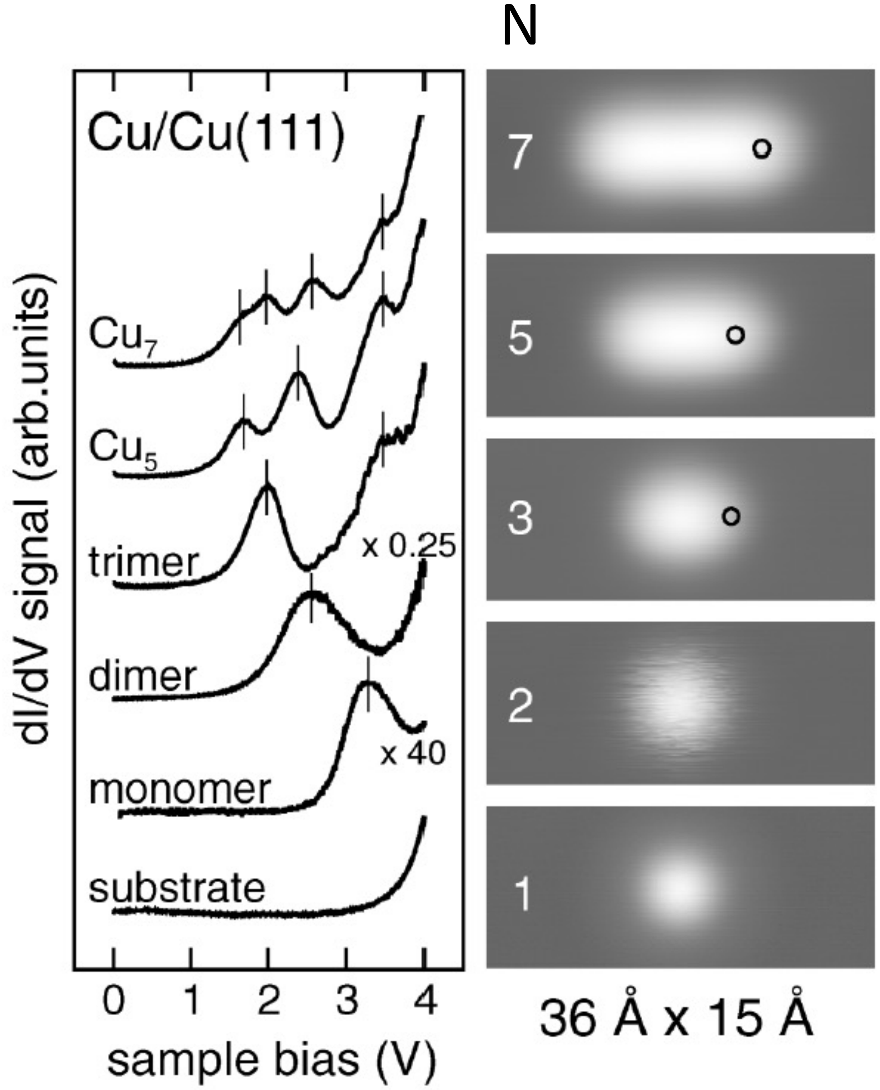
- Continuous energy levels (bands)
- Electrons delocalized

How the electronic properties change
when going from atoms to bulk ?

Where is the frontier ?

Can STM and STS help find an answer?

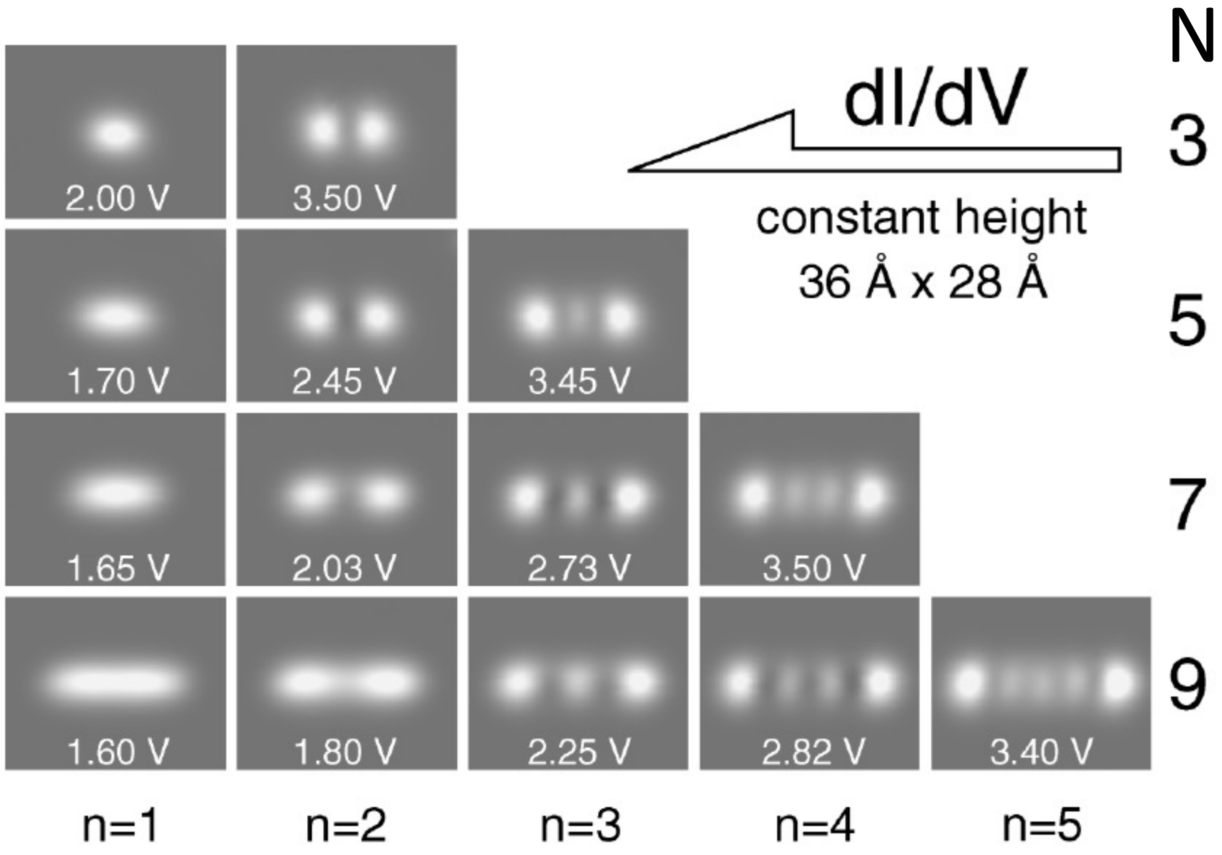
1D chain of Cu atoms

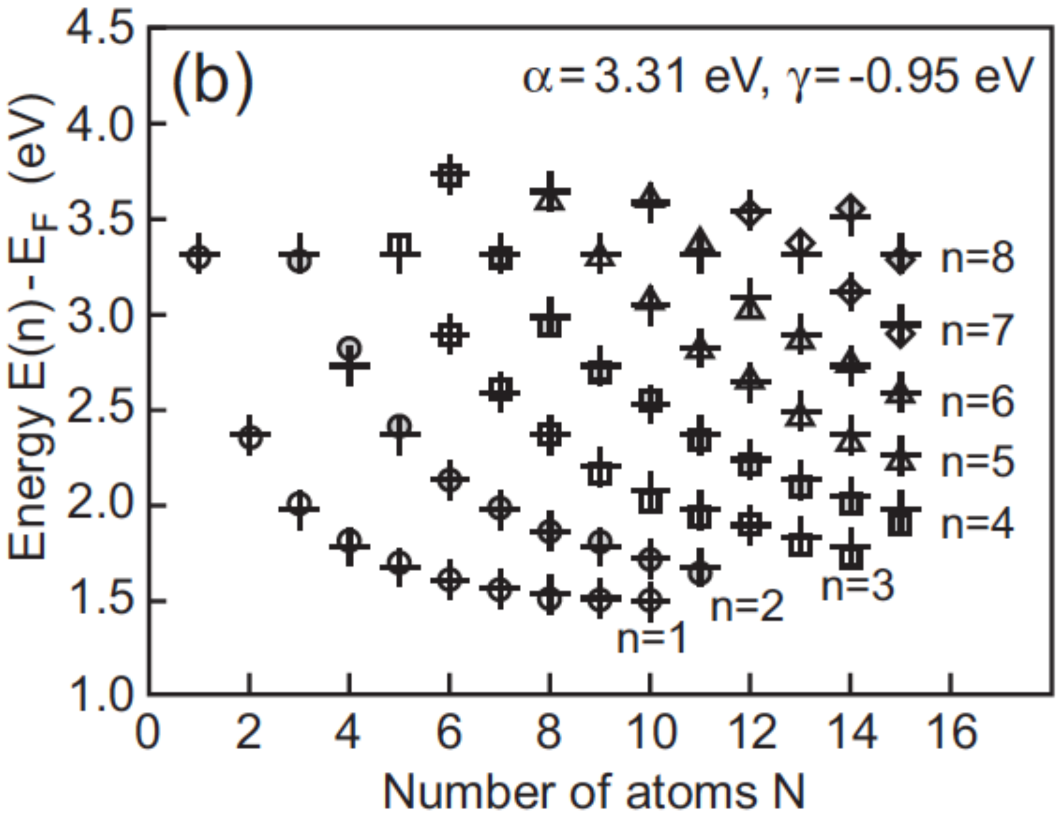


Cu adatom:
wavefunction (state) ψ of s nature

S. Fölsch et al., Phys. Rev. Lett. **92**, 056803 (2004)

1D chain of Cu atoms





The dI/dV maps show increasing number of nodes for increasing n:
n=1 → 0 nodes
n=2 → 1 node
n=3 → 2 nodes
...

