KONDO EFFECT IN TRANSPORT THROUGH CoPc AND TBrPP-Co ADSORBED ON METAL SURFACES

(EFFECTS OF MOLECULE CONFIGURATION)

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OUTLINE

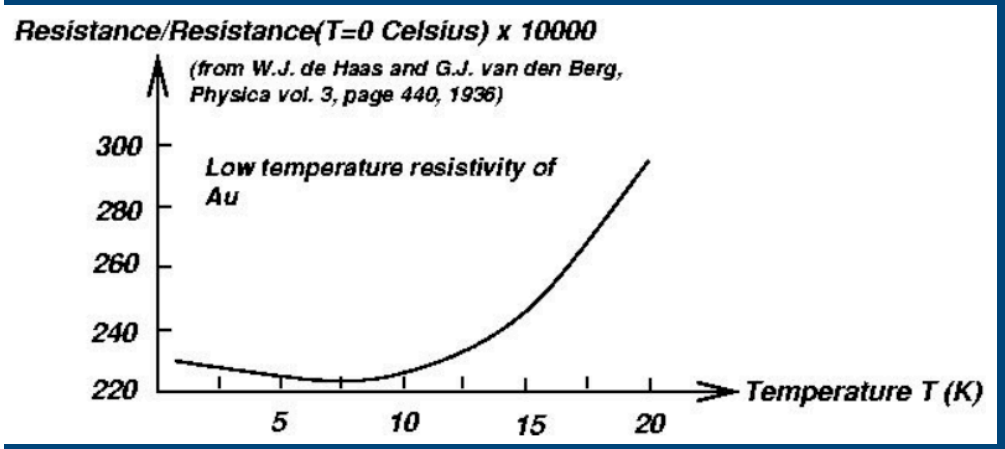
- Kondo physics
- Survey and Summary of experiments:
  CoPc/Au(111) and TBrPP-Co/Cu(111)

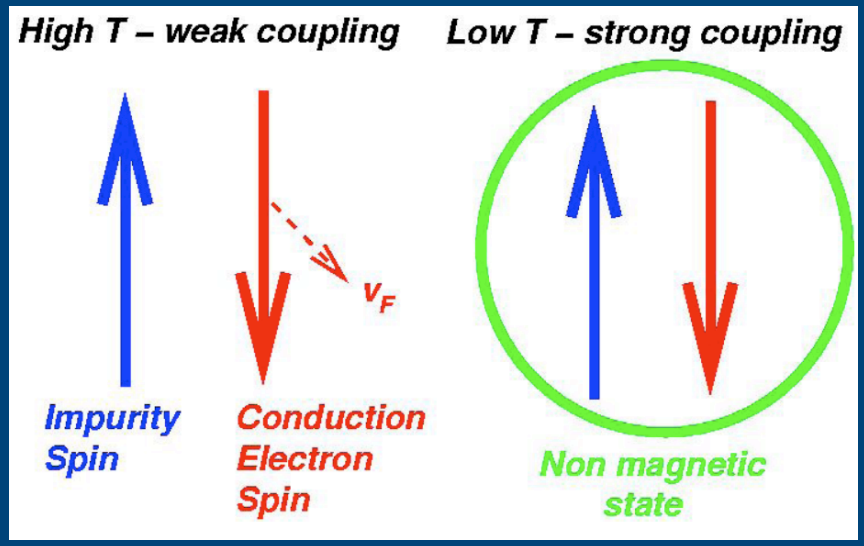
- A simple model

  CoPc/Au(111): the role of quantum interference

  TBrPP-Co/Cu(111): Fano dip versus Kondo peak
  Isolated versus molecule clusters
  The role of molecule conformation

The Kondo effect: metals with magnetic impurities





- Minimum in resistance at low T (1936)
- 1964: Jun Kondo "solves" the Kondo problem

The Kondo Physics

- A genuine many-body effect.

