Manipulating Molecular Spins at the Nanometer Scale

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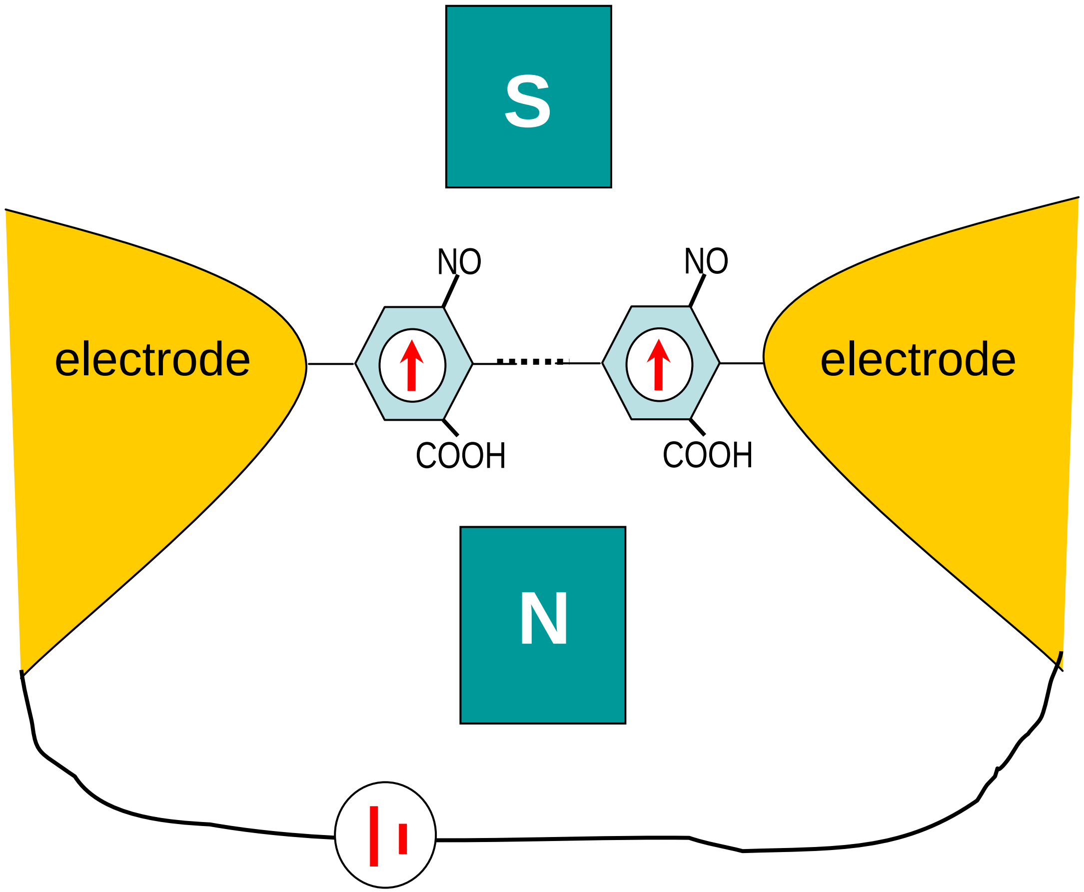
张 平 *(Institute of Appl. Phys. & Computa. Math. Beijing)*

Molecule Based Spintronics



1. **Molecule-electrode (metal) interaction**
2. **Molecule-molecule interaction**
3. **Spin-polarized electrons**

   (injection, transport, manipulation, detection…)

   (under external fields)

……

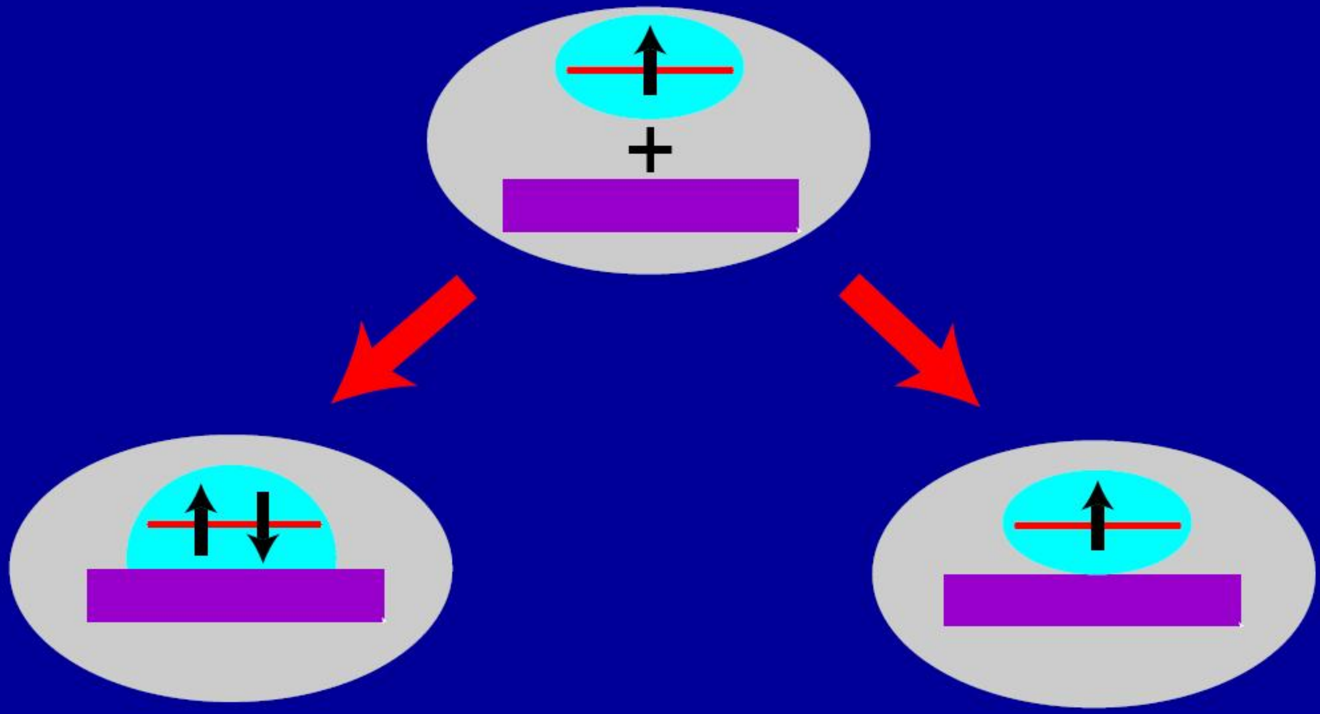
Essential but Challenging!

Content

I. Introduction
II. Experiment
III. Kondo Effect (MnPc)
IV. Zeeman Effect (CoPc)
V. *Gap States (Mn & Cr)*
VI. Summary

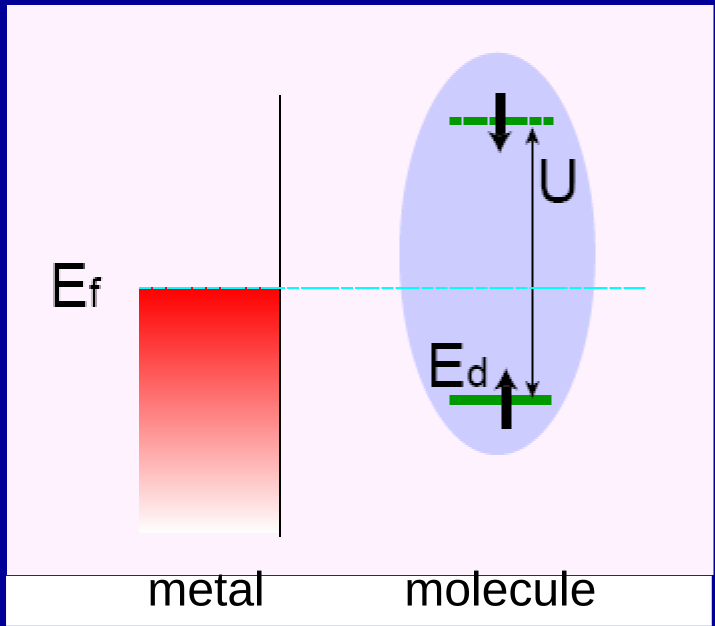
I. Introduction

localized spin + surface



I. Introduction

Anderson Model



$$
\begin{aligned}
H &= H_c + H_{mix} + H_d + H_U \\
H_c &= \sum_{k\sigma} \epsilon_k c^\dagger_{k\sigma} c_{k\sigma} \\
H_{mix} &= \sum_{\sigma} V_k c^\dagger_{k\sigma} d_\sigma + h.c. \\
H_d &= E_d \sum_{\sigma} n_\sigma \\
H_U &= U n_{d\uparrow} n_{d\downarrow}
\end{aligned}
$$

Three parameters:

E_d: energy of molecular level

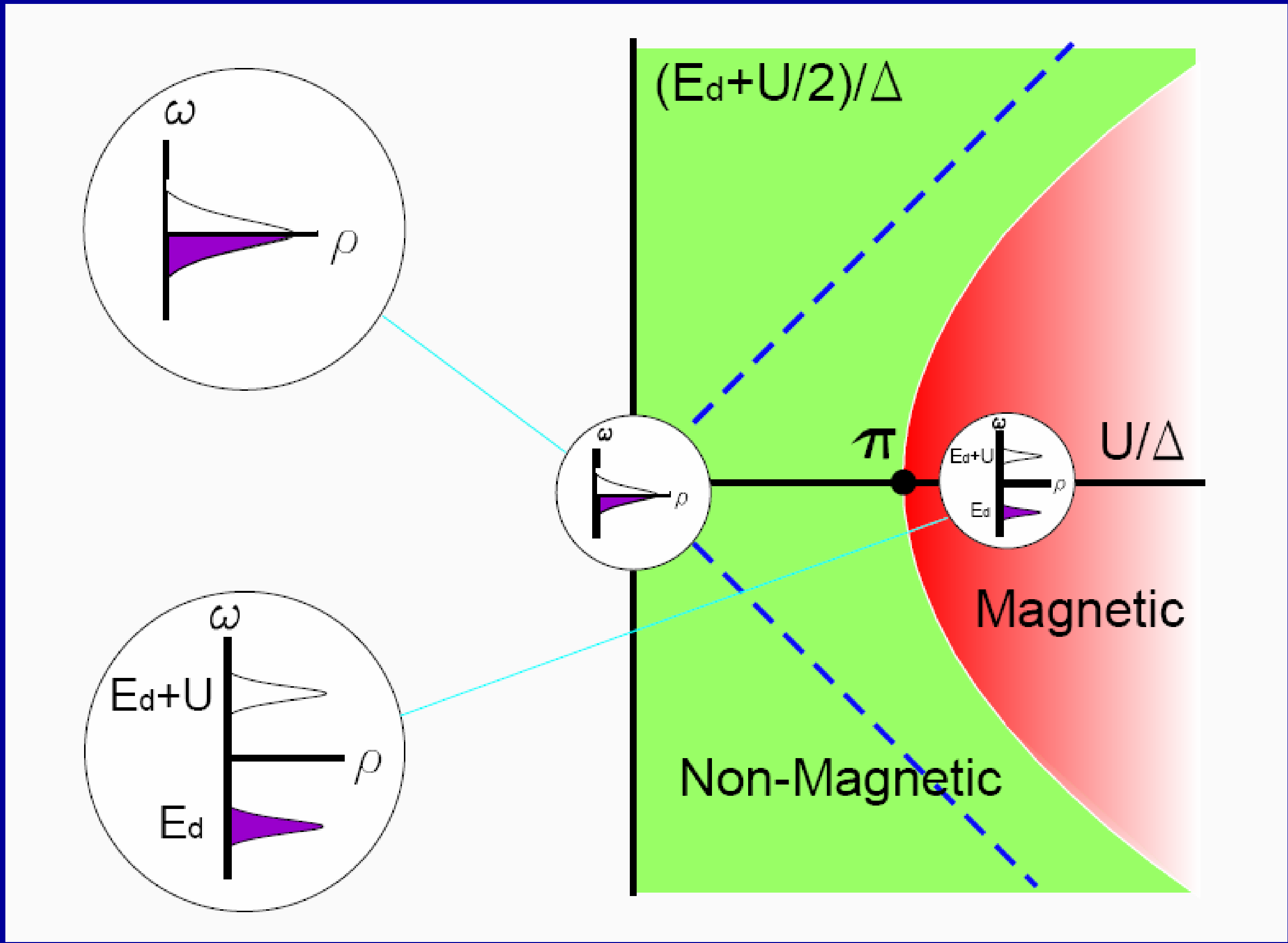
U: Coulomb energy

$\triangle \sim |V|^2 N$: peak width

I. Introduction

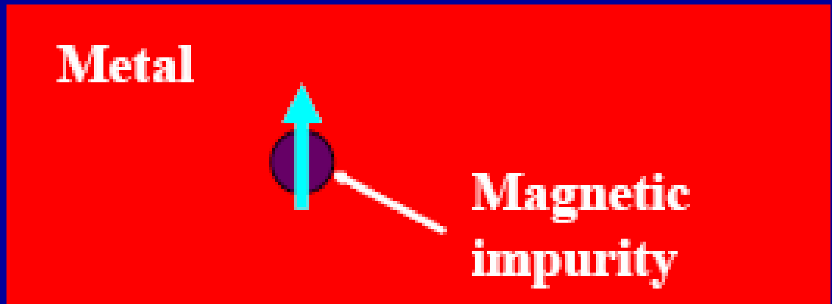
Anderson Model

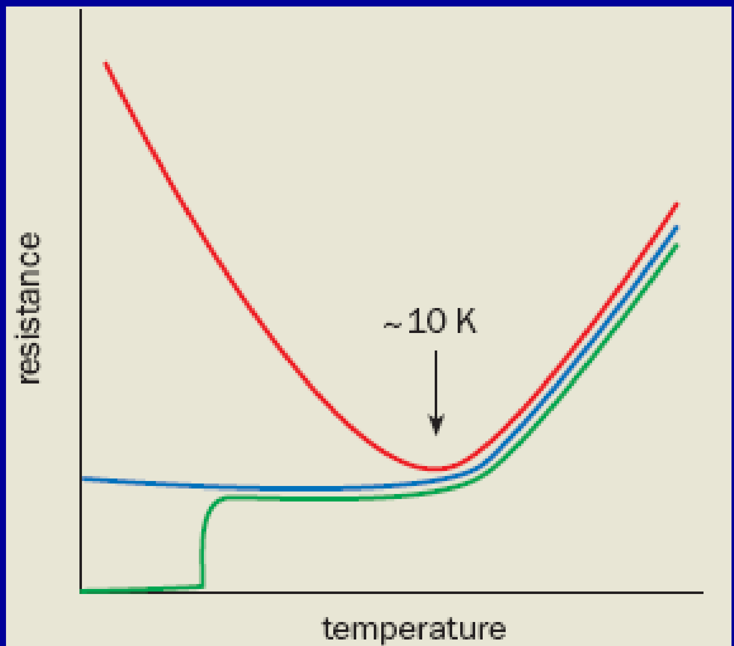
Parameters: E_d , U, $\triangle$



I. Introduction

Kondo Effect





Discovered in the 1930s

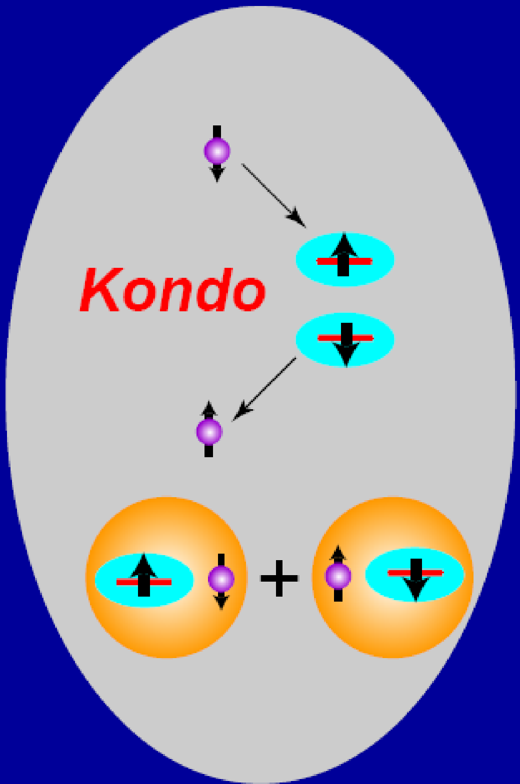
Explained in the 1960s

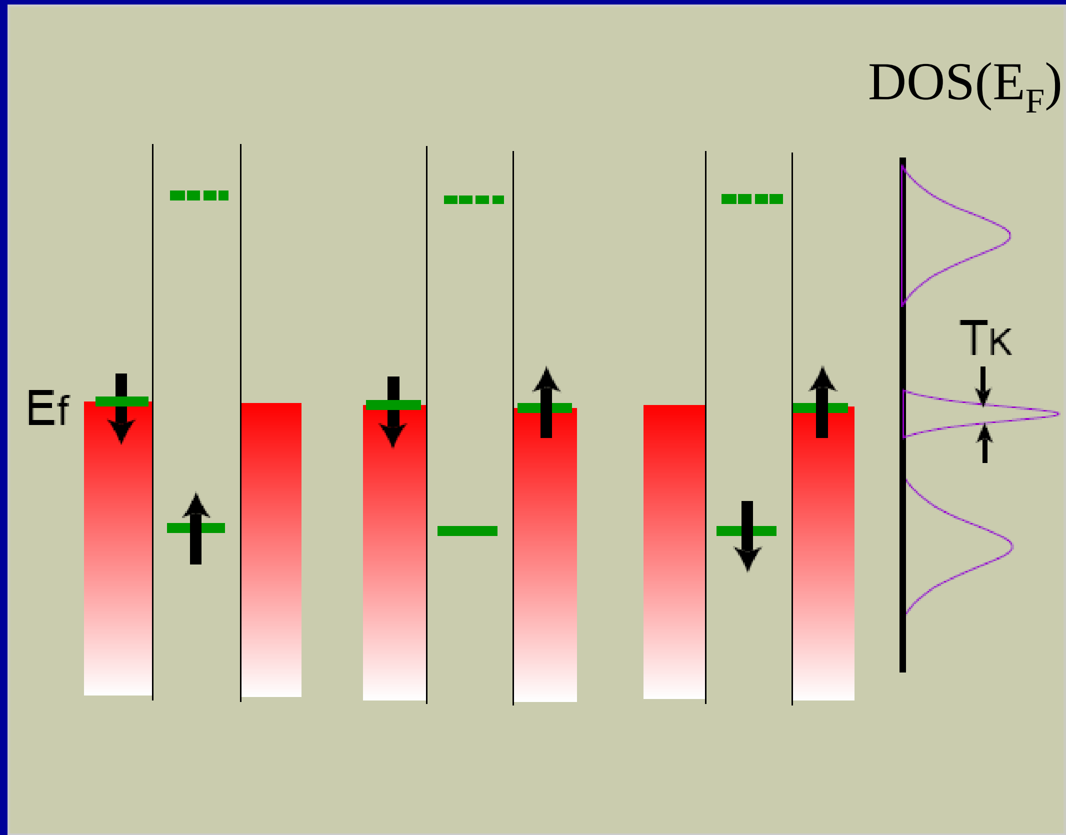
Interaction between spin and environment

I. Introduction

Kondo

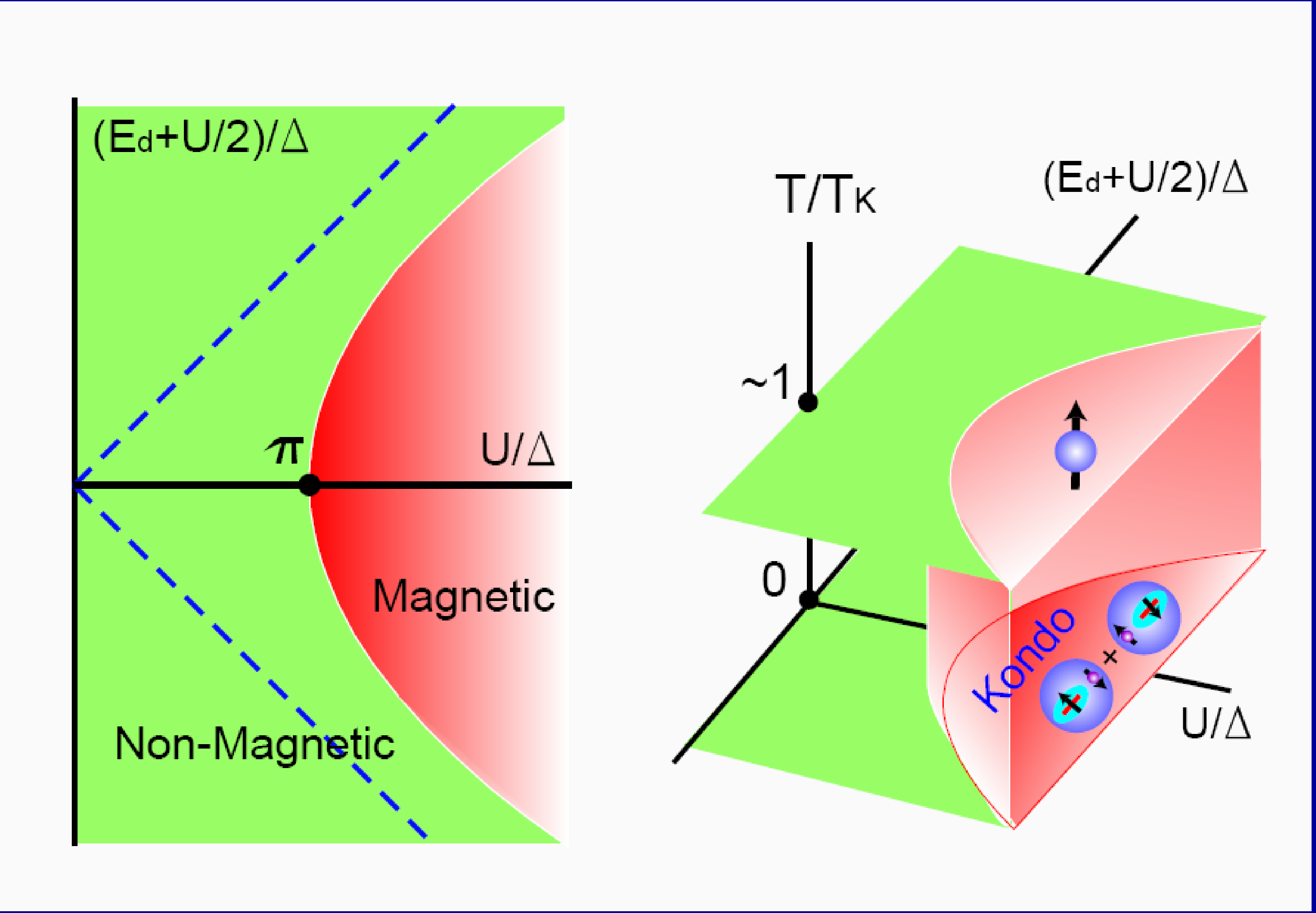
$$T_K = \sqrt{\frac{\Delta U}{2}} \exp\left(\frac{\pi}{2\Delta U} E_d (E_d + U)\right)$$