For a given n, the energy decreases for increasing length

S. Fölsch et al., Phys. Rev. Lett. **92**, 056803 (2004)
J. Lagoute et al., Phys. Rev. B **74**, 125410 (2006)

Does a band structure develop in these 1D chains?

Electrons in solids are delocalized (band structure): *E(k)*

Is it possible to derive the band structure of the 1D chains?

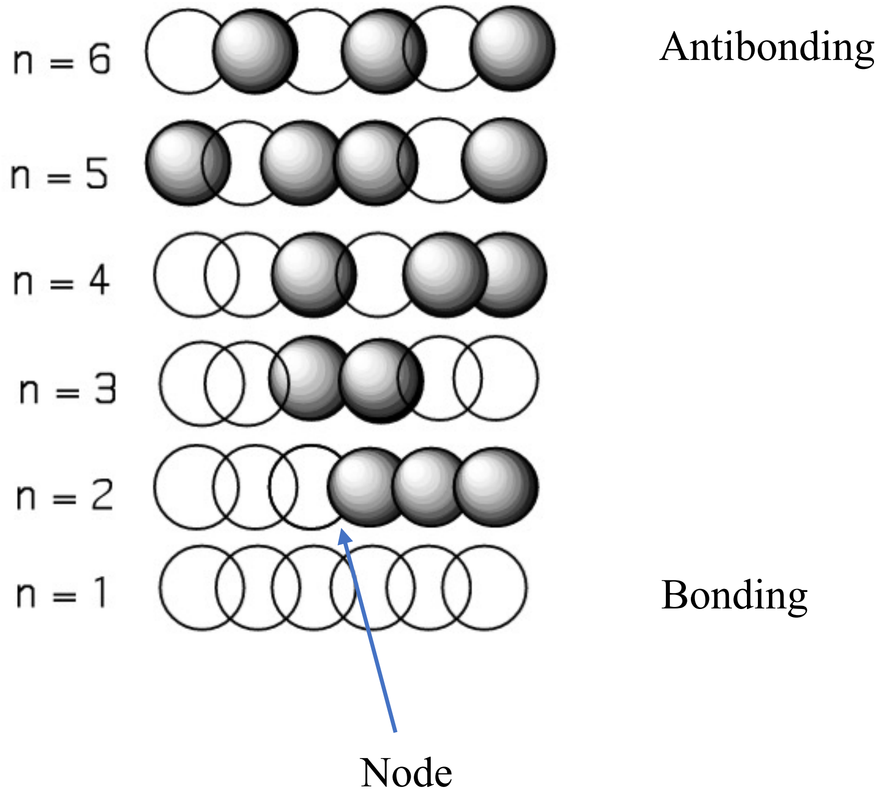
We need to link $E(n)$ to k-vector

- wavefunctions have positive and negative amplitudes (phase)
- bonding results from wavefunctions of the same sign
- nodes result from wavefunctions of adjacent atoms of opposite sign
- a periodicity (wavelength) can be deduced from the images

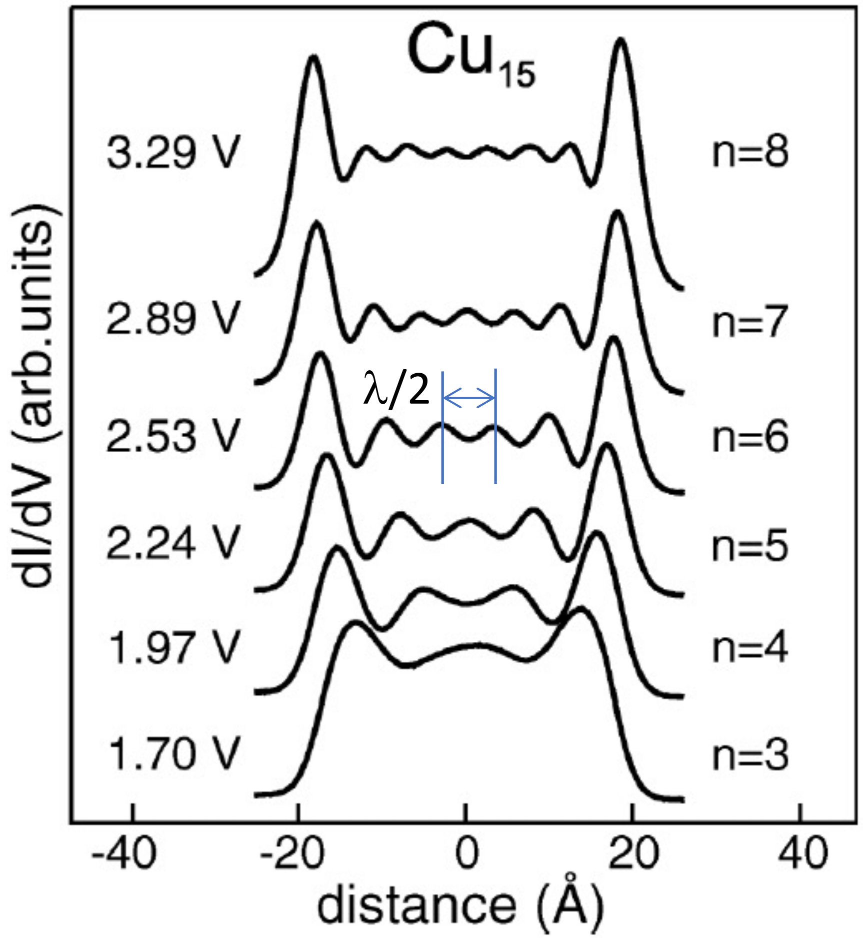
- STM/STS measures the LDOS: $\rho(x) \propto |\psi(x)|^2$
- consequently in STM / STS we see $\lambda/2$

- link wavelength λ to wavevector k : $k = 2\pi/\lambda$
- then plot $E(k)$ vs k

Example with (6 atoms, 1 orbital per atom):



1D chain of Cu atoms



deduce k from λ

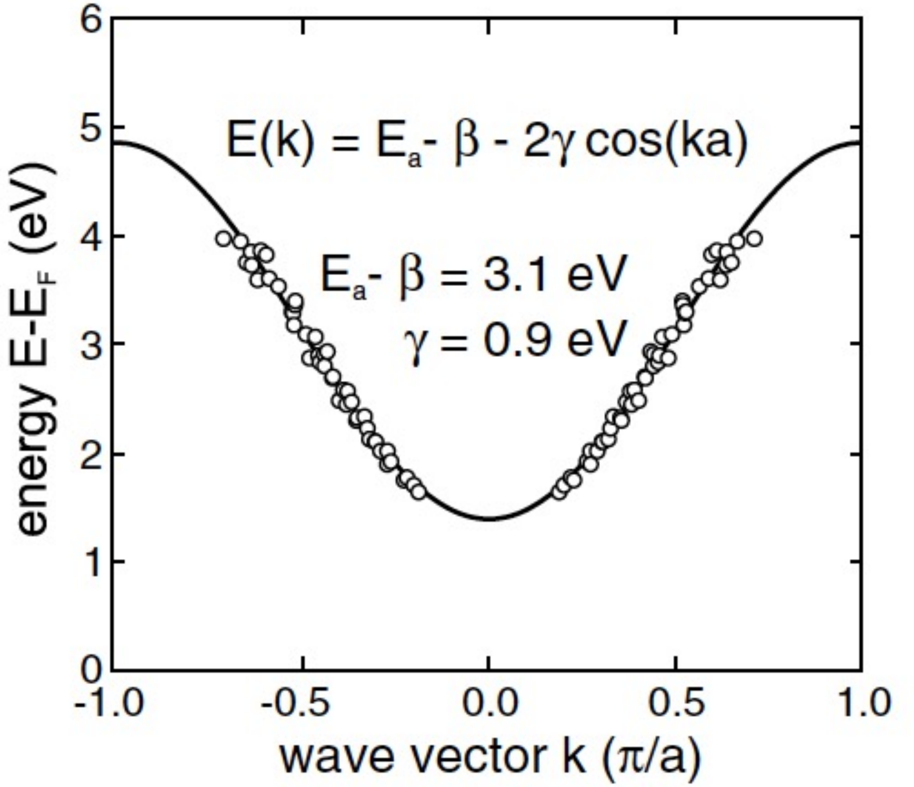


FIG. 3. The 1D band dispersion extracted from the characteristic wavelength for chain lengths from 5 to 15 atoms and $n = 3$ to $n = 8$, the wave vector is given in quantities of π/a ($a = 2.55$ Å is the Cu-Cu spacing). The experimental data are well fitted within the tight binding approximation yielding a band centered at 3.1 eV and an effective electron mass of $m^* = 0.68m_e$.

