4

Spectroscopy at the atomic scale

using

Scanning Tunneling Microscopy (STM)

Spectroscopy at the atomic scale

Introduction to Scanning Tunneling Microscopy
C. Julian Chen
Oxford University Press

Scanning Probe Microscopy and Spectroscopy
R. Wiesendanger
Cambridge University Press

Scanning Probe Microscopy
B. Voigtländer
Springer

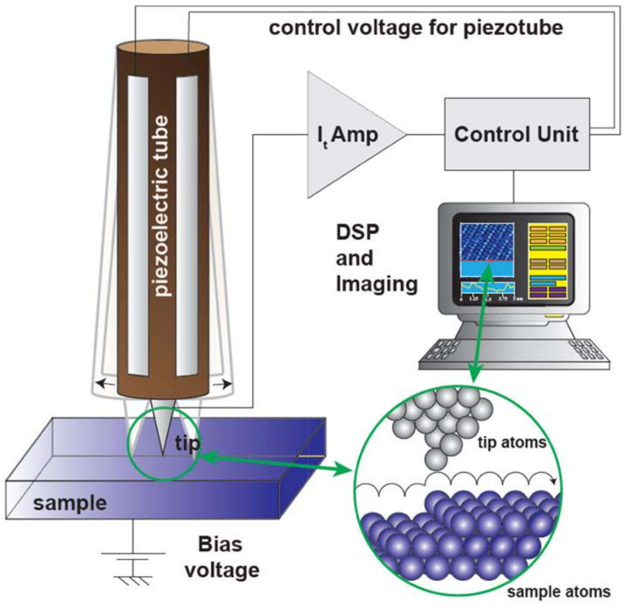
Review articles:

manipulation
[DOI: 10.1002/pssb.201248392]

quantum simulator
[DOI: 10.1038/ s42254-019-0108-5]

STM: a powerful multitask tool for nanoscience

EPFL



Atomically resolved

Topography → shape

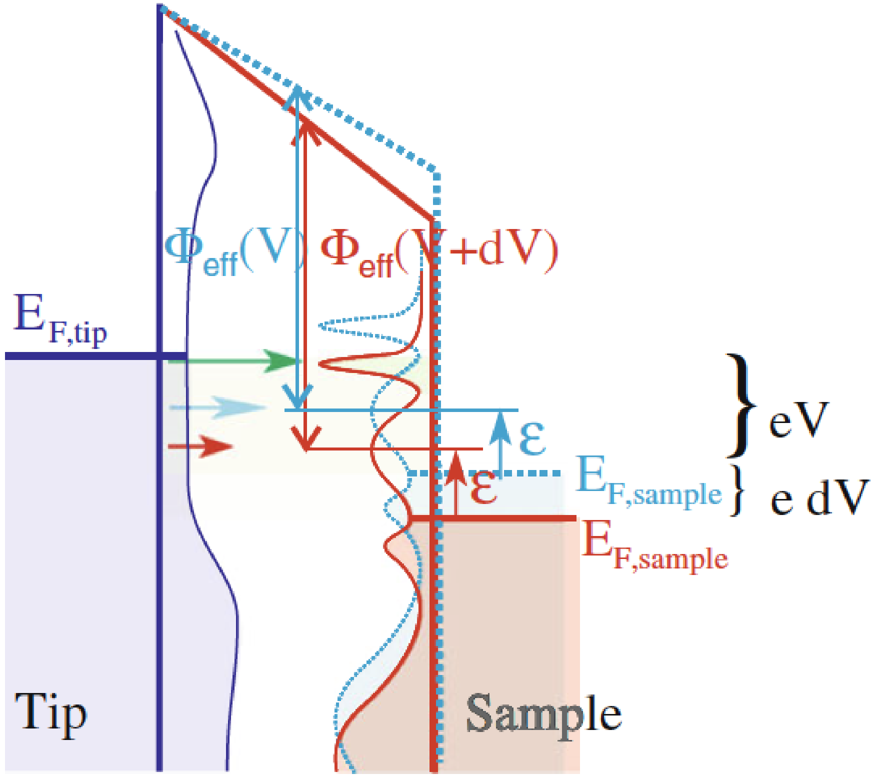
Spectroscopy → electronic properties
- electronics
- spintronics
- chemistry

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

....

Scanning tunneling spectroscopy (STS)

$$I = \frac{4\pi e}{\hbar}\int_0^{eV} \rho_t(\varepsilon - eV)\rho_s(\varepsilon)\,T(\varepsilon, V)\,d\varepsilon$$



How to determine the density of states of the sample?

Measuring the current-vs-voltage characteristic of the tunneling junction: I vs V curves

The current variation upon a small bias voltage variation can be expressed as

$$\frac{dI}{dV} = \frac{4\pi e^2}{\hbar}\rho_t(0)\;\rho_s(eV)\,T(eV, V)$$

In the simplest approximation, the density of states of the tip and the transmission factor are considered voltage independent

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

The differential conductance dI/dV measures the sample density of states at the energy eV relative to the Fermi energy of the sample

STS: acquisition

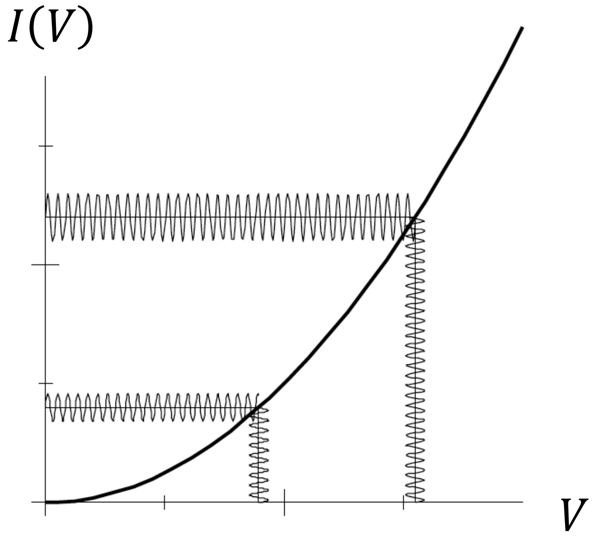
$$\frac{dI}{dV} \propto \rho_s(eV)$$

Experimentally:
Acquisition technique: small ac-modulation voltage added to V bias, lock-in detection, 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 → LDOS vs energy

- dI/dV mapping → spatial variation of the LDOS at a given energy

Assumptions/conditions:
- the density of states of the tip is constant in the chosen voltage range
- small modulation voltages



The amplitude of the resulting modulated (tunneling) current is proportional to the slope of the $I - V$ curve, i.e, to dI/dV

More formally: $$I \propto \int_0^{eV+eV_m \sin(\omega_m t)} \rho_s(\varepsilon)d\varepsilon$$

Taylor expansion

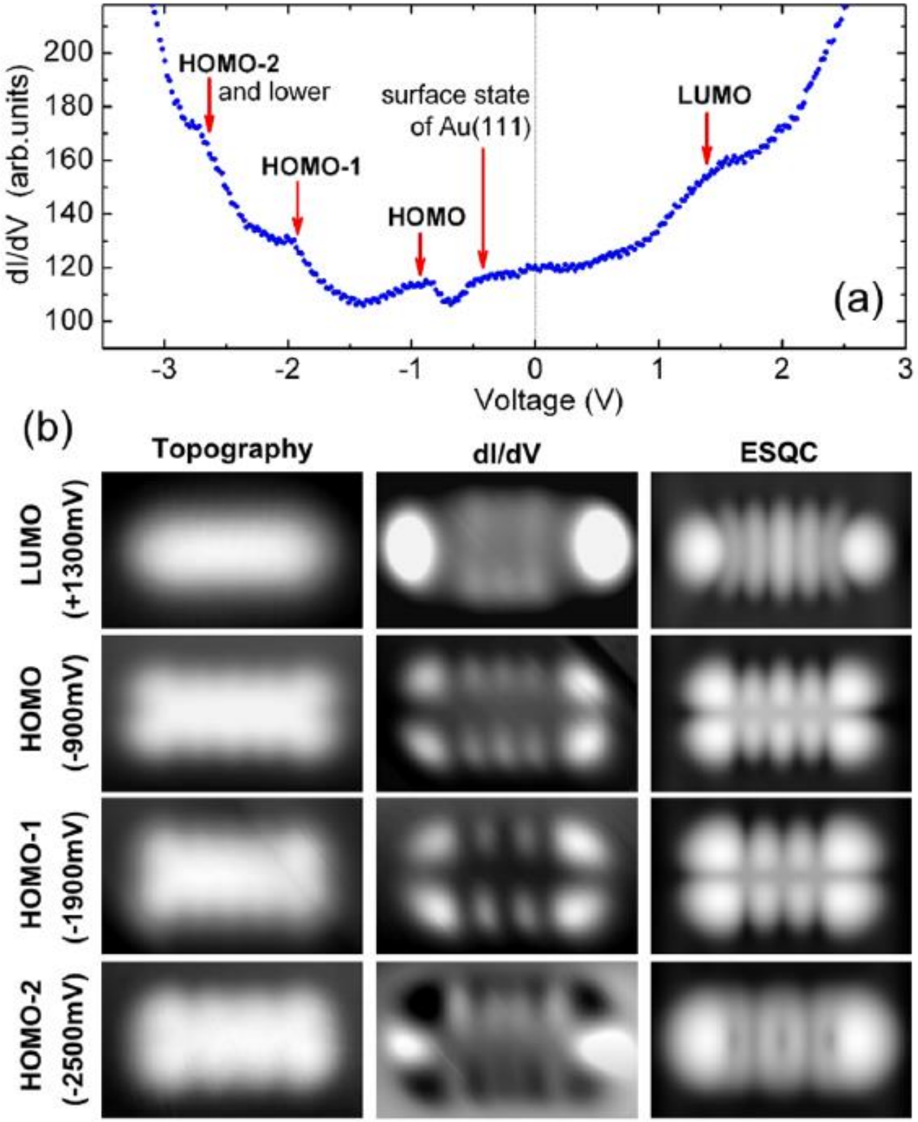
$$I \propto I(V) + \boxed{I'(V)\, eV_m \sin(\omega_m t)} + \ldots$$

$$I \propto \int_0^{eV} \rho_s(\varepsilon)d\varepsilon + \boxed{\rho_s(eV)\, eV_m \sin(\omega_m t)} + \ldots$$

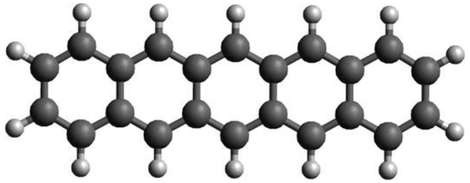
The amplitude of the ac current is proportional to the LDOS

Example: Pentacene molecular orbitals

Pentacene / Au(111)



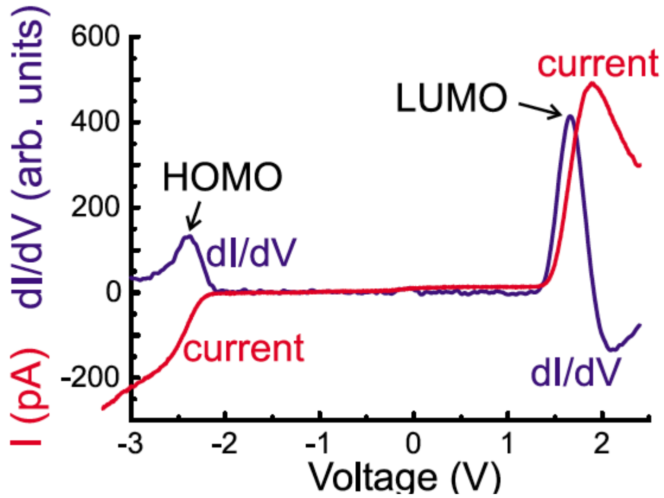
DOI: 10.1103/PhysRevLett.102.176102

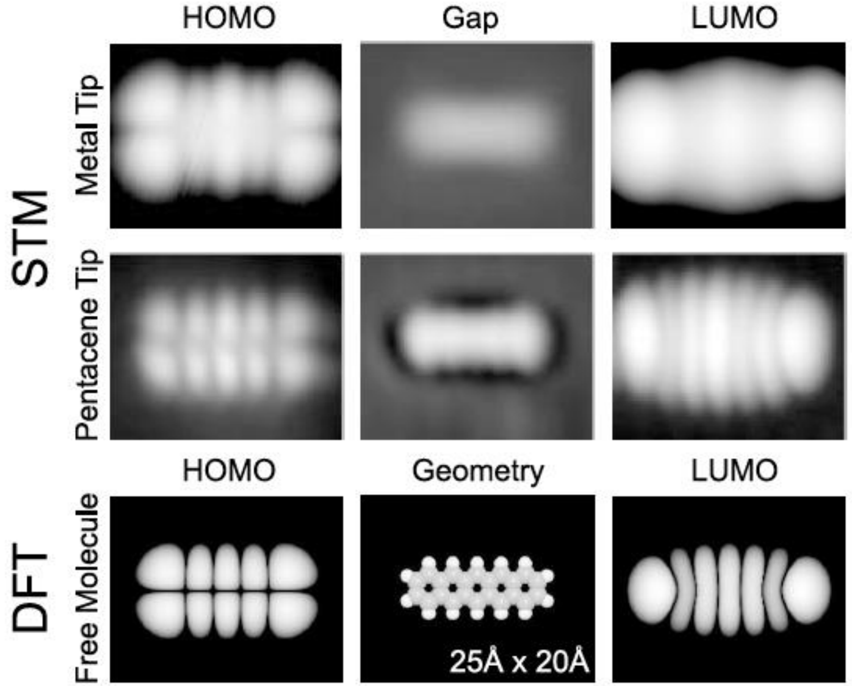


The NaCl decoupling layer prevents hybridization and increases the lifetime of the electron in the MOs.

The presence of the NaCl decoupling layer allows to better detect and resolve the MOs directly in the topographic images.

Pentacene / NaCl(100) / Cu(111)