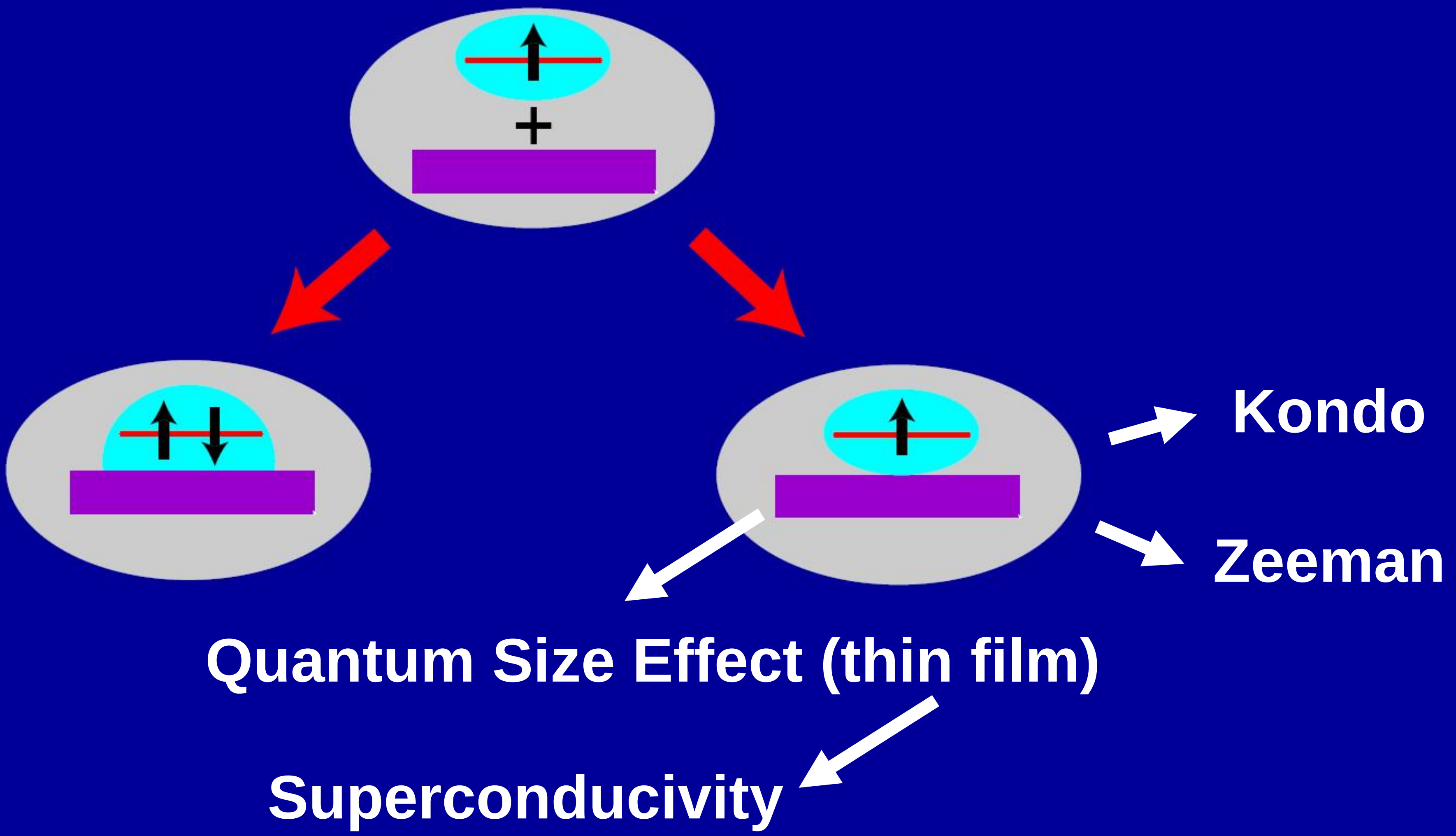
I. Introduction

Anderson Model



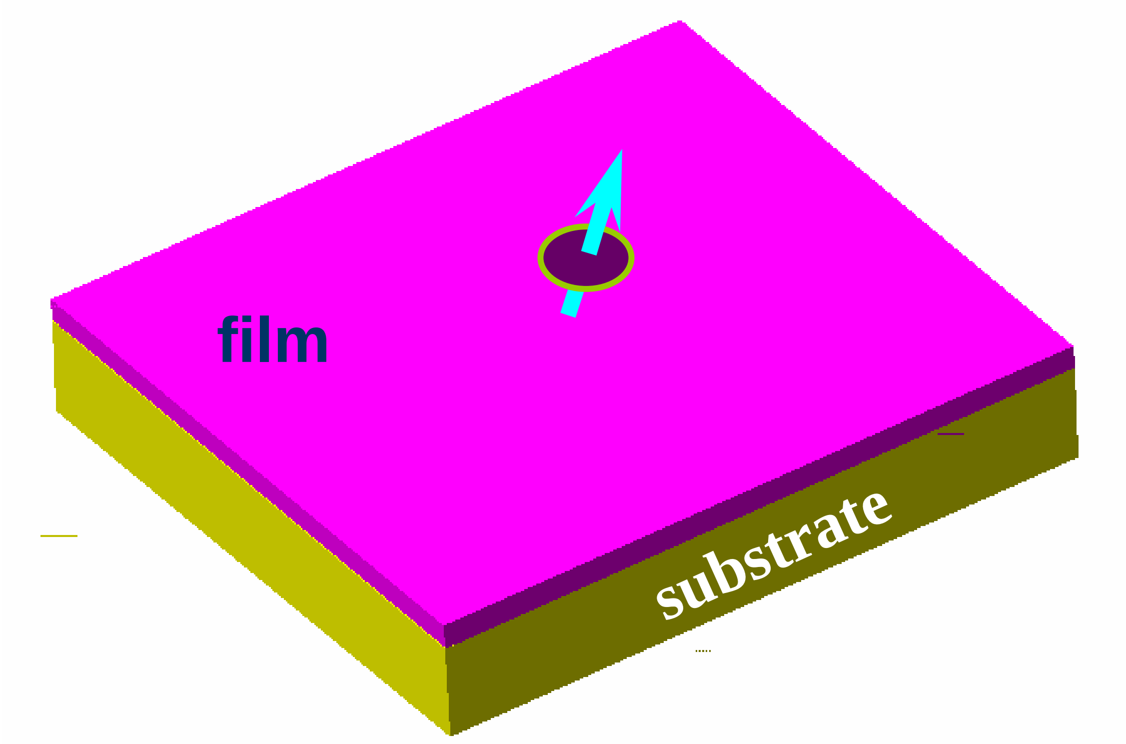
I. Introduction

localized spin + surface

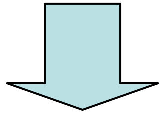


I. Introduction

localized spin + surface



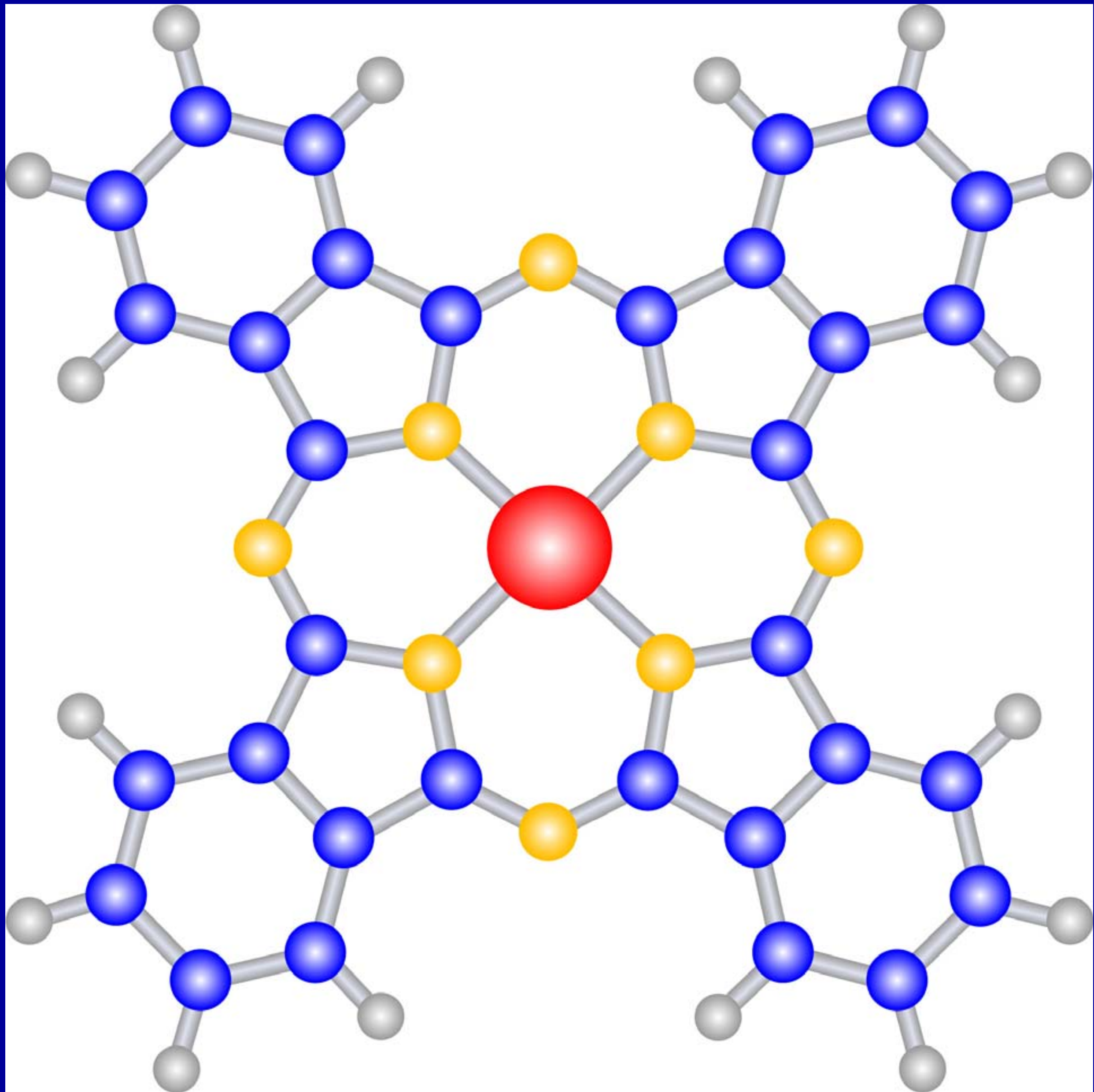
Platform



Quantum Size Effect
Zeeman
Kondo
Magnetism
Superconductivity
....

II. Experiment

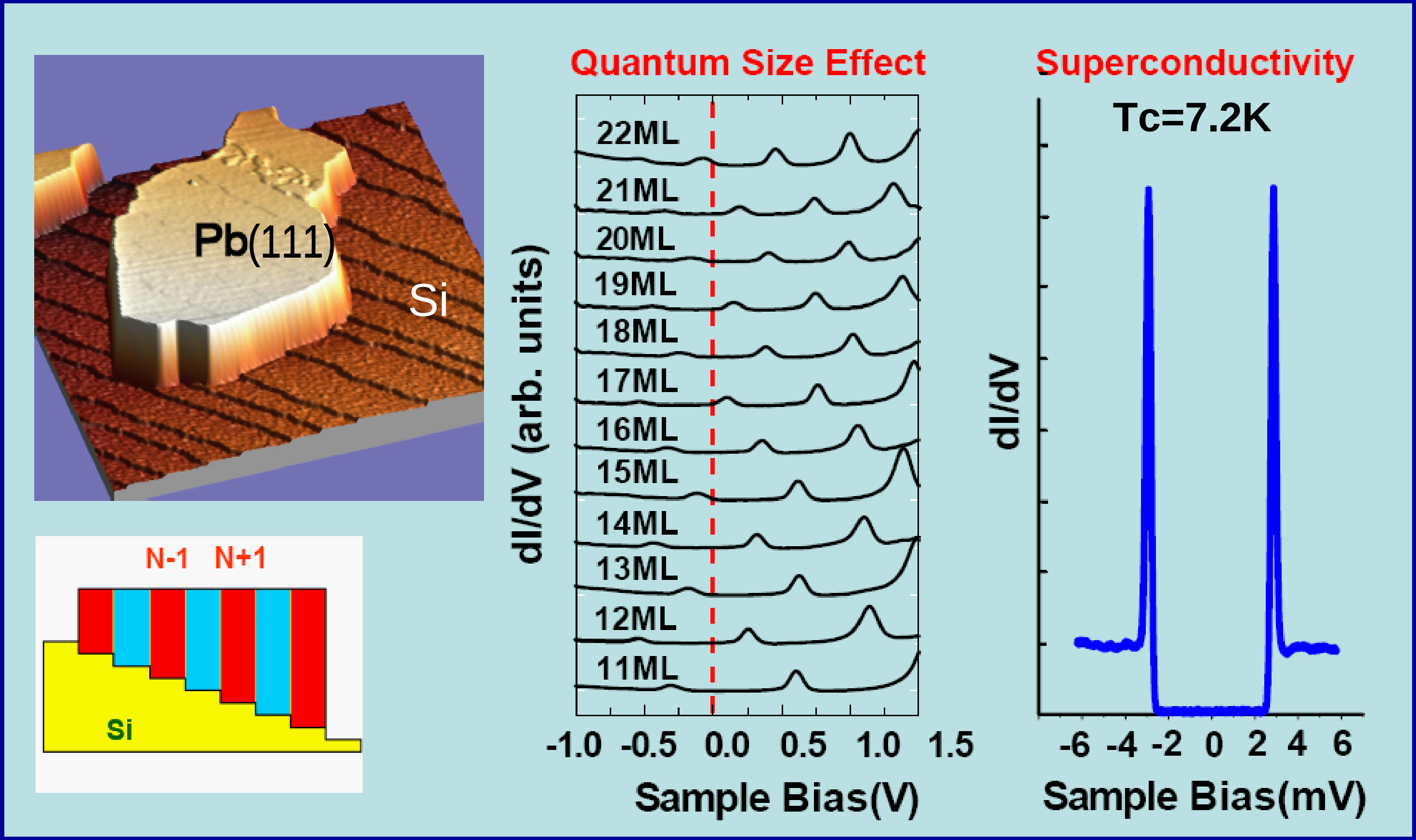
Our Molecules



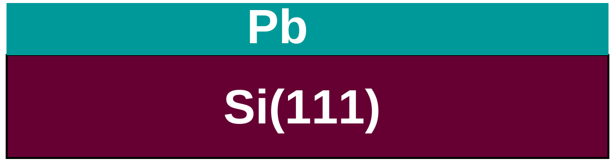
II. Experiment

Our Surface

Pb (111) thin films on Si



Pb thin films on Si



Material Properties Modulated by QSE

Superconductivity (Tc): *SCIENCE 306, 1915 (2004)*

Growth kinetics: *PRL 92, 106104 (2004)*

Electron-phonon coupling : *PRL 95, 096802 (2005)*

Upper critical field : *PRL 95, 247005 (2005)*

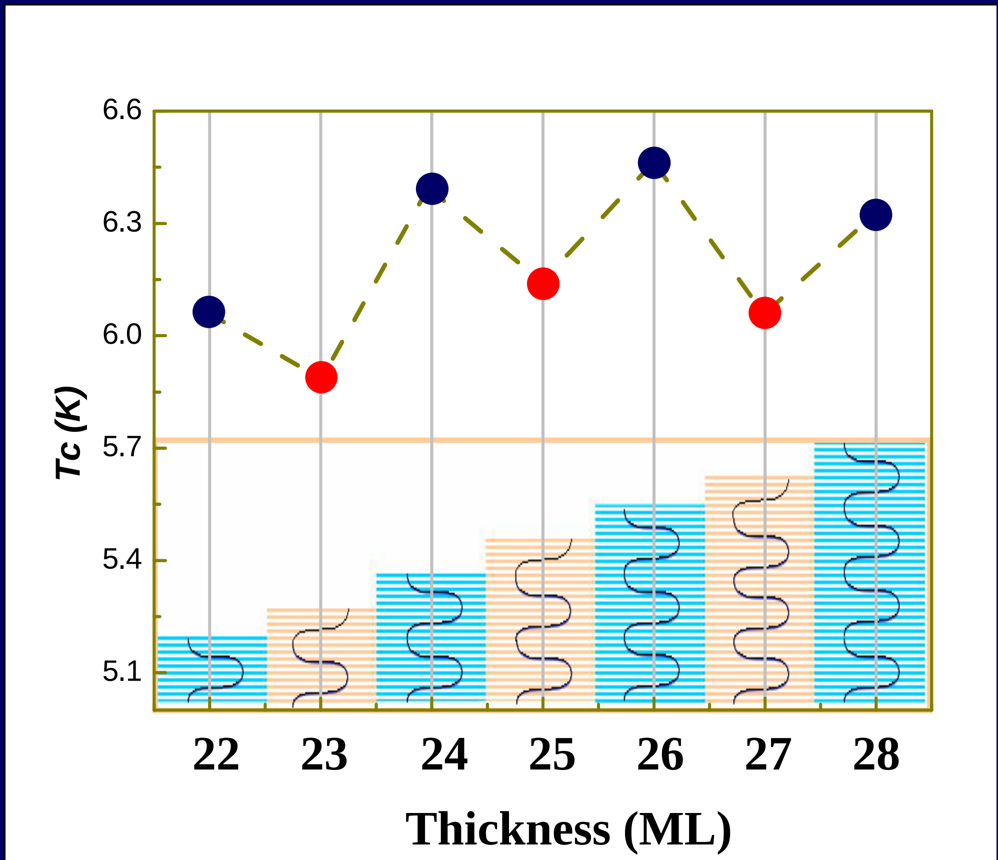
Surface diffusion: *PRL 95, 266102 (2006)*

Kondo resonance: *PRL 99, 156601 (2007)*

Surface chemical reactivity: *PNAS 104, 9204 (2007)*

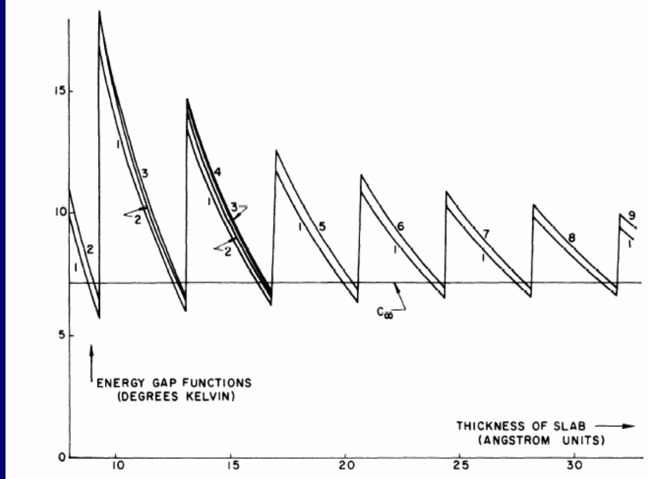
……

Superconductivity (Tc) oscillation



Guo, Zhang et al., ***SCIENCE 306****, 1915 (2004)*
Zhang et al., ***PRL 96****, 096802 (2005)*

PHYSICAL REVIEW LETTERS 15 April 1963

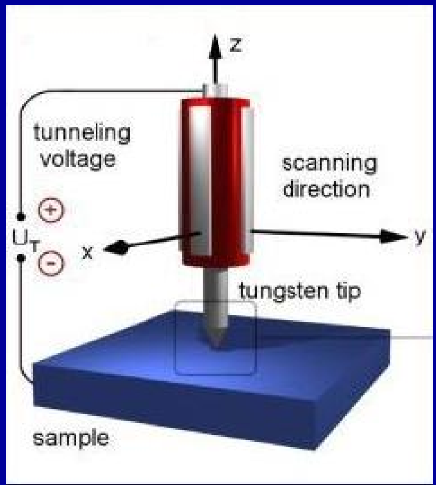


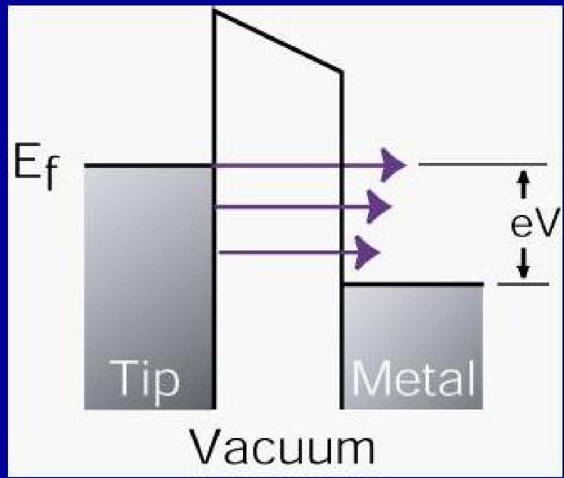
perconducting energy gap parameters C_n, vs thickness of film. At each resonance, a new value of ntribute. All values of C_n are shown for small thicknesses; thereafter, only the largest and smallest , to avoid confusion. The peak heights lie well above the bulk value, C_∞, which is also shown on the troughs are only slightly below C_∞. The width of the resonances is too small to show on the scale of The distance between resonances equals one half of the deBroglie wavelength of an electron at the e. The parameters used for this figure were $N/V = 2 \times 10^{22}$ electrons/cm^3, $\rho = 0.3$, and $\hbar\omega_c = 100$°K.