S. Fölsch et al., Phys. Rev. Lett. **92**, 056803 (2004)

Other approach to describe electronic states in solids (and nanostructures)?

from localized atomic orbitals

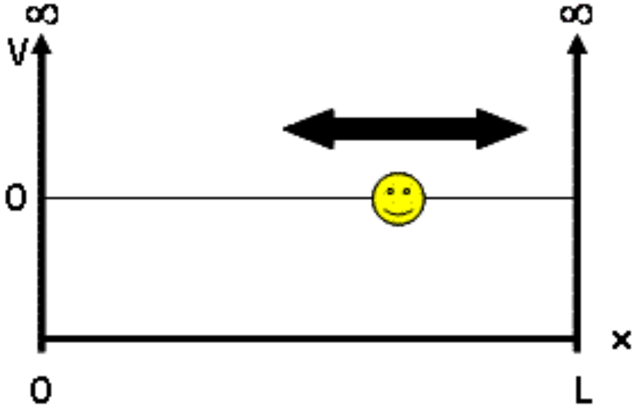
tight-binding model

from delocalized electrons

nearly-free-electron model

electronic band structure

Confined electrons: particle in a box

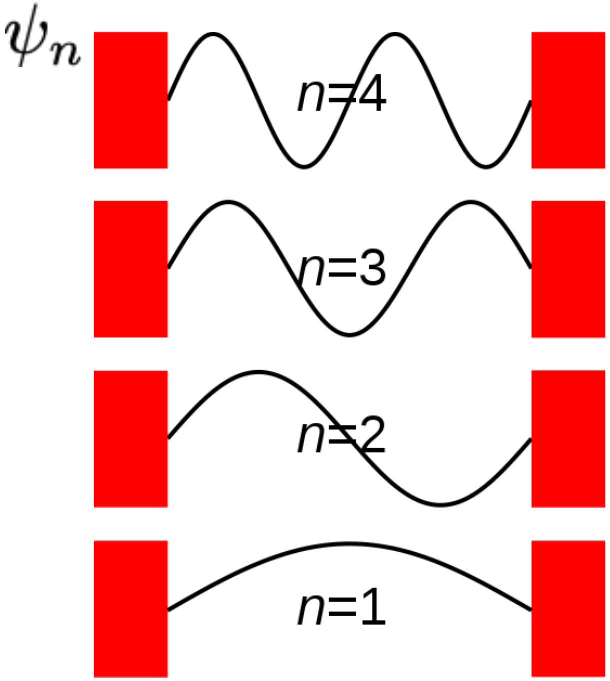


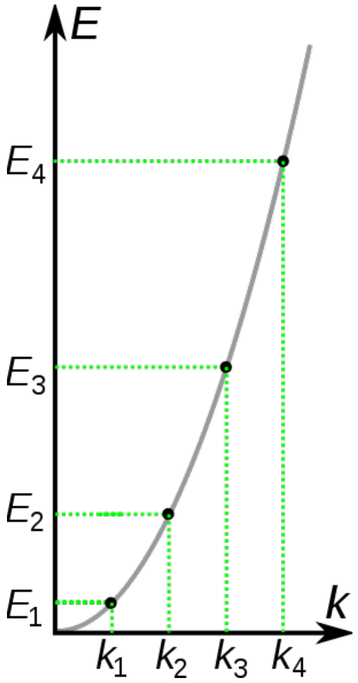
The potential energy is *0 inside the box* (*V*=0 for 0<*x*<*L*)
and *goes to infinity at the walls of the box* (*V*=∞ for *x*<0 or *x*>*L*).

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+V(x)\psi(x)=E\psi(x)$$

$$\psi(0)=\psi(L)=0$$

$$\psi_n(x)=\sqrt{\frac{2}{L}}\sin\frac{n\pi}{L}x$$

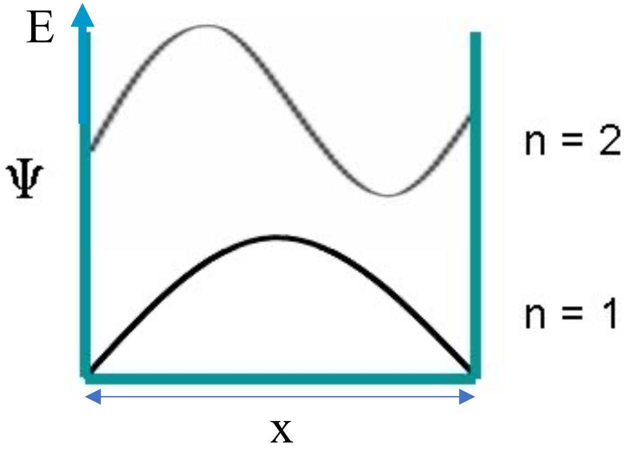




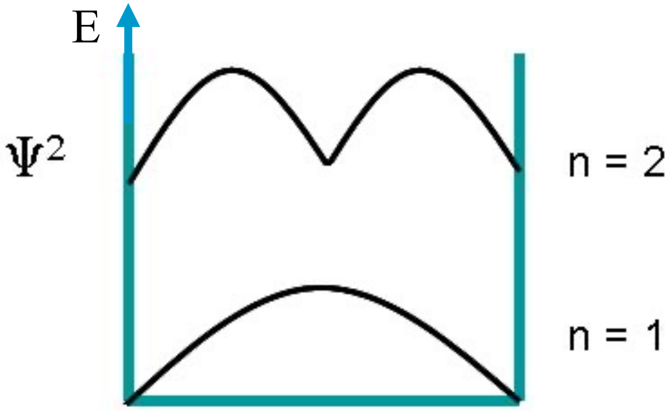
$$k_n=\frac{\pi}{L}n \qquad E_n=\frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 n^2, \quad n>0$$

The energy of a particle in a box (black dots) and a free particle (grey line) both depend on wave vector in the same way. However, the particle in a box may only have certain, discrete energy levels.

STS mapping



Wavefunctions for a particle in a box
corresponding to the n=1 and n=2 energy levels



The spatial map intensity corresponds to the local DOS
which is proportional to $|\Psi_n(x)|^2$

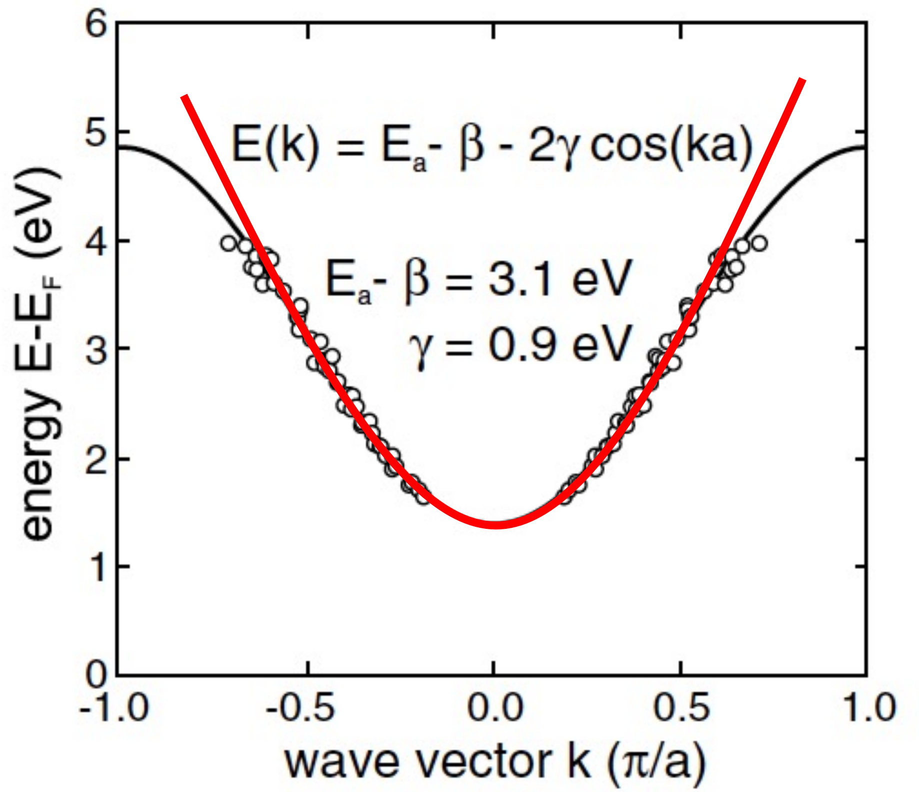
1D chain of Cu atoms

the observed quantized states can be described fairly well also by the model of an electron gas confined in a 1D box

- spatial dependence
- energy dependence

- the energy band is parabolic and is described using the effective mass m*

$$E_n = \frac{\hbar^2 k_n^2}{2m^*}$$



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S. Fölsch et al., Phys. Rev. Lett. **92**, 056803 (2004)

How the frontier discrete state-continuous band depends on the element?

Energy spectrum depends on the chemical element or on the material via m^*

$$E_n = \frac{\hbar^2}{2m^*}\left(\frac{\pi}{L}\right)^2 n^2, \qquad n > 0$$

$$E_2 - E_1 = 3\frac{\hbar^2}{2m^*}\left(\frac{\pi}{L}\right)^2$$

$$m_e = 9.1 \cdot 10^{-31}\mathrm{kg}$$

$$m^* = 0.68\, m_e$$

$$\hbar = 1 \cdot 10^{-34}\mathrm{J \cdot s}$$

For the previous Cu chains ($L \sim 5$ nm)
we get $E_2 - E_1 \sim 60$ meV

To be compared with thermal broadening $\sim 4k_BT$
At room temperature $\sim 4k_BT = 100$ meV

What happens if we consider a semiconductor ?