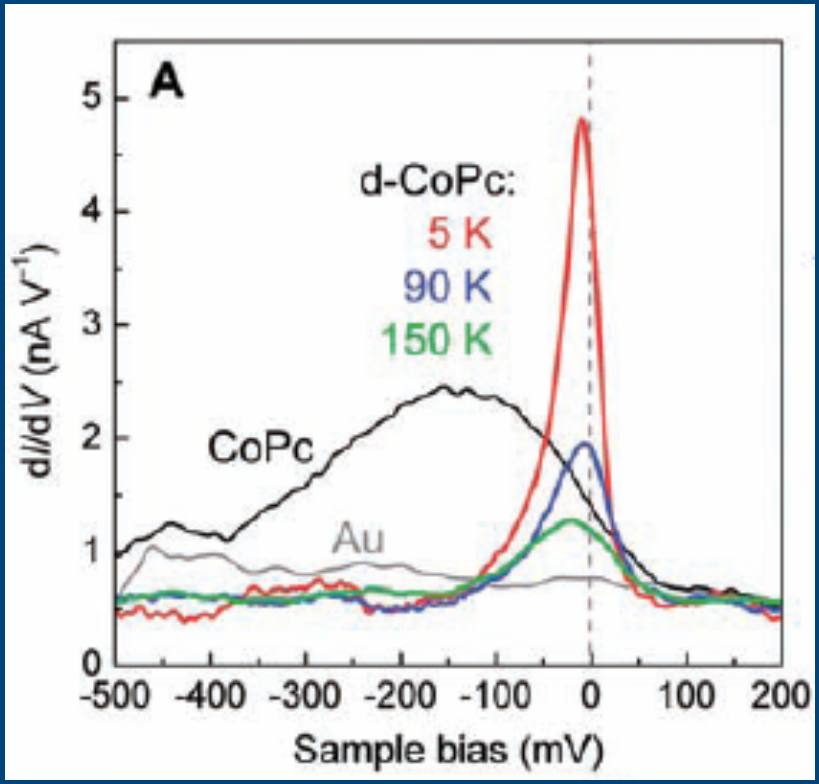
MESOSCOPIC AND NANOSCOPIC PHYSICS

- A conductance feature at the Fermi level E_F that may show up either as a peak or a dip (Fano dip)
- Whose width is related to the Kondo temperature T_K (50-250 K)

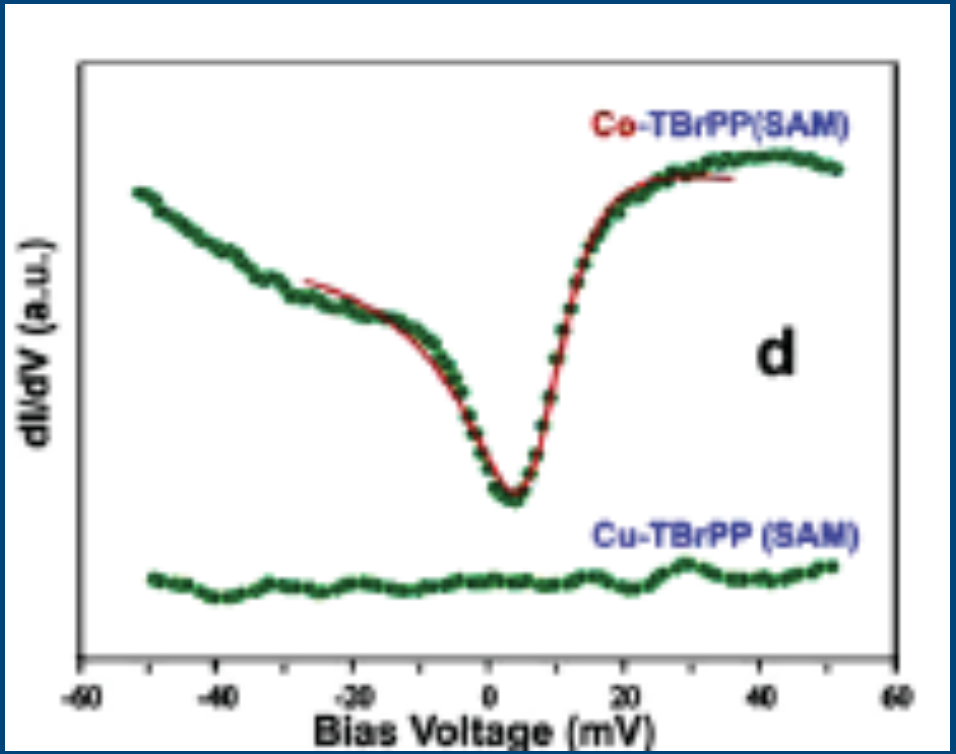
- AF coupling between strongly correlated atom and leads

Kondo resonance: dips and peaks

STM-CoPc/Au(111)