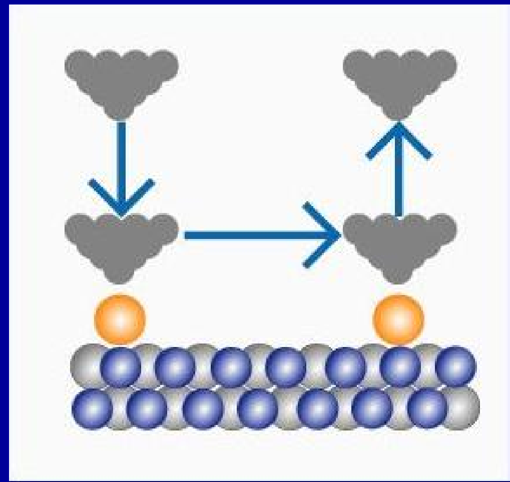
J. M. Blatt and C. J. Thompson
PRL 10, 332 (1963)

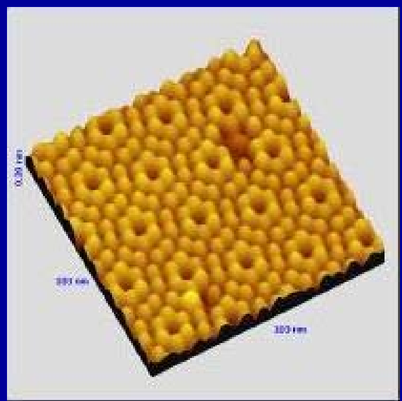
II. Experiment

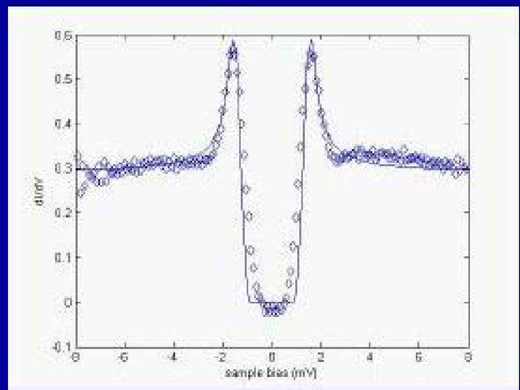
Our tool: STM

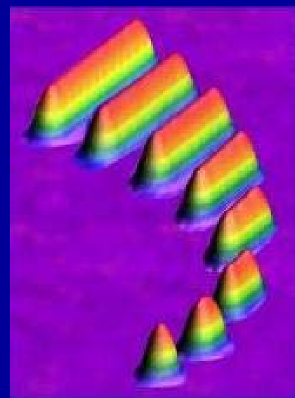












Imaging **Spectroscopy** **Manipulation**

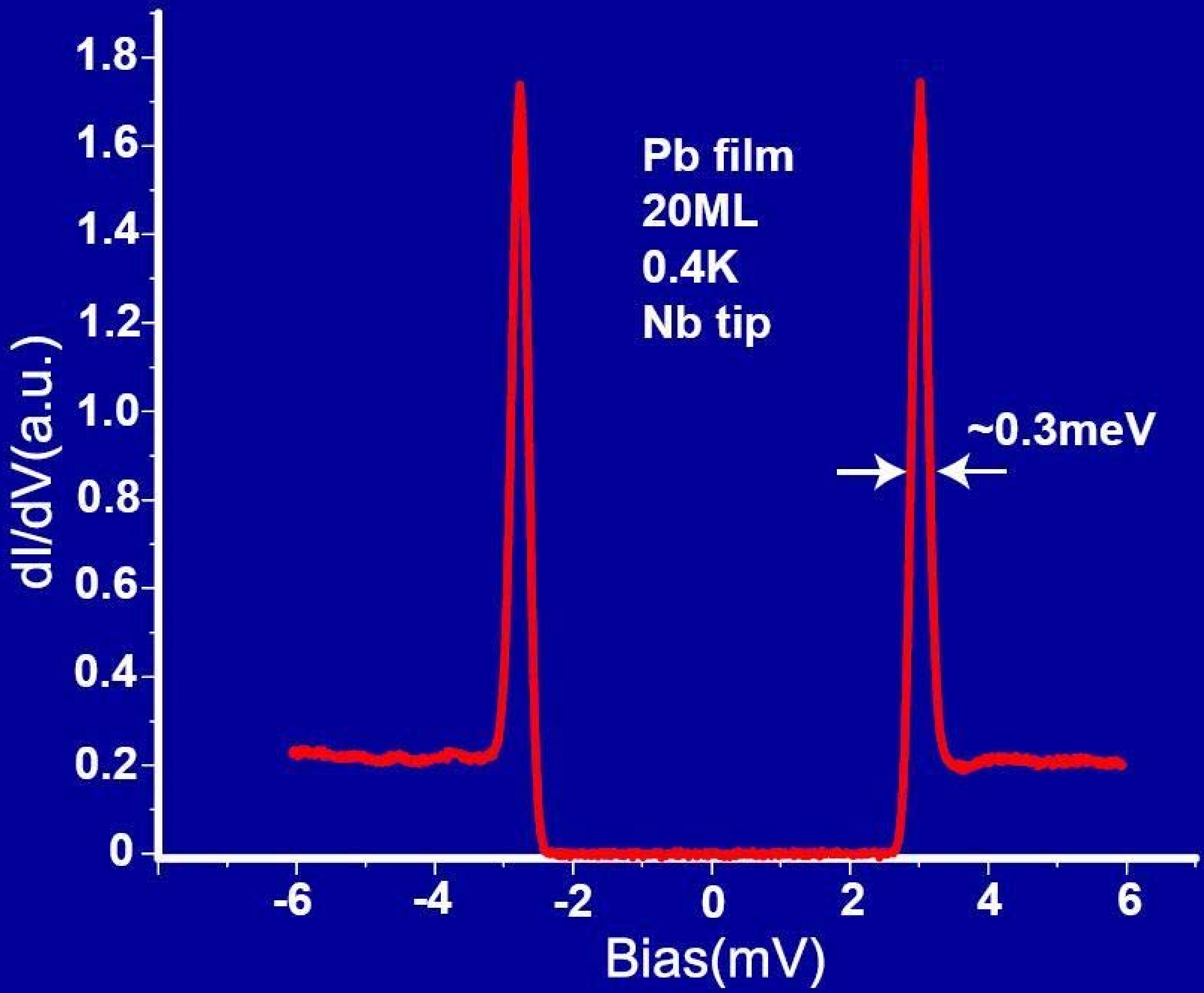
II. Experiment

Our Instrument

Unisoku UHV ultra-LT (400mK) high magnetic field (11T) STM

II. Experiment

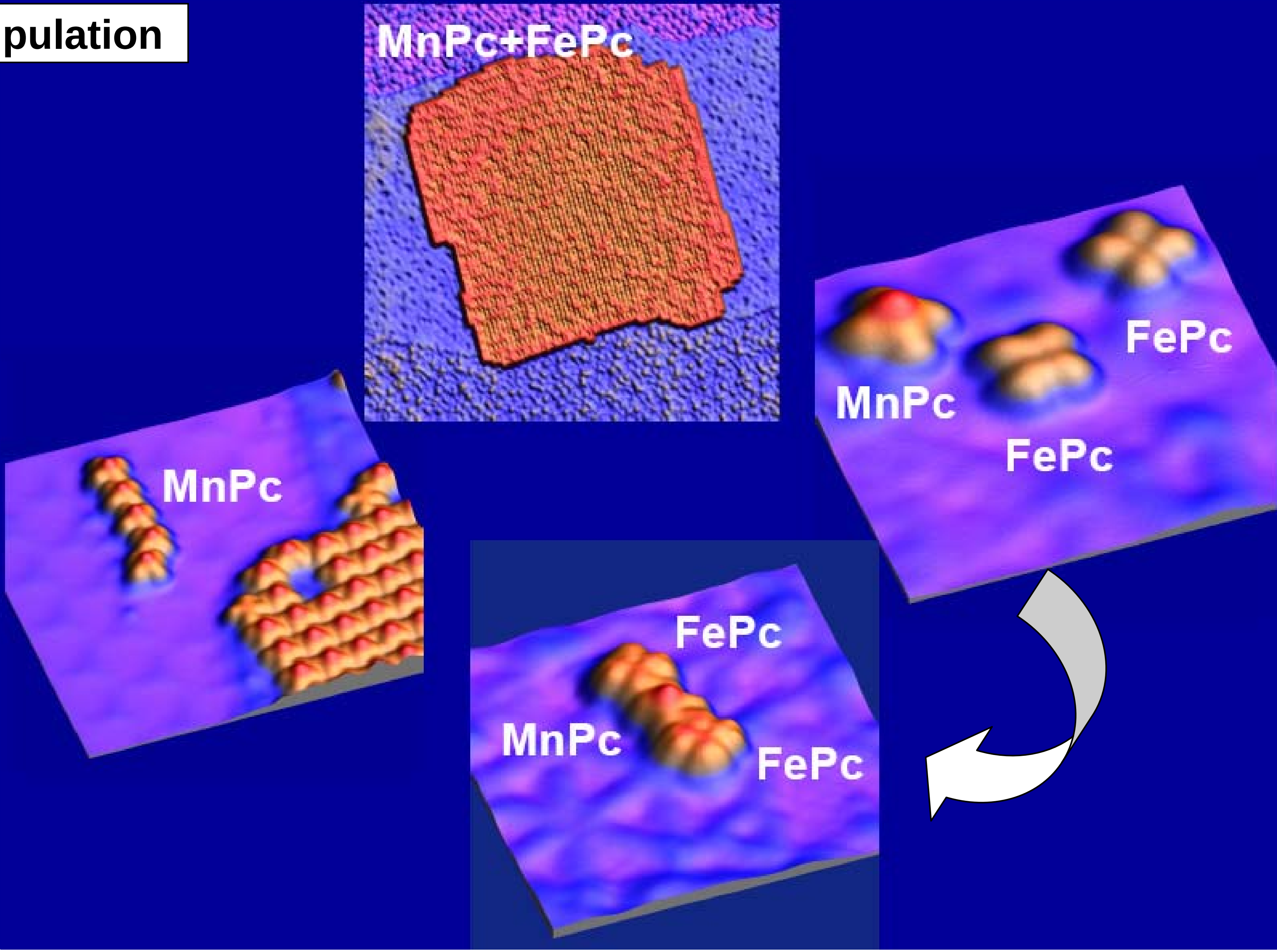
Our Instrument



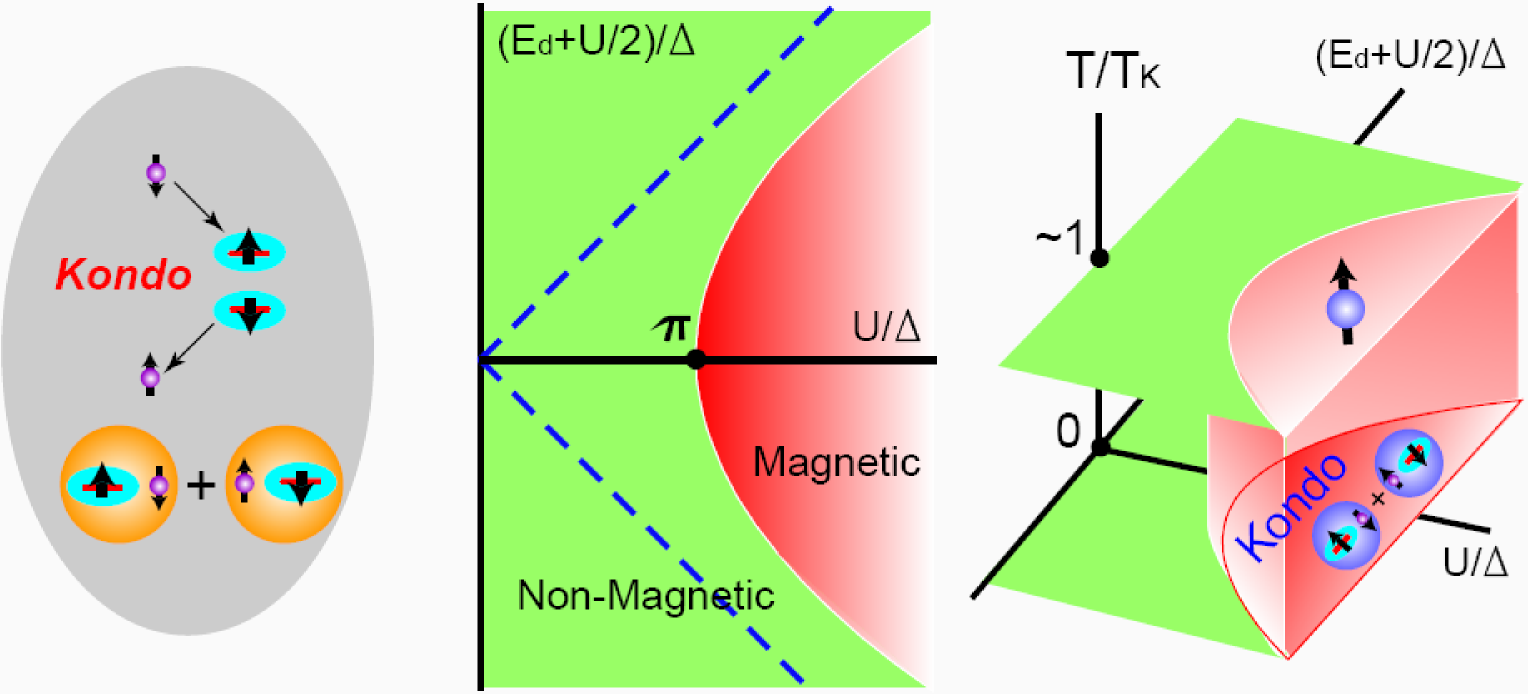
Ji et al., PRL (in press)

III. Kondo Effect

Manipulation



III. Kondo Effect



Kondo Effect

$$T_K = D\sqrt{\frac{2\Delta}{\pi D}}e^{-\frac{1}{2J\rho_0}}$$

***J*:** coupling of spins and conduction electrons

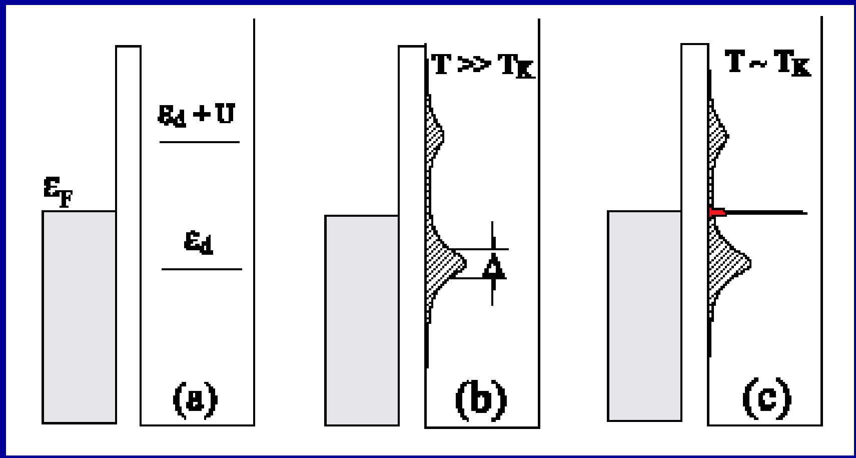
***ρ_0*:** density of states of host

$$J = \frac{\Delta}{\pi\rho_0}\left(\frac{1}{|\bar{\varepsilon}_d|}+\frac{1}{|\bar{\varepsilon}_d+U|}\right)$$

$$\Delta = \pi|V|^2\rho_0$$

$$T_K = \sqrt{2D|V|^2\rho_0}\,e^{-\frac{1}{2|V|^2\left(\frac{1}{|\bar{\varepsilon}_d|}+\frac{1}{|\bar{\varepsilon}_d+U|}\right)\rho_0}}$$

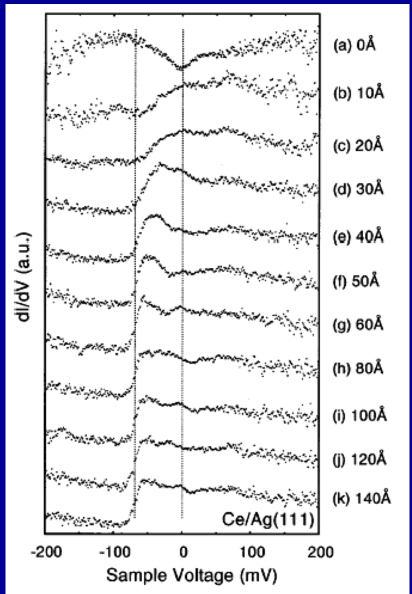
Energy spectra for an Anderson impurity system



Without hybridization — With hybridization — In the Kondo regime below T_K.

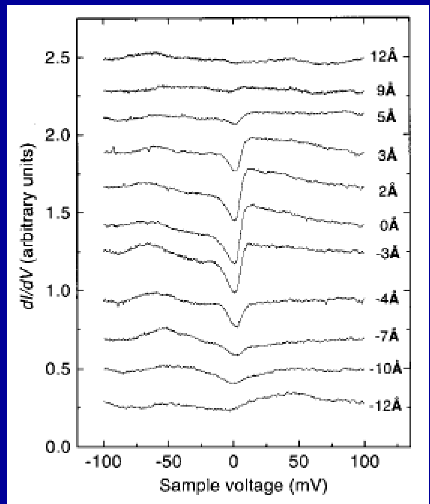
Direct observation at single atoms/molecule level by STM

Ce/Ag(111)

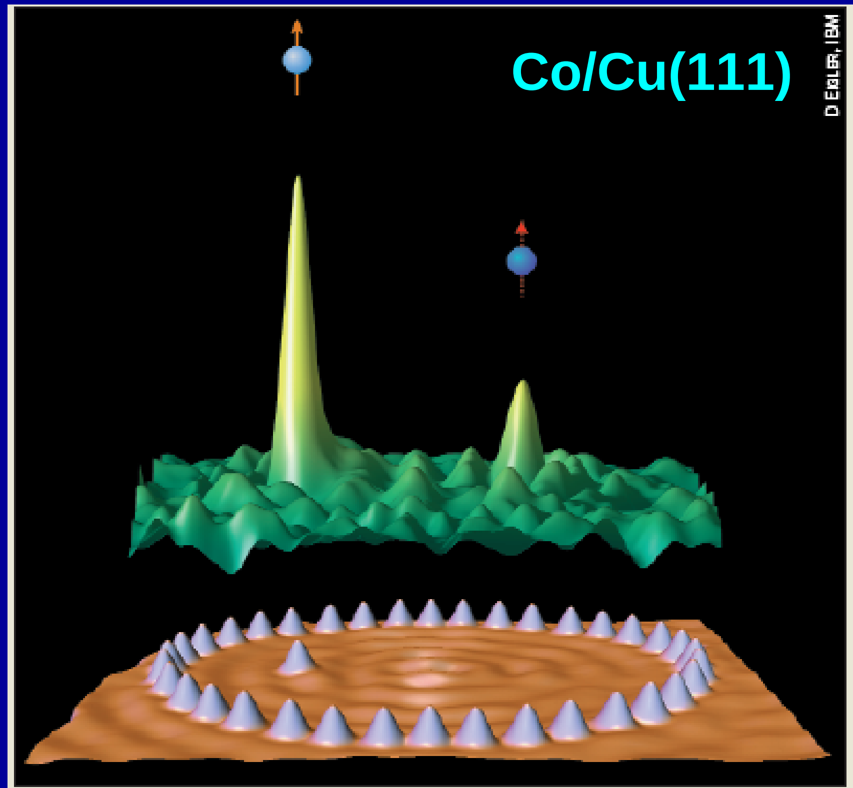


PRL80, 2893 (1998)
Wolf-Dieter Schneider

Co/Au(111)



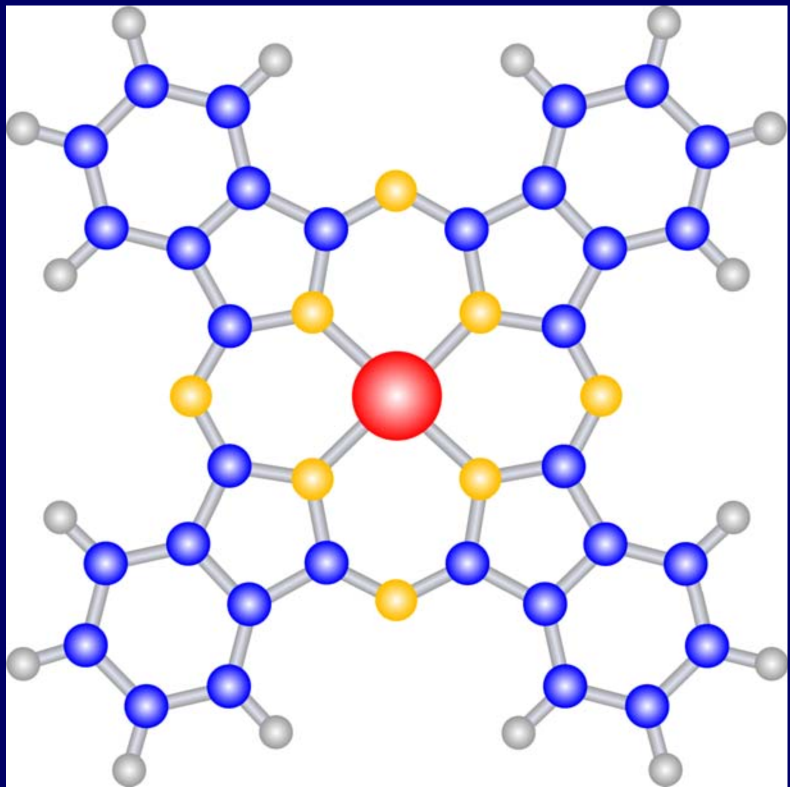
Science **280,** 567(1998)
M. Crommie

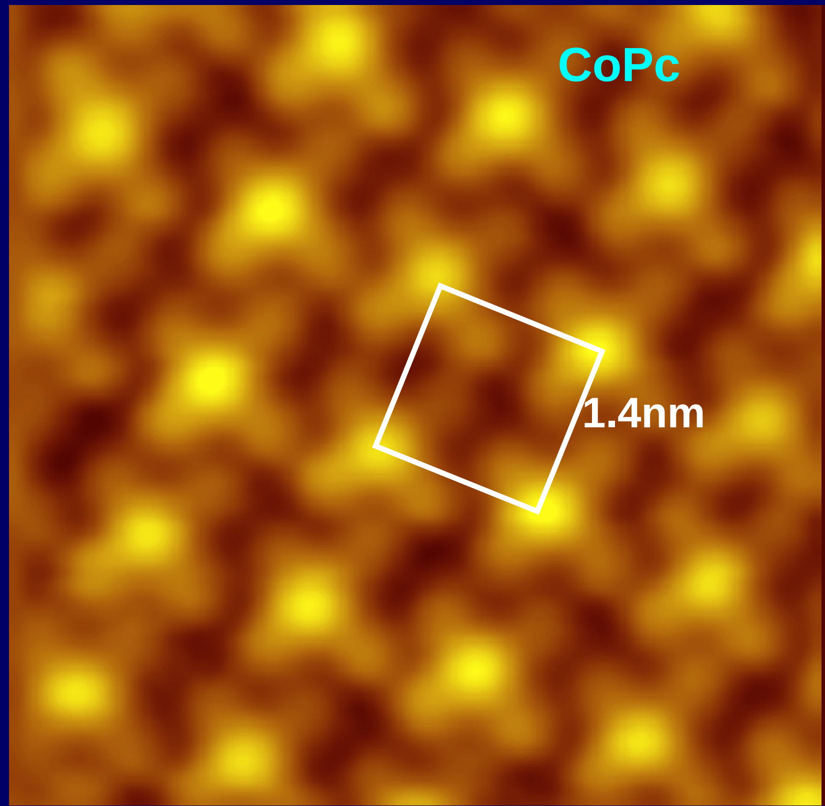


Nature 403, 512(2000) D. M. Eigler

3d transition metal on Au (111):
Ti, V, Cr, Mn, Fe, Co, and Ni.