III-V

GaAs $m^* = 0.067\, m_e$

InSb $m^* = 0.013\, m_e$

m^* is reduced ⇨

Size can be larger to get the same energy splitting ⇨

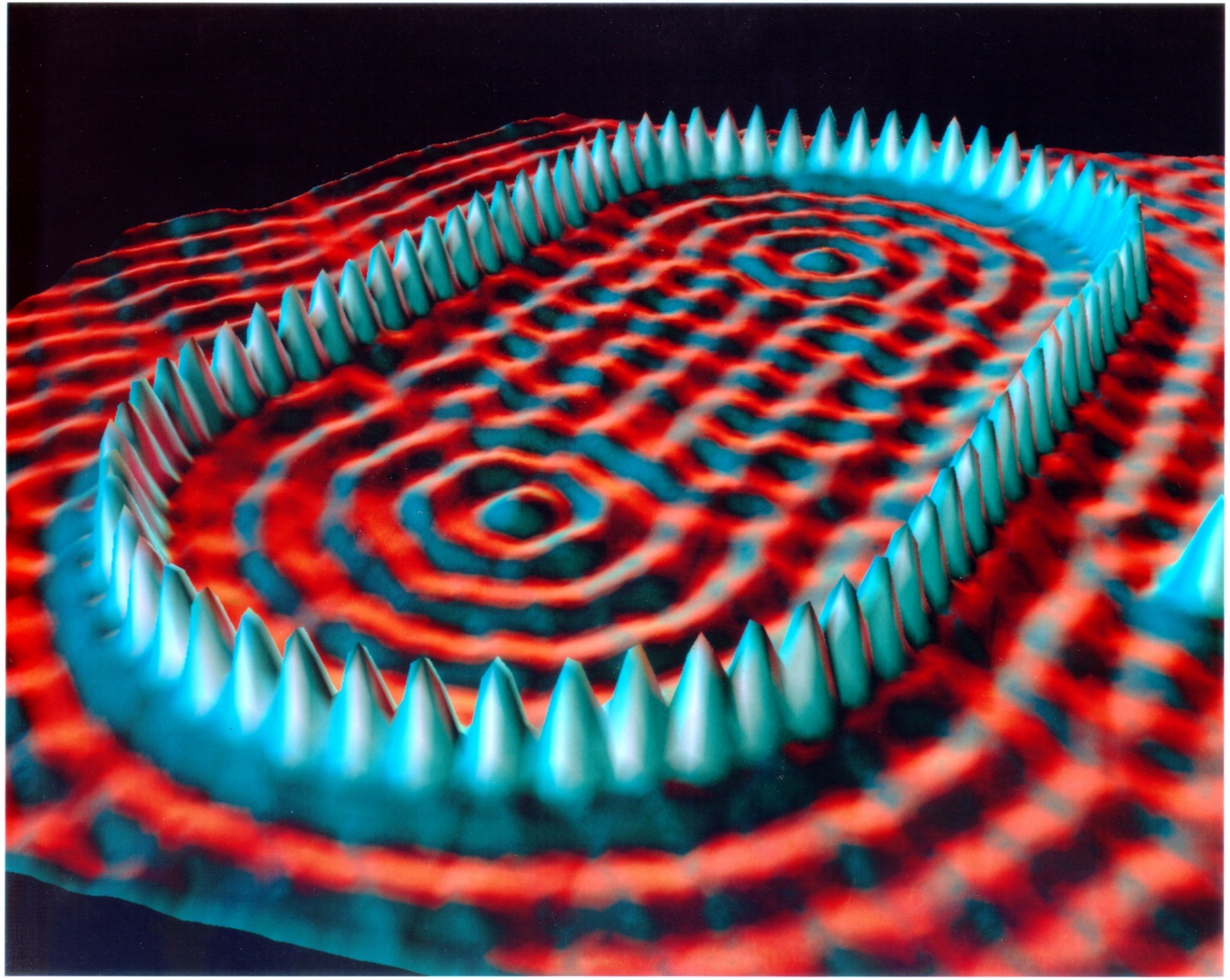
quantum world starts at different sizes:
metals → nanometers
semiconductors → tens of nanometers

2023 Nobel Prize in Chemistry “for the discovery and synthesis of quantum dots” (semiconductors, fluorescence)

Electrons in a 2D box

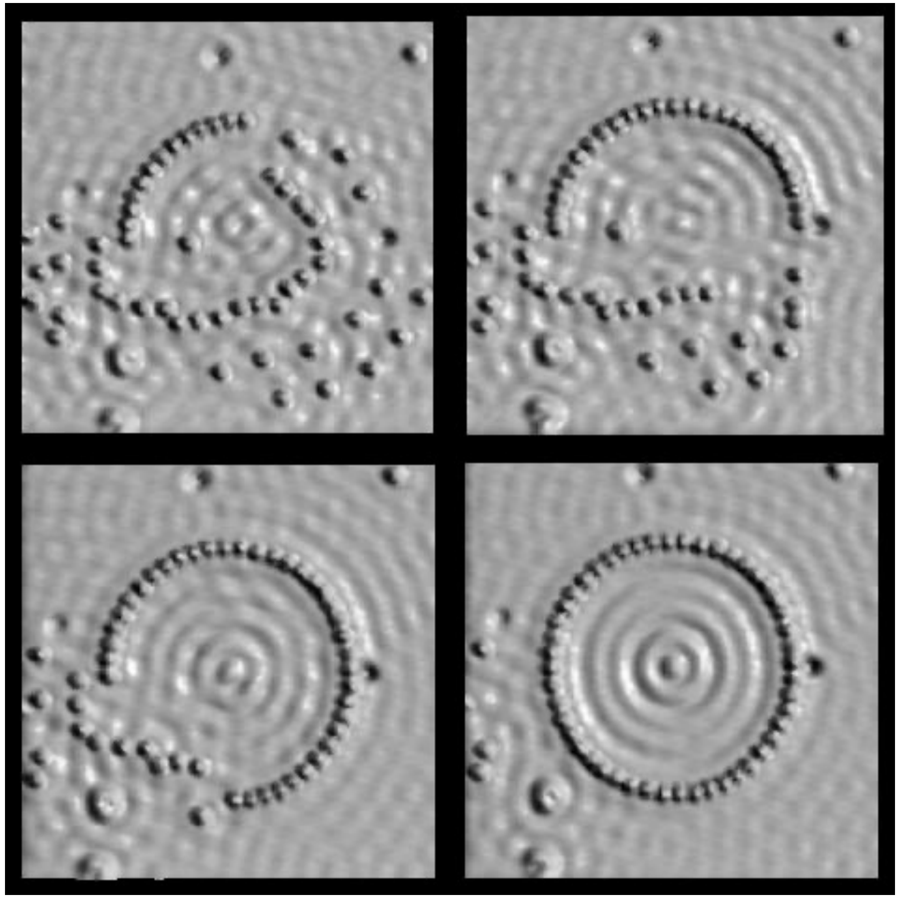
The quantum corral

Fe adatoms (blue) on
Cu(111) (red)

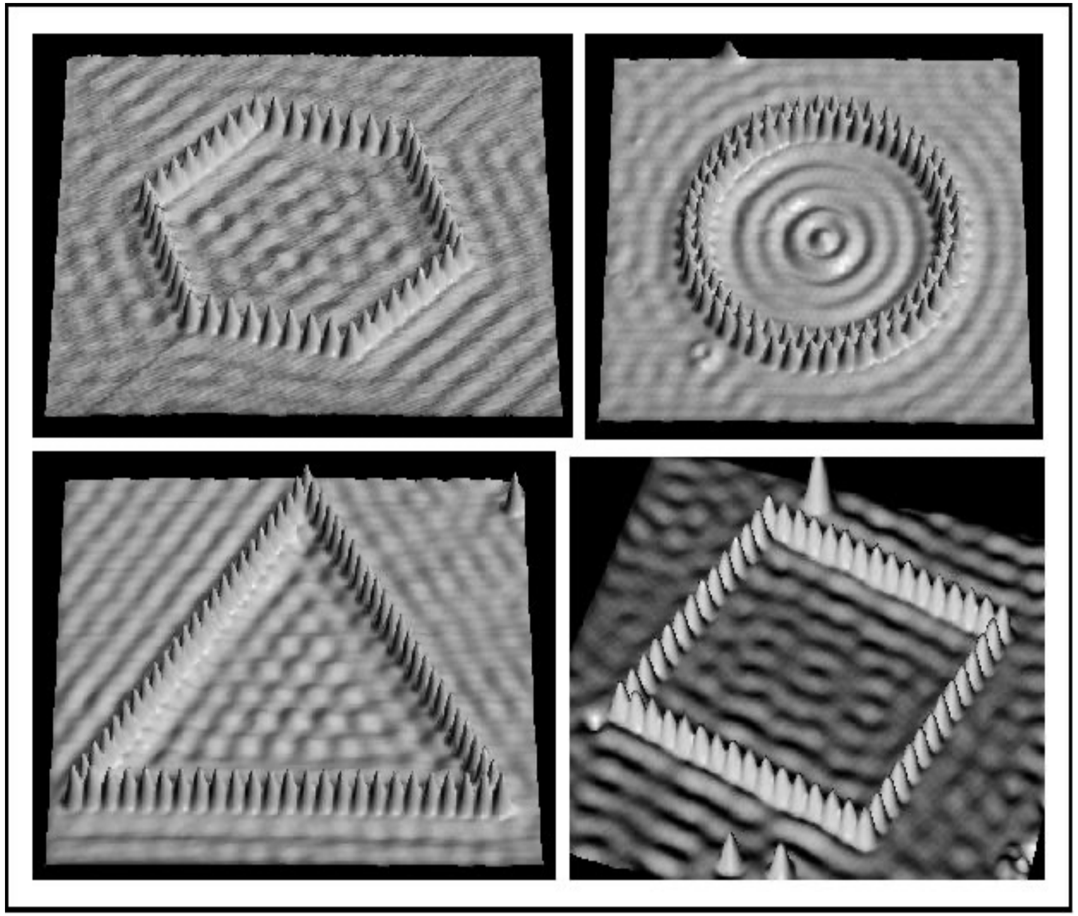


http://www.almaden.ibm.com/vis/stm/corral.html

Quantum corral: electron confinement



The corral is made by moving, with the STM tip, the Fe adatom one by one at the desired position



Standing waves formed by free **surface** electrons confined by the corral

Why we have free electrons confined at the surface of a bulk Cu(111) crystal?