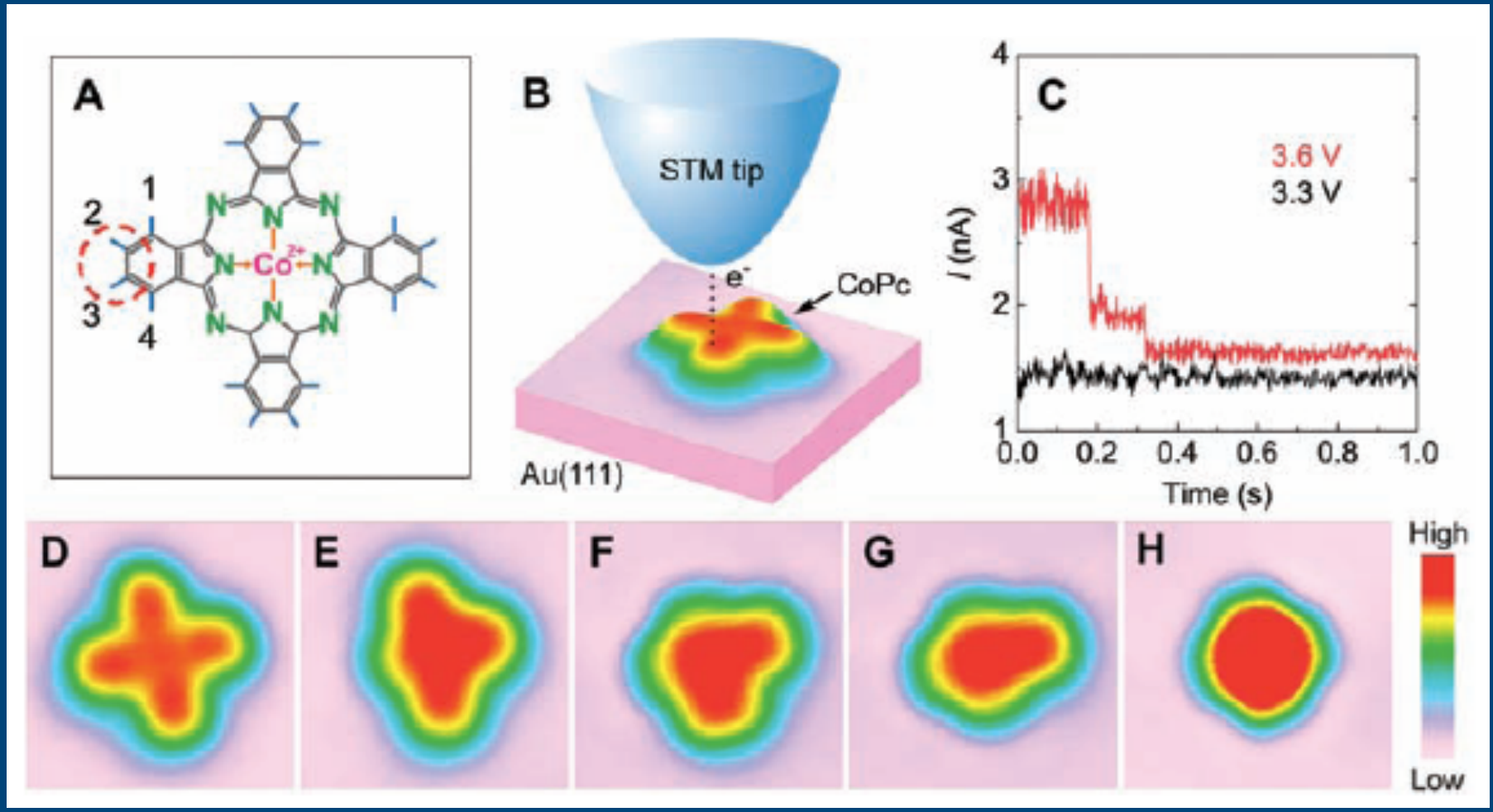


STM-TBrPP-Co/Cu(111)