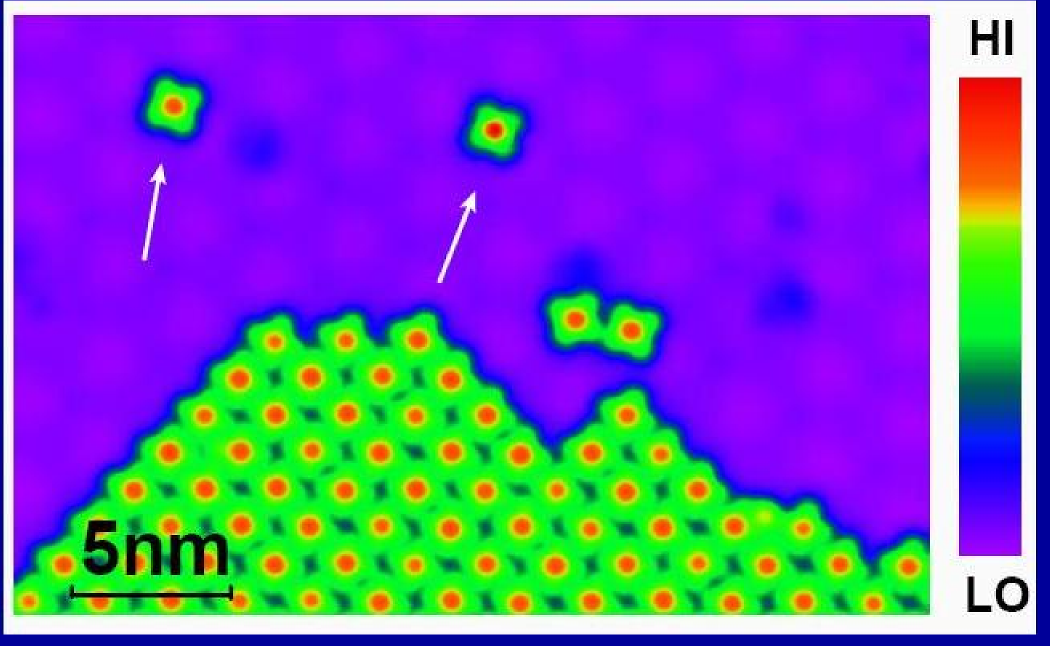
MnPc on Pb(111)

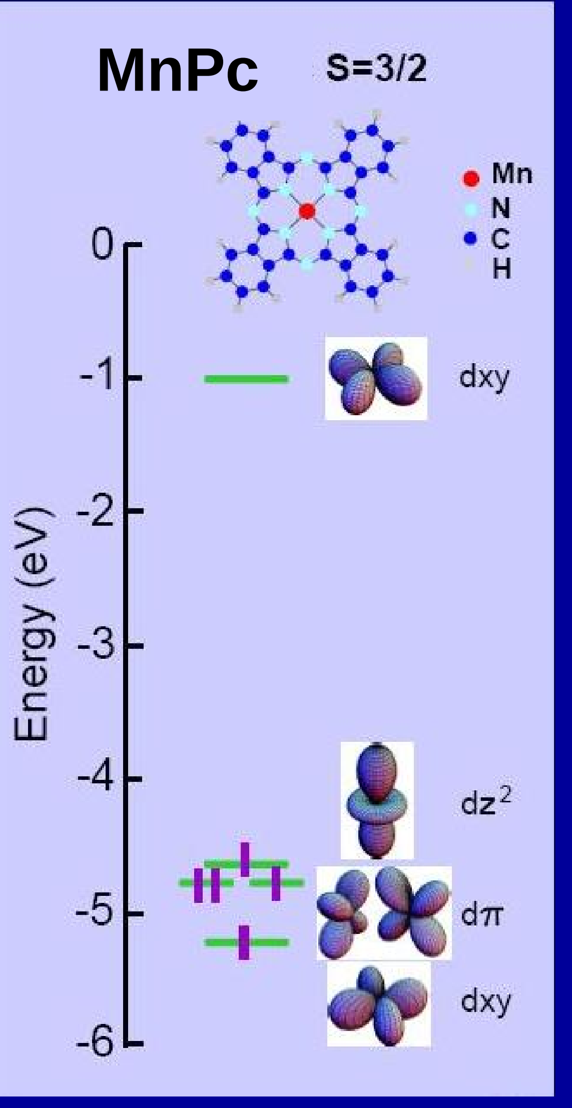




III. Kondo Effect

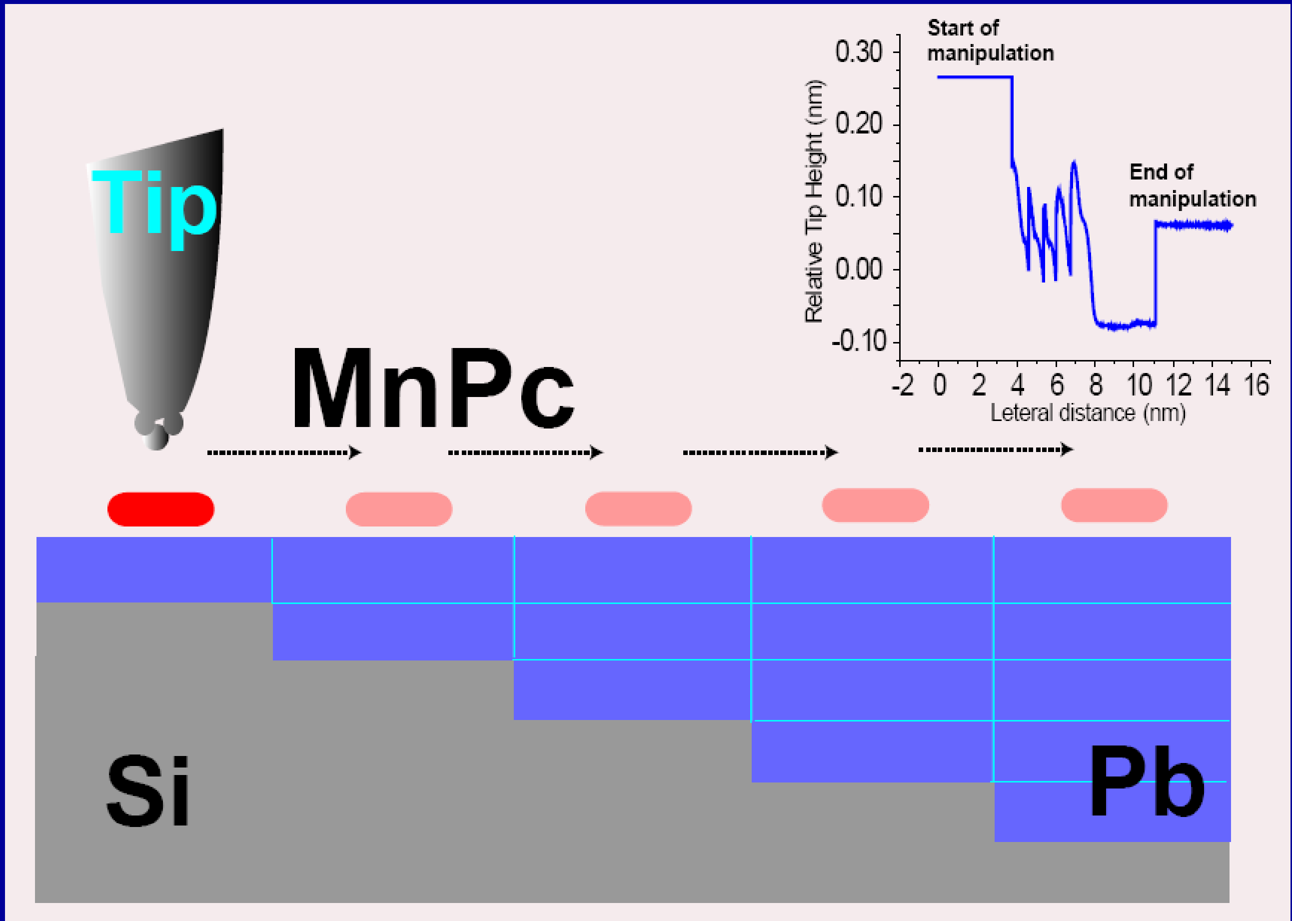
Modulation of Kondo Effect by QSE





III. Kondo Effect

STM Manipulation

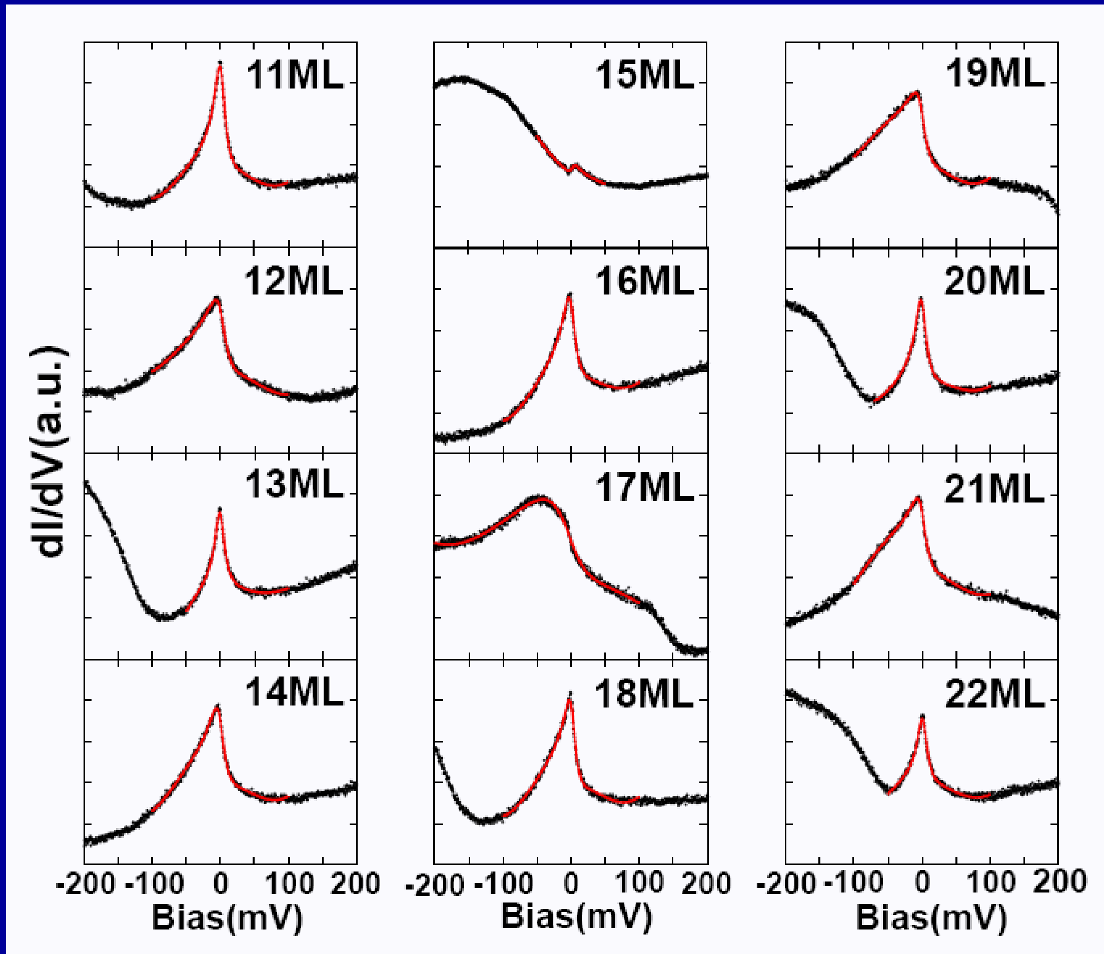


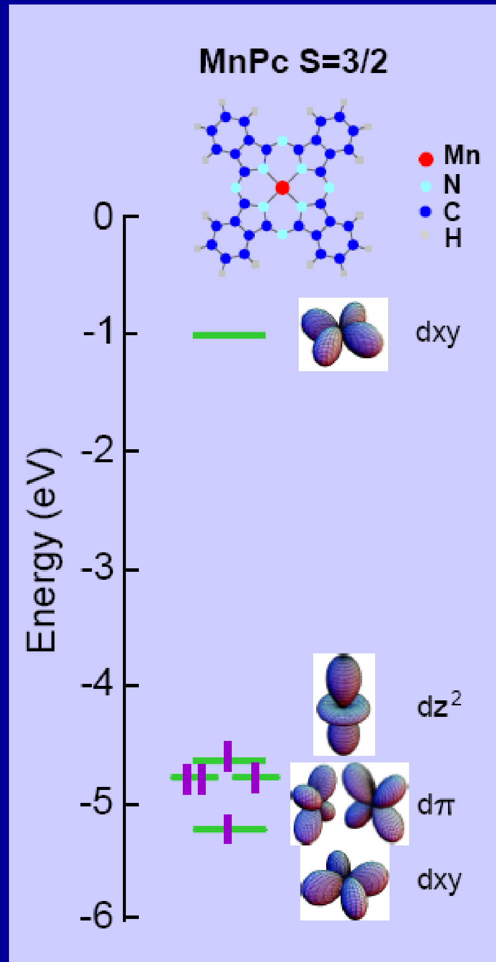
III. Kondo Effect

The same molecule

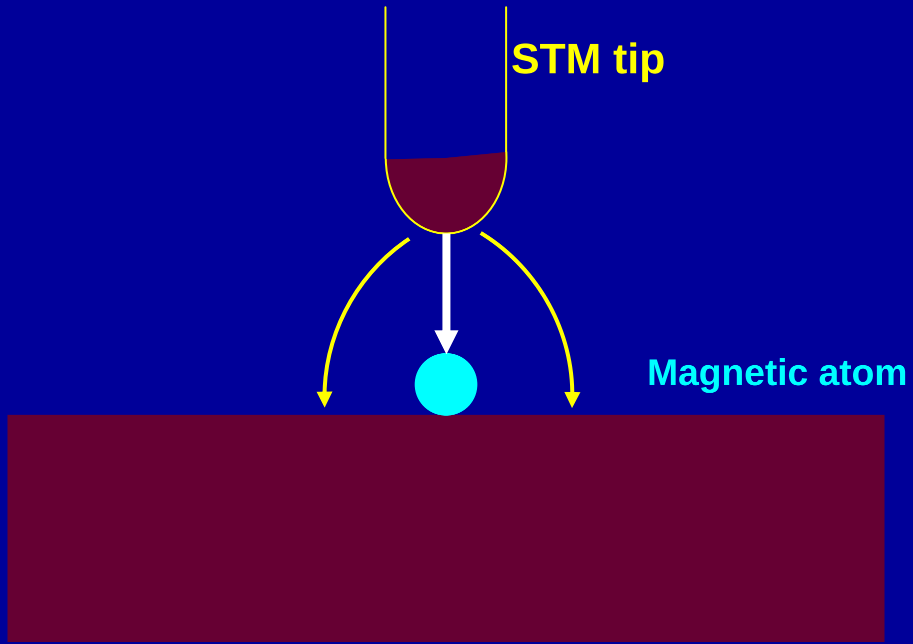
on the same surface under the same measurement conditions!

Kondo Resonance





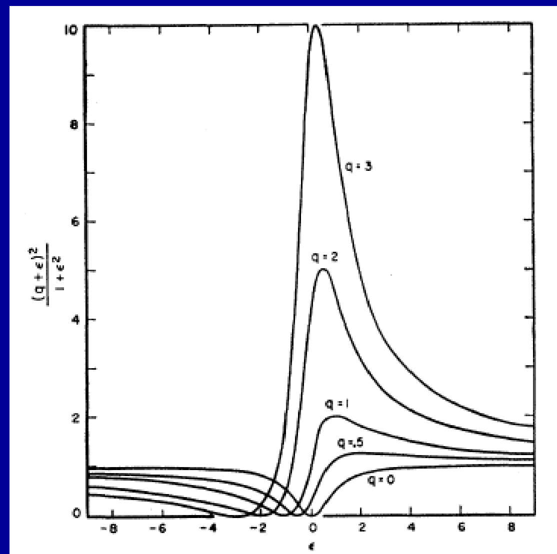
Fano Lineshape



In tunneling experiments:

$$\frac{dI}{dV}(V) \propto \frac{(\varepsilon' + q)^2}{1+\varepsilon'^2} \qquad \varepsilon' = \frac{eV - E_0}{K_B T_K}$$

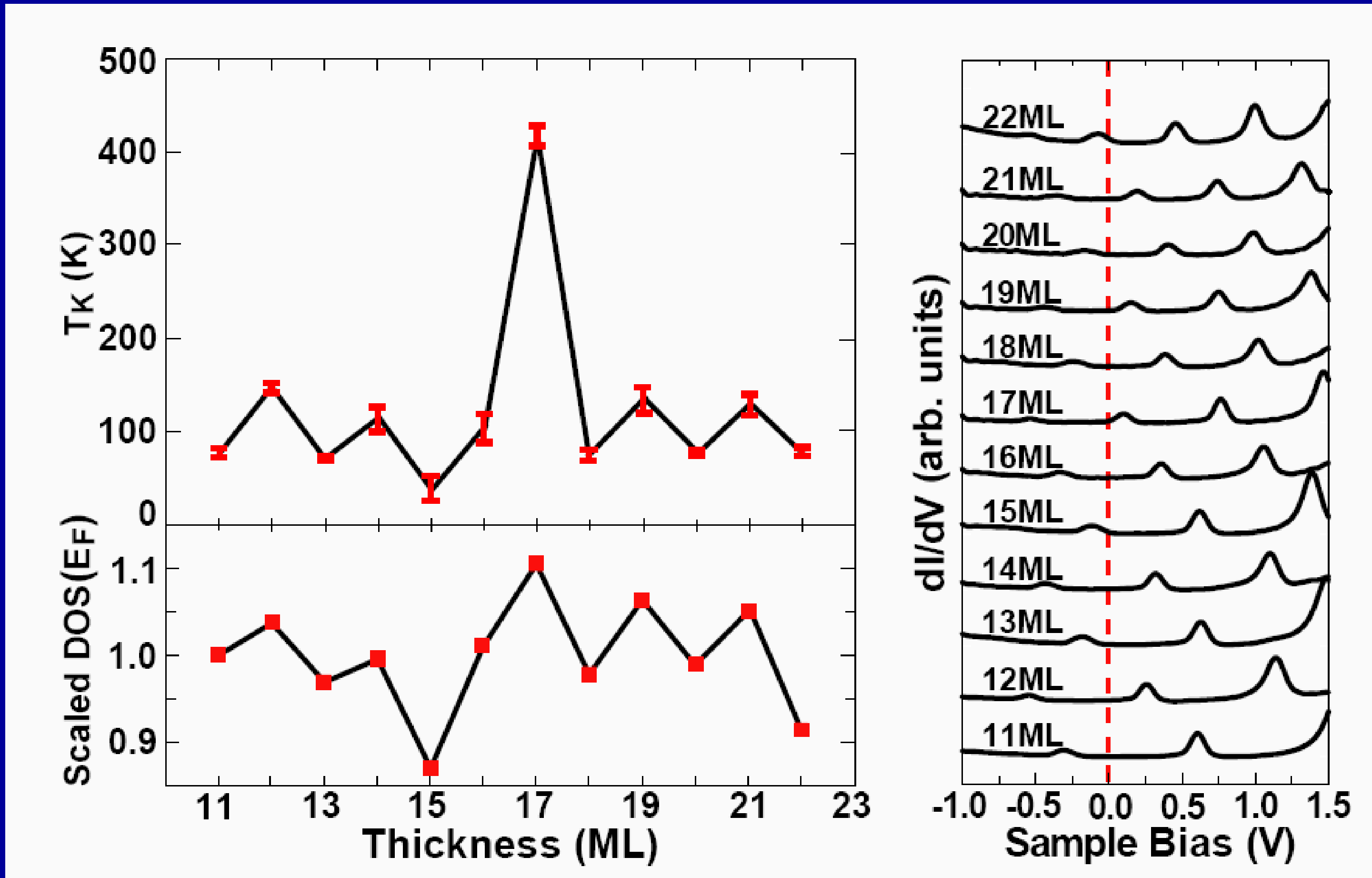
Resonance width: $2\Gamma = 2K_B T_K$



III. Kondo Effect

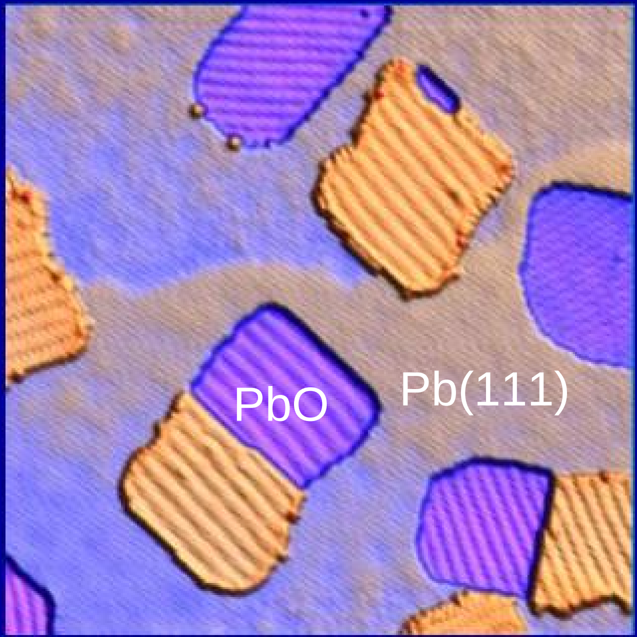
Kondo Temperature

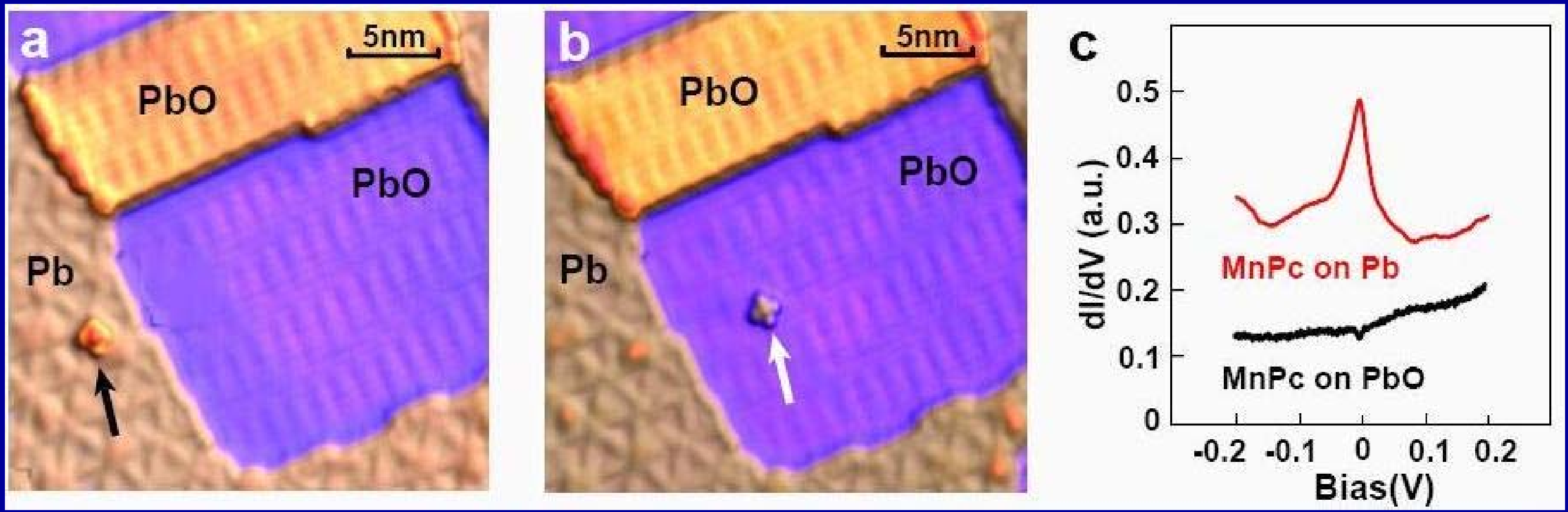
Fu et al., PRL 99, 156601 (2007)