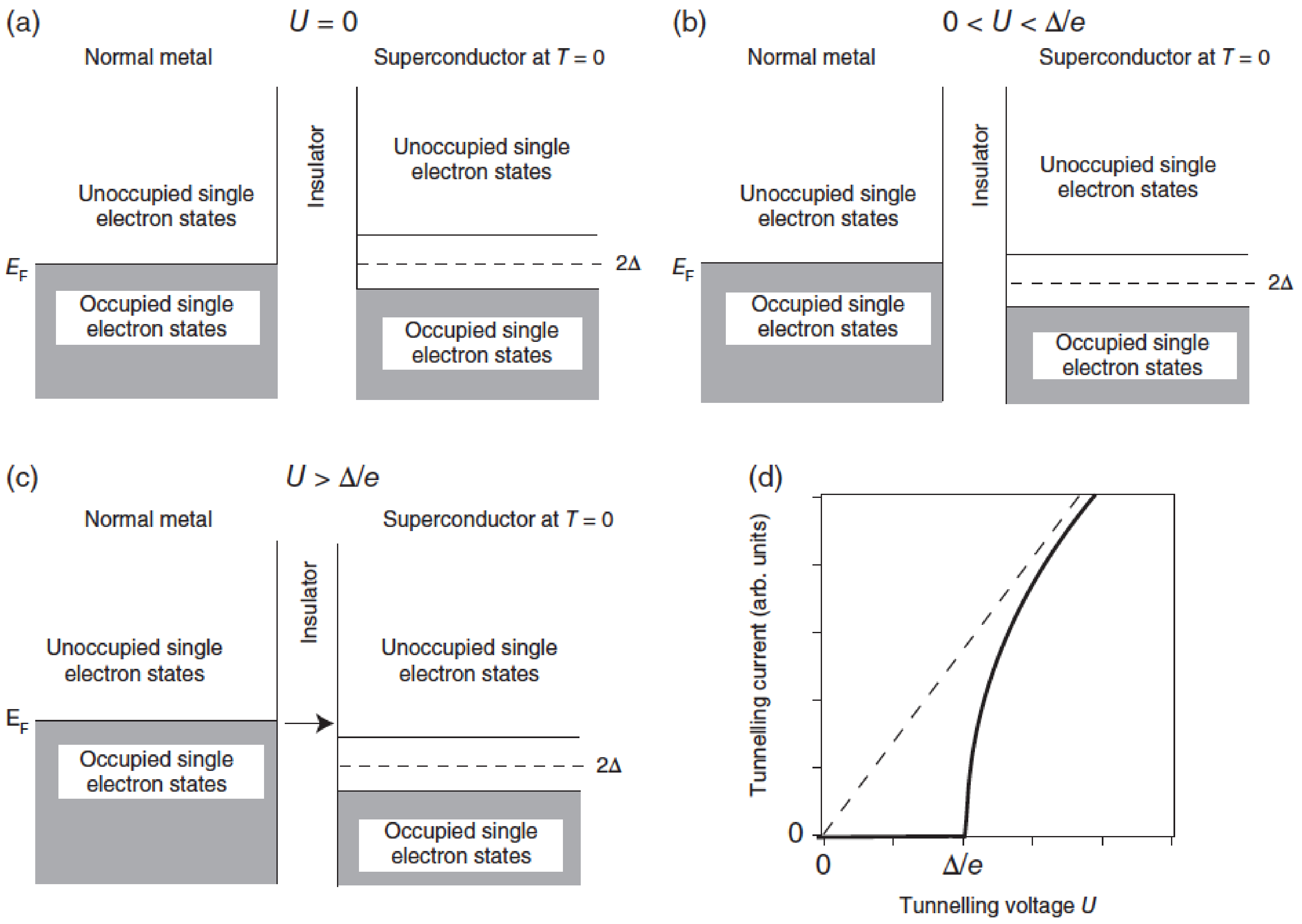




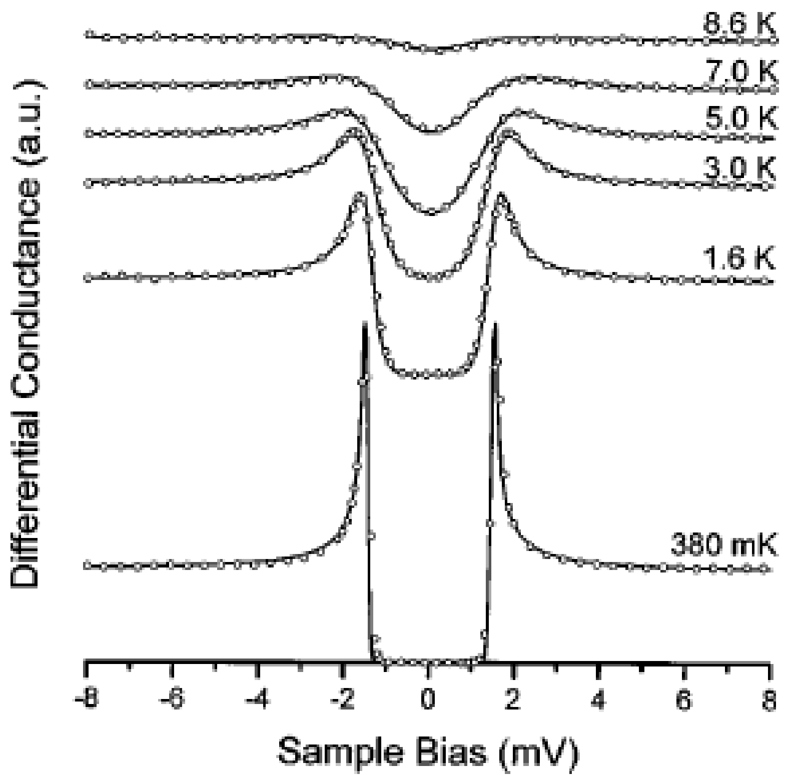
DOI: 10.1103/PhysRevLett.94.026803

Example: Superconductivity

Exercise 4.1

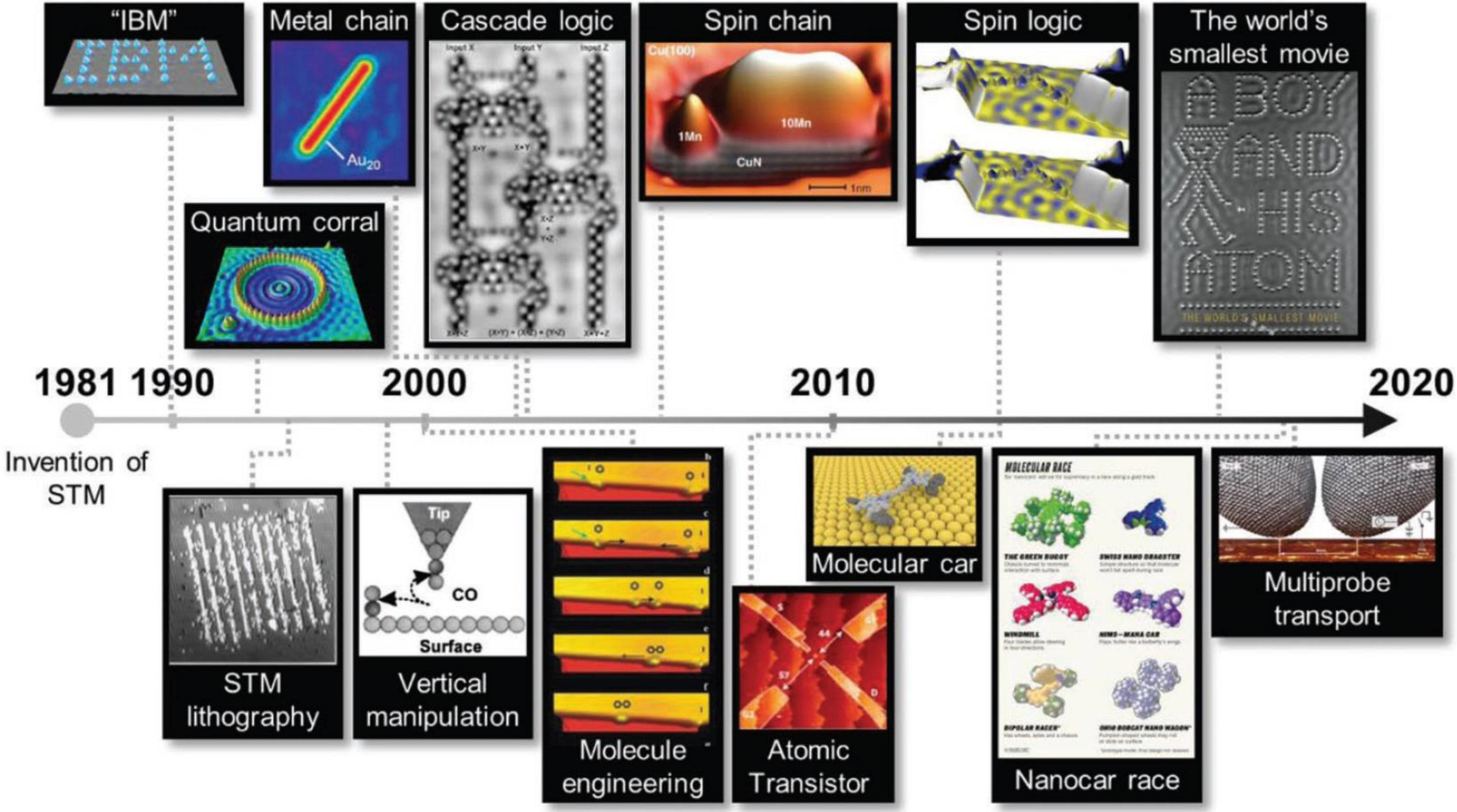


Niobium (Nb) tip on a gold (Au) surface
(bulk Nb is superconducting at T < 10 K)



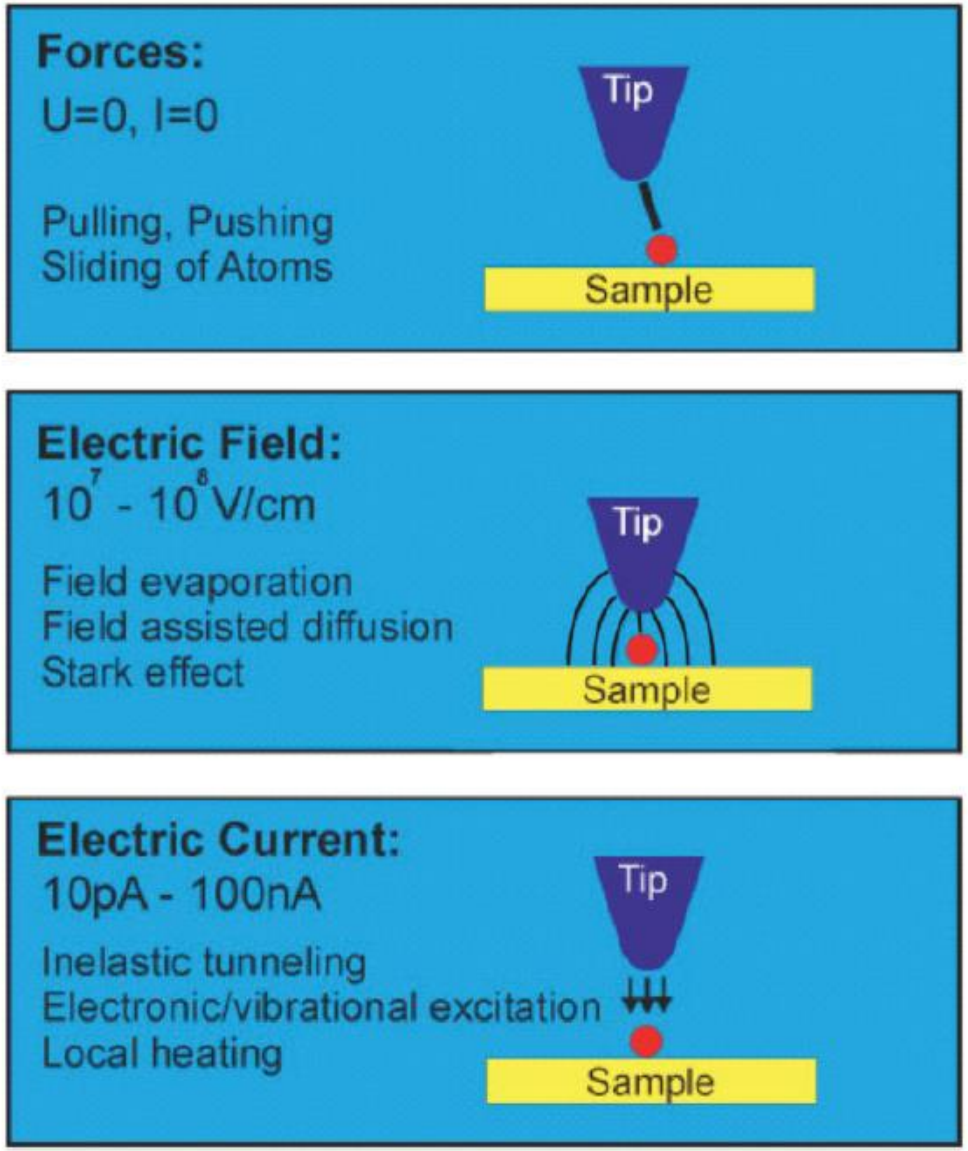
Pan et al., APL **73**, 2992 (1998)

Atomic-scale manipulation



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

Atomic-scale manipulation



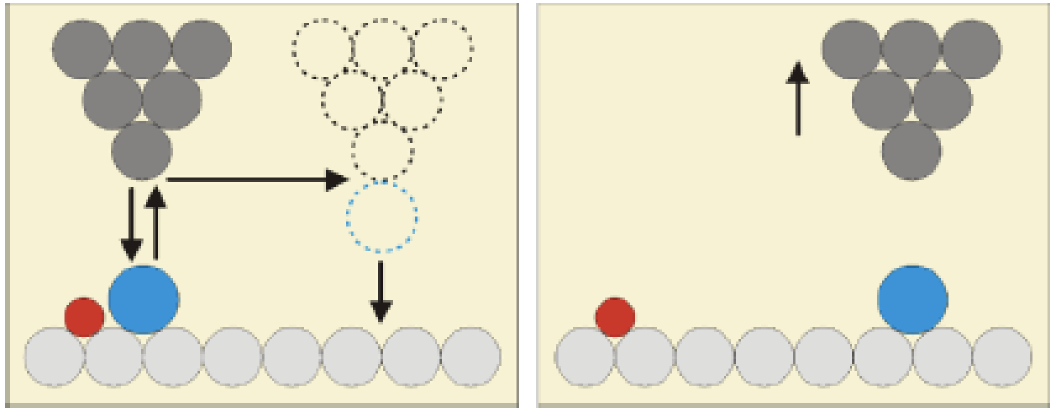
DOI: 10.1002/pssb.201248392
K. Morgenstern et al., Phys. Status Solidi B **250**, 1671 (2013)

Vertical manipulation

Transfer of the atom from the surface to the tip, move laterally, transfer atom back on the surface

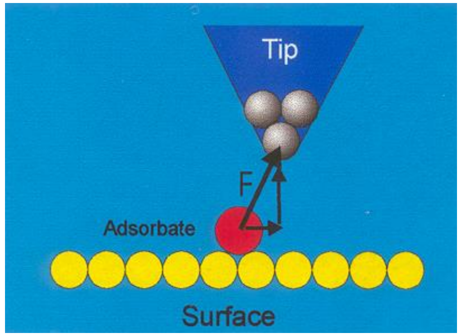
pick-up: contact

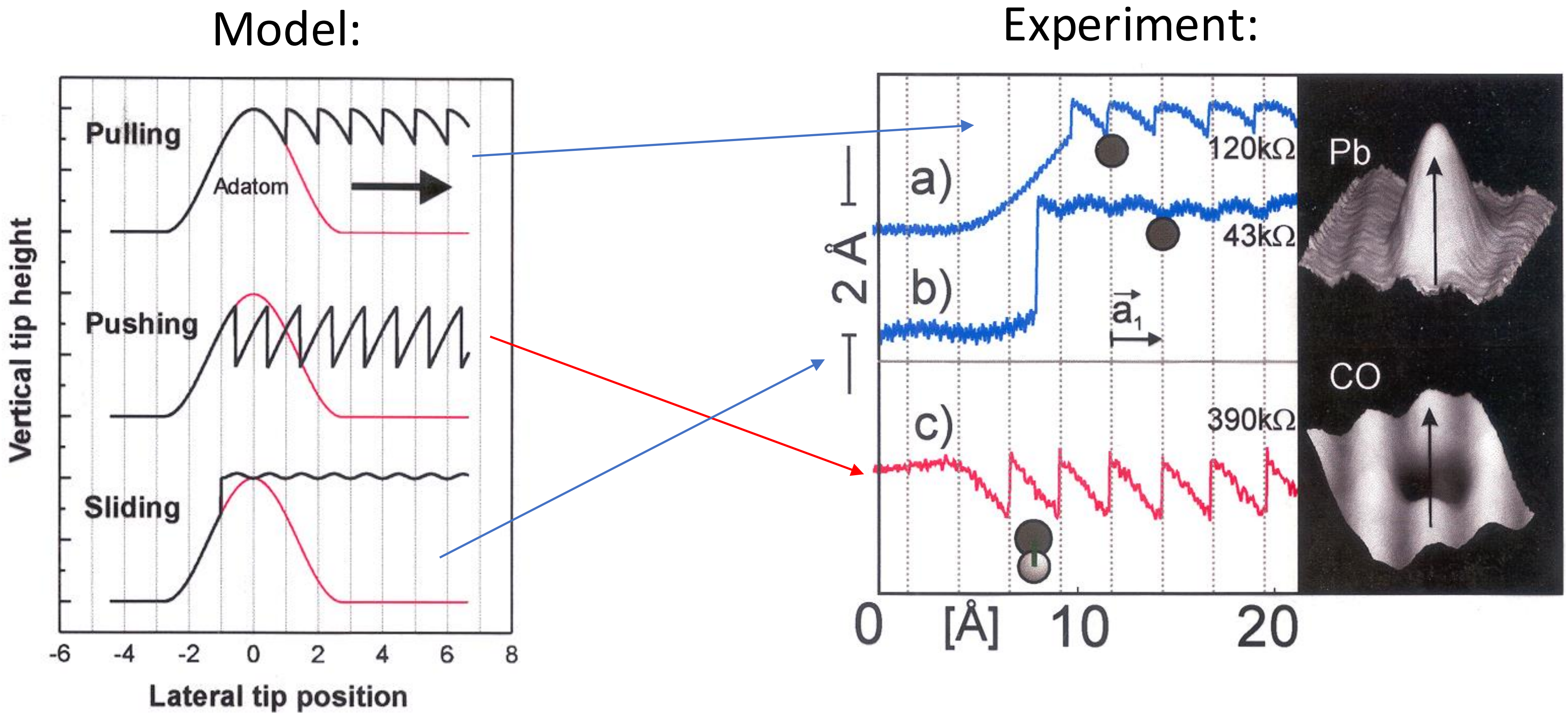
drop-off: in general, less controlled



DOI: 10.1002/pssb.201248392
K. Morgenstern et al., Phys. Status Solidi B **250**, 1671 (2013)

Lateral manipulation



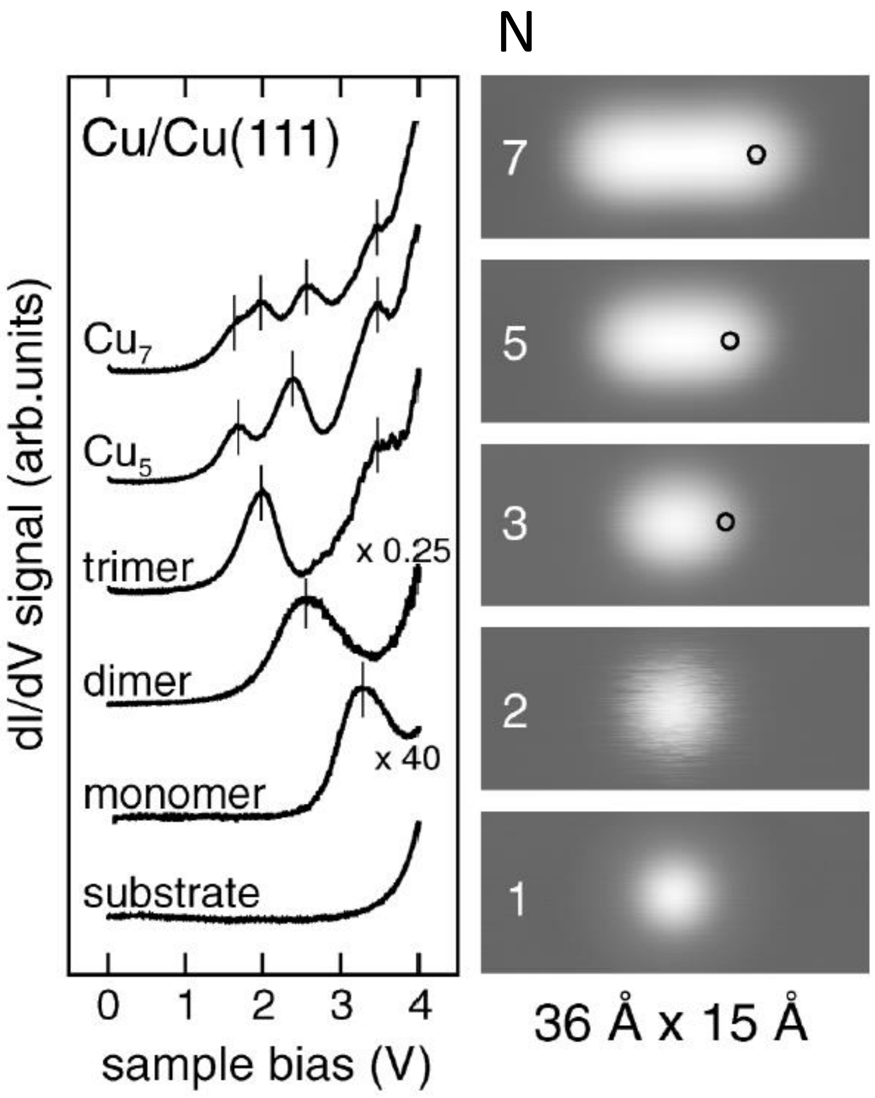


attractive interaction → pull
even stronger interaction→ slide
repulsive interaction → push

higher tunneling resistance: tip further away
lower tunneling resistance: tip closer

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

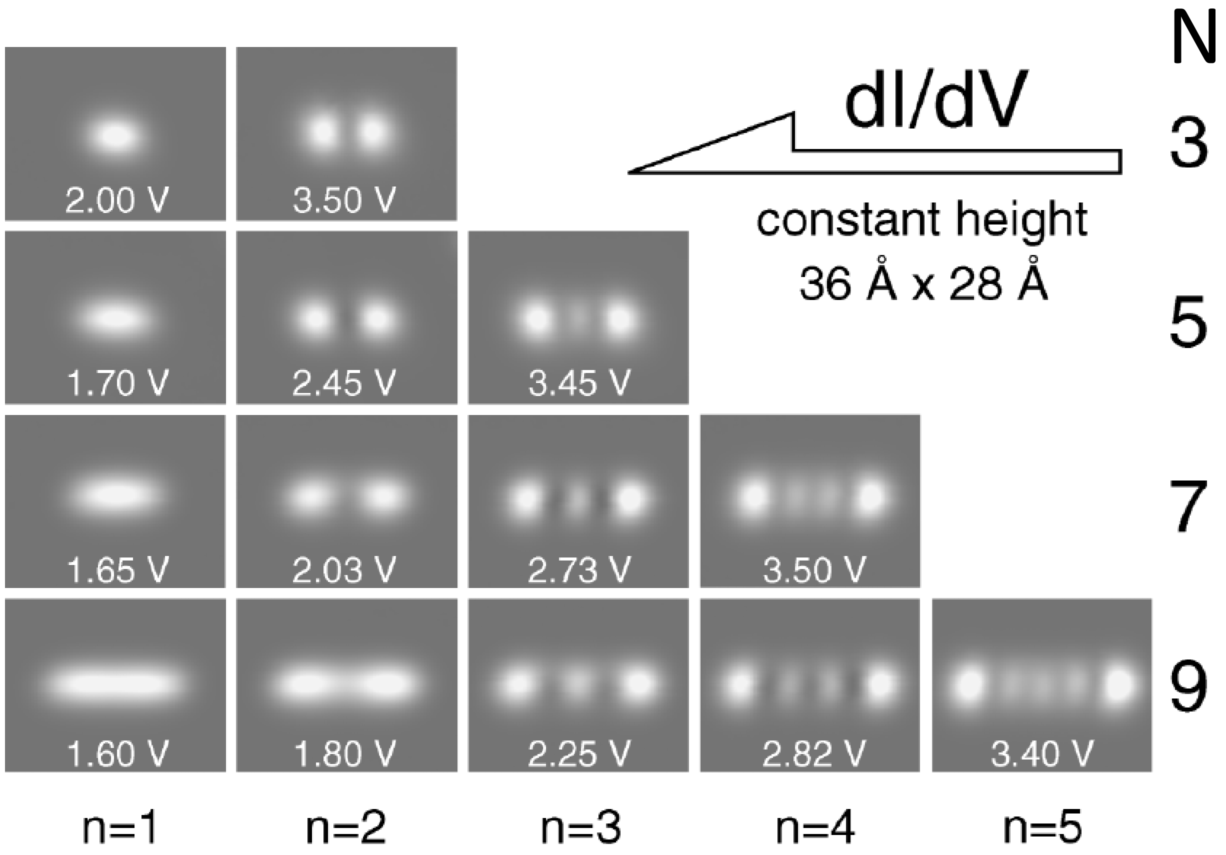
K. Morgenstern et al., Phys. Status Solidi B **250**, 1671 (2013)