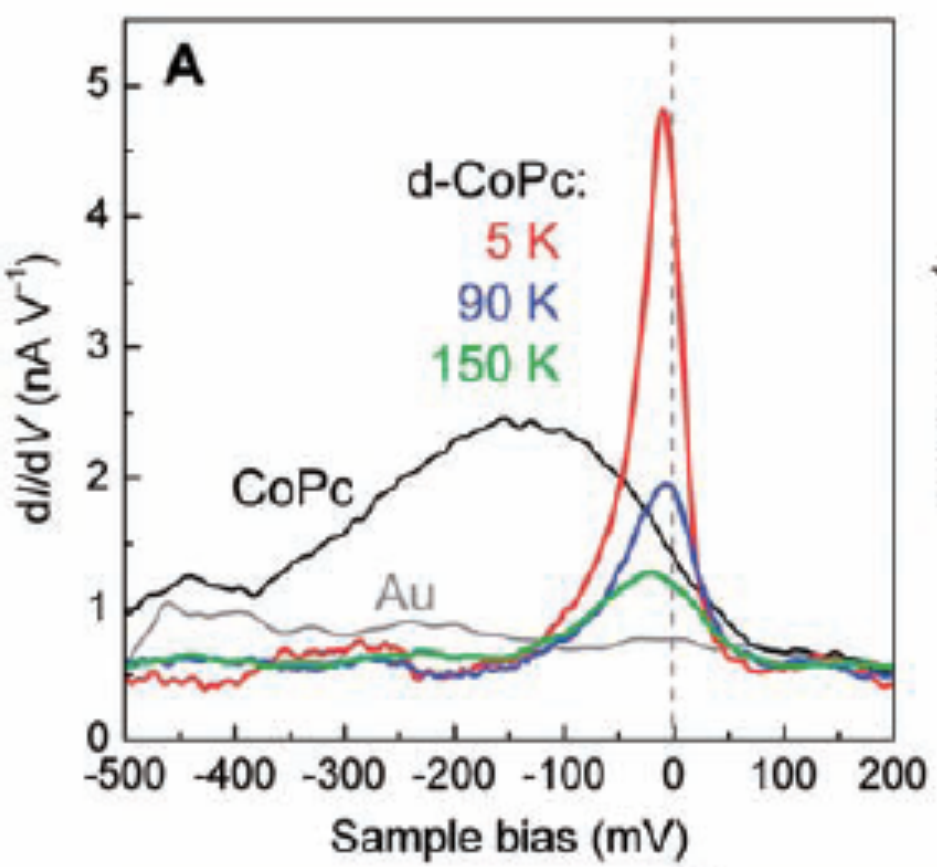


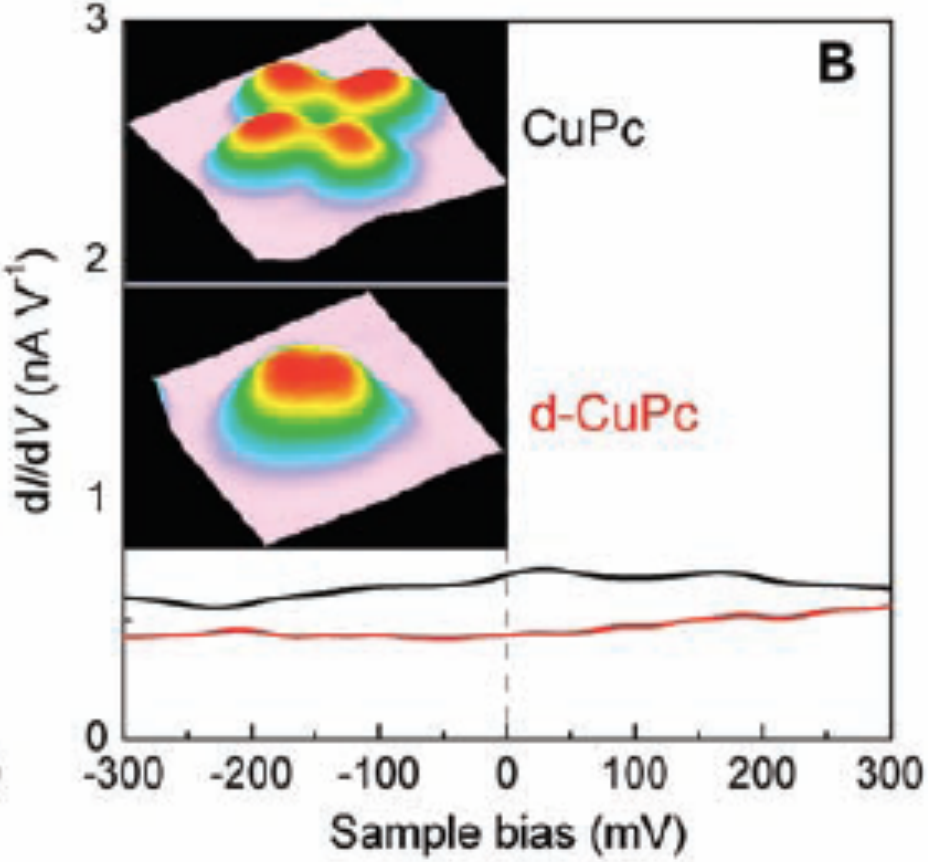
Experiments: CoPc/Au(111)

(Zhao et al, Science 309, 1542 (2005))



Experiments: CoPc/Au(111)