III. Kondo Effect

Oxide surface

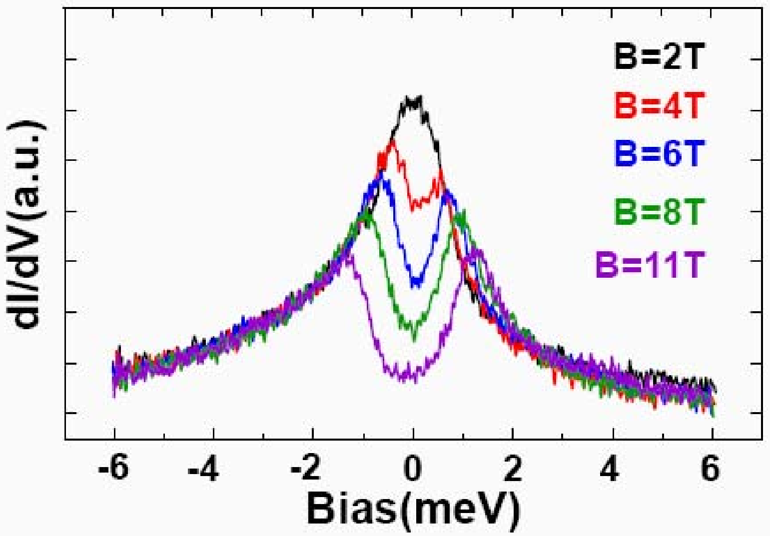


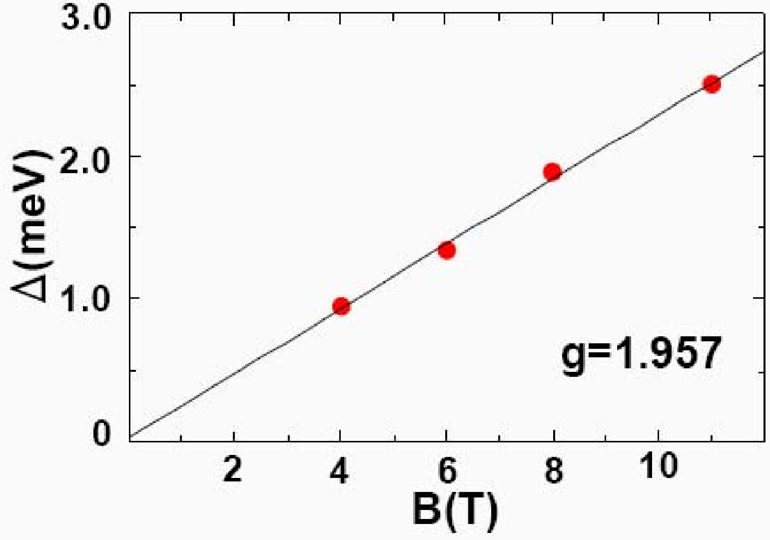


III. Kondo Effect

Splitted Kondo

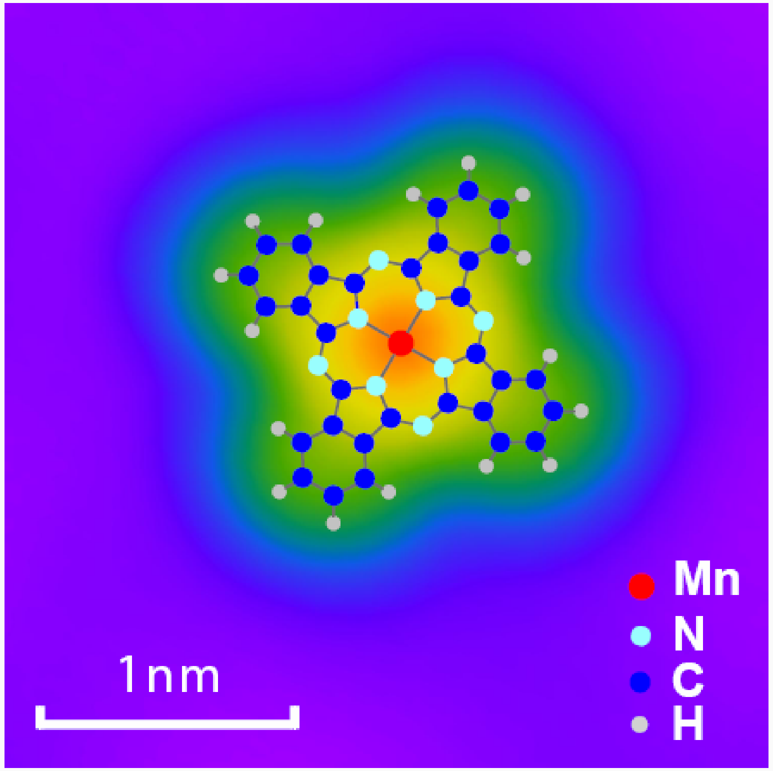
$$\Delta = 2g\mu_B B$$

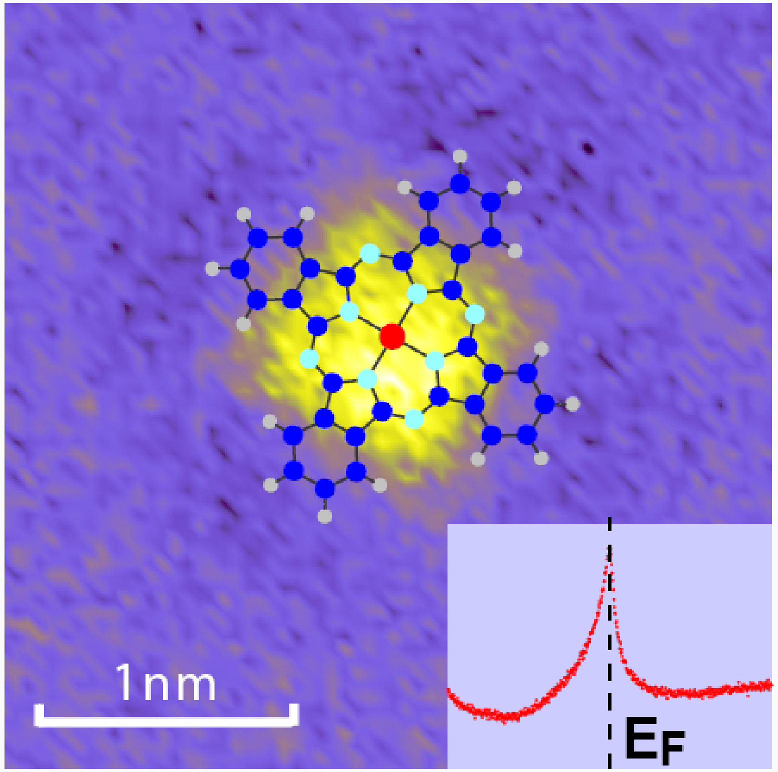




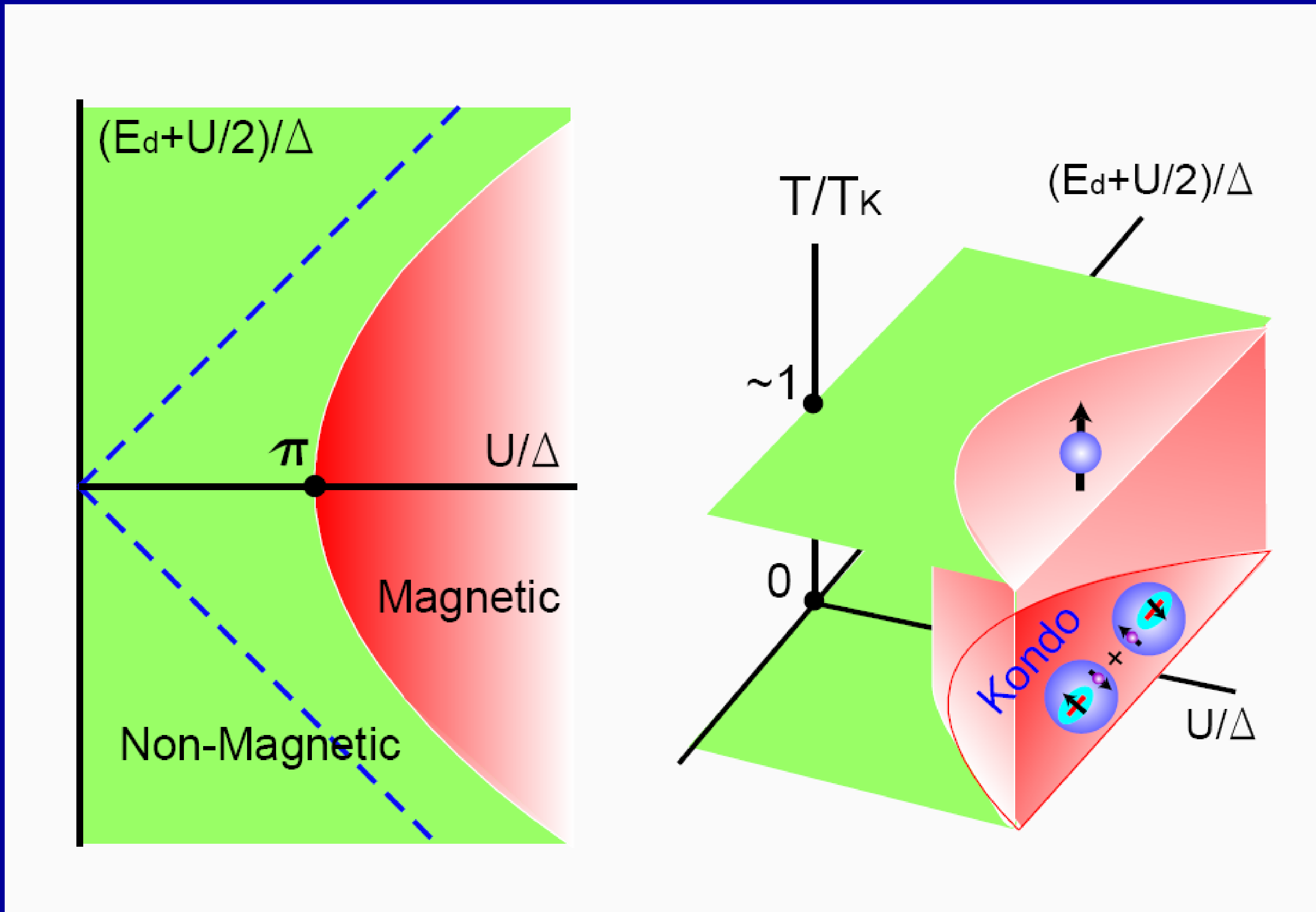
III. Kondo Effect

Kondo Mapping



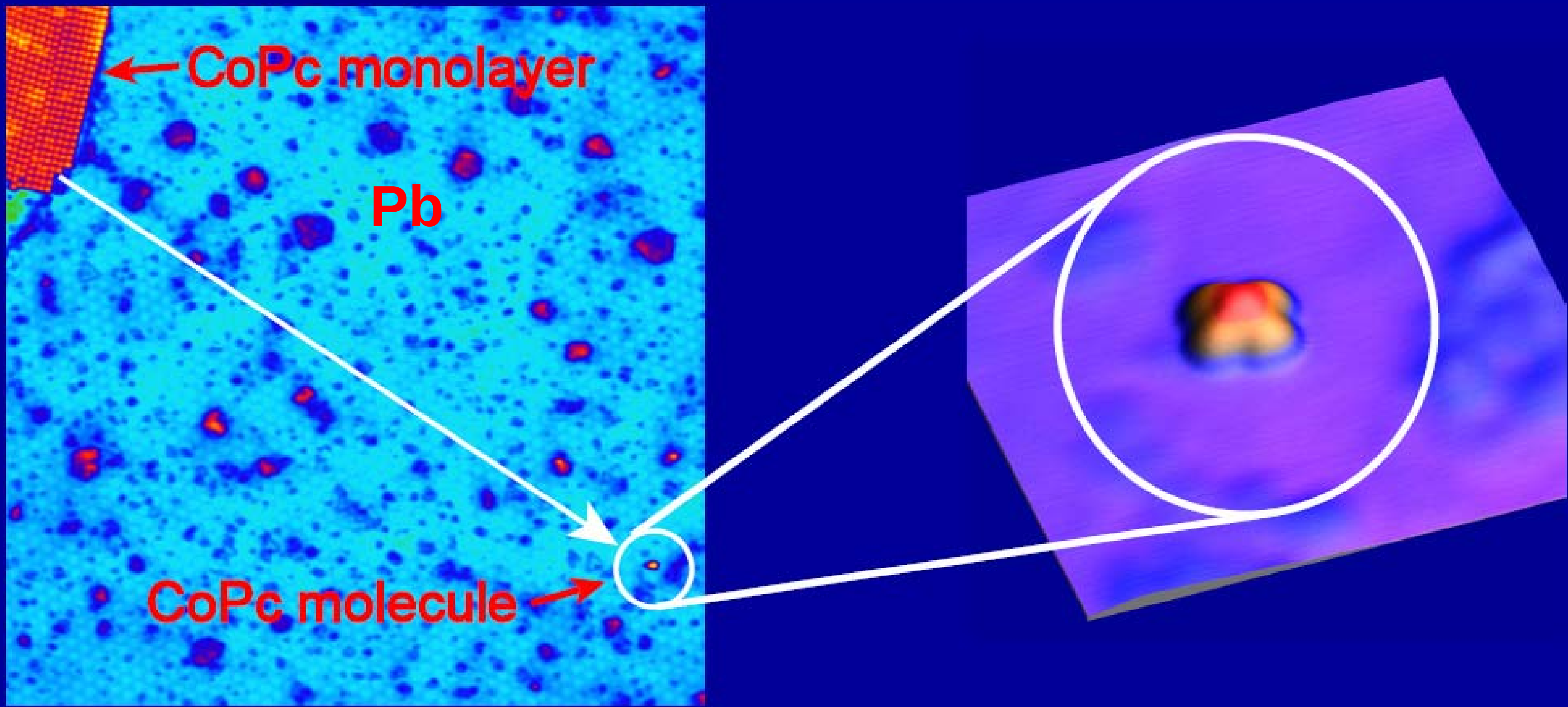


IV. Zeeman

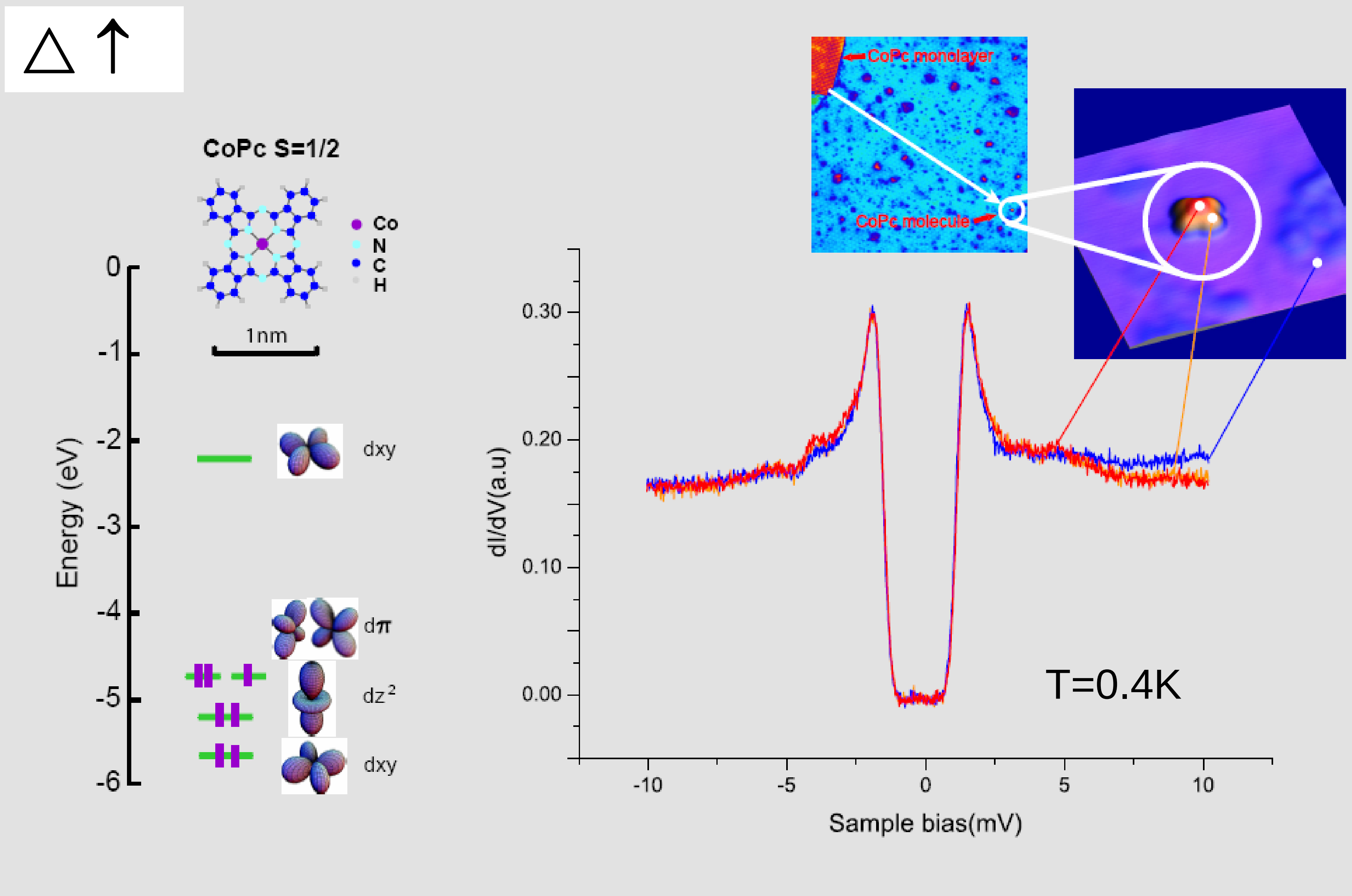


IV. Zeeman

CoPc/Pb(111)



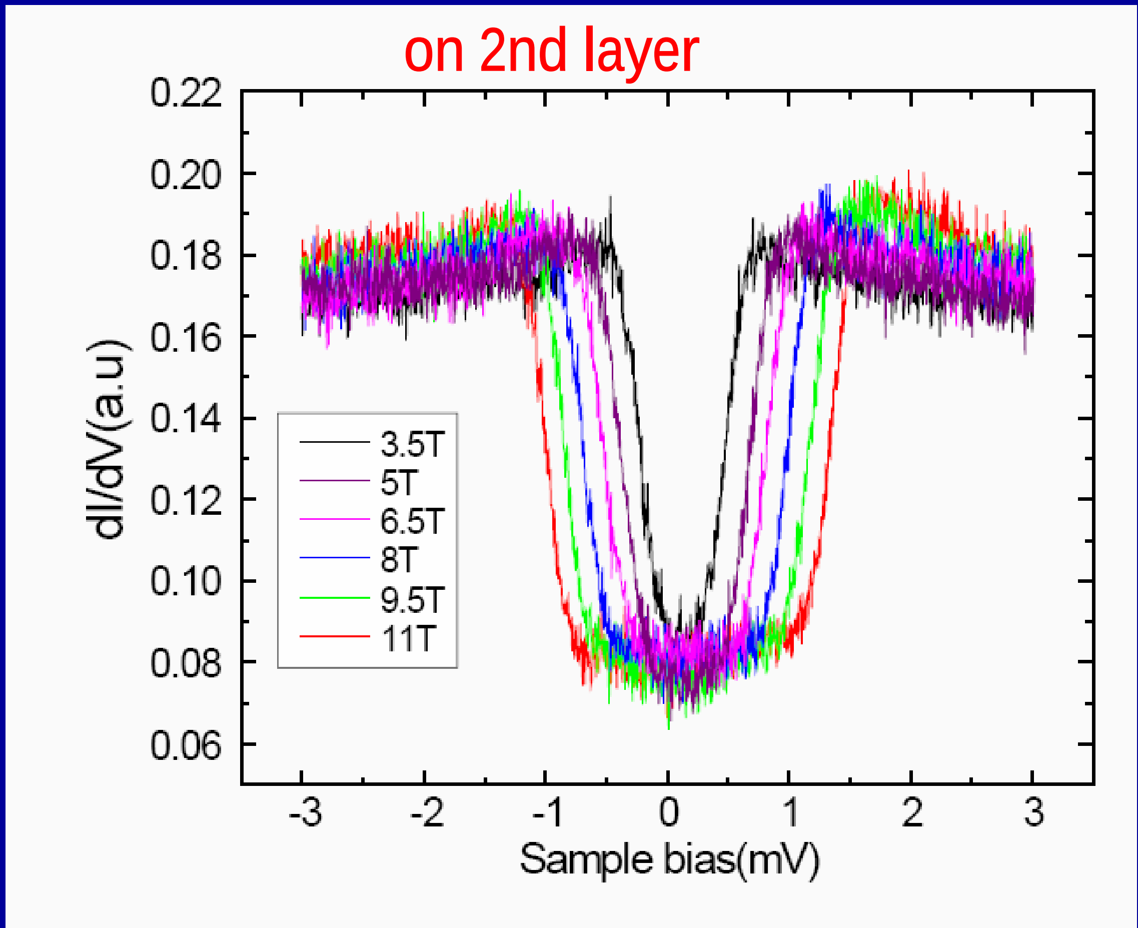
IV. Zeeman

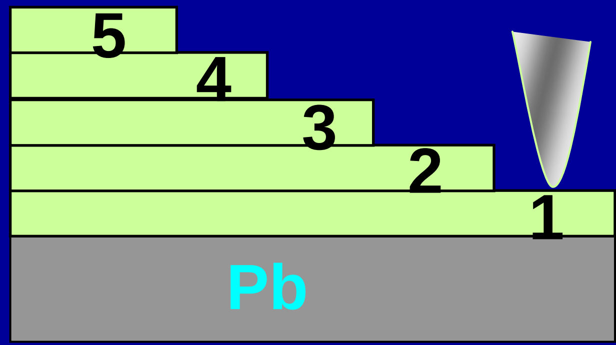


△ ↑
CoPc S=1/2
Co
N
C
H
1nm
Energy (eV)
0
-1
-2
-3
-4
-5
-6
dxy
dπ
dz²
dxy
CoPc monolayer
CoPc molecule
dI/dV(a.u)
0.30
0.20
0.10
0.00
-10
-5
0
5
10
Sample bias(mV)
T=0.4K