Surface states

- Electronic states: plane waves (free electron model): $\psi_{\boldsymbol{k}}(\boldsymbol{r}) \propto e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$

- Infinite crystal (bulk):
  Born-von-Karman periodic boundary conditions in all directions → k_x, k_y, k_z real

- Semi-infinite crystal:
  Introduce surface in the *z* direction: **finite** potential wall → k_x, k_y real, k_z complex

➡

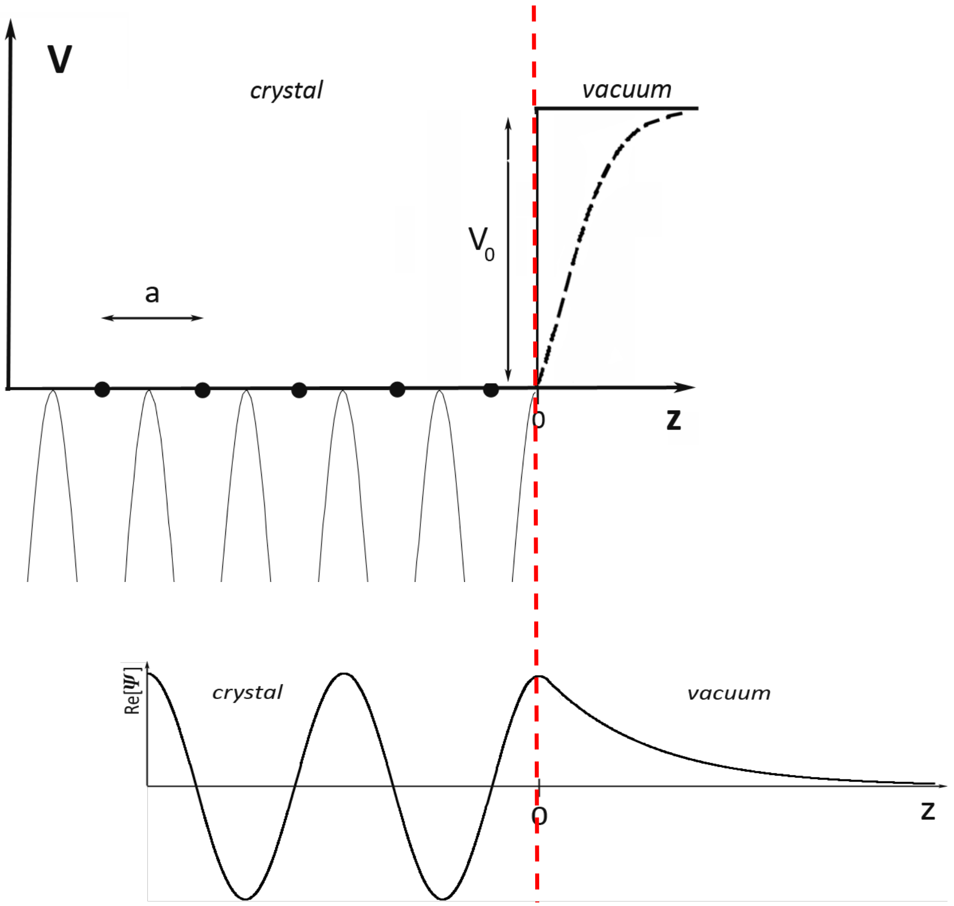
Parallel to the surface, $\boldsymbol{k}_{\parallel} = (k_x, k_y)$
→ 2D free electrons

Perpendicular to the surface
→ vacuum side: decaying wave

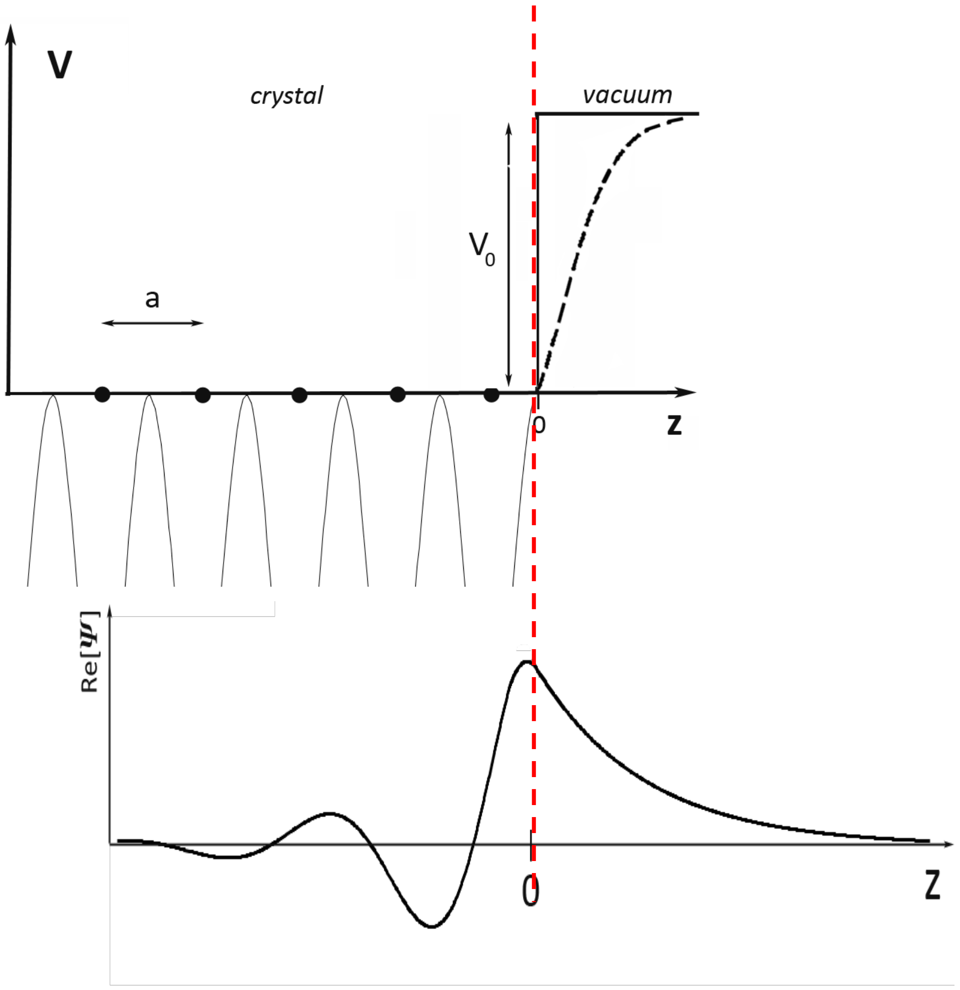
crystal side : real wavevector → bulk state (plane wave)
imaginary wavevector → surface state (decaying wave)