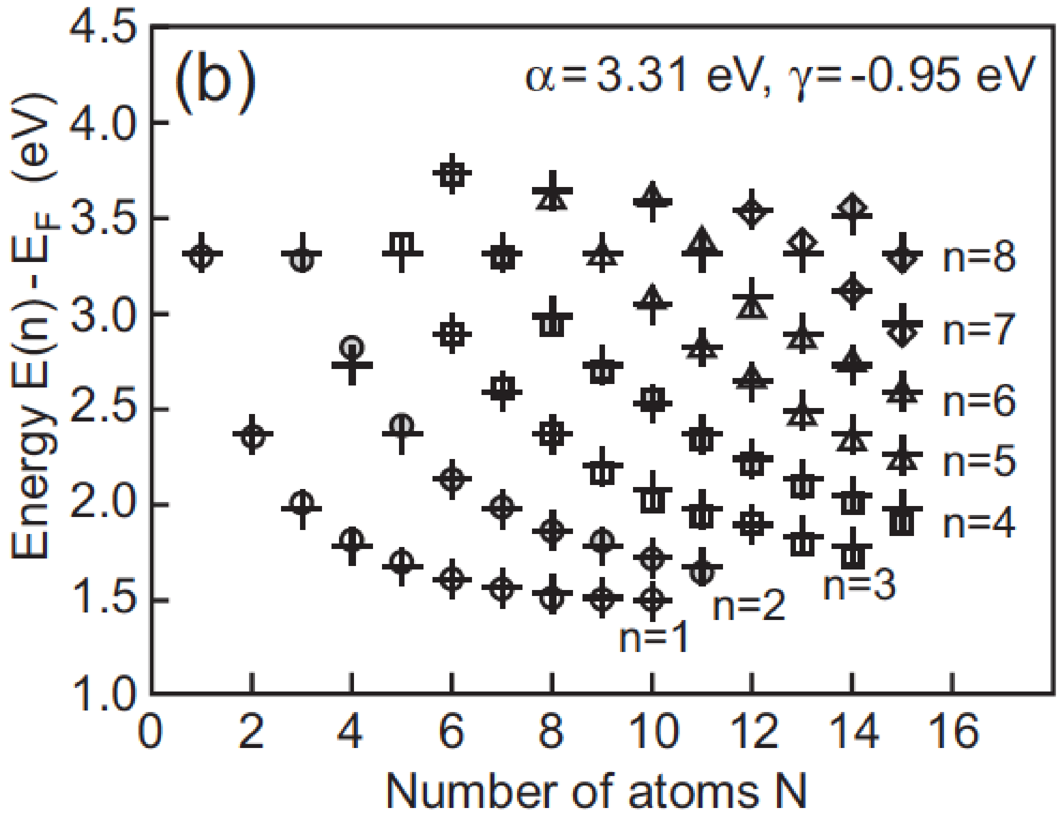


Cu adatom:
wavefunction (state) of s nature

DOI: 10.1103/PhysRevLett.92.056803
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

DOI: 10.1103/PhysRevLett.92.056803
S. Fölsch et al., Phys. Rev. Lett. **92**, 056803 (2004)
DOI: 10.1103/PhysRevB.74.125410
J. Lagoute et al., Phys. Rev. B **74**, 125410 (2006)

1D chain of Cu atoms: How to deduce the electronic band

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

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

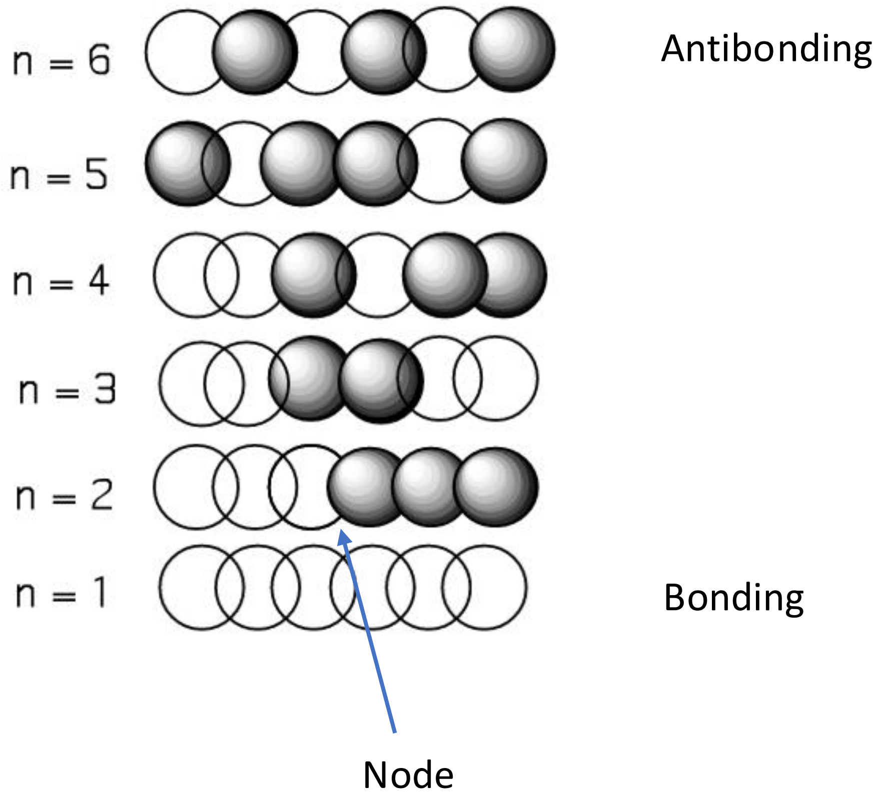
We need to link $E(n)$ to k-vector

- 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

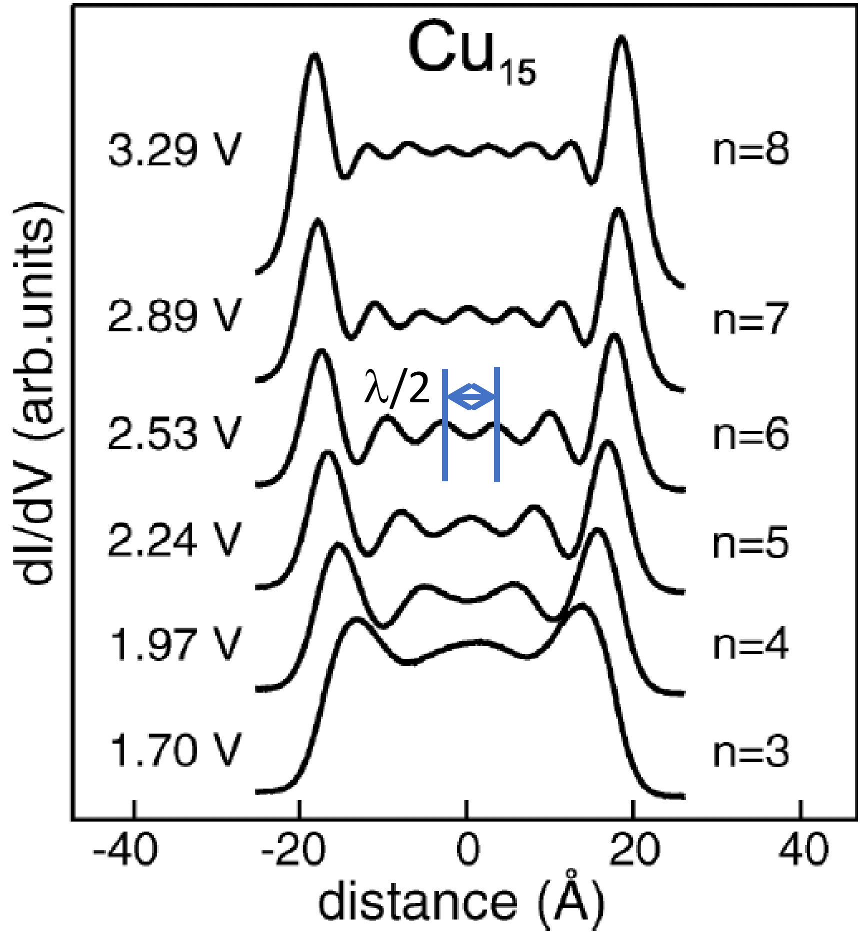
- STM and STS measure the LDOS: $\rho(x) \propto |\psi(x)|^2$ consequently, we see $\lambda/2$

- 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: Electronic band



deduce k from λ

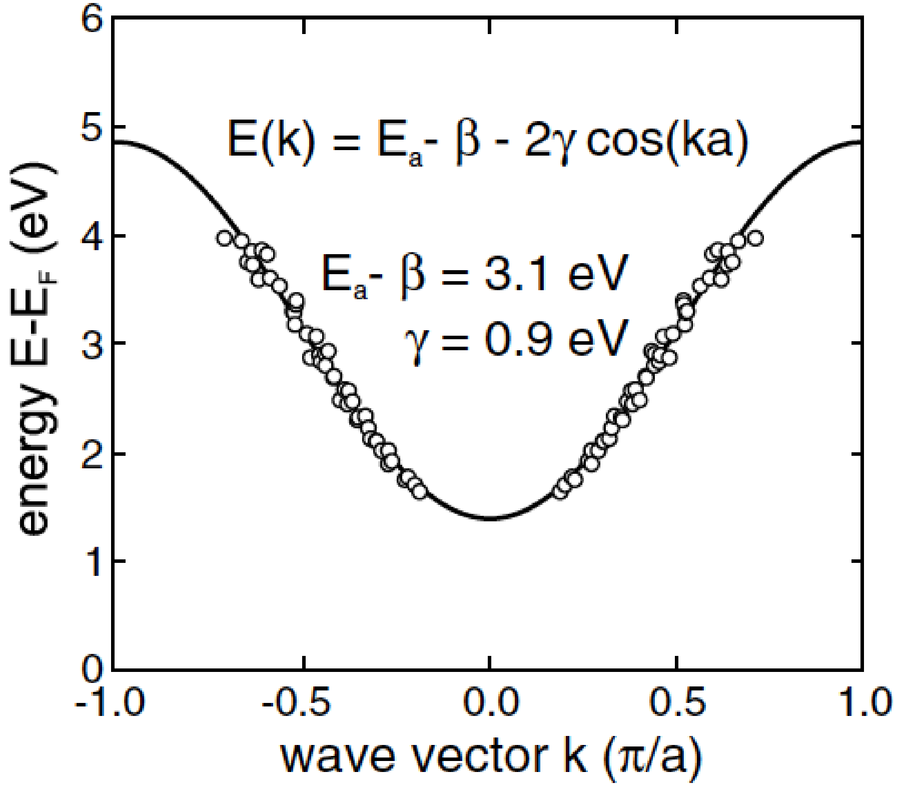
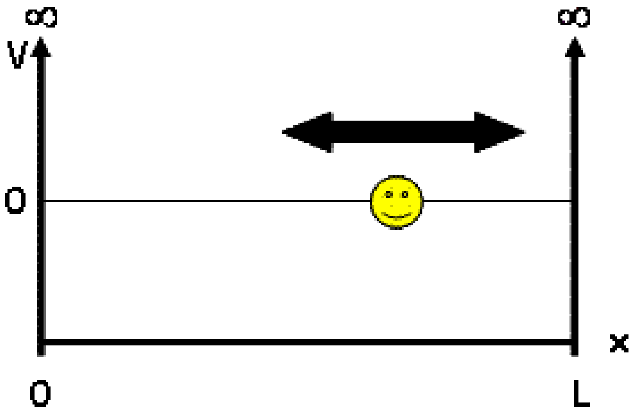


FIG. 3. The 1D band dispersion extracted from the characteristic wavelength for chain lengths from 5 to 15 atoms and $n = 3$ to $n = 8$, the wave vector is given in quantities of π/a ($a = 2.55$ Å is the Cu-Cu spacing). The experimental data are well fitted within the tight binding approximation yielding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

Confined electrons: Particle in a box



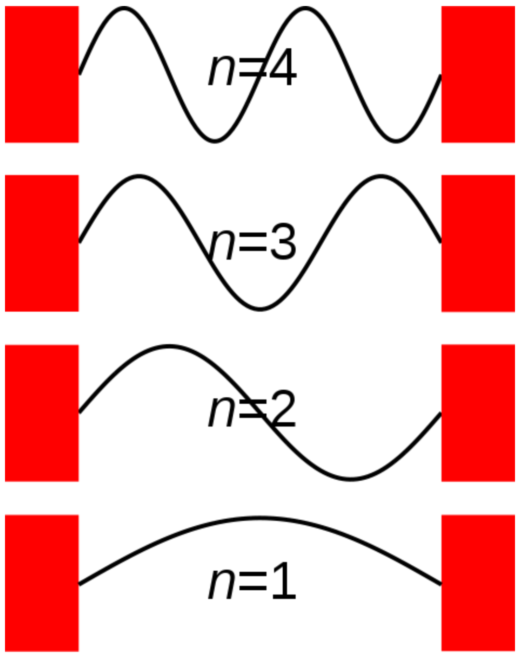
The potential energy is *0 inside the box* ($V = 0$ for $0 < x < L$) and *goes to infinity at the walls of the box* ($V = \infty$ for $x < 0$ and $x > L$).

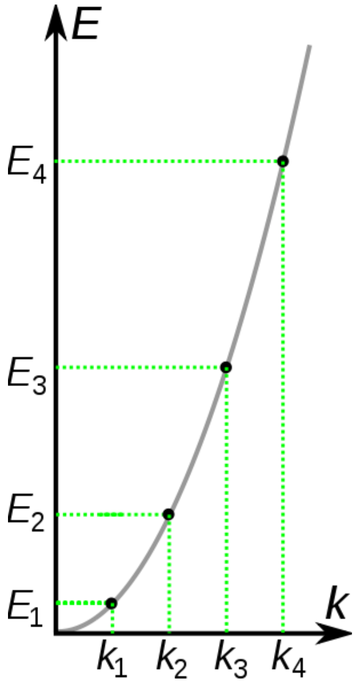
$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)$$

boundary conditions

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

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





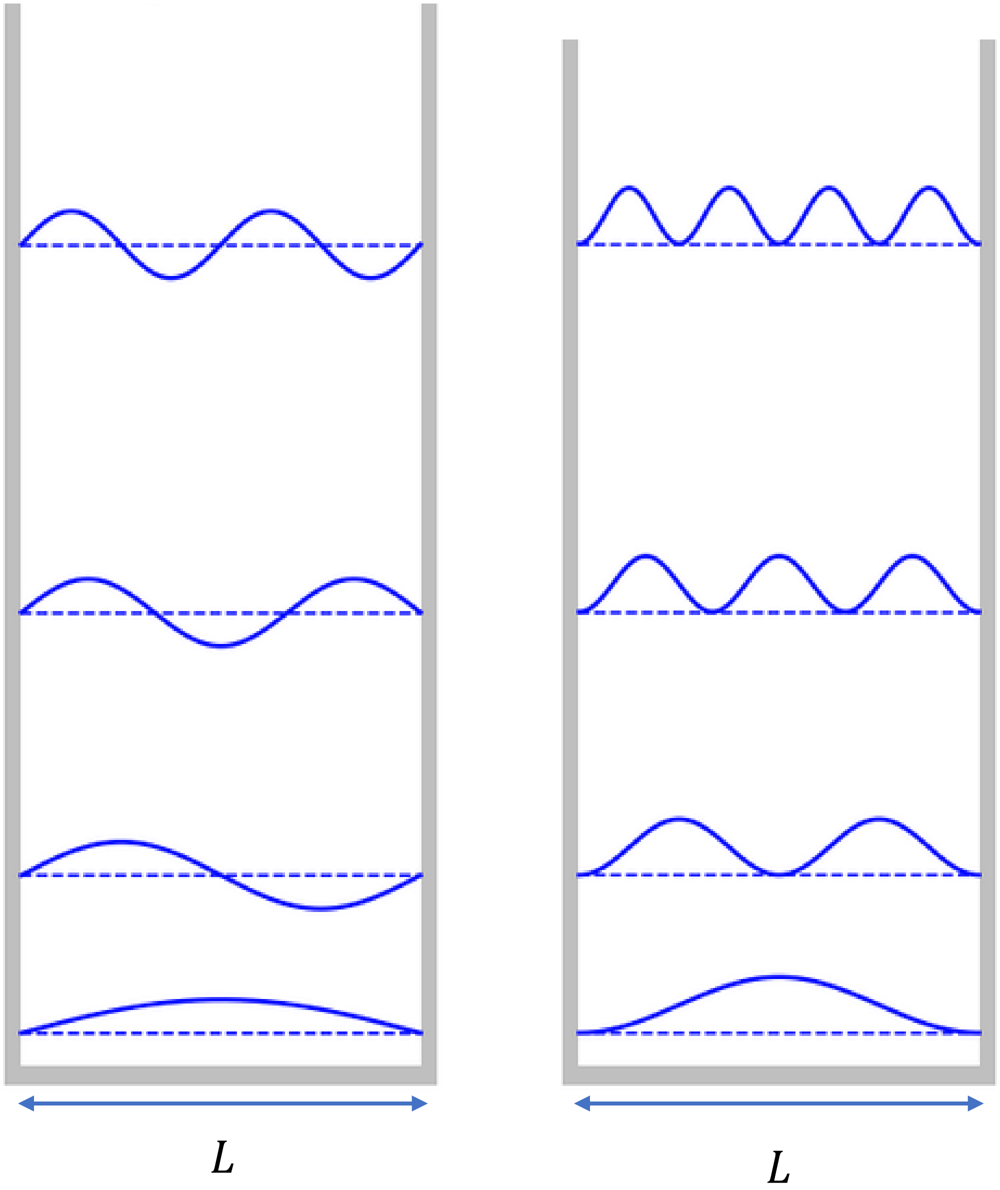
$$k_n = \frac{\pi}{L}n \qquad E_n = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 n^2, \qquad n > 0$$

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.