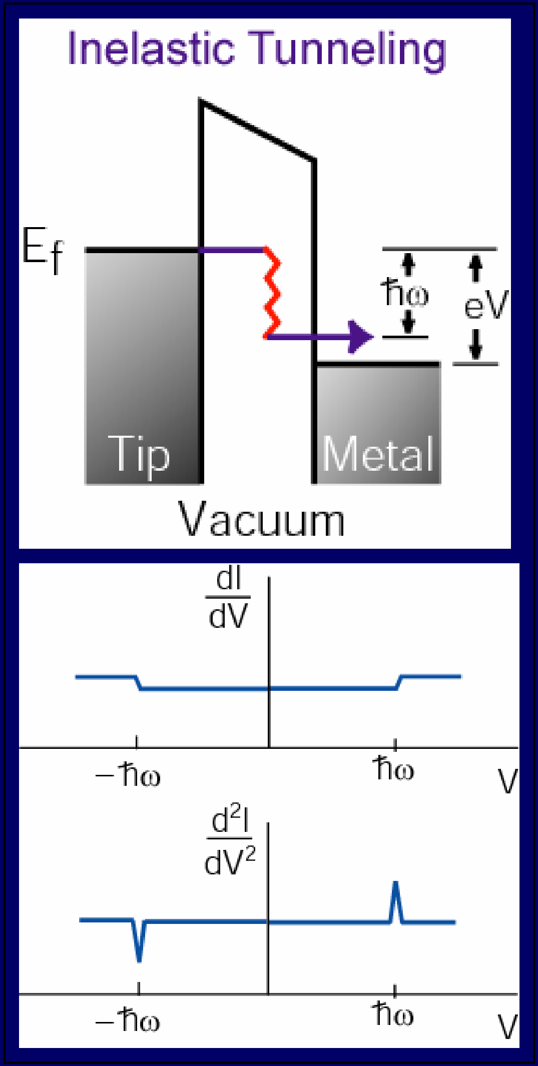
IV. Zeeman

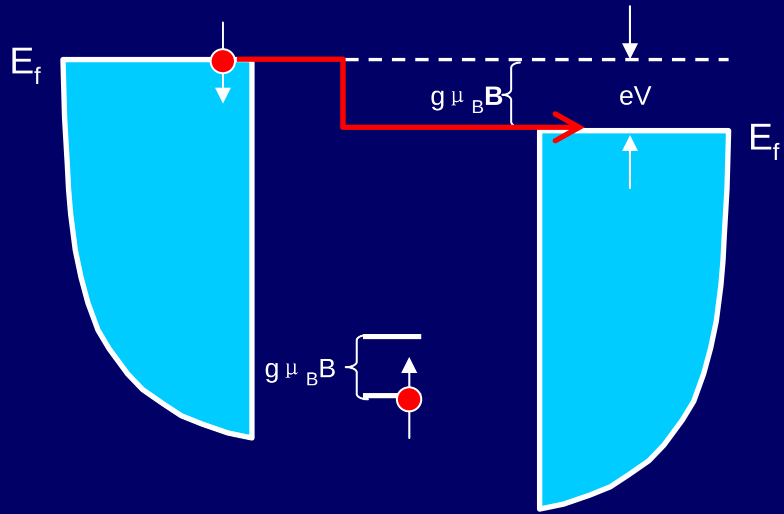
IETS via Single Spin Flipping

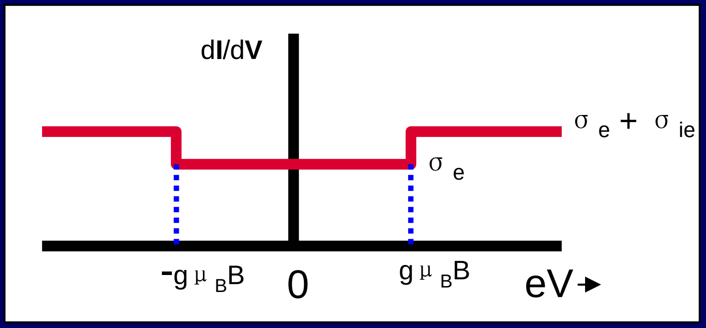




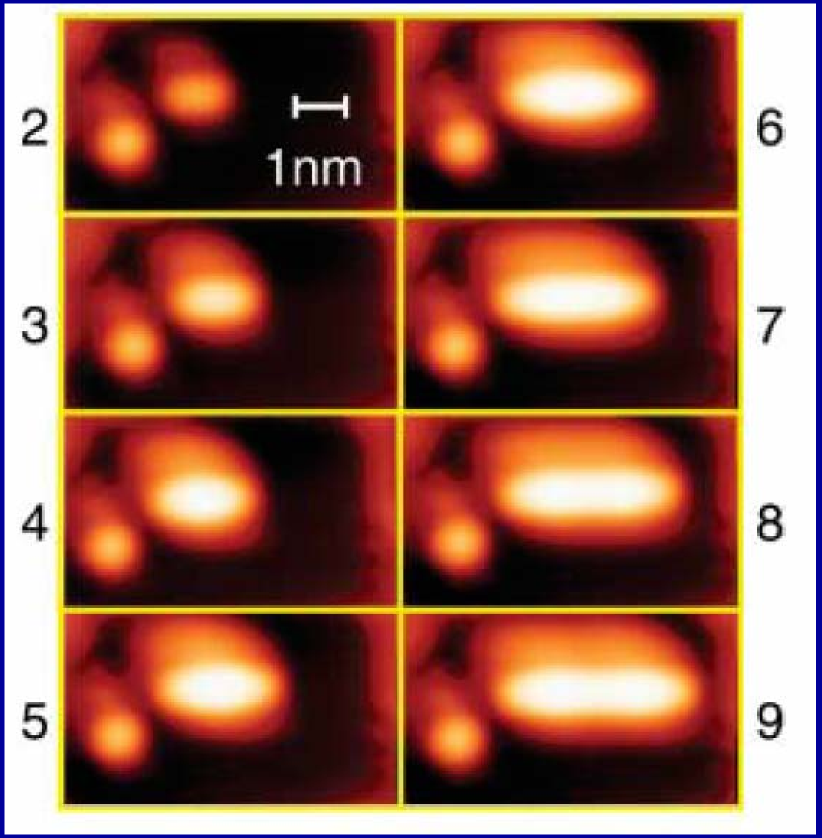
Spin-flip IETS

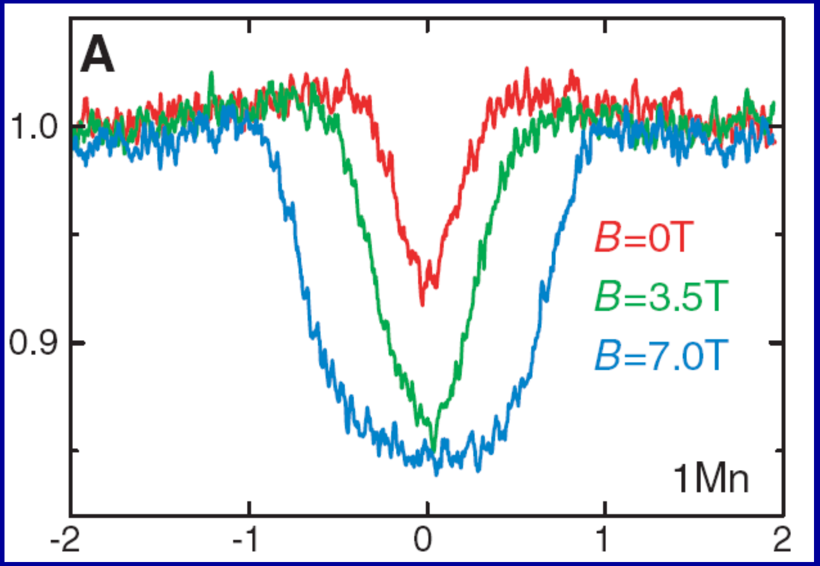






Mn Atom Chains

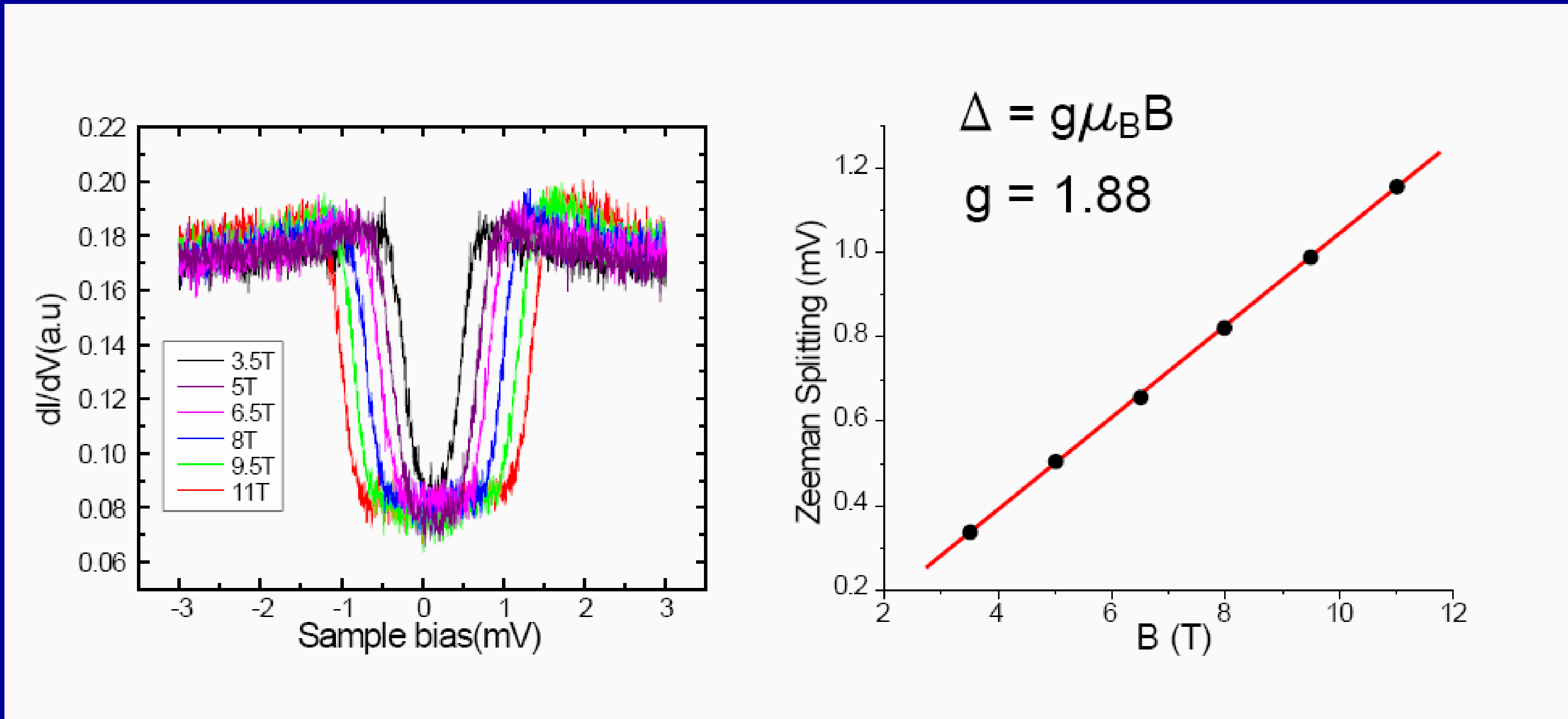




Hirjibehedin et al., Science 312, 1021(2006)

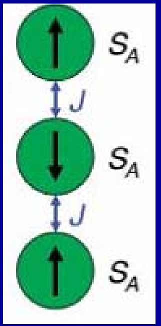
IV. Zeeman

Measurement of g-factor of single molecule



Model Calculations

Heisenberg model: $$H_N = J\sum_{i=1}^{N-1} S_i \cdot S_{i+1}$$



Dimer:
(3rd layer CoPc)

$$H = \frac{J}{2}[(S_1 + S_2)^2 - S_1{}^2 - S_2{}^2]$$

$$\Delta E_1 = J$$

Trimer:
(4th layer)

$$H = \frac{J}{2}[(S_1 + S_2 + S_3)^2 - (S_1 + S_3)^2 - S_2{}^2]$$

$S_A > \frac{1}{2}$ $\quad \Delta E_1 = JS_A$

$S_A = \frac{1}{2}$ $\quad \Delta E_1 = J$

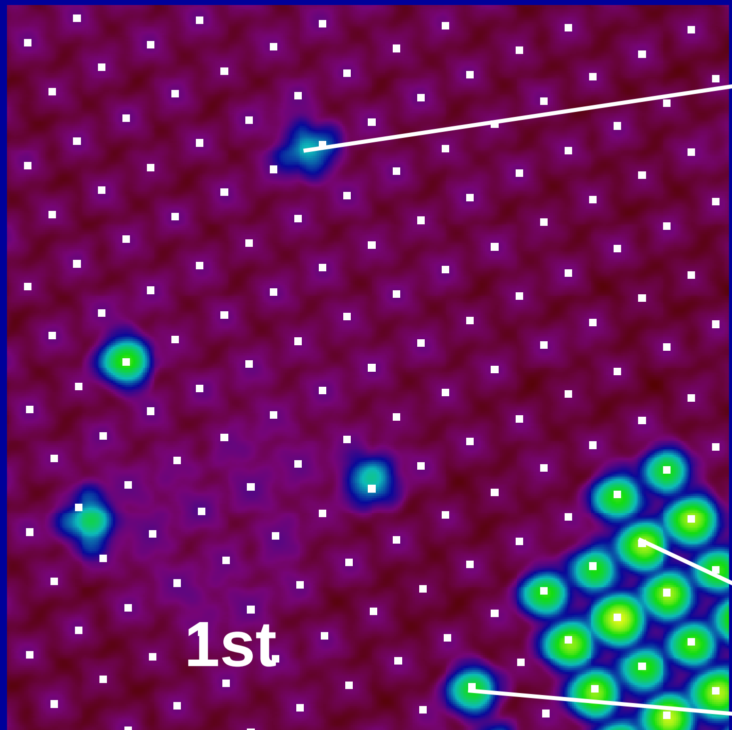
Tetramer:
(5th layer)

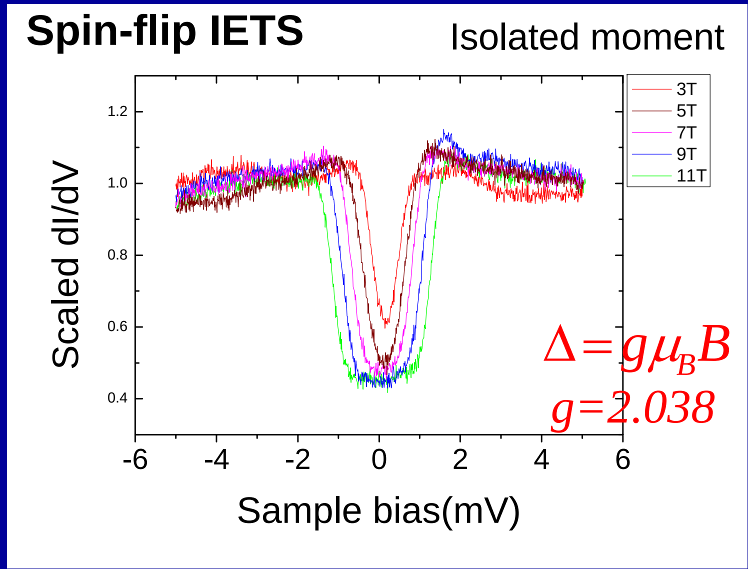
$$H = \frac{J}{2}[(S_1 + S_2 + S_3)^2 - (S_1 + S_3)^2 + (S_2 + S_3 + S_4)^2 - (S_2 + S_4)^2 - (S_2 + S_3)^2]$$

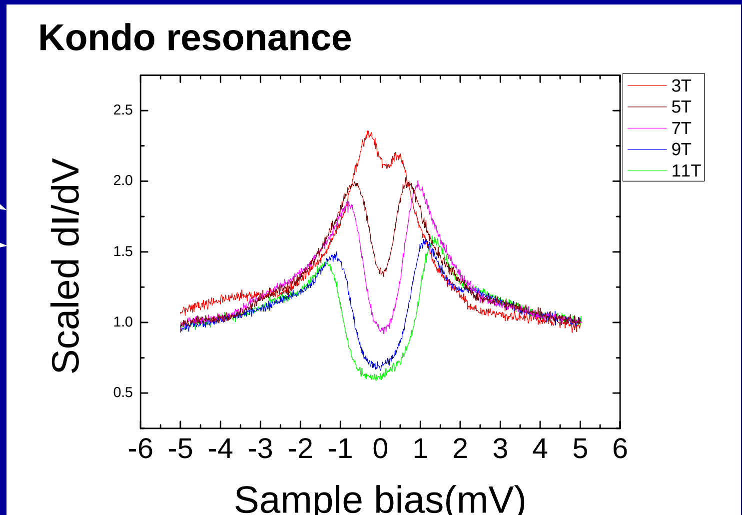
only for $S_A = \frac{1}{2}$ $\quad \Delta E_1 = J \quad \Delta E_2 = 1.5J$

Manipulation of single-molecule spin-states

Zeeman ↔ Kondo







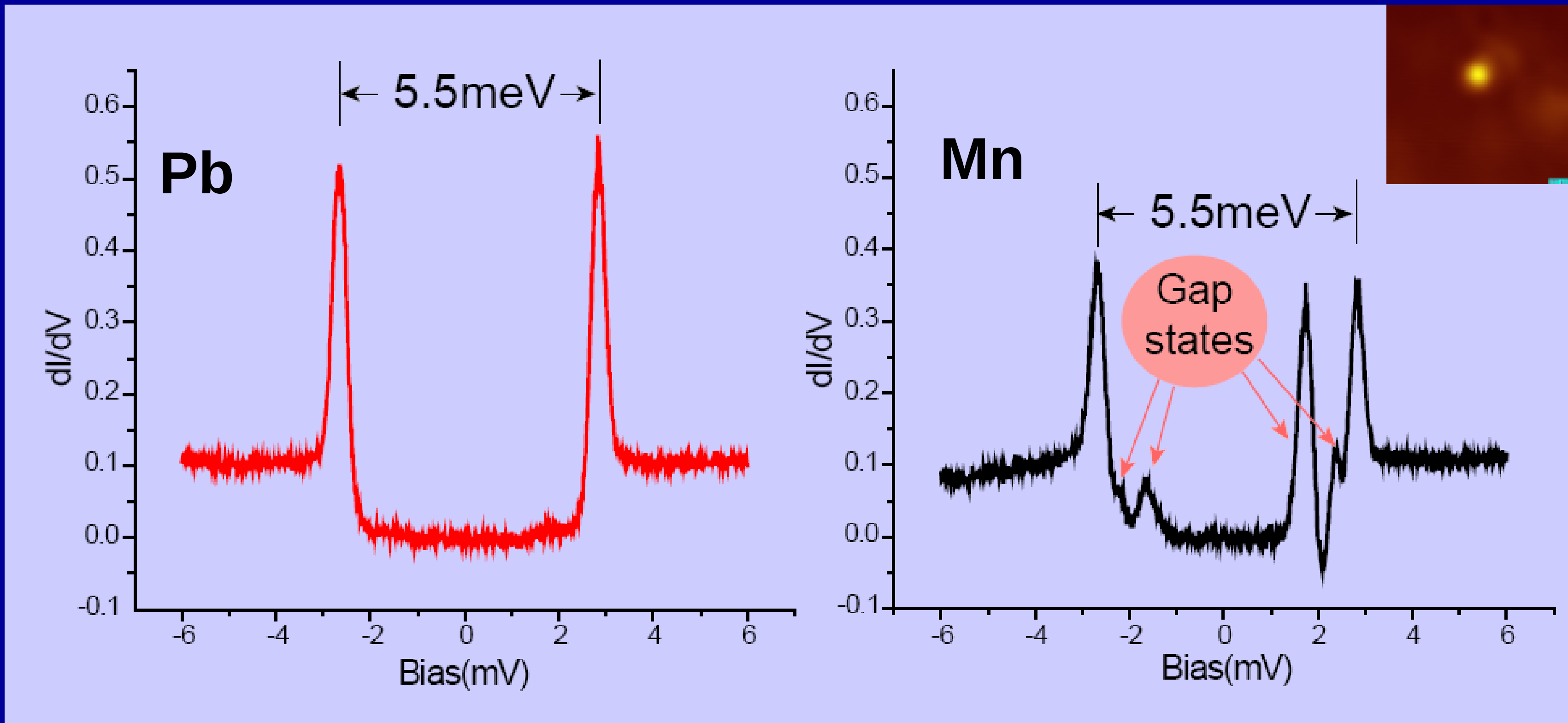
Ji et al., PRL (in press)