Surface states

bulk state



surface state

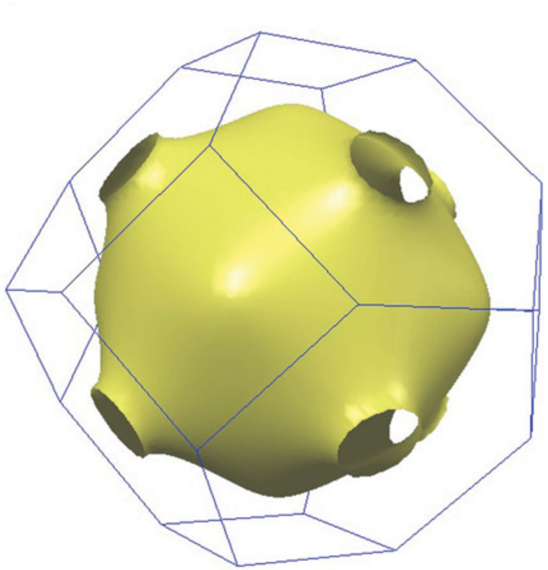


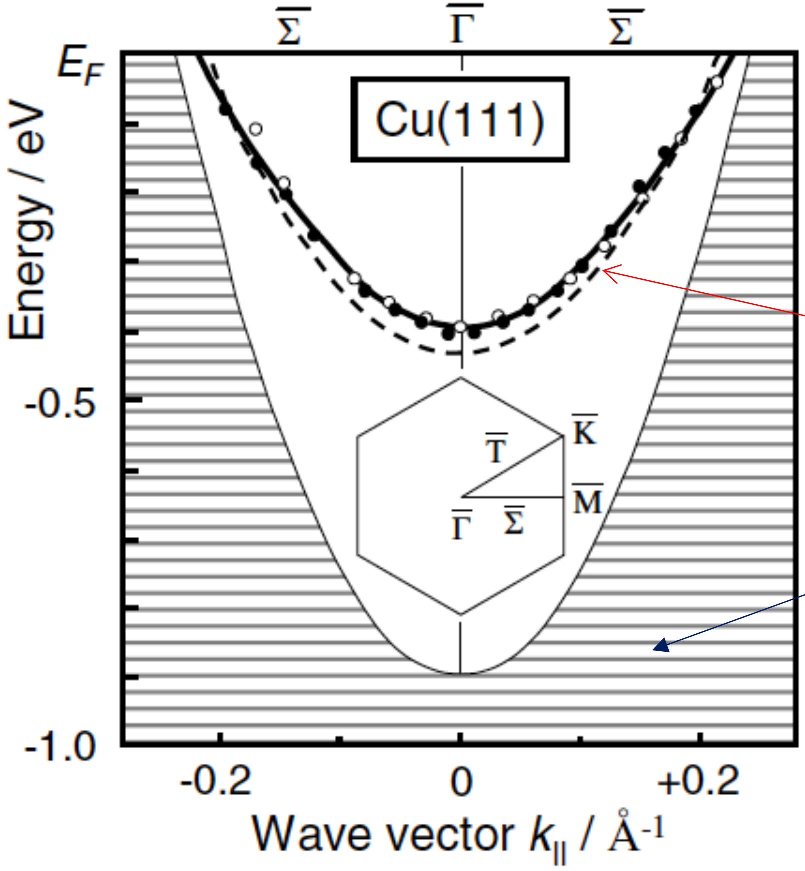
Shockley surface state:
a 2D free electron gas confined at the surface

Why surface states are easily observed on the (111) noble metal surfaces?

Ideal case (free electrons): the Fermi surface is a sphere of radius $k_F = (3\pi^2 n)^{1/3}$ (n is the electron density)

Real case (quasi-free electrons, Bloch waves): the Fermi surface of noble metals deviates from a sphere with gaps at the L points of the Brillouin zone (Γ-bar point in the surface Brillouin zone)





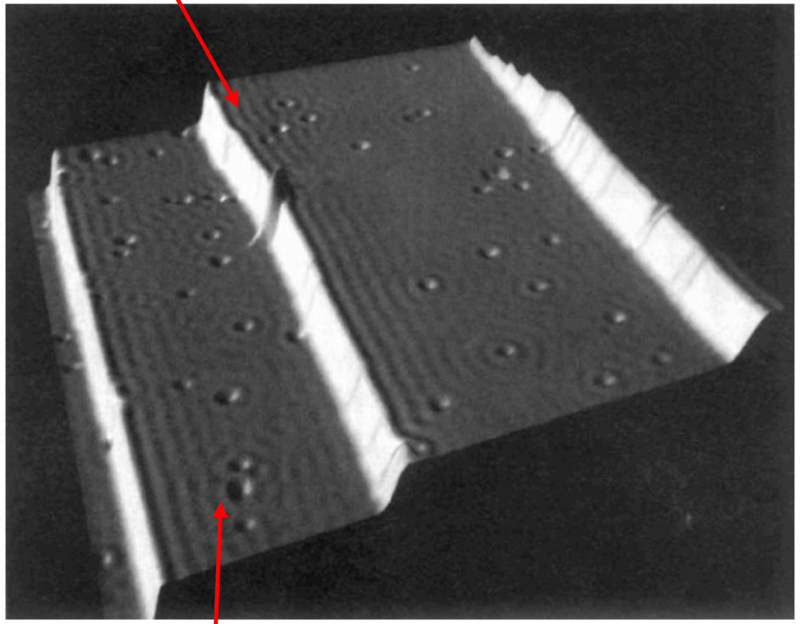
Surface state

Projected bulk states

D. Shoenberg (1962) http://www.jstor.org/stable/73177

Friedel oscillations of surface states

Reflection by a step edge



Scattering by a point defect

FIG. 1 Constant-current 500 Å × 500 Å image of the Cu(111) surface (V=0.1 V, I=1.0 nA). Three monatomic steps and about 50 point defects are visible. Spatial oscillations with a periodicity of ~15 Å are clearly evident. The vertical scale has been greatly exaggerated to display the spatial oscillations more clearly.

The periodicity of the oscillations is related to the wave vector k → determine E *vs* k for the surface states

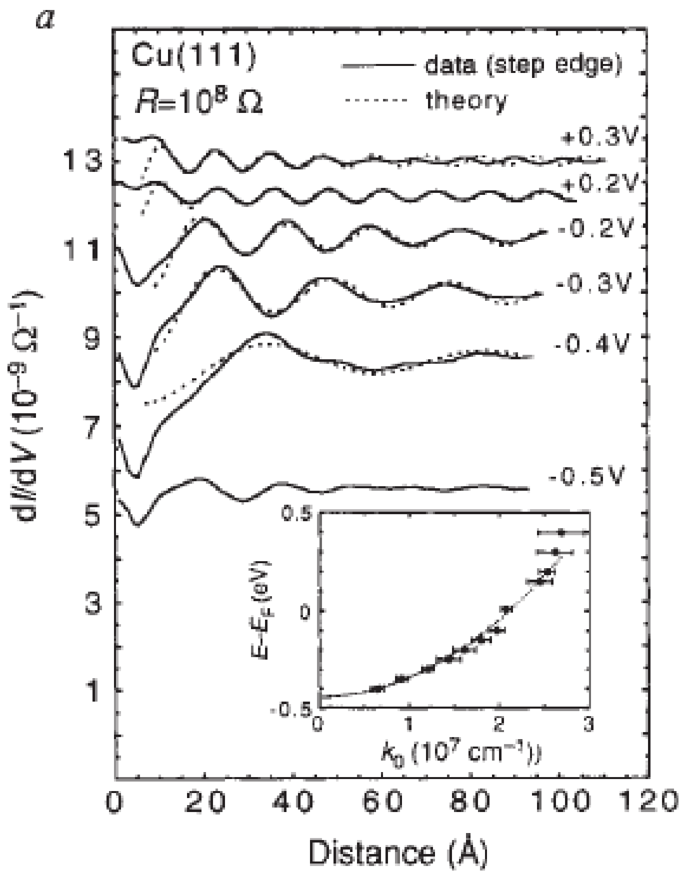
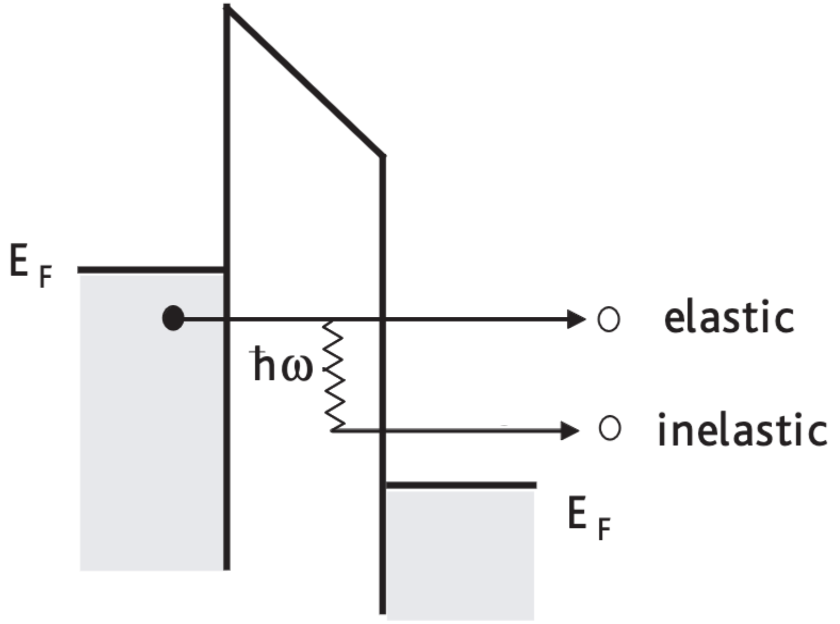


FIG. 2 *a*, Solid lines: spatial dependence of dI/dV, measured as a function of distance (along upper terrace) from step edge at different bias voltages. Zero distance corresponds to the lower edge of the step.

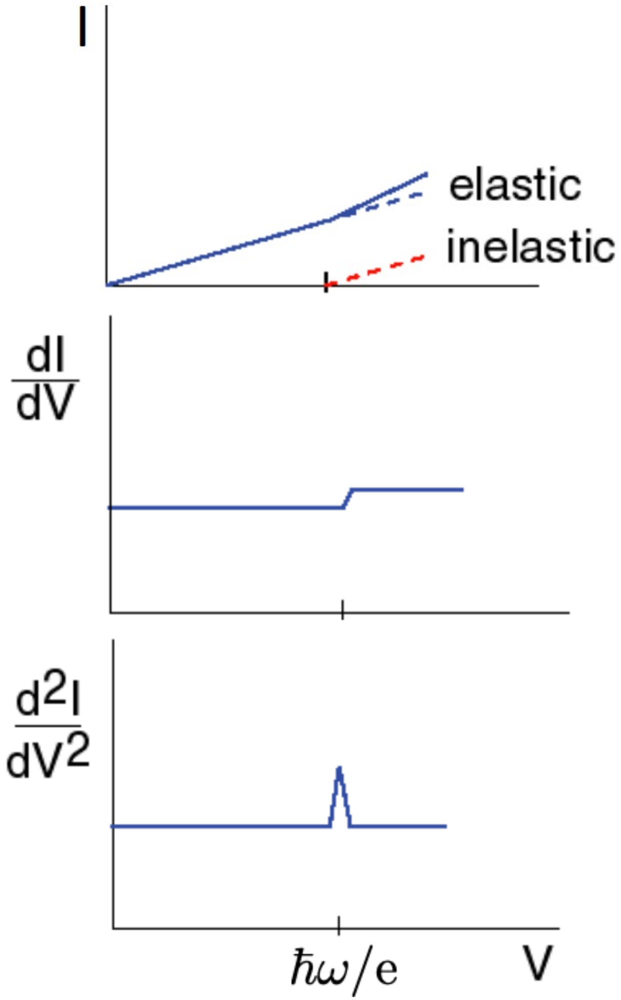
M. F. Crommie, Nature **363** (1993) 524.