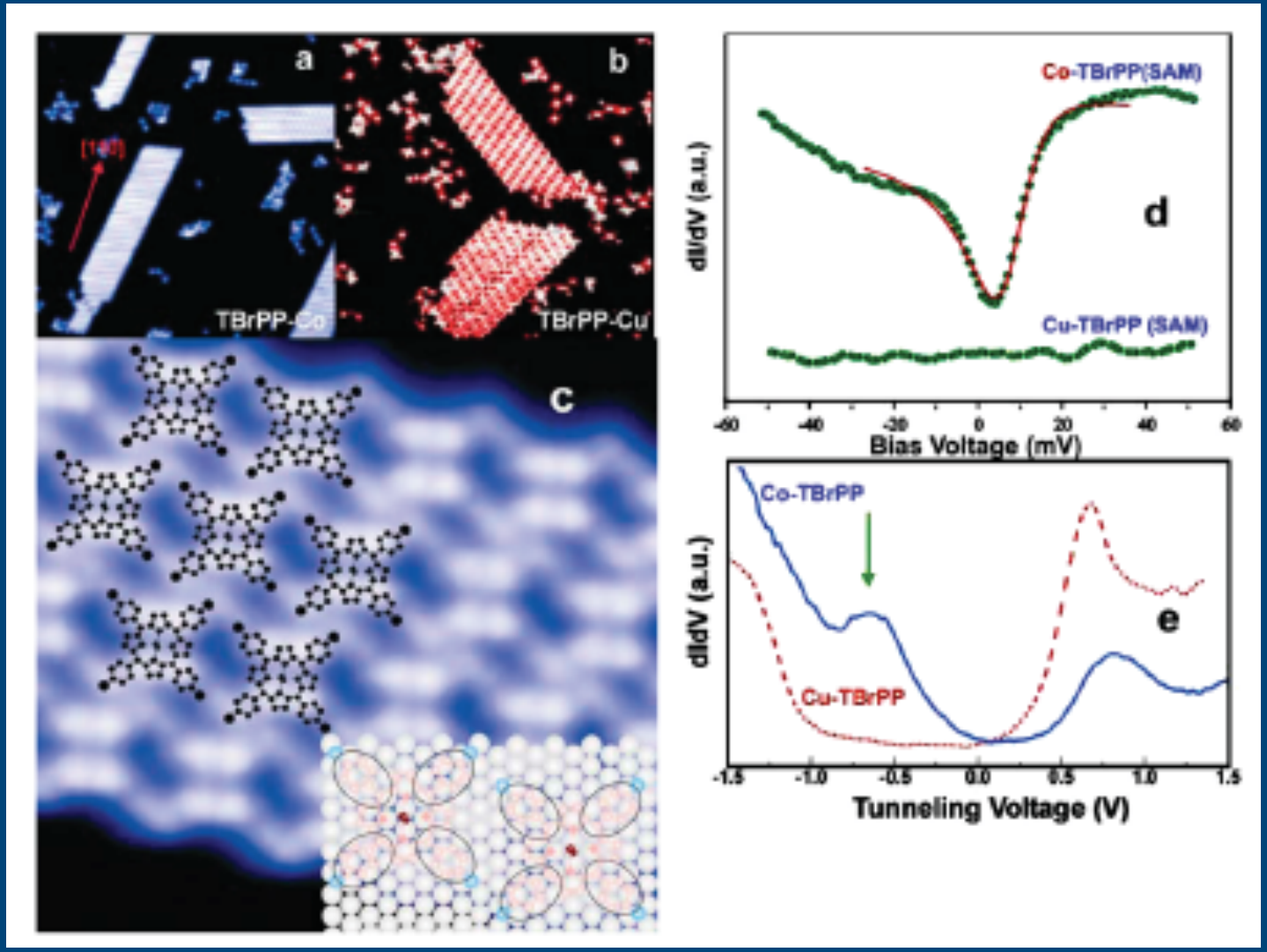


$$\Gamma = 2\sqrt{(\pi k_B T)^2 + 2(k_B T_K)^2}$$

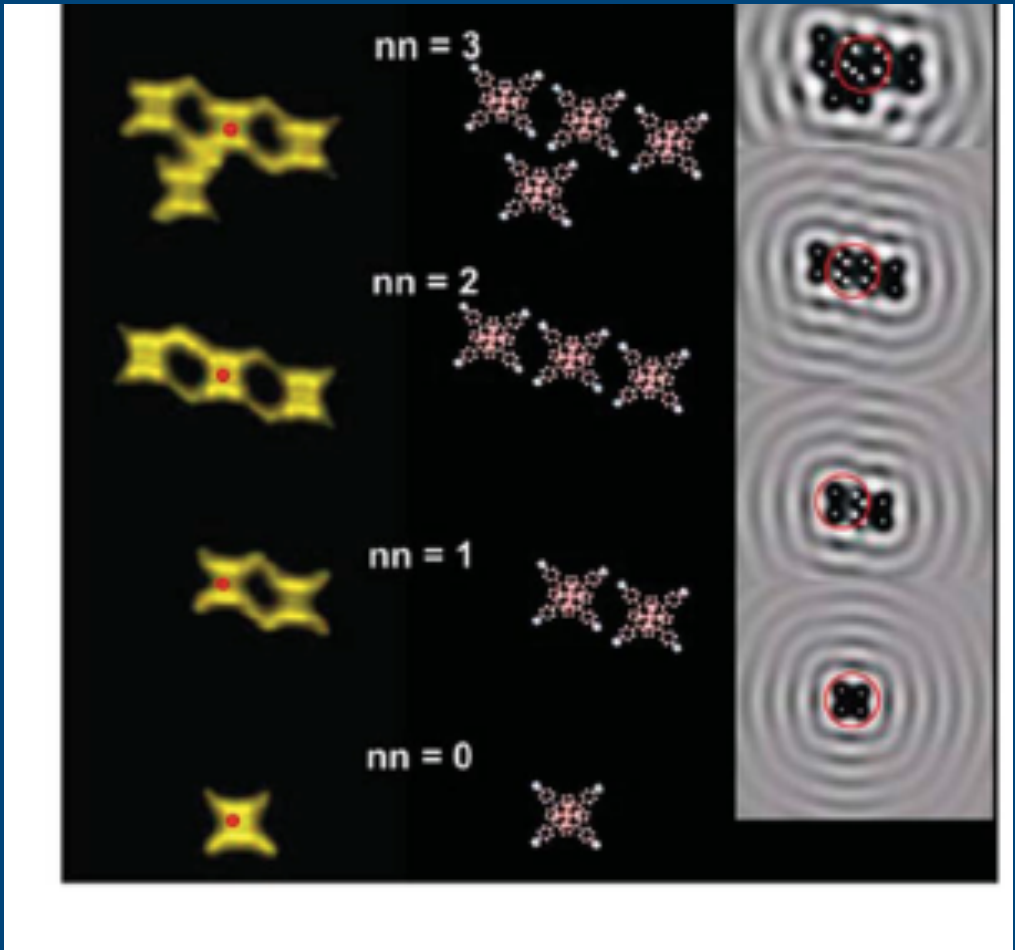
A very high T_K (> 200 K)