Confined electrons: STS mapping

wavefunctions $\psi_n(x)$ for a particle in a box (infinite walls) for $n = 1, 2, 3, 4$

$$E_n \propto \left(\frac{\pi}{L}\right)^2 n^2$$



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

1D chain of Cu atoms

Exercise 4.2

The observed quantized states can be described 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^*

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

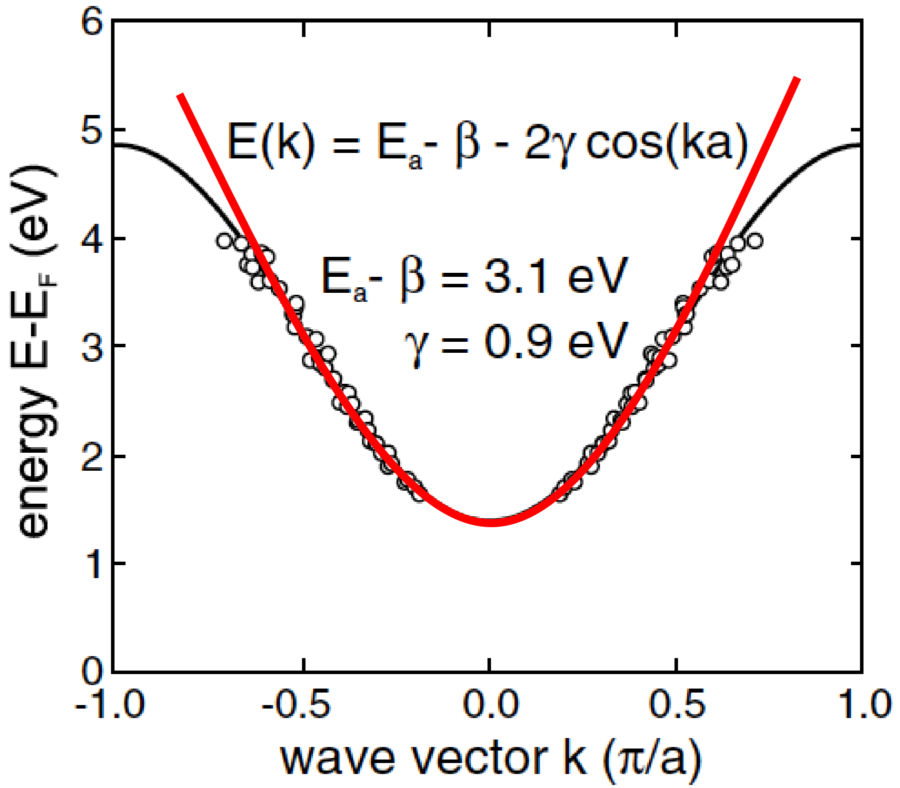
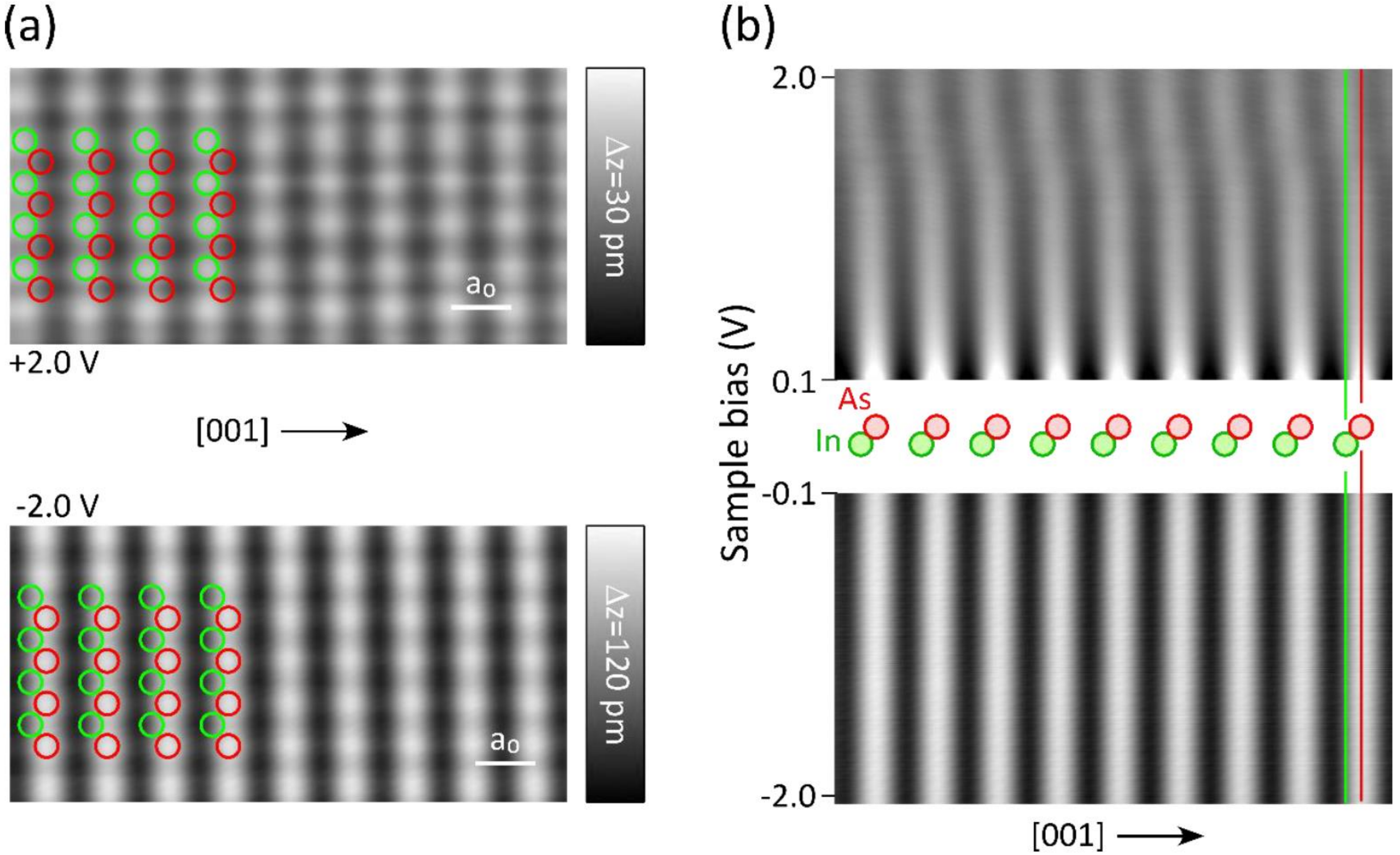


FIG. 3. The 1D band dispersion extracted from the characteristic wavelength for chain lengths from 5 to 15 atoms and $n = 3$ to $n = 8$, the wave vector is given in quantities of π/a ($a = 2.55$ Å is the Cu-Cu spacing). The experimental data are well fitted within the tight binding approximation yielding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

DOI: 10.1103/PhysRevLett.92.056803
S. Fölsch et al., Phys. Rev. Lett. **92**, 056803 (2004)

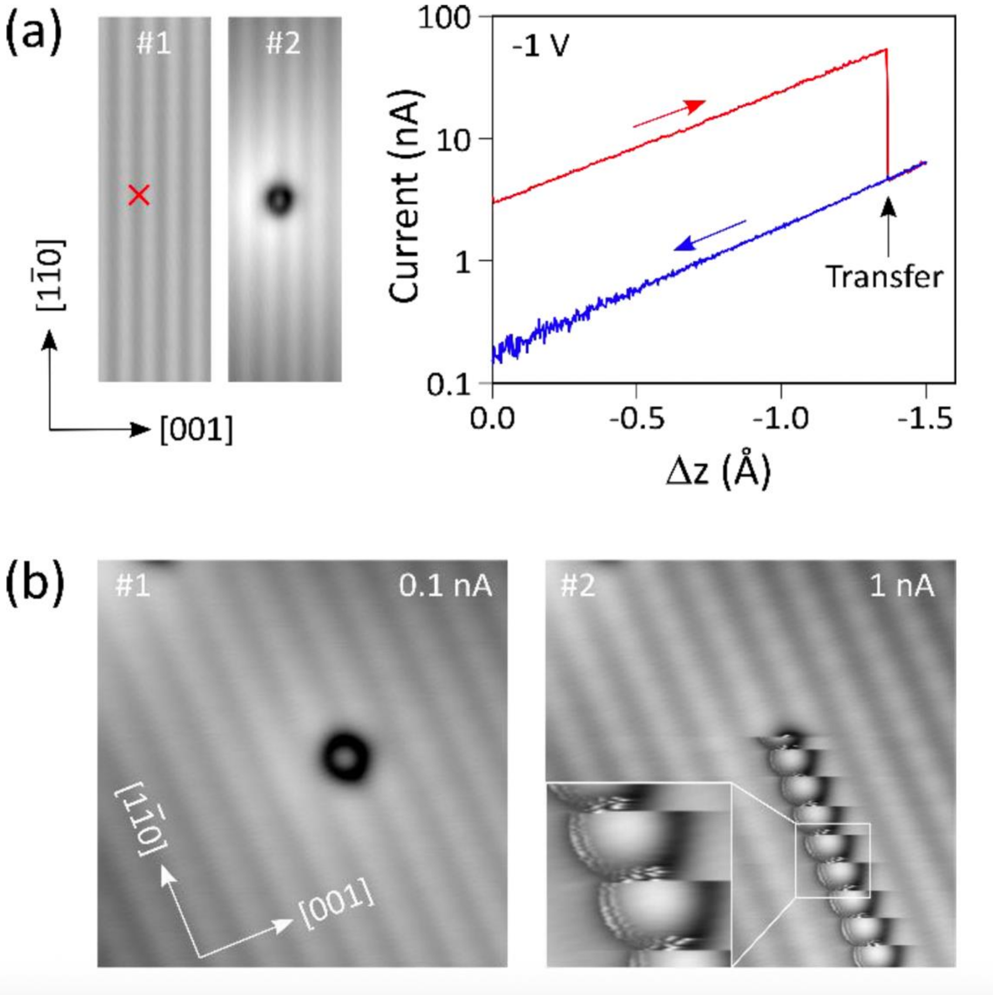
Quantum dots on the InAs(110) cleavage surface created by atom manipulation

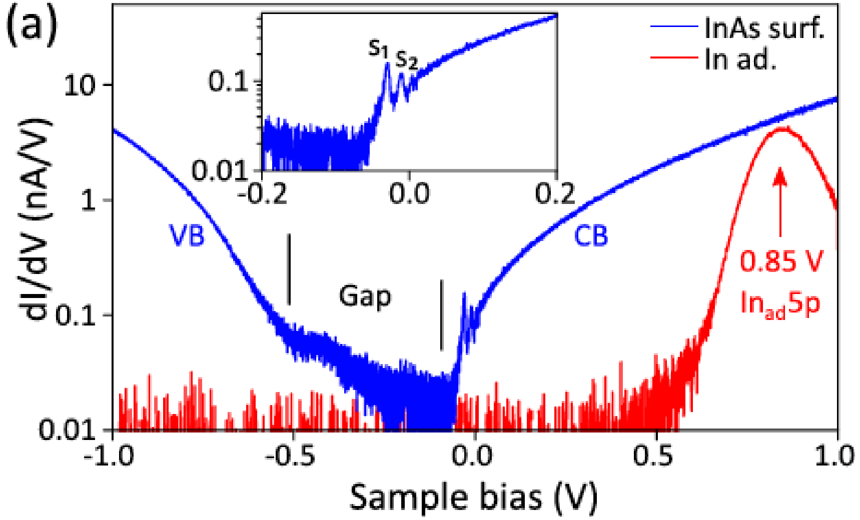
Bias dependent imaging



DOI: 10.1103/PhysRevResearch.6.013269
Phys. Rev. Research **6**, 013269 (2024)

Indium atom transfer from tip to surface



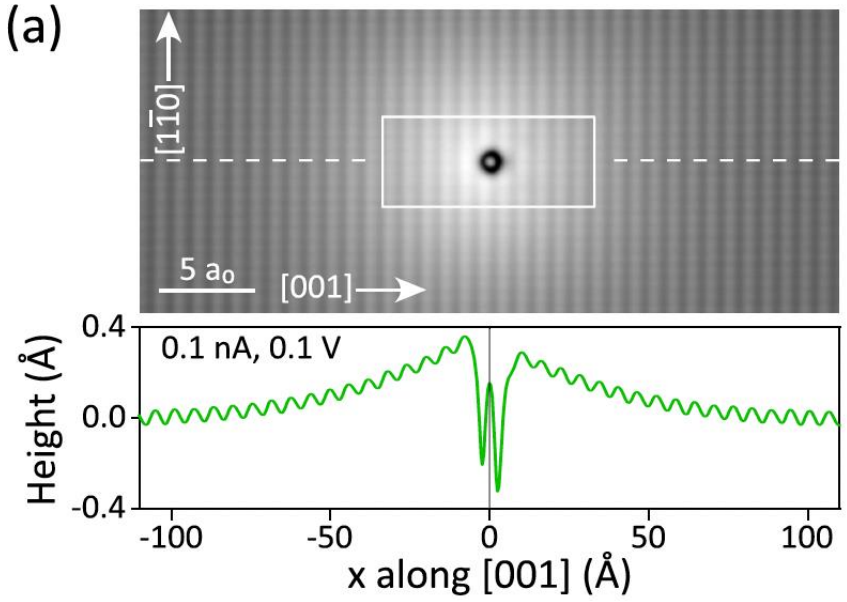


Conductance spectra on a logarithmic scale recorded with the tip probing the bare surface (blue) and a In adatom (red)

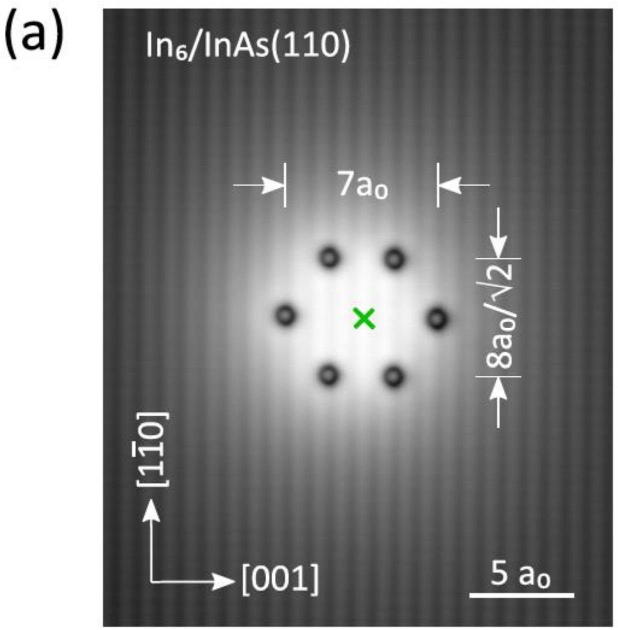
DOI: 10.1103/PhysRevResearch.6.013269
Phys. Rev. Research **6**, 013269 (2024)

Quantum dots: Artificial atoms and molecules

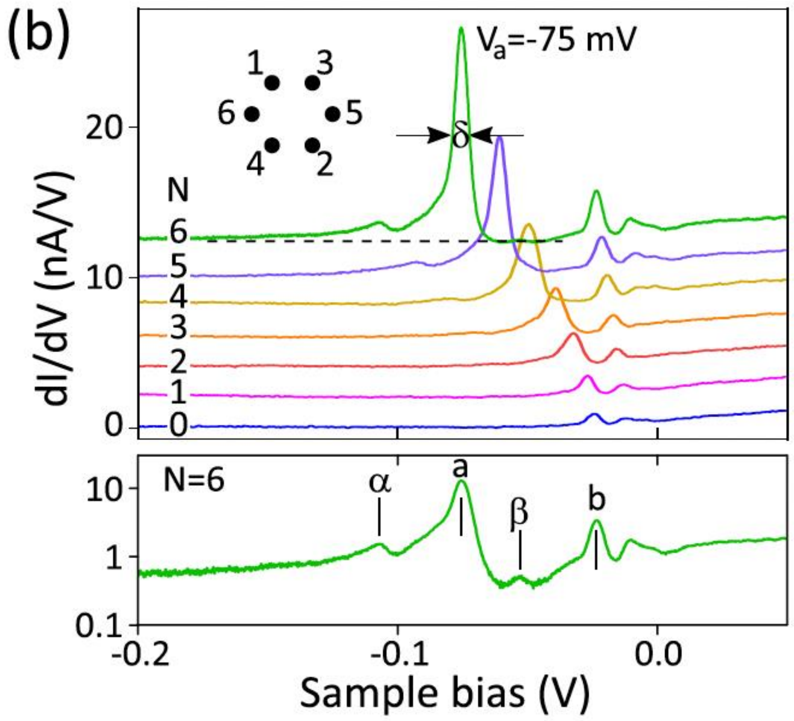
six In adatoms on InAs(110) assembled into a hexagon “dot”



In adatoms on InAs(110) are positively charged (screened Coulomb potential)

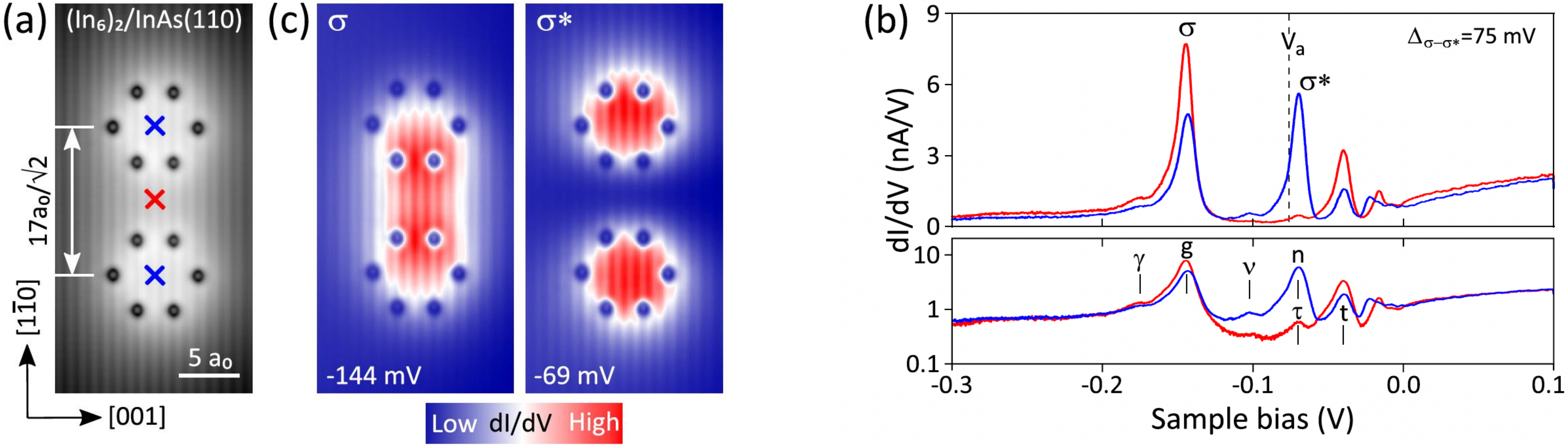


-0.3V



The attractive potential induced by the assembled adatoms confines electrons at the InAs(110) surface in an atomic-like potential.
The hexagon acts as a quantum dot—an “artificial atom”— that creates a bound state of discrete energy

DOI: 10.1103/PhysRevResearch.6.013269
Phys. Rev. Research **6**, 013269 (2024)