IETS: Inelastic Electron Tunneling Spectroscopy

Density of states for a system composed by the STM tip, a metal surface and an adsorbate

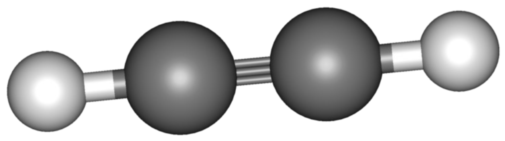


Consider an object at the surface (molecule, adatom, nanostructure...).
The tunneling electrons trigger an excitation of the adsorbate (vibration, rotation, spin flip, magnetic excitation...): they couple to the excitation mode, loose their energy, so that an additional tunneling channel is created.
This results in an increase of the tunneling current with respect to the elastic channel.

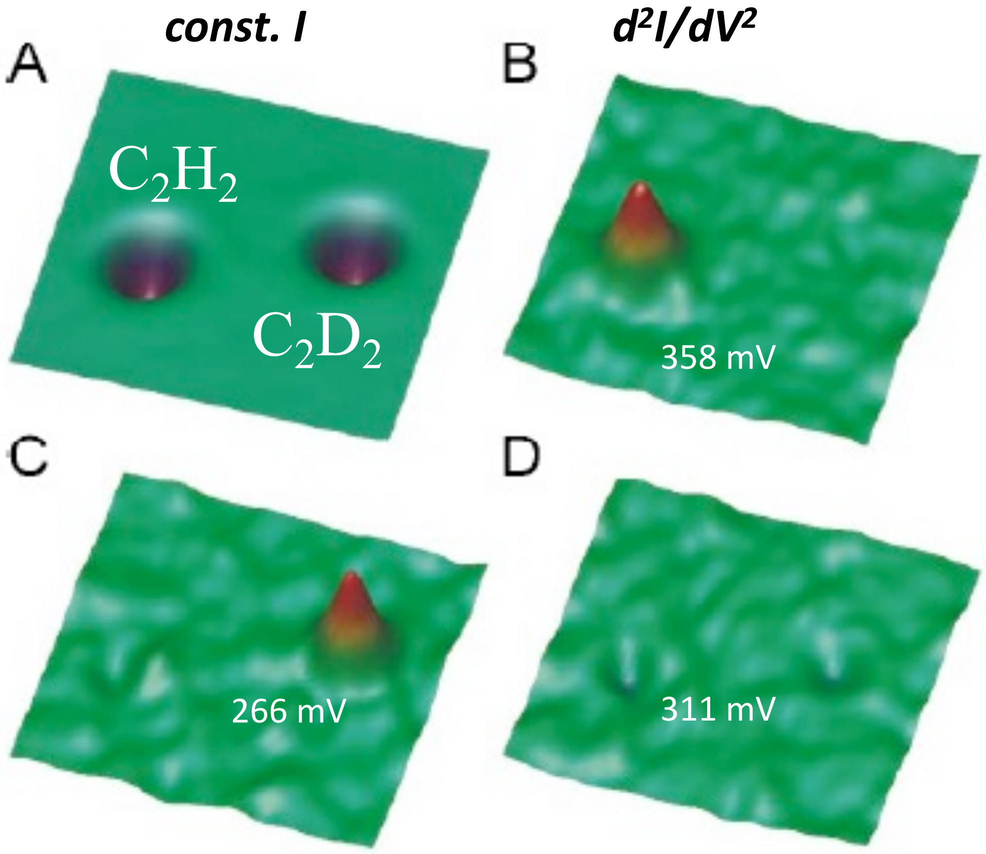


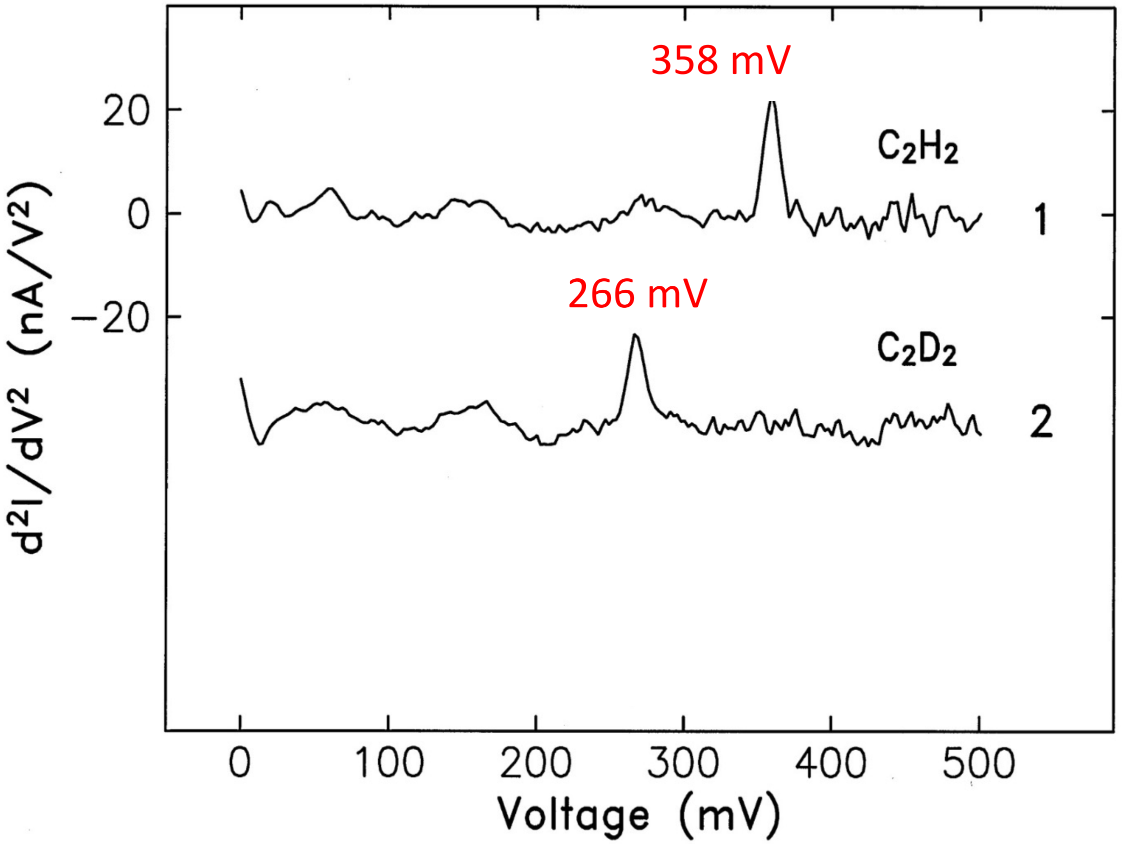
An inelastic tunneling channel opens, at a specific energy, in addition to the elastic one. The inelastic feature is present in both bias polarities.

Vibrations: chemical contrast



acetylene C_2H_2





Isotopic substitution (hydrogen → deuterium):

C_2H_2: C-H stretch @ 358 mV
C_2D_2: C-D stretch @ 266 mV

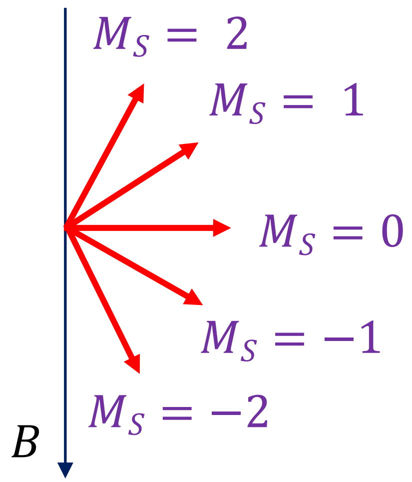
$$\hbar\omega \propto \frac{1}{\sqrt{m_{reduced}}}$$

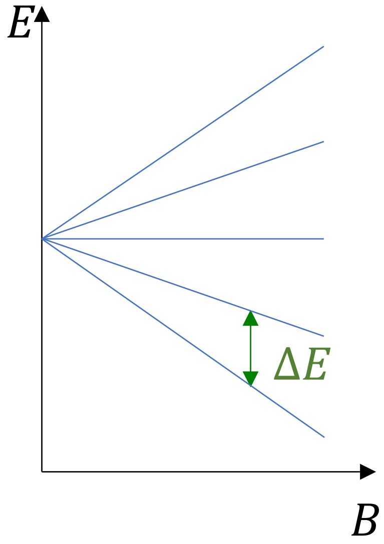
B. C. Stipe *et al.*, Science **280**, 1732 (1998)
B. C. Stipe, *et al.*, Phys. Rev. Lett **82**, 1724 (1999)

Magnetism: spin-flip excitation by STM

Zeeman energy for a paramagnetic spin $|S, M_S\rangle$
(Note that the magnetic moment $\boldsymbol{\mu} = -g\mu_B \boldsymbol{S}$)