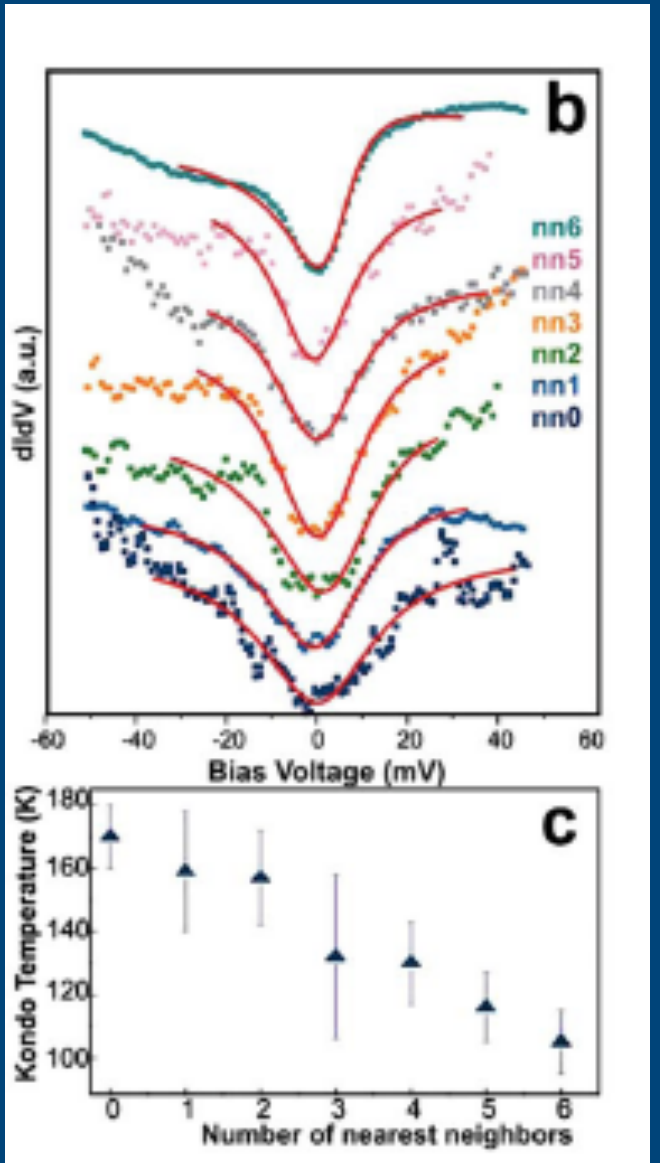
Experiments: TBrPP-Co/Cu(111)

(Iancu et al, PRL, 97, 266603 (2006))



Experiments: TBrPP-Co/Cu(111)