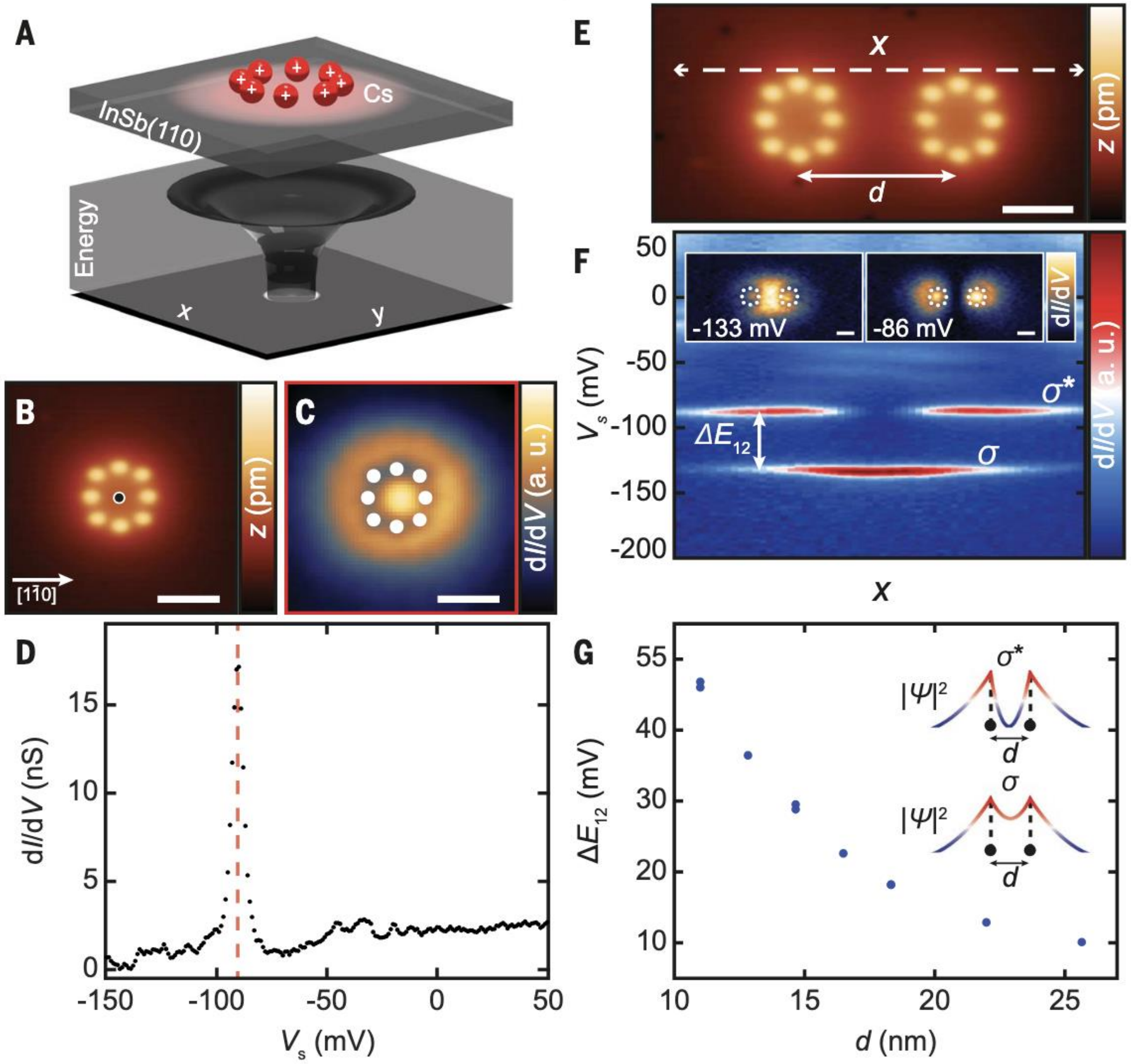


Molecular electronic states can be created by bound-state coupling in quantum-dot dimers.

Emergence of a bonding (σ) and an antibonding state (σ*) as expected for the symmetric and antisymmetric superposition of the bound states belonging to the two dots

DOI: 10.1103/PhysRevResearch.6.013269
Phys. Rev. Research **6**, 013269 (2024)

Quantum simulator



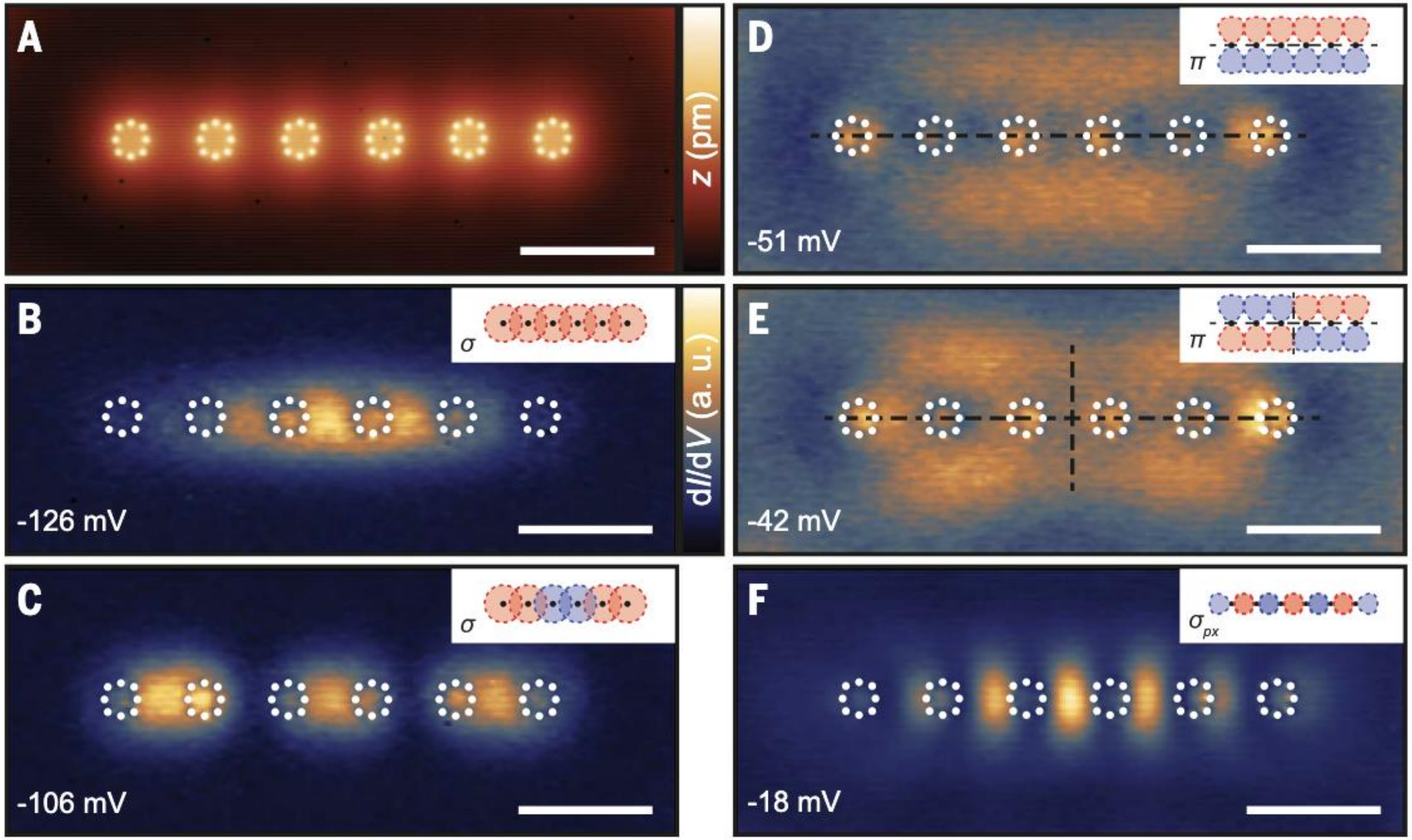
Cs atoms on InSb(110)

Cs transfer charge: Cs^+

The ring structures create a potential energy landscape that mimics the $1/r$ potential of an atom in two dimensions

DOI: 10.1126/science.adf2685
Science **380**, 1048 (2023)

Quantum simulator



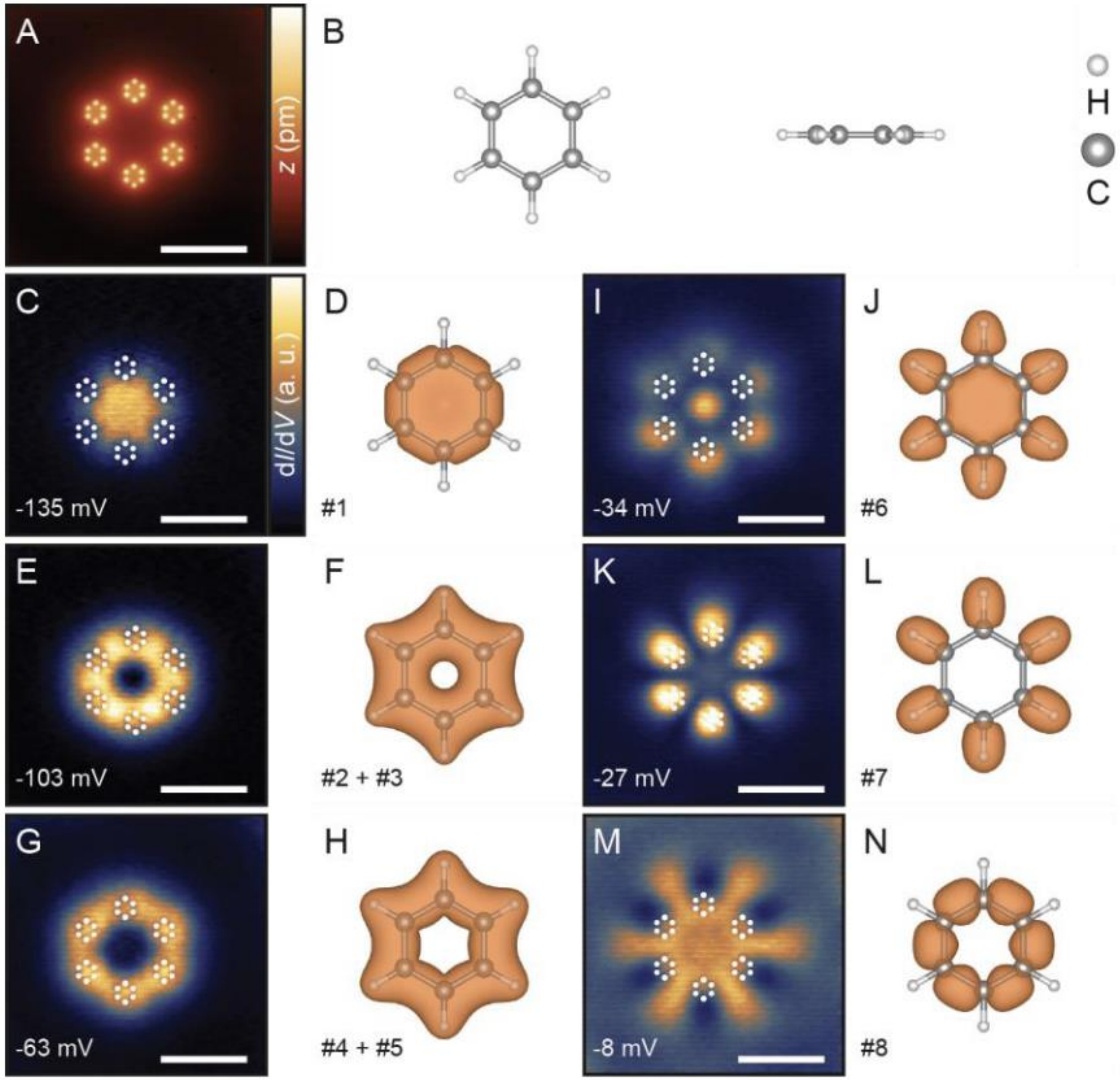
emergence of
σ and π orbitals

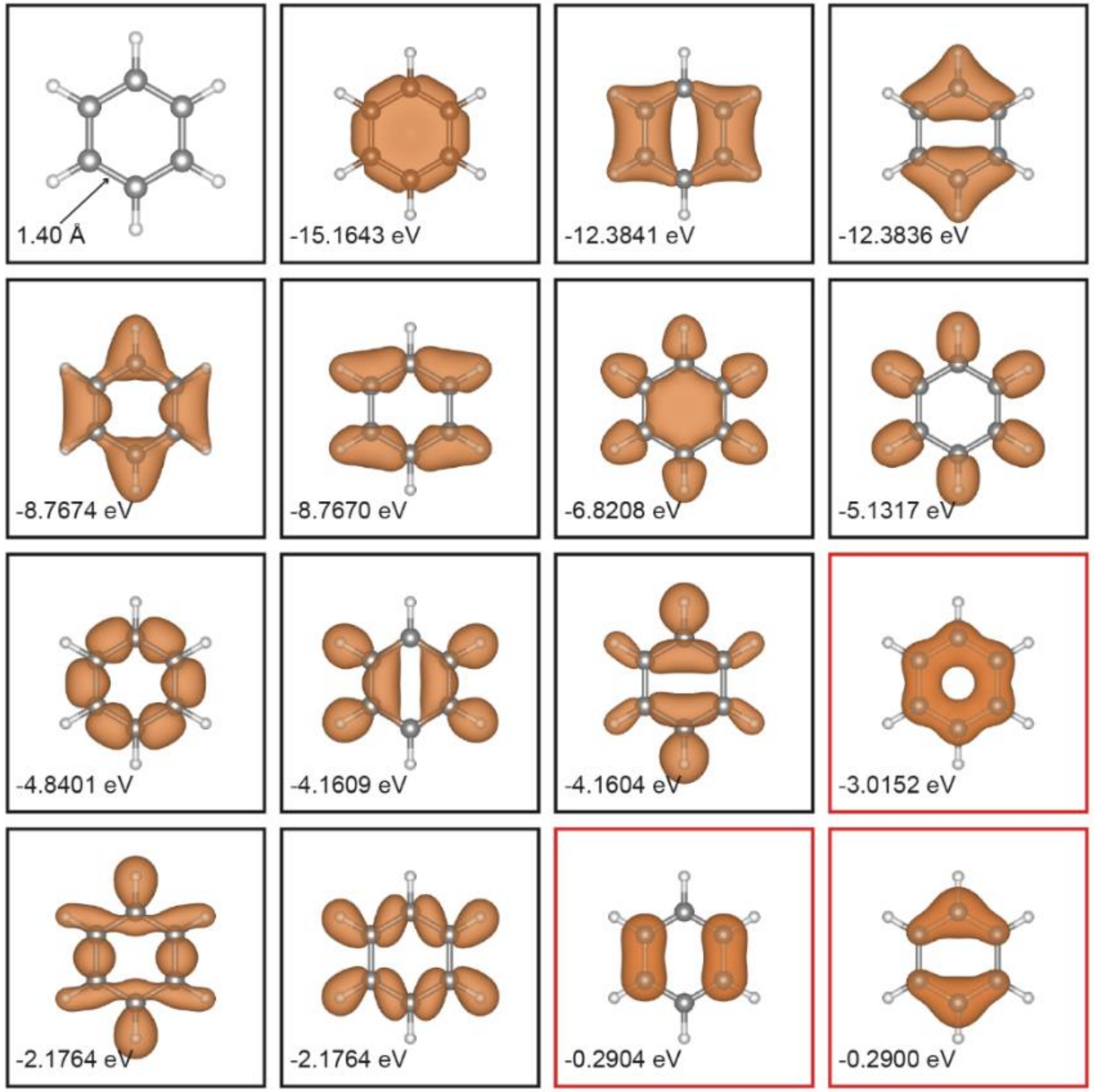
DOI: 10.1126/science.adf2685
Science **380**, 1048 (2023)

Quantum simulator: Benzene

EPFL

Exercise 4.3

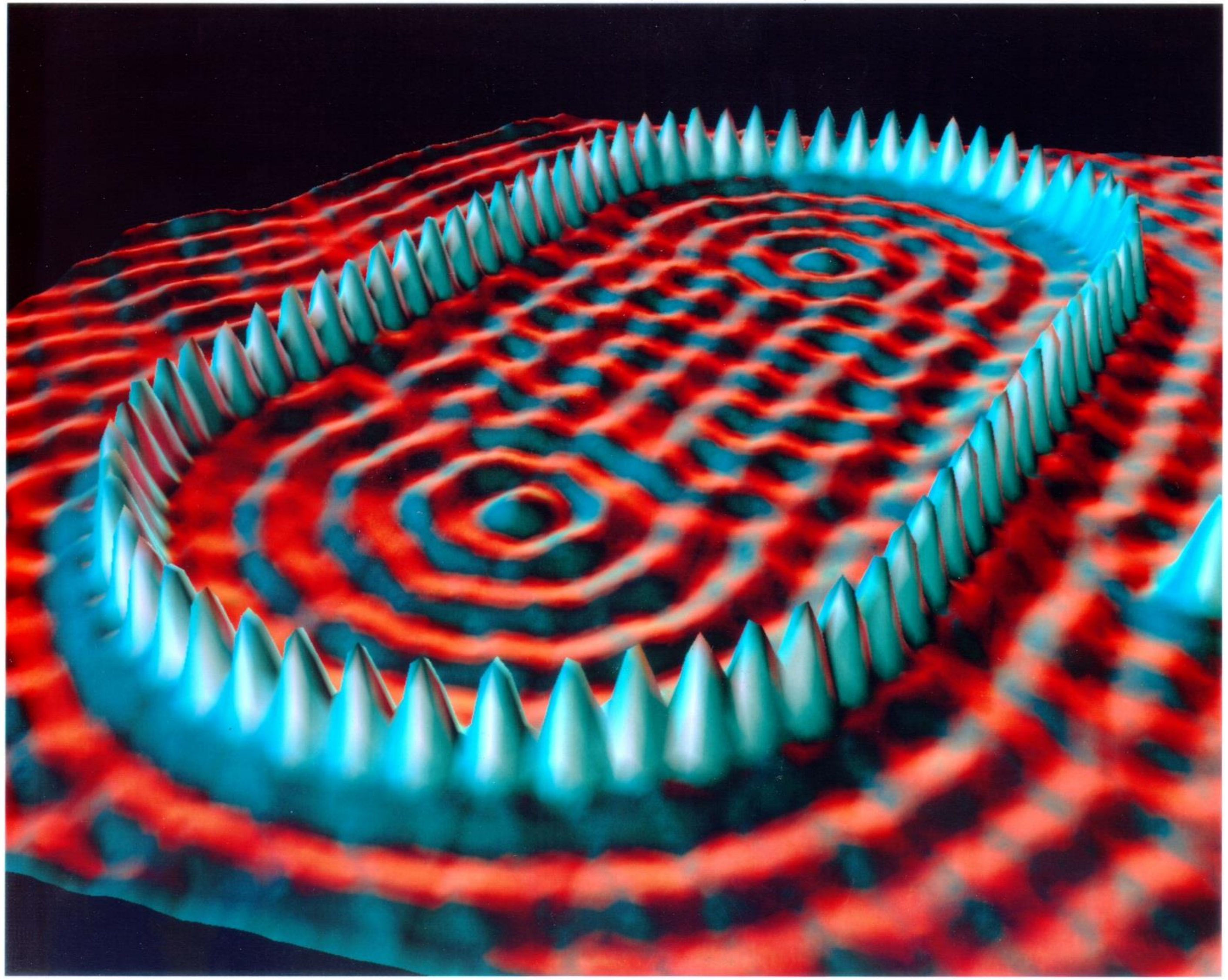




DOI: 10.1126/science.adf2685
Science **380**, 1048 (2023)