V. Gap States

$U \uparrow$

Gap States

$$\epsilon_\ell = \Delta\left[1 - \cos(\delta_\ell^+ - \delta_\ell^-)\right]$$



V. Magnetic

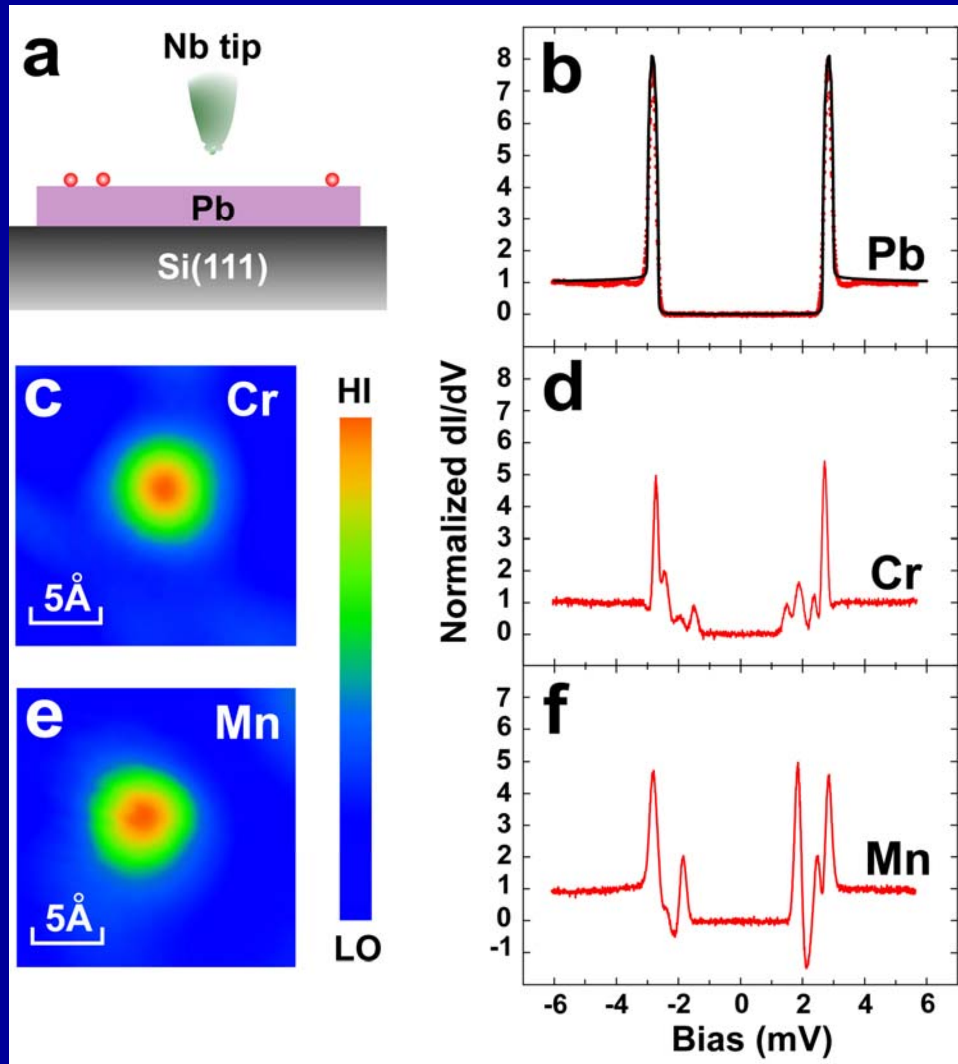
$U \uparrow$

Superconductor Gap States

$$\epsilon_\ell = \Delta\left[1 - \cos(\delta_\ell^+ - \delta_\ell^-)\right]$$

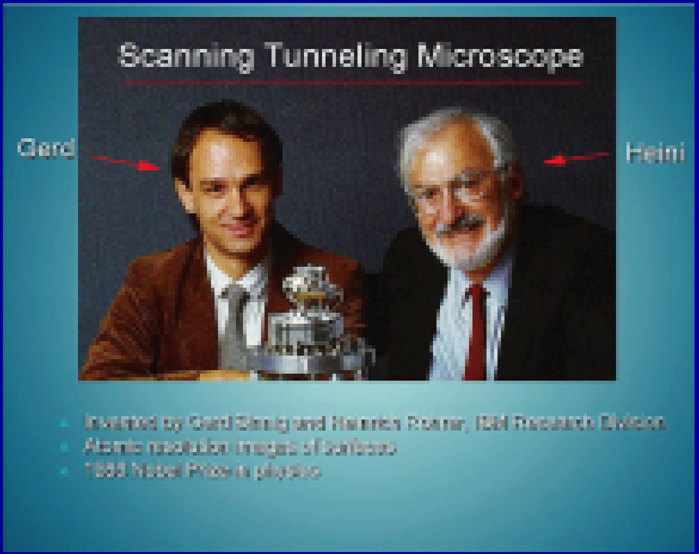
Single Atom Spectroscopy

Cr, Mn on Pb(111)

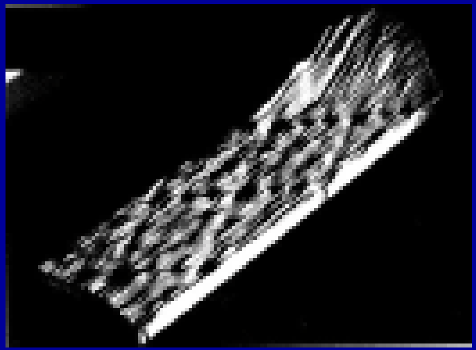


Three Functions & Three Milestones

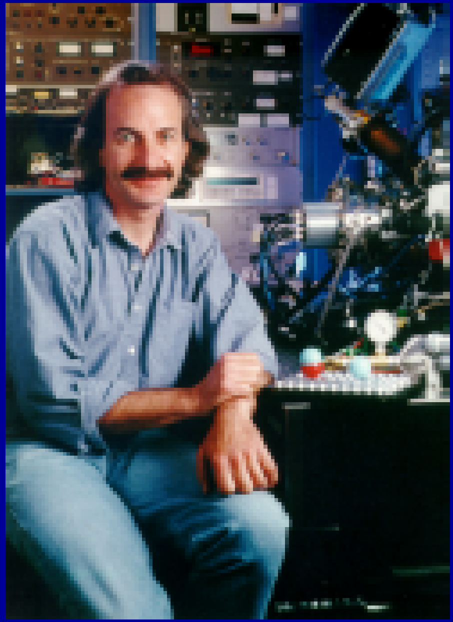
Imaging



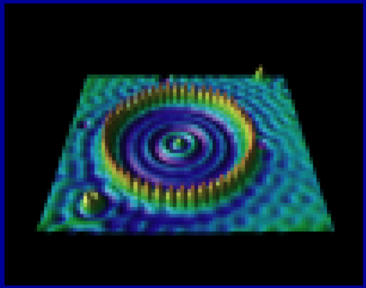
Invention of STM (1981)



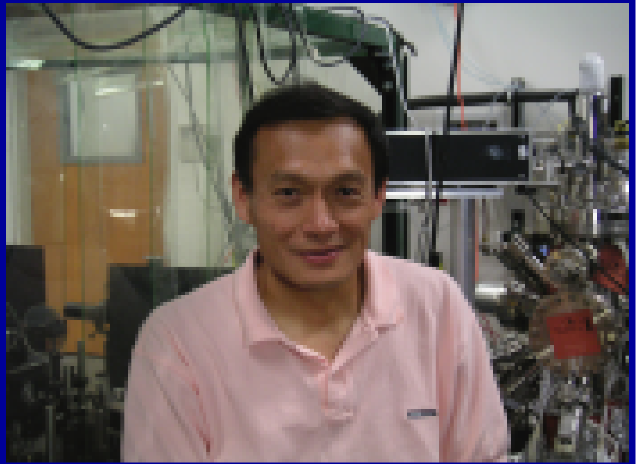
Manipulation



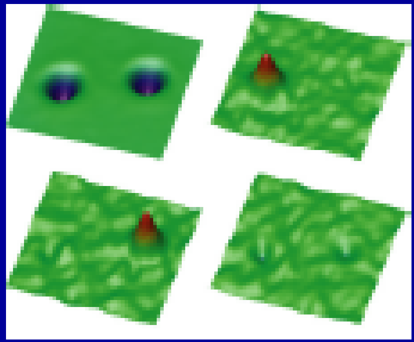
Quantum Corral (1990)



Spectroscopy



IETS (1997)



VI. Summary

Topic

Spin states of adsorbates

Toolbox

Low temperature (B) STM

Single molecule manipulation

Scanning tunneling spectroscopy

Inelastic tunneling spectroscopy (IETS) via single spin flip

Gap states in superconductor

Progress

Kondo effect modulation via QSE

Magnetic coupling between molecules

Manipulating spin states at single molecular level

Perspective

Organic magnetism

Molecular spintronics

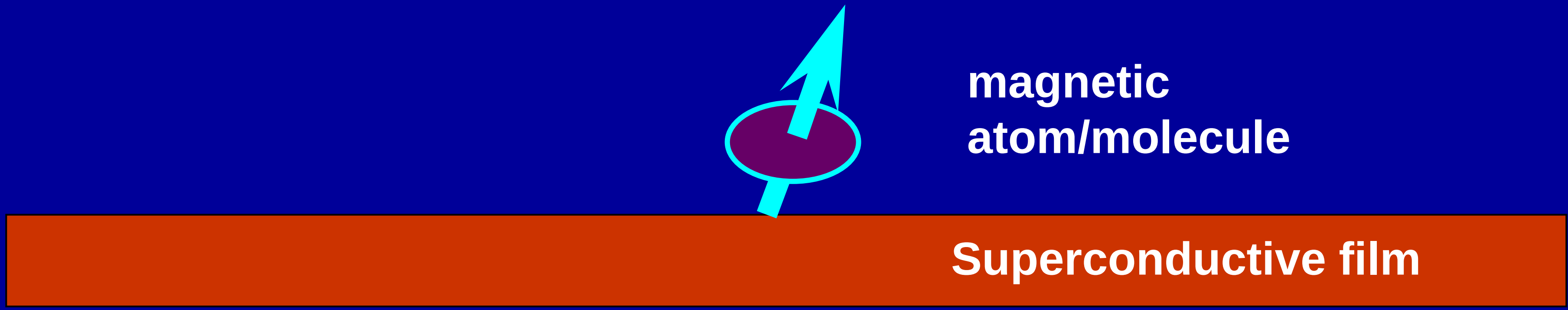
Molecular recognition

Single atom reaction detection……

Thank you very much!!!

I. Introduction

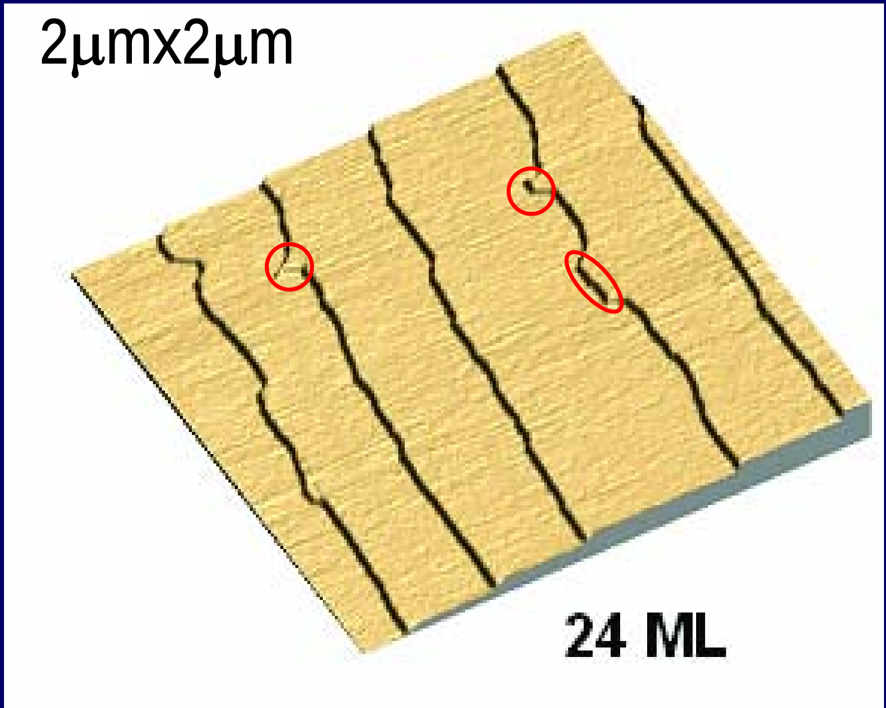
localized spin + surface



Platform ⇨

Quantum Size Effect
Zeeman
Kondo
Magnetism
Superconductivity
………

Atomically flat Pb films on Si(111)



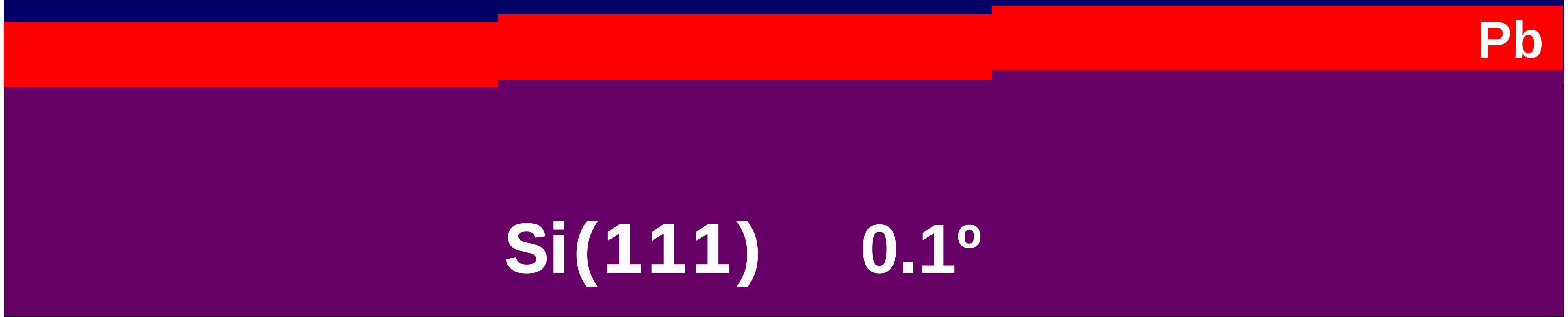
Thickness: 7nm (24ML)

Uniformity: ~centimeter

Pb(bulk): coherent length 87nm

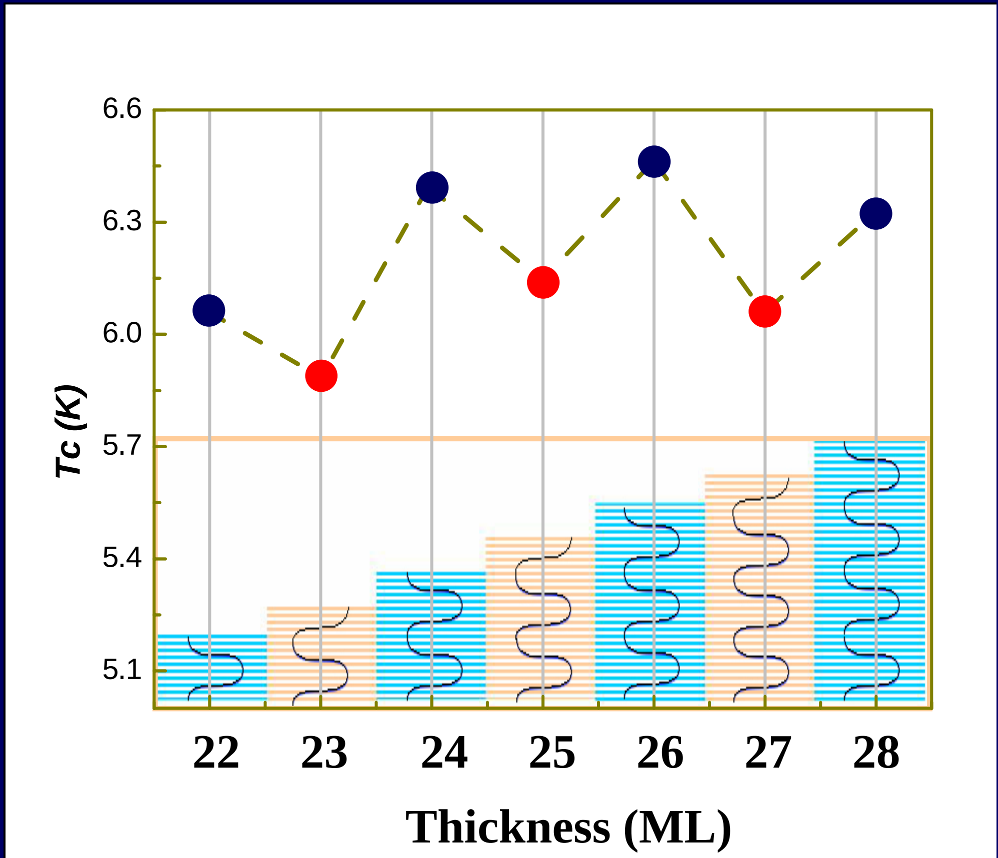
2D electronic system

1D Square Potential Well-tunable L



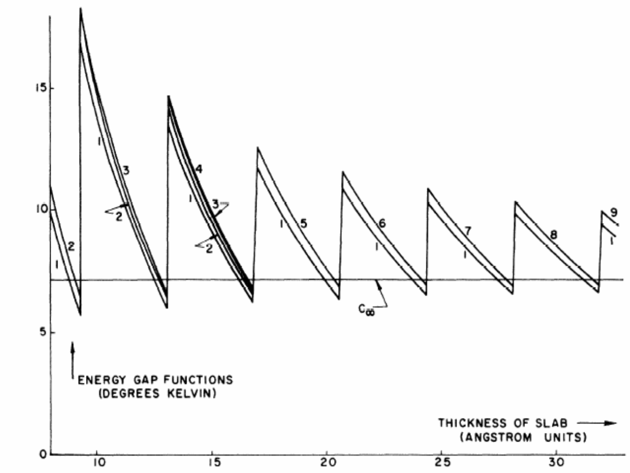
QSE对电子结构和超导的影响

Superconductivity (Tc) oscillation



Guo, Zhang et al., ***SCIENCE 306****, 1915 (2004)*
Zhang et al., ***PRL 96****, 096802 (2005)*

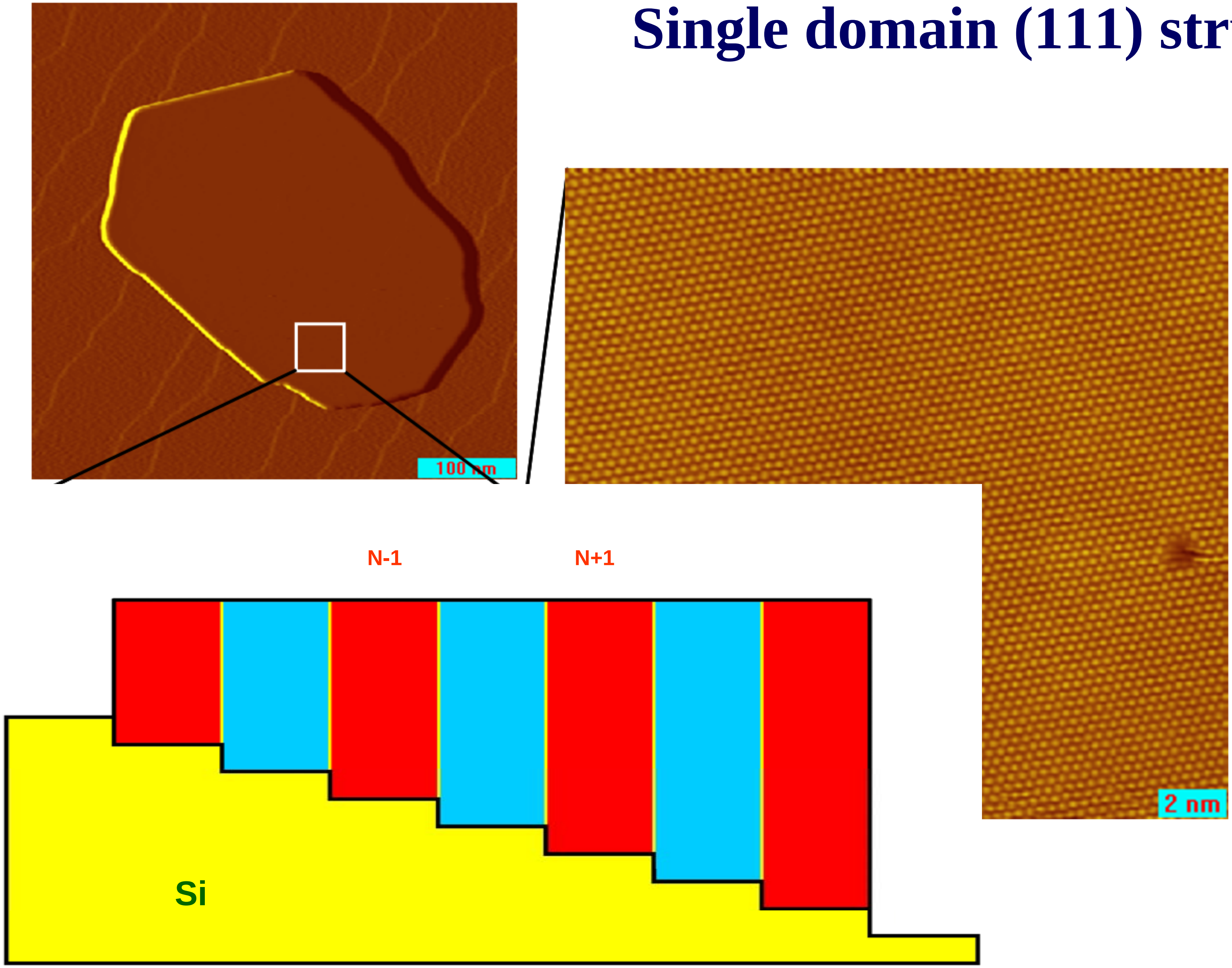
PHYSICAL REVIEW LETTERS **15 April 1963**



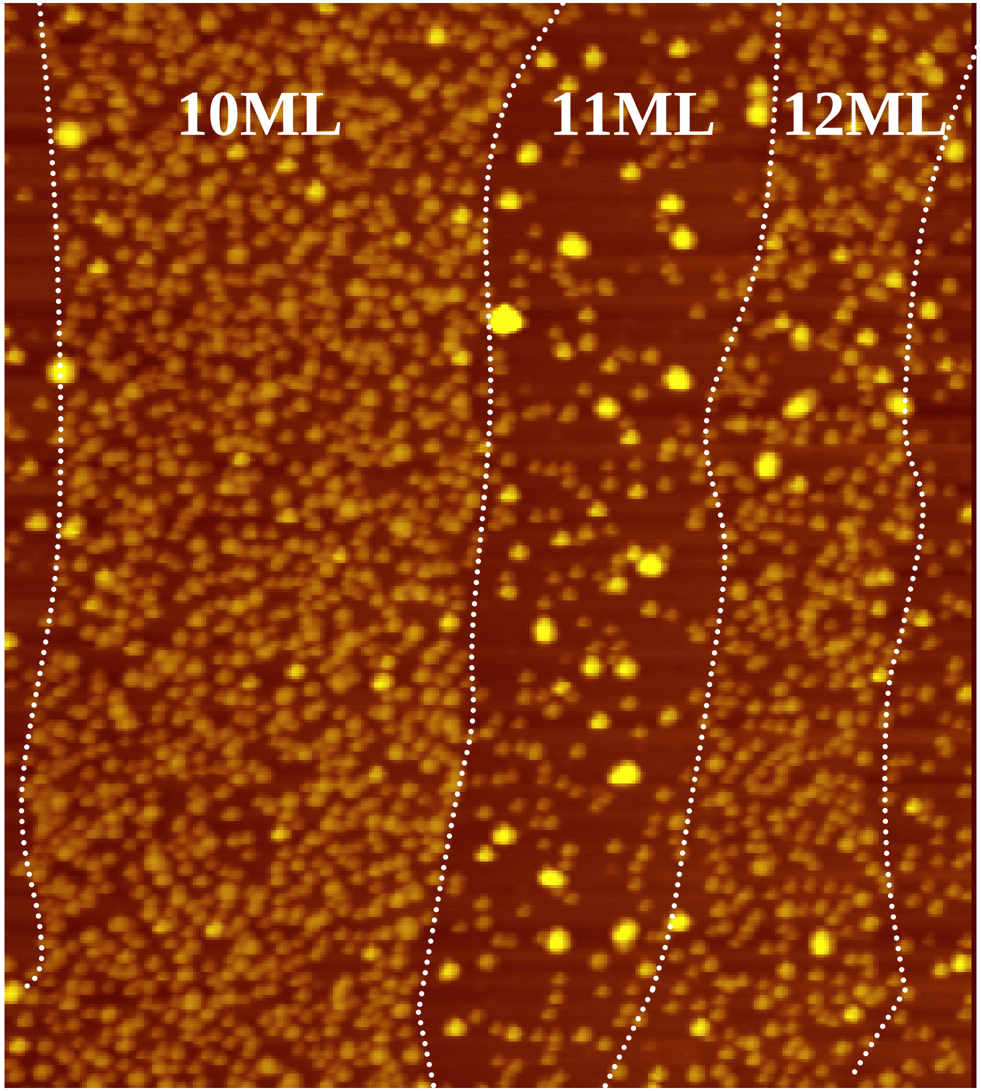
perconducting energy gap parameters C_n, vs thickness of film. At each resonance, a new value of ntribute. All values of C_n are shown for small thicknesses; thereafter, only the largest and smallest , to avoid confusion. The peak heights lie well above the bulk value, C_∞, which is also shown on the troughs are only slightly below C_∞. The width of the resonances is too small to show on the scale of The distance between resonances equals one half of the deBroglie wavelength of an electron at the e. The parameters used for this figure were $N/V = 2 \times 10^{22}$ electrons/cm^3, $\rho = 0.3$, and $\hbar\omega_c = 100°$K.