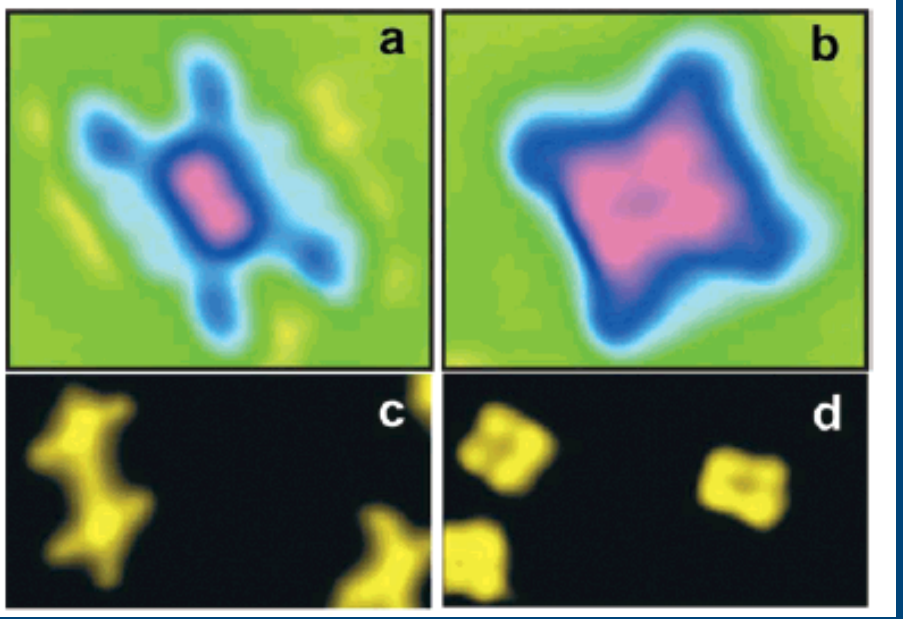


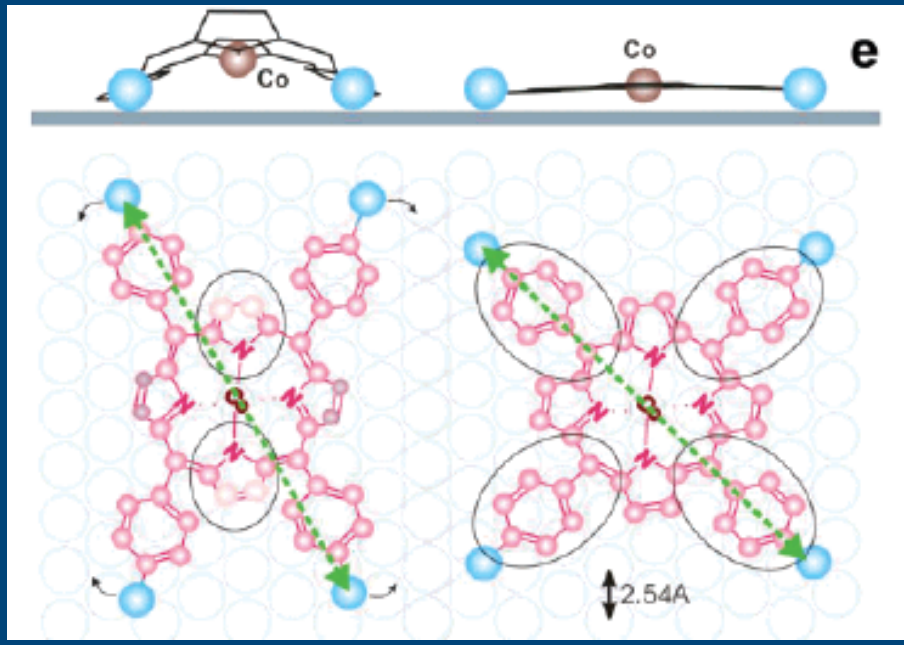


Experiments: TBrPP-Co/Cu(111)

(Iancu et al, Nanoletters, 6, 820 (2006))