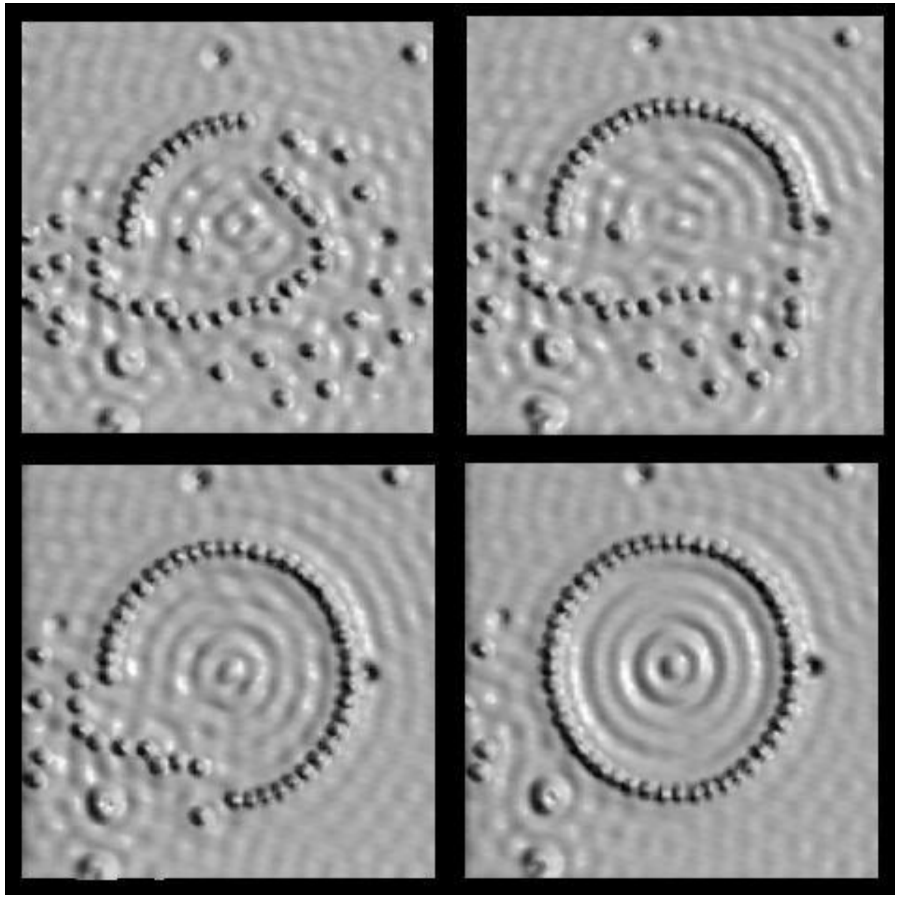
The quantum corral

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

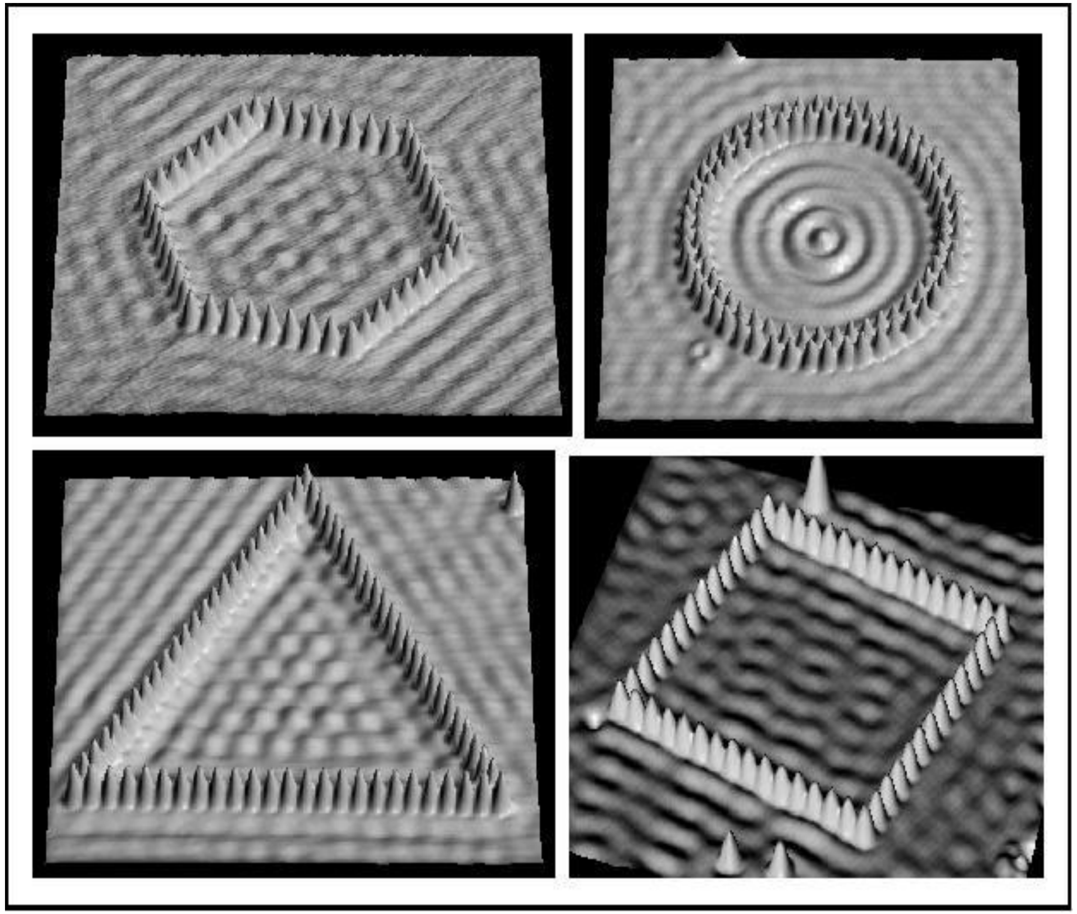


IBM Almaden

2D-electron gas in a box



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 are there 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):
  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

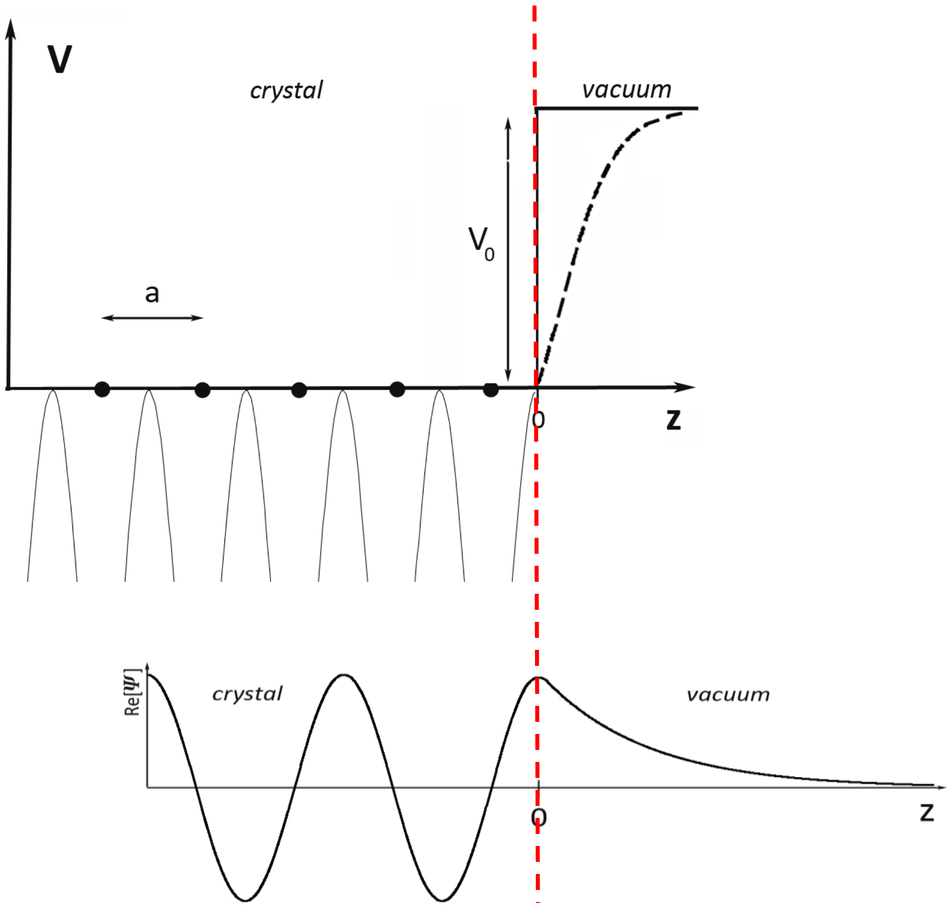
➡

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

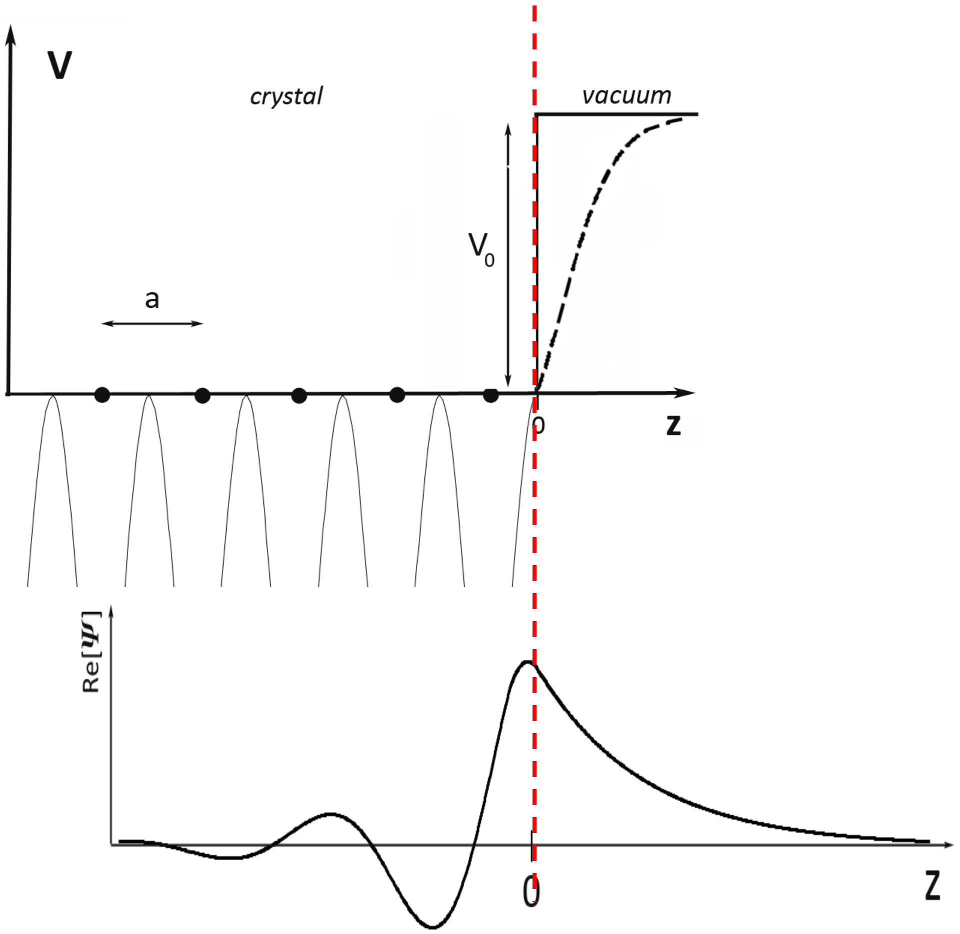
Perpendicular to the surface
→ vacuum side: decaying wave

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

bulk state



surface state

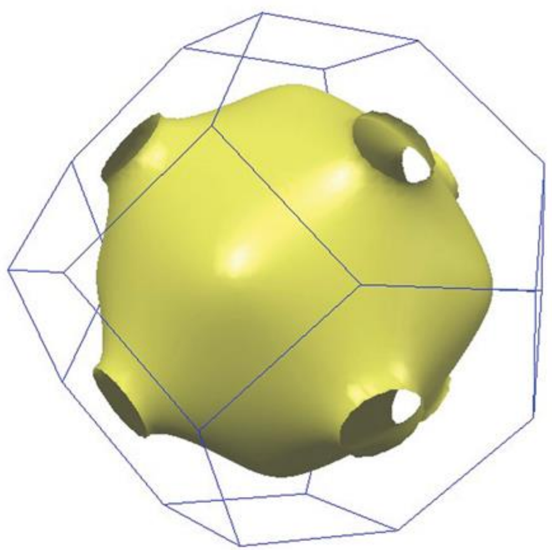


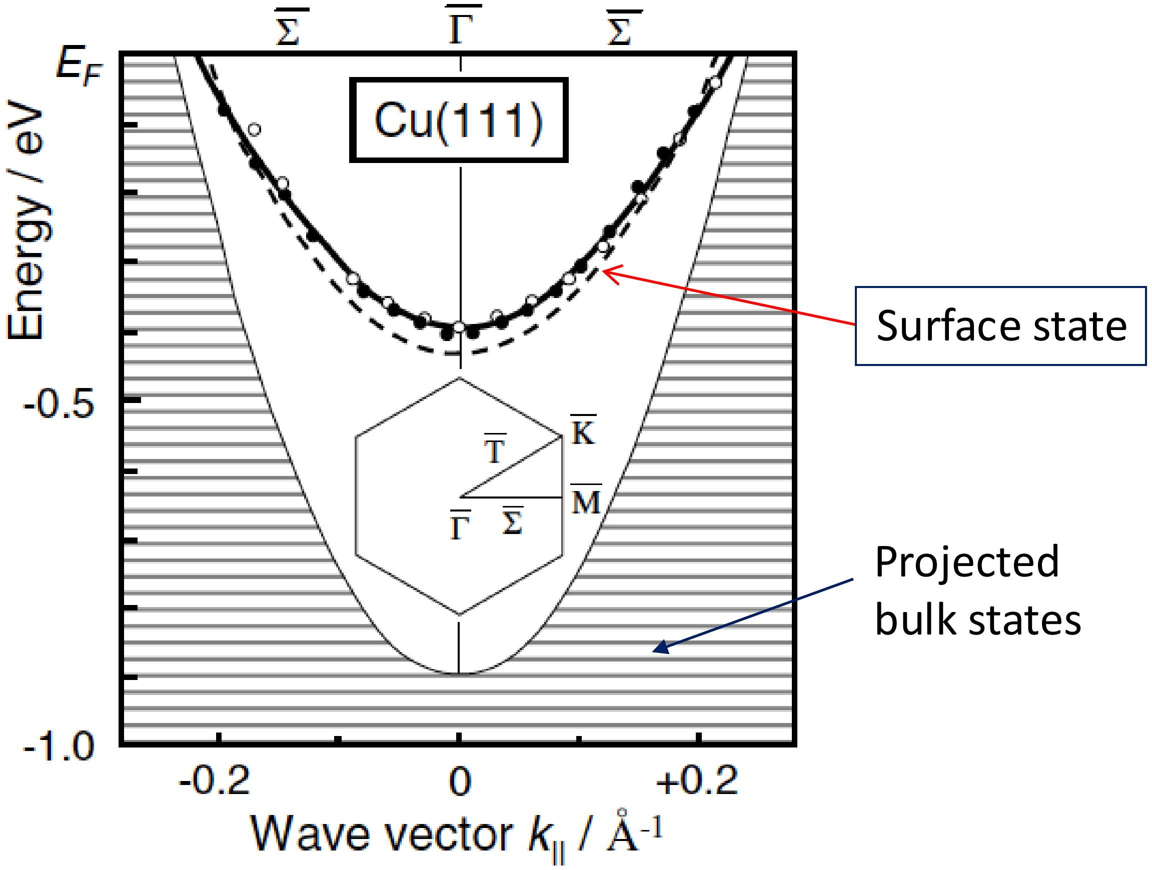
Shockley surface state:
a 2D free electron gas confined at the surface