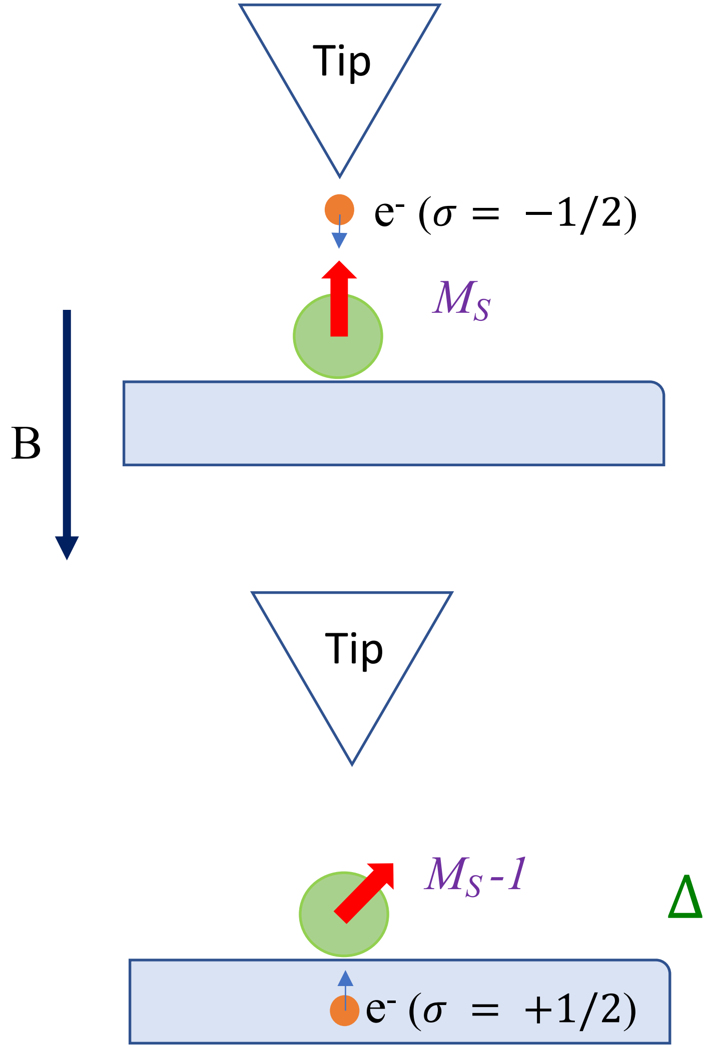
$S = 2; \quad M_S = -2, .., 2$

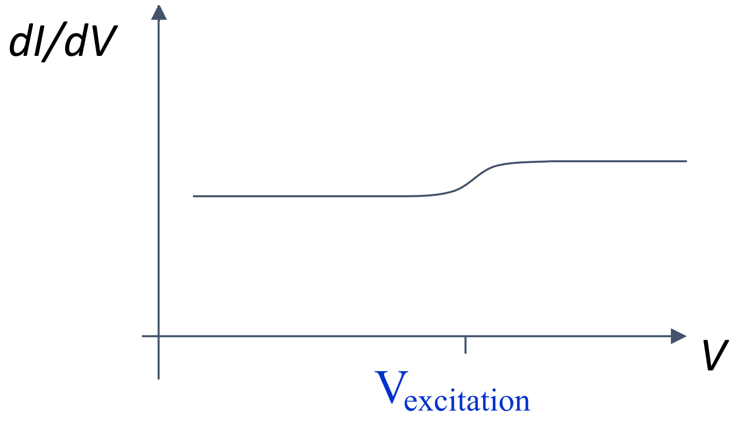




$$E = -\boldsymbol{\mu} \cdot \boldsymbol{B} = g\,\mu_B M_S\, B$$

$$\Delta E = g\mu_B B\, \Delta M_S = g\mu_B B$$





$$eV_{\text{excitation}} = g\,\mu_B B$$

$$\Delta\sigma = +1 \rightarrow \Delta M_S = -1$$

An inelastic tunneling process can involve energy and momentum transfer from the tunneling electron to the atom spin which flips from the ground to an excited state (spin-flip). The threshold energy for spin-flip processes depends on the crystal field, that is, the coordination of adjacent atoms and their chemical composition, and the magnetic field.

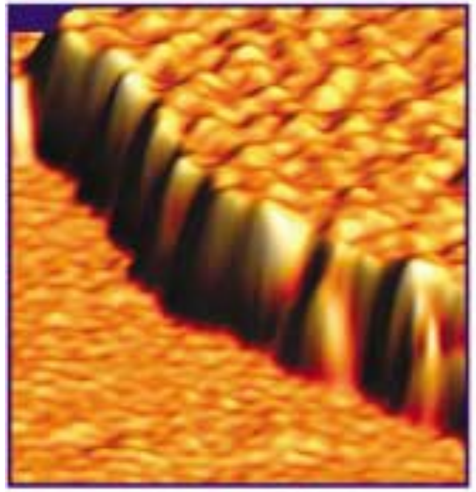
Single-atom spin-flip spectroscopy

free atom:

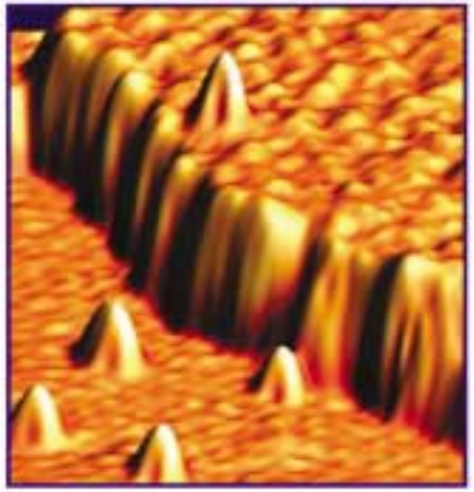
Mn: [Ar] $3d^5\,4s^2$

$S = 5/2, \qquad L = 0$

$Al_2O_3/Ni_3Al(111)$



$Mn/Al_2O_3/Ni_3Al(111)$



T = 0.6 K

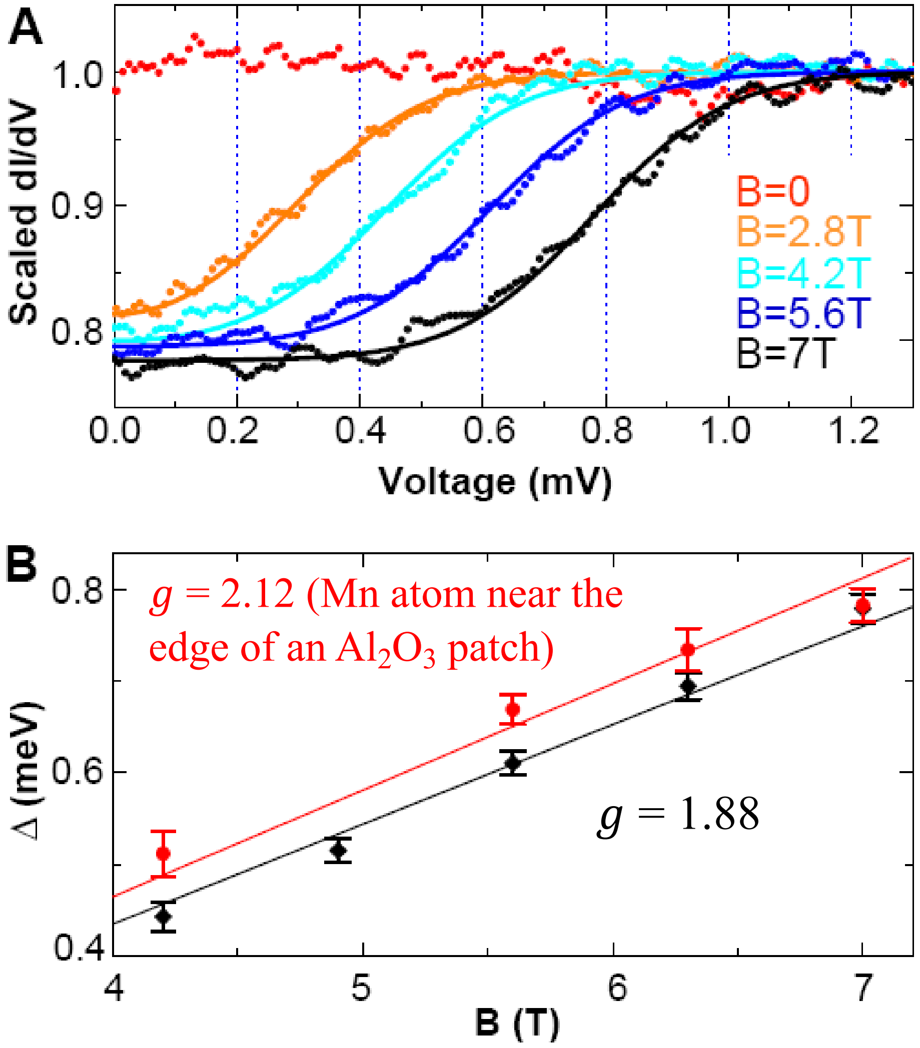
$$eV_{\text{excitation}} = g\,\mu_B B$$

g is the Landé g-factor; it reflects the spin and orbital contributions to the total magnetic moment

$$g = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

For $L = 0 \rightarrow g = 2$

Shift of the spin-flip conductance step with magnetic field



A.J. Heinrich *et al.*, Science **306**, 466 (2004).