J. M. Blatt and C. J. Thompson
PRL 10, 332 (1963)

Single domain (111) structure



Oxygen adsorption on Pb



500nm x500nm

O_2 (~120L @LN_2)

10ML, 12ML: more sites

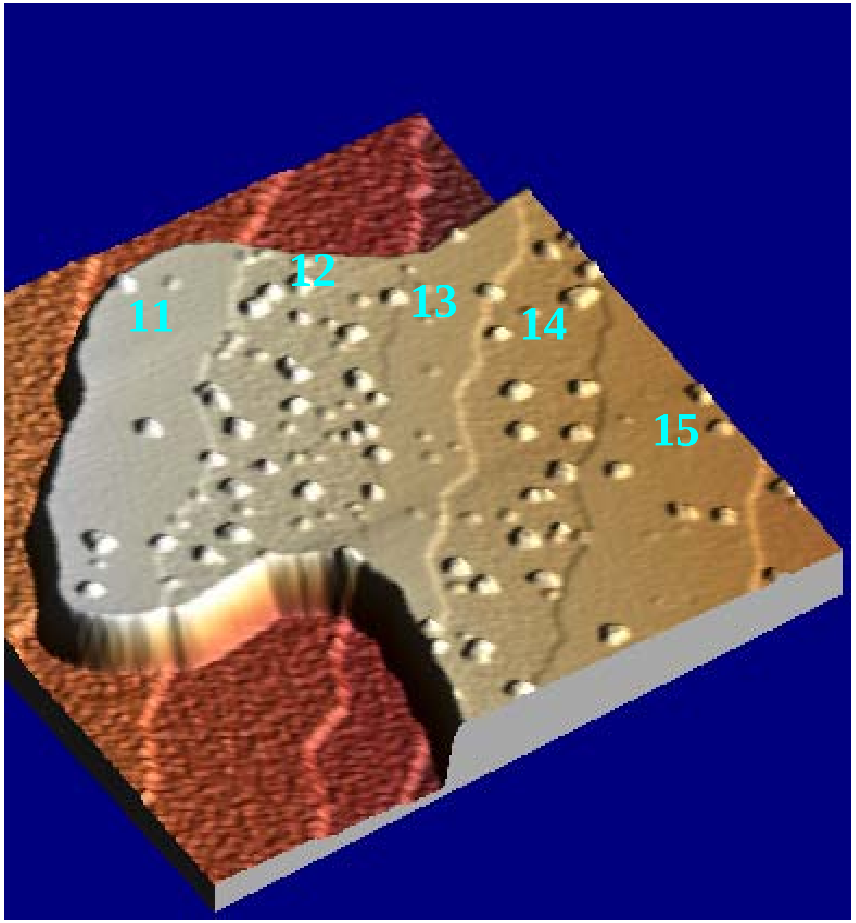
11ML: less sites

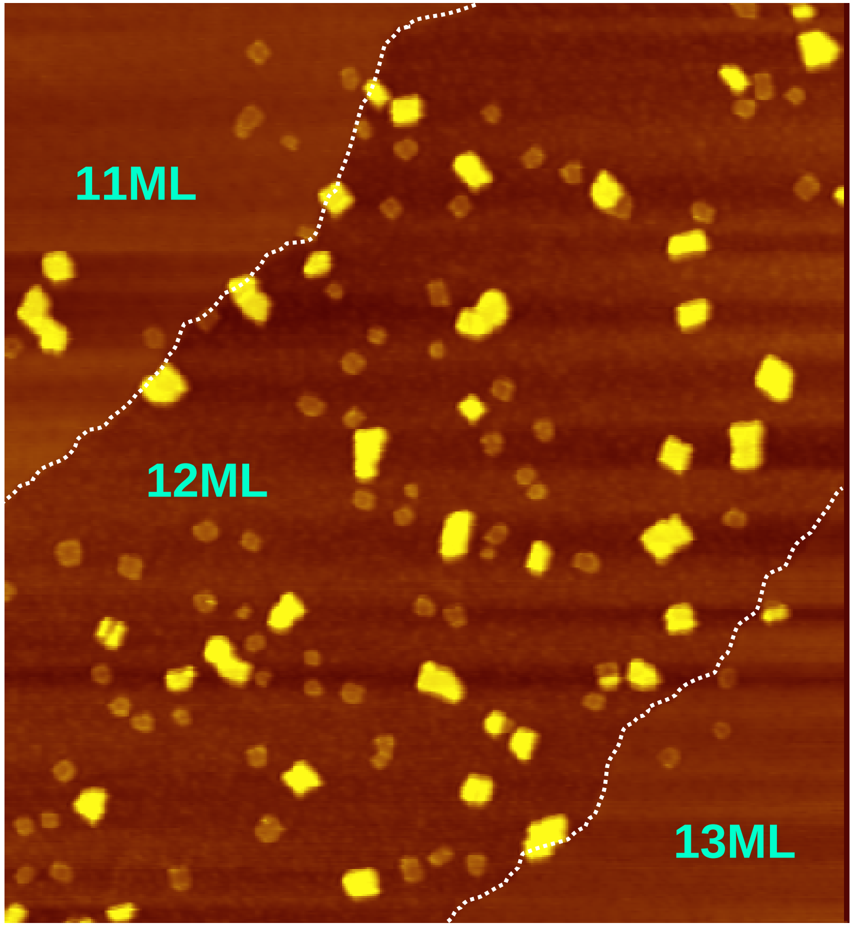
10ML: θ=0.2453

11ML: θ=0.0831

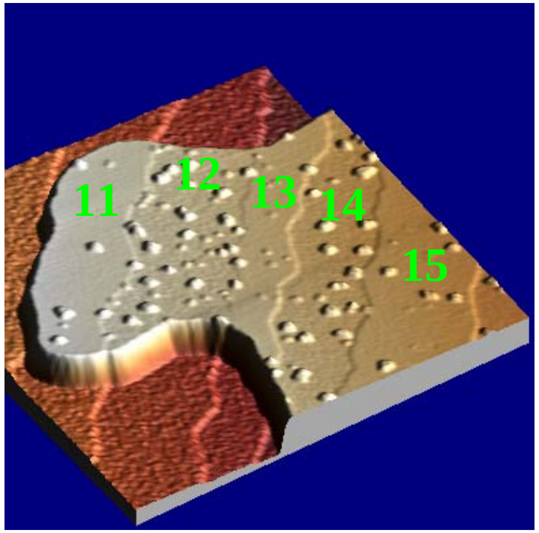
3 times!

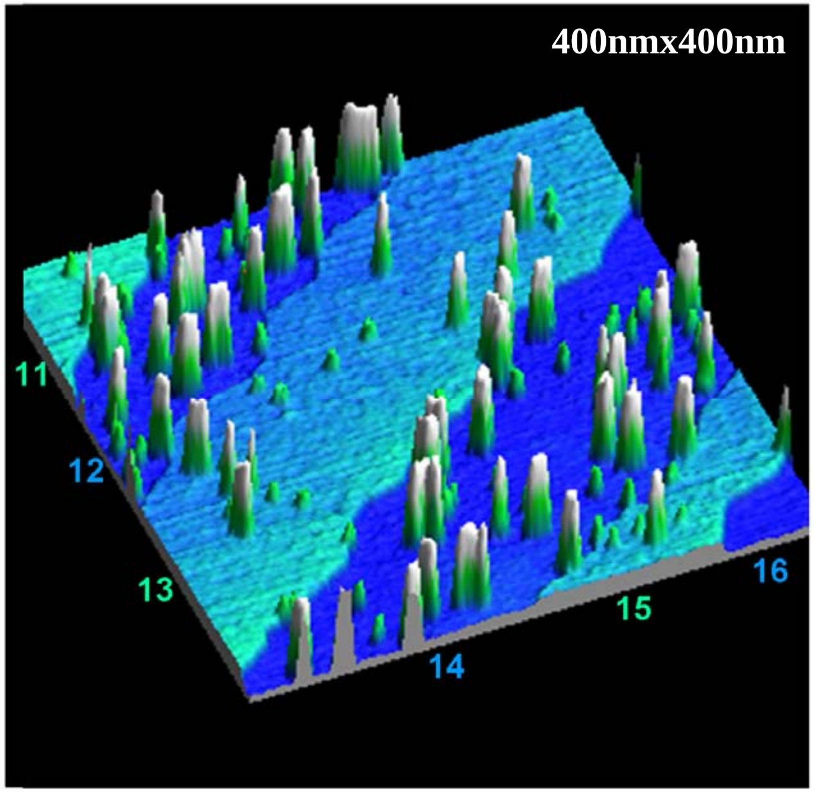
Oscillating oxidation on Pb(111) surface





QSE on Surface Oxidation of Pb(111)



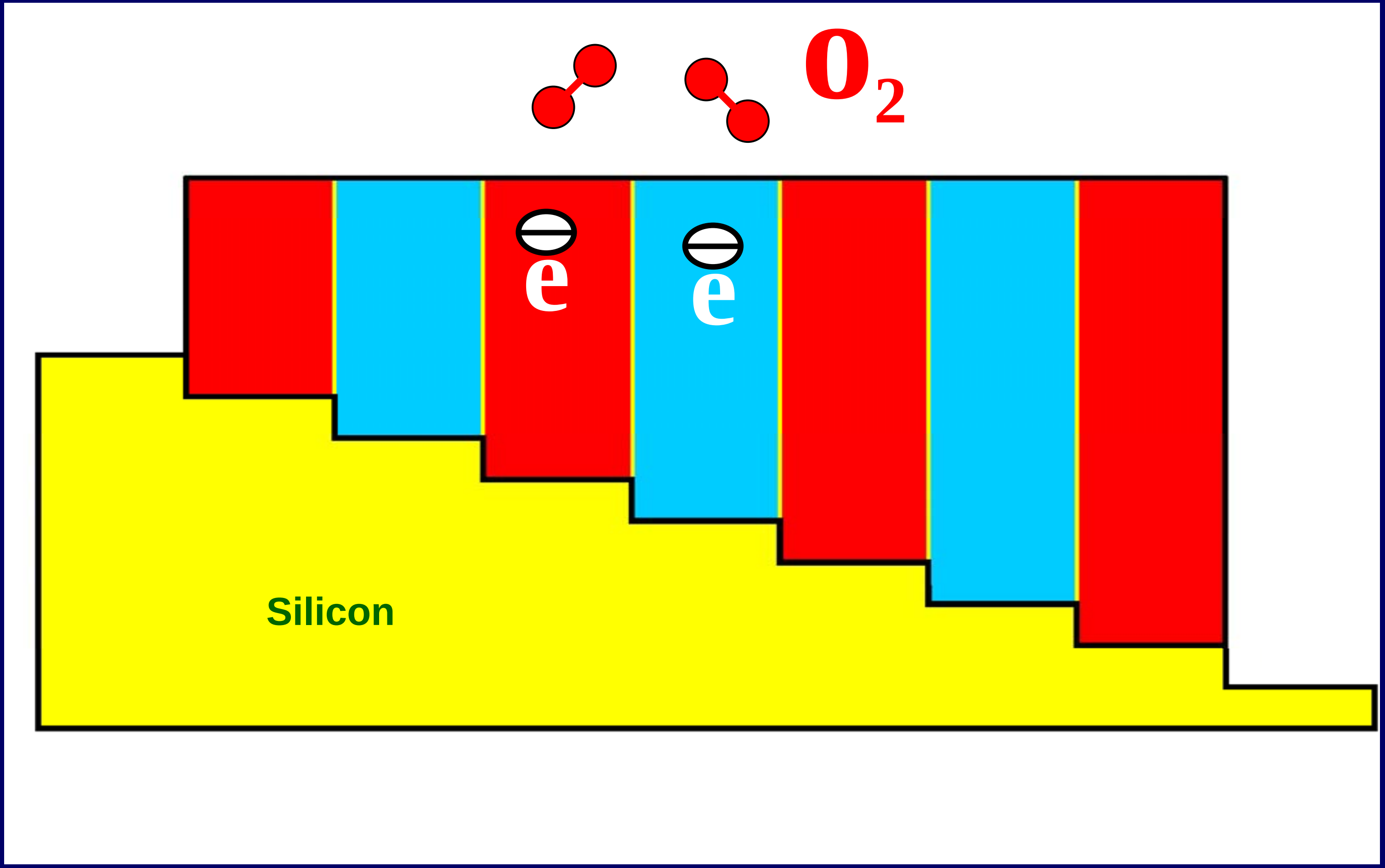


Xucun Ma et al.,

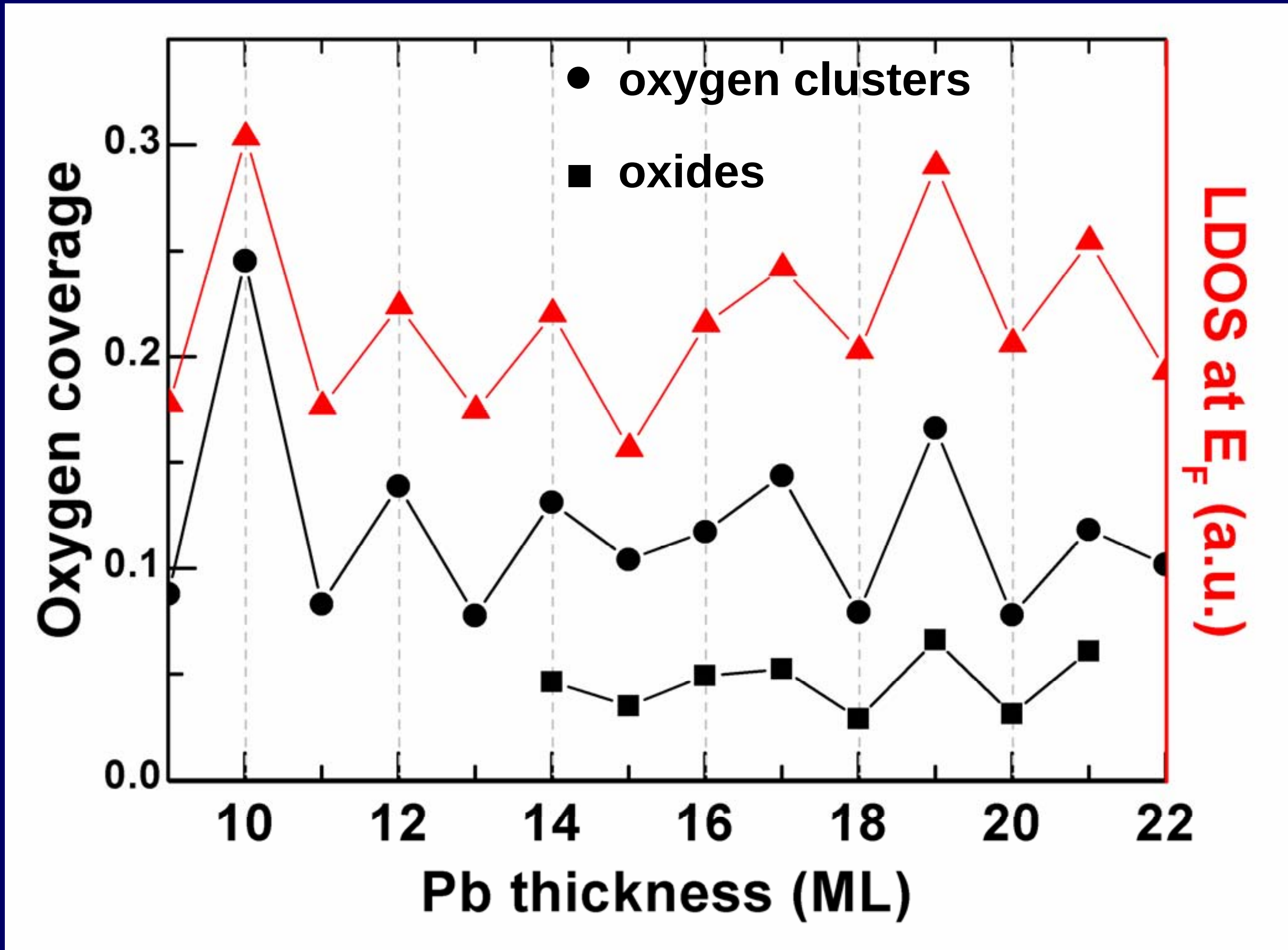
PNAS 104, 9204 (2007)

In the same metal Pb island,

the behaviors of electrons are different



Surface Reactivity & LDOS at E_F (O_2/Pb)

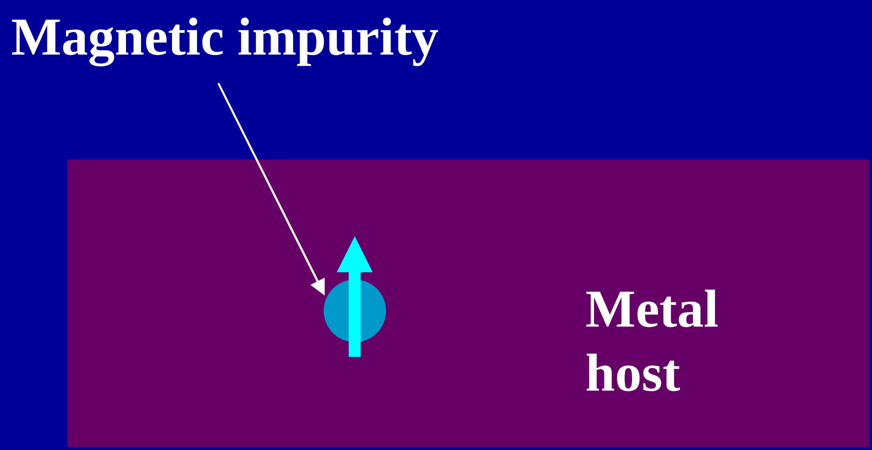


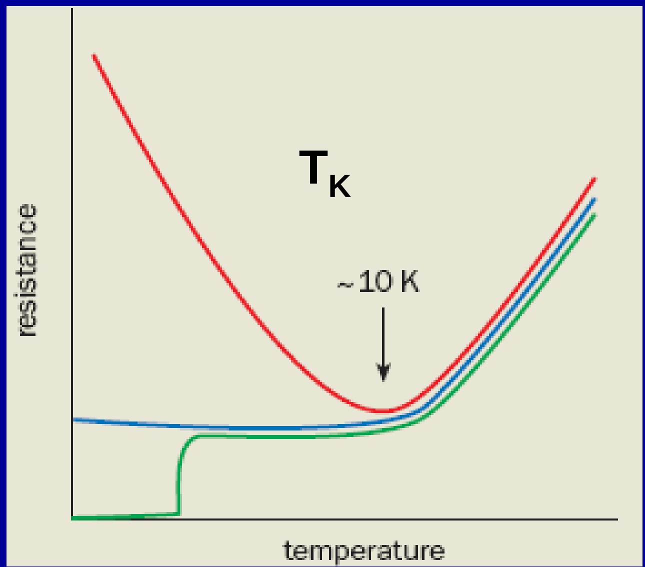
↑ LDOS at E_F

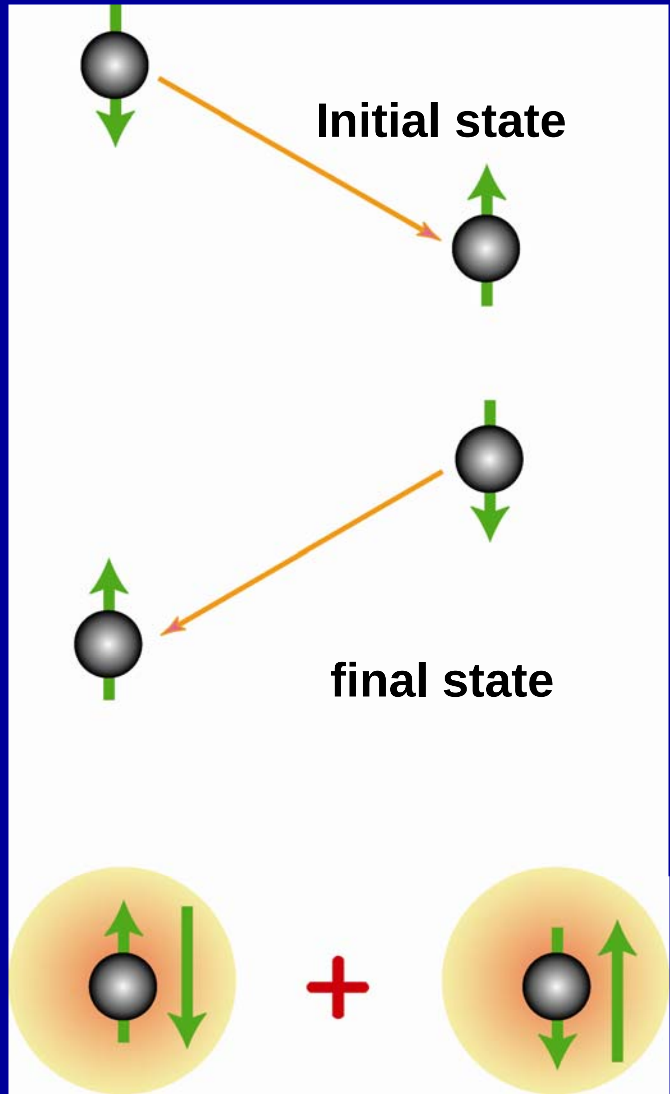
↑ Reactivity

Xucun Ma et al., PNAS 104, 9202 (2007)

Kondo Effect







Kondo Temperature T_K