Surface states at (111) noble metal surfaces

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

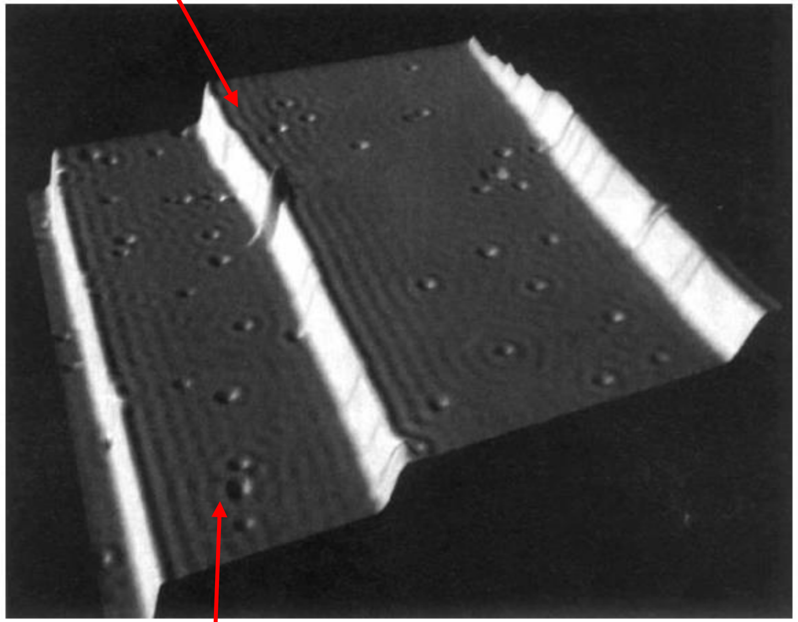




D. Shoenberg (1962) http://www.jstor.org/stable/73177

Friedel oscillations

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 state

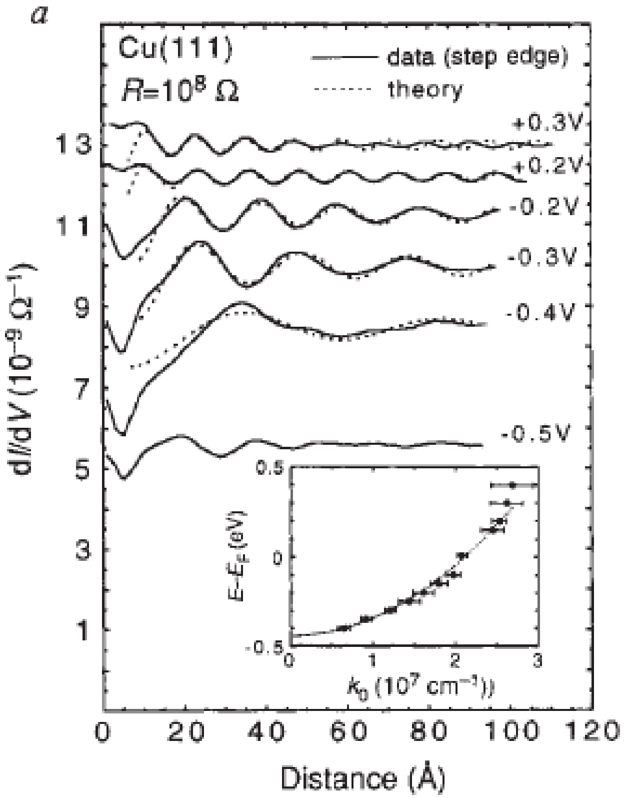
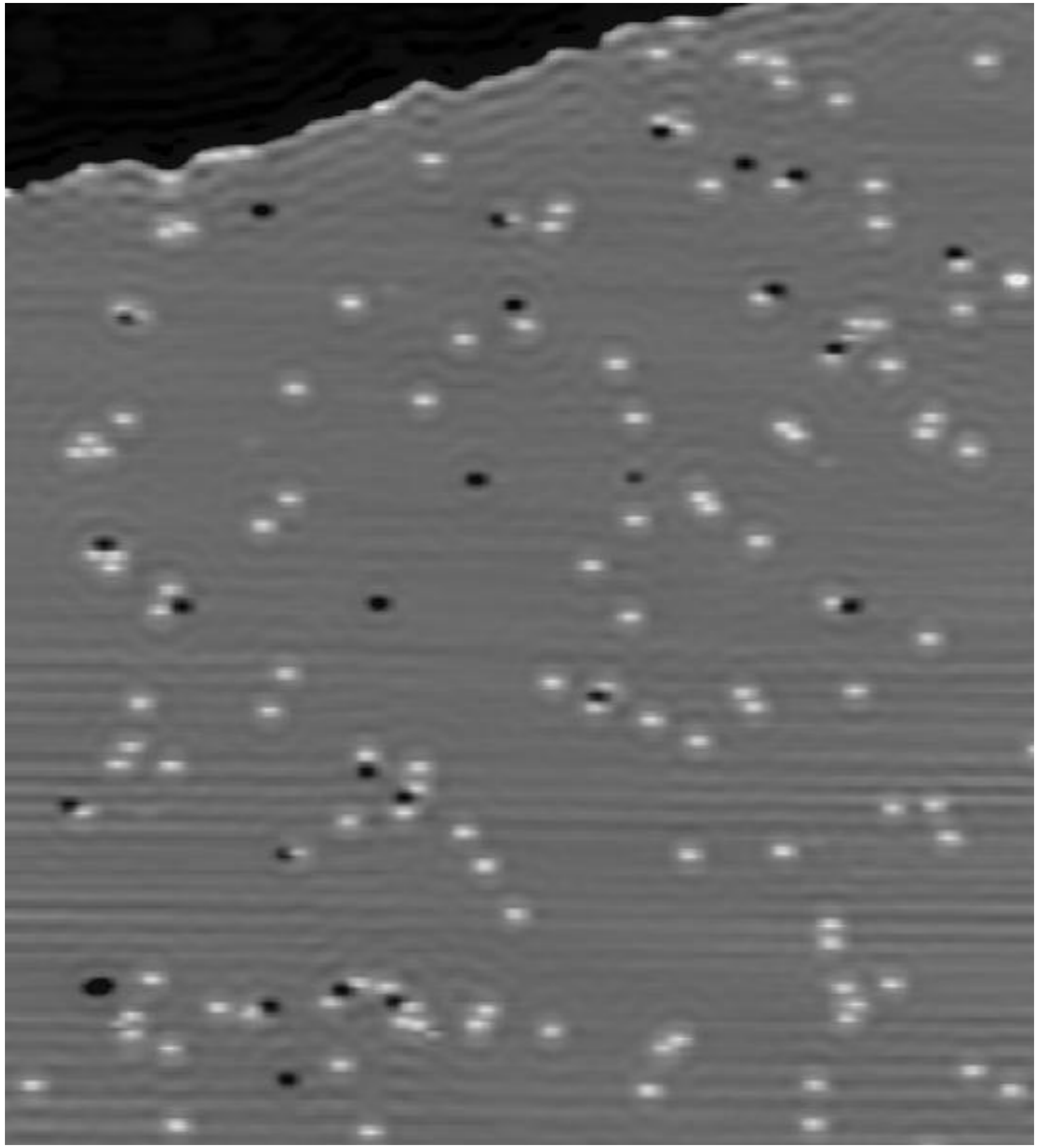


FIG. 2 *a*, Solid lines: spatial dependence of dI/dV, measured as a function of distance (along upper terrace) from step edge at different bias voltages. Zero distance corresponds to the lower edge of the step.

DOI: 10.1038/363524a0
M. F. Crommie, Nature **363,** 524 (1993)

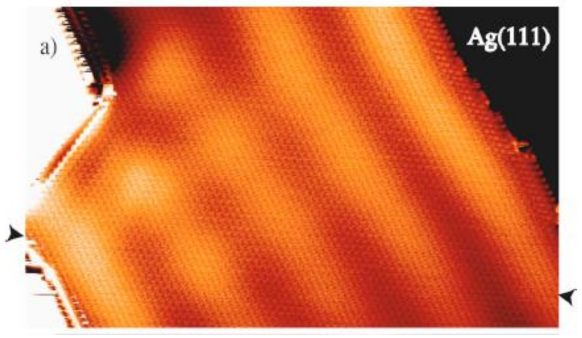


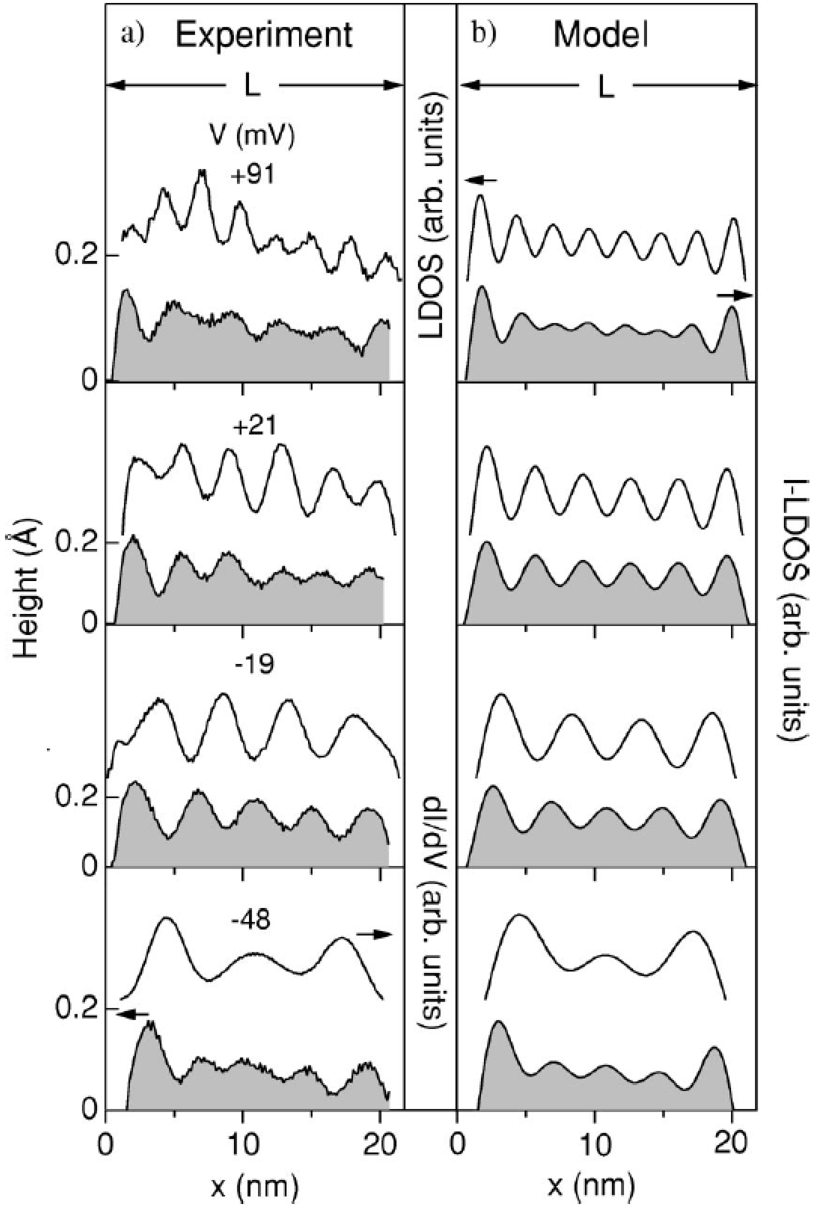
bright dots are Cu adatoms diffusing at the surface (hopping between equivalent adsorption sites)

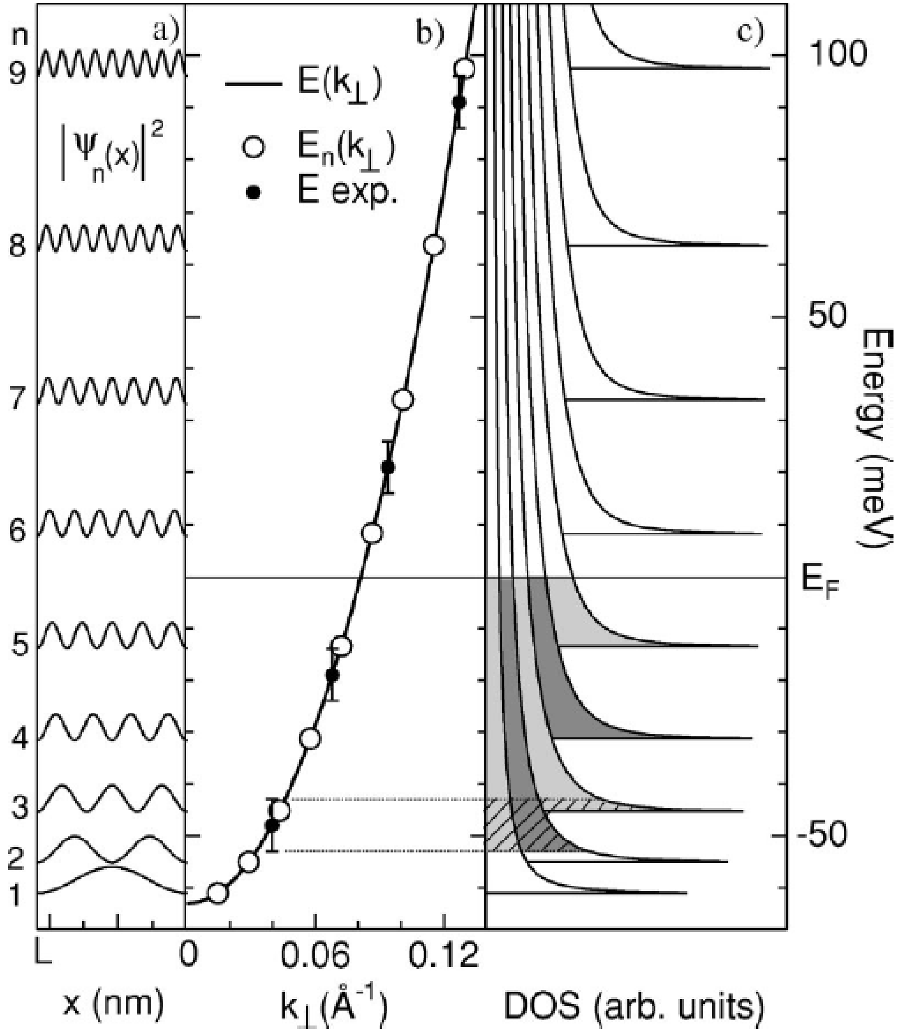
black spots are CO molecules (contamination)

Ag(111) surface state confinement

Exercises 4.4 – 4.6



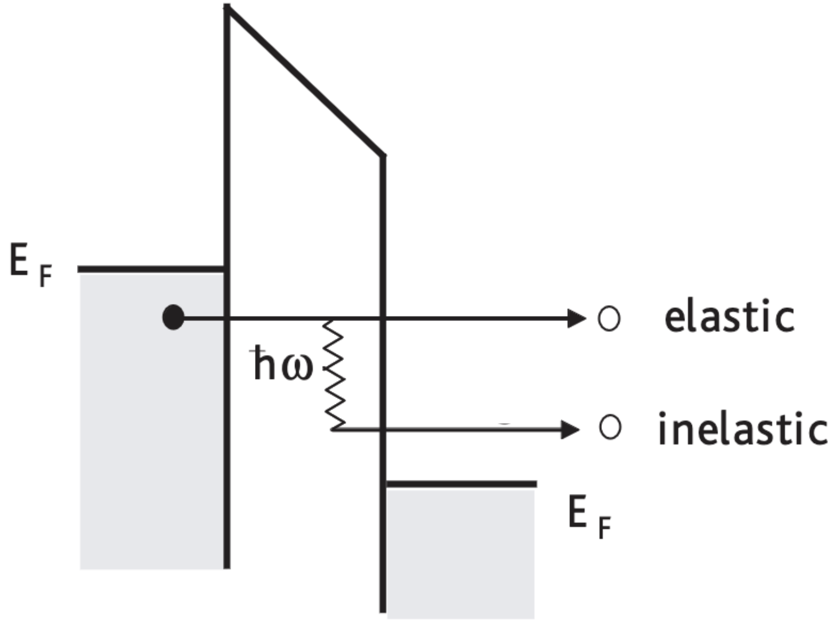




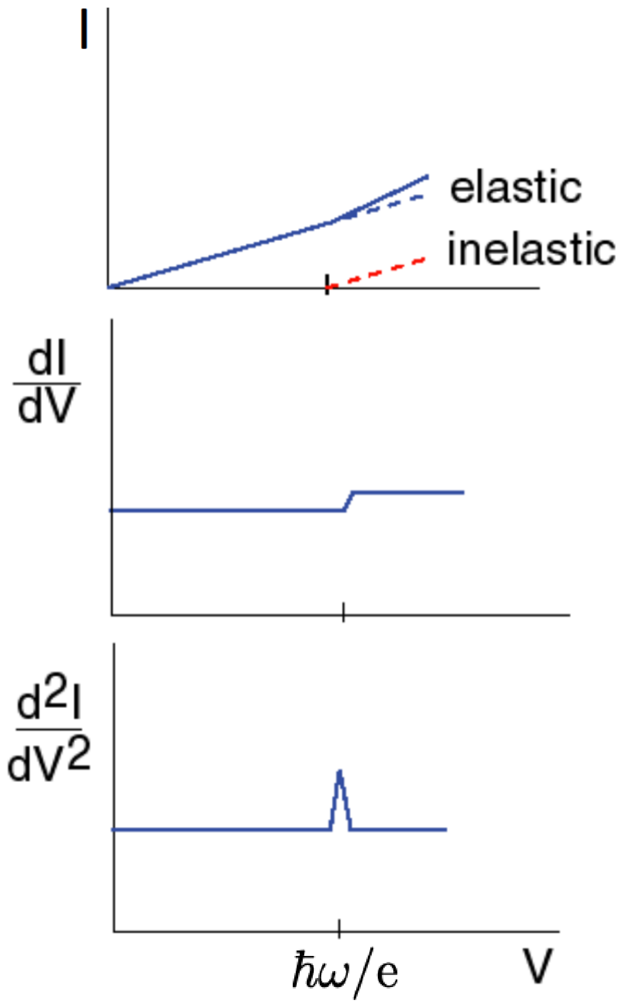
DOI: 10.1103/PhysRevB.67.193402

Inelastic Electron Tunneling Spectroscopy (IETS)

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



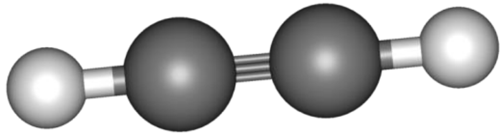
Consider an object at the surface (molecule, adatom, nanostructure...).
The tunneling electrons trigger an excitation of the adsorbate (vibration, rotation, spin flip, magnetic excitation...): they couple to the excitation mode, loose their energy, so that an additional tunneling channel is created.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



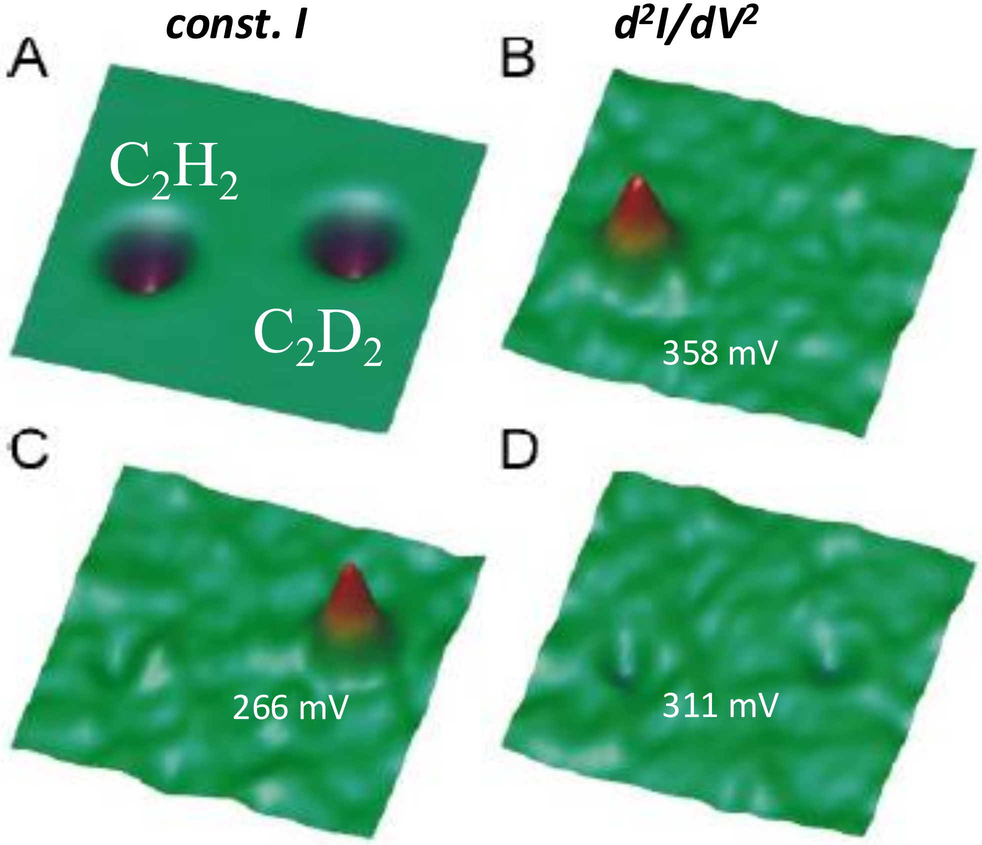
An inelastic tunneling channel opens, at a specific energy, in addition to the elastic one. The inelastic feature is present in both bias polarities.

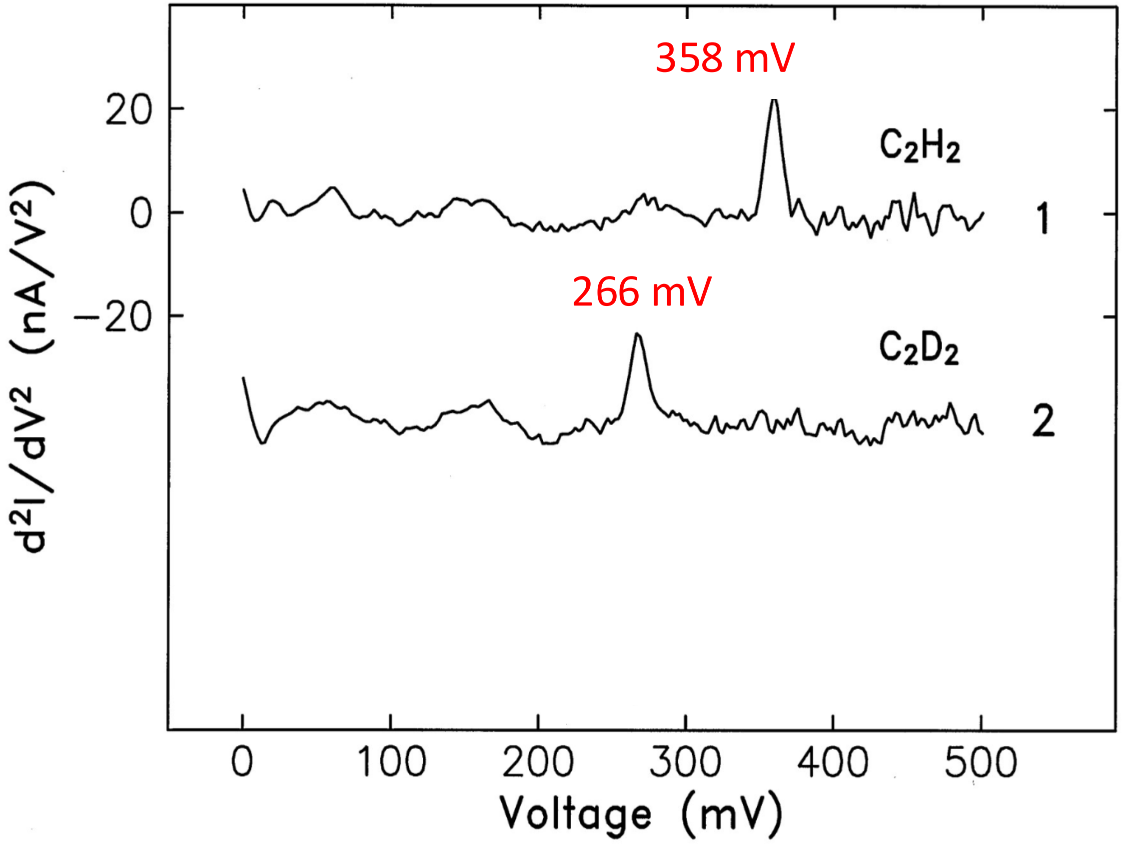
Vibrations: chemical contrast

Exercise 4.7



acetylene C_2H_2





Isotopic substitution (hydrogen → deuterium):

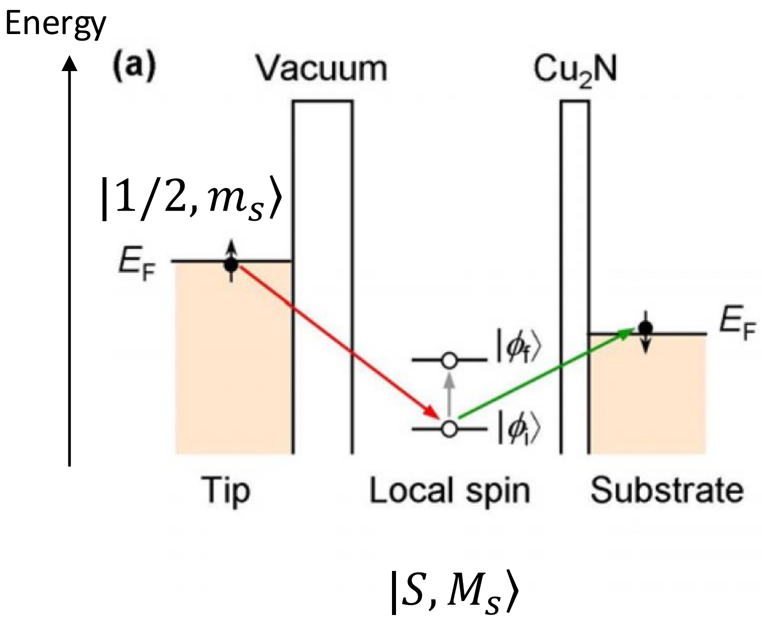
C_2H_2: C-H stretch @ 358 mV
C_2D_2: C-D stretch @ 266 mV

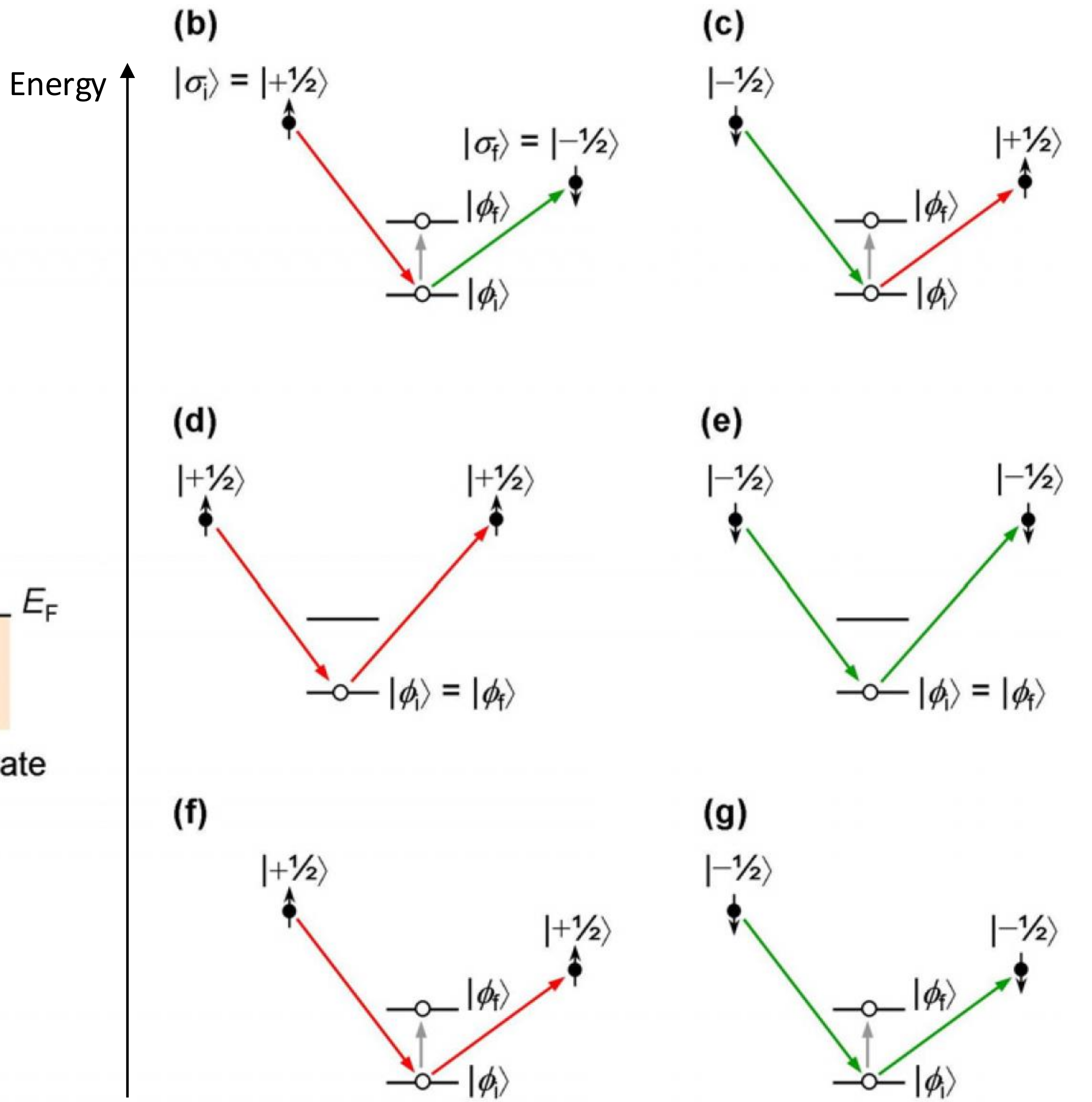
$$\hbar\omega \propto \frac{1}{\sqrt{m_{reduced}}}$$

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

IETS: spin excitations

hamiltonian for s-e scattering: $J_{exc}\, S_z s_z + 1/2\, J_{exc}\, (S_+ s_- + S_- s_+)$





$\Delta m_s = \mp 1$
$\Delta M_s = \pm 1$
$\Delta E \neq 0$

$\Delta m_s = 0$
$\Delta M_s = 0$
$\Delta E = 0$

$\Delta m_s = 0$
$\Delta M_s = 0$
$\Delta E \neq 0$

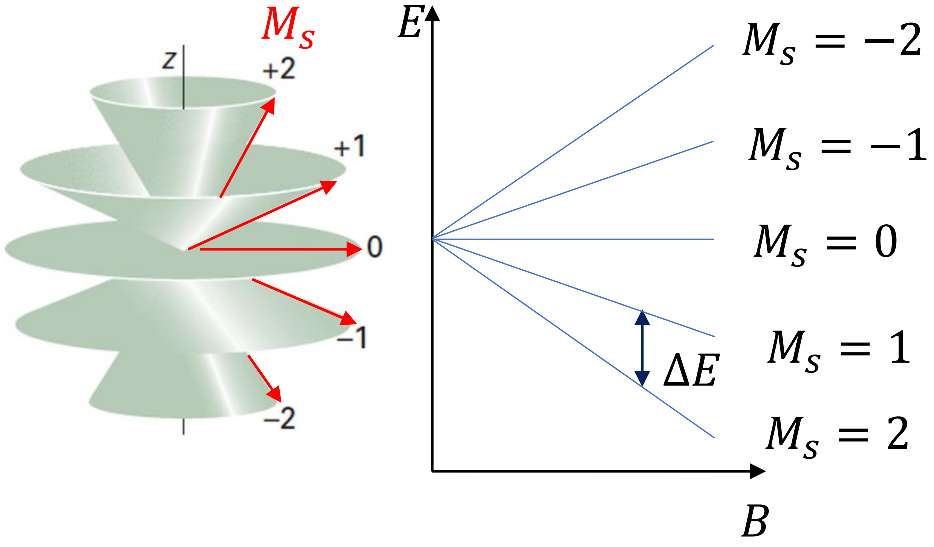
Loth et al., New J. Phys. **12**, 125021 (2010)

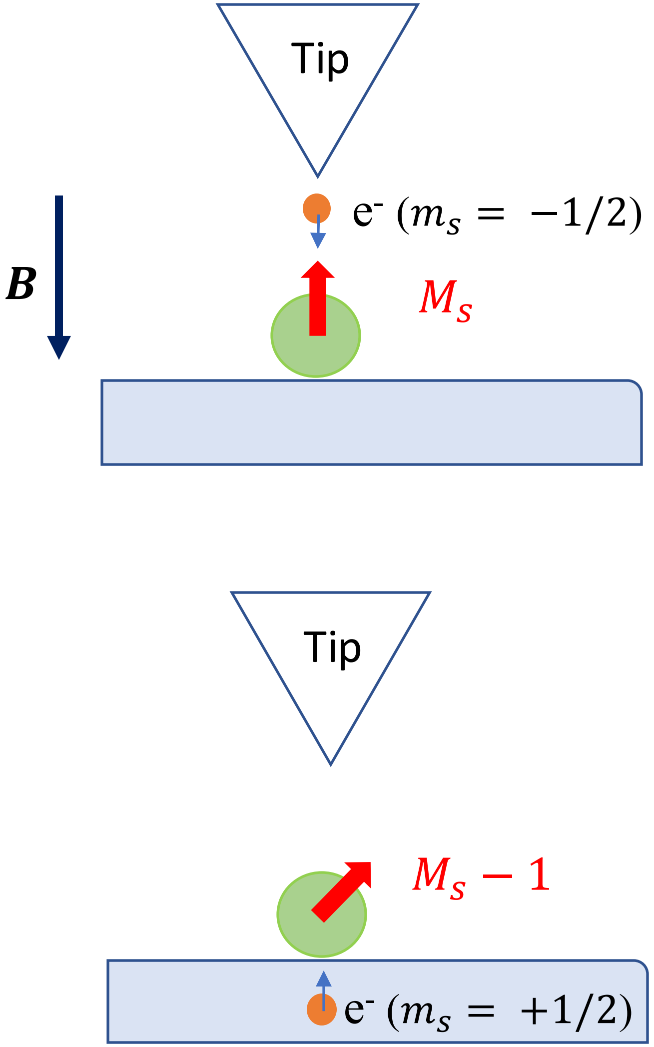
IETS: spin excitations

Exercise 4.8

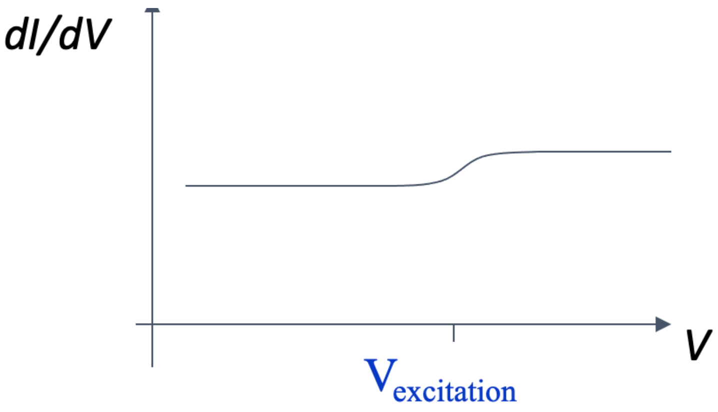
Zeeman energy for a paramagnetic spin $|S, M_s\rangle$ (magnetic moment $\boldsymbol{\mu} = -g\mu_B \boldsymbol{S}$)

example: $S = 2; \quad M_s = -2,..,2$





we expect:



$$\mathrm{e}V_{excit} = g\mu_B B$$

$$\Delta m_s = +1 \rightarrow \Delta M_s = -1$$

$$\Delta E = |g\mu_B B|$$

$$H_{Zee} = g\mu_B \boldsymbol{S} \cdot \boldsymbol{B}$$

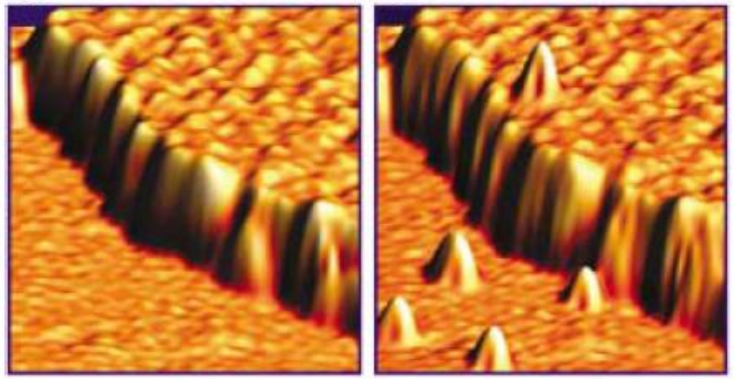
$$E(M_s) = g\,\mu_B M_s B$$

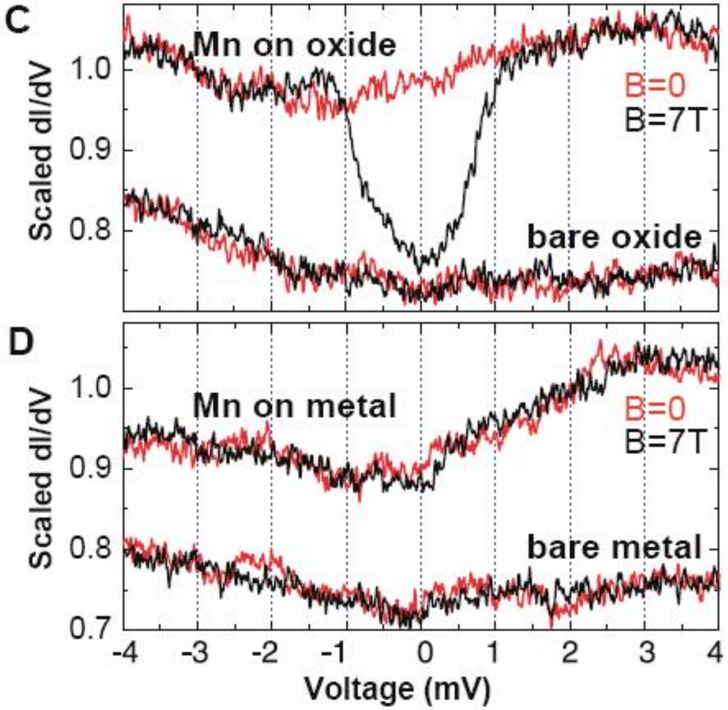
$$\Delta E = |g\mu_B B\, \Delta M_s|$$

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.

Example: Mn/Al_2O_3

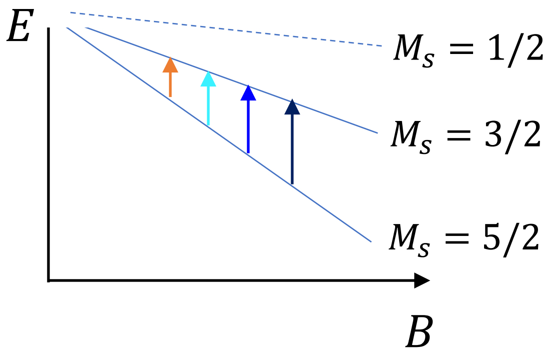
$Mn/Al_2O_3/Ni_3Al(111)$





free Mn atom: [Ar]3d[5] 4s[2]

$$S = \frac{5}{2}, L = 0$$



$$eV_{excit} = g\mu_B B$$

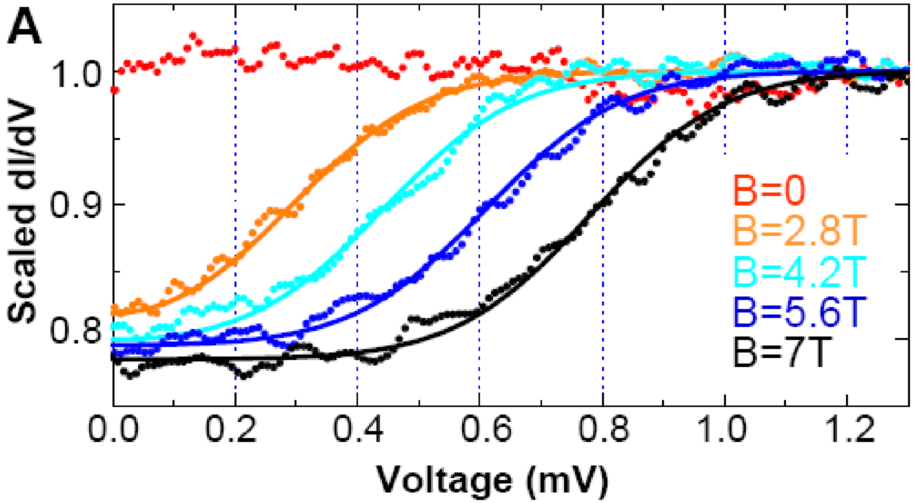
$$g = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

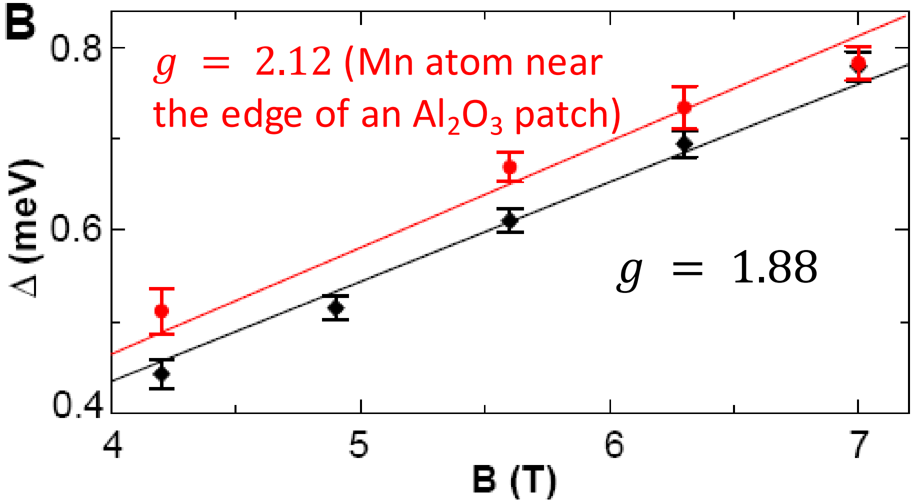
g is the Landé g-factor.

For $L = 0 \rightarrow g = 2$

T = 0.6 K

Shift of the spin-flip conductance step with magnetic field





weak influence of the crystal field (local environment)

[Heinrich et al., Science 2004 10.1126/science.1101077]