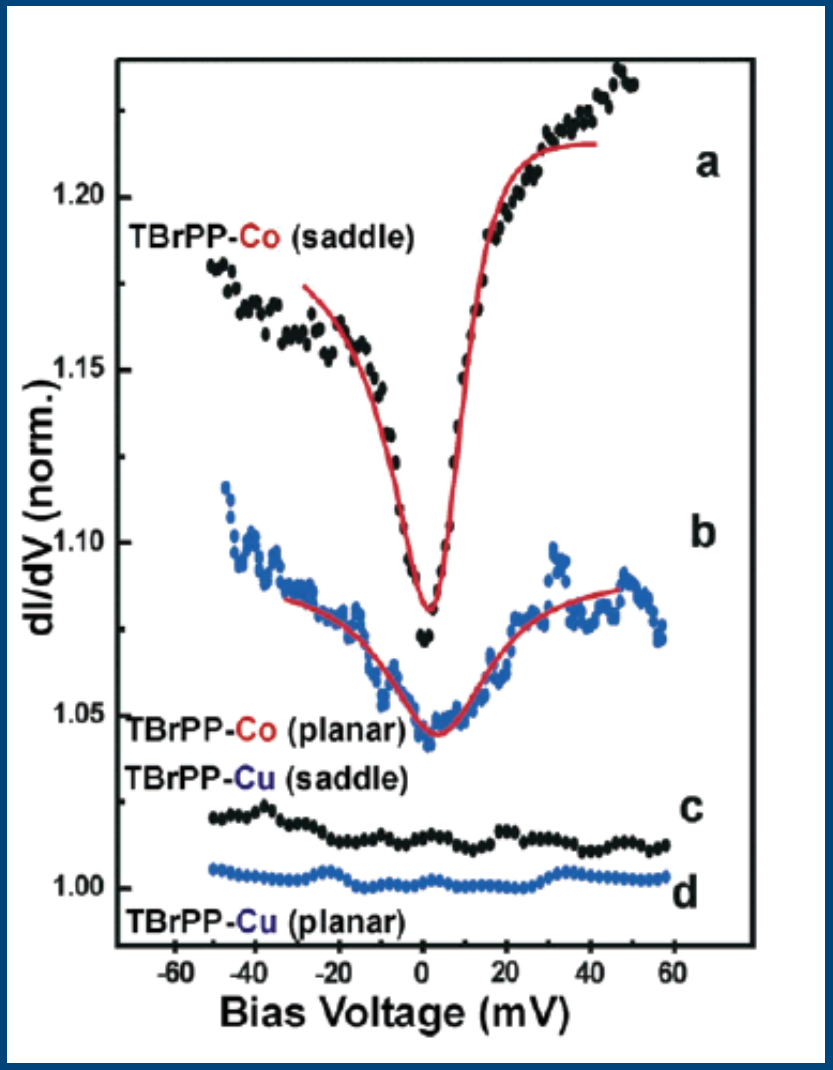
Two conformations

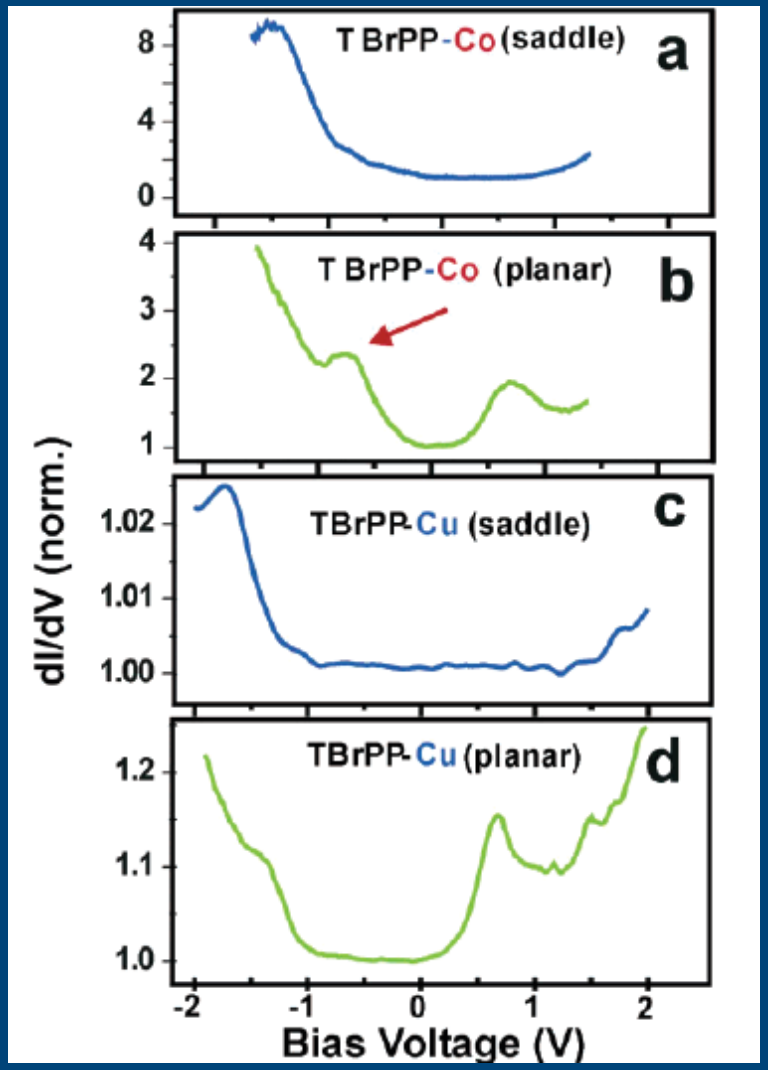




Switched from saddle
to planar by applying voltage pulses

Experiments: TBrPP-Co/Cu(111)

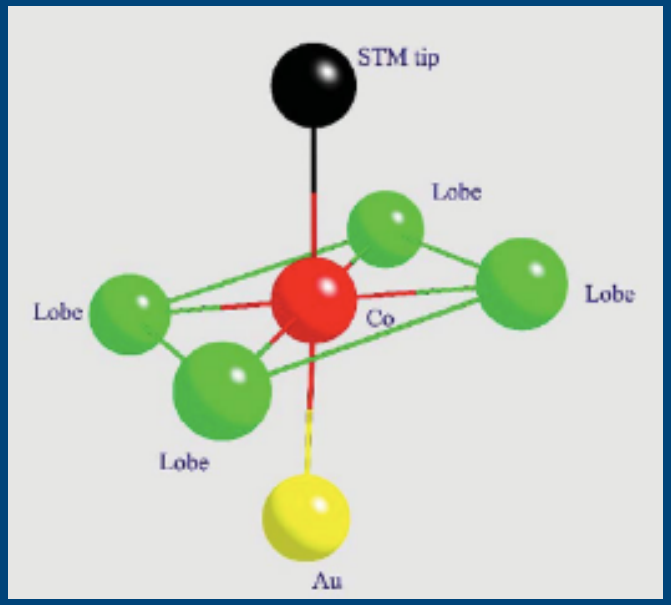




Summary of Experimental data

- Molecules: i) both four-lobed structure, ii) d-active orbital at -0.15 eV (CoPc) and -0.7 eV (TBrPP-Co).
- CoPc/Au(111): Kondo peak shows up upon distortion (cutting out H at the lobes ends).
- TBrPP-Co/Cu(111): Kondo Temperature changed by either distortion or by varying the number of neighboring molecules.

CoPc/Au(111): Model and Hamiltonian



$$\hat{H} = \sum_{i\sigma} \epsilon_i c^{\dagger}_{i\sigma} c_{i\sigma} + \sum_{\langle ij\rangle;\sigma} t_{i,j} c^{\dagger}_{i\sigma} c_{j\sigma} + U n_{\mathrm{Co}\uparrow} n_{\mathrm{Co}\downarrow},$$

- Molecule: 5 orbitals, Co and 4 lobes
- 2 additional orbitals: Au and STM tip
- Selfenergies attached to STM tip, Au and 4 lobes

Lobe/lobe hopping switched on upon distortion
No direct coupling STM tip/lobes

Model parameters

- Lobes orbitals lying at E_F
- Co orbital at -U/2 (symmetric case)

- Lobe/lobe hopping varied (*related to molecule distortion*)

- Actual values fitted to give the experimental energy scale

Conductance Calculations

At T=0 and zero bias voltage

$$T(E) = \frac{2e^2}{h}\mathrm{Tr}[t^\dagger t]$$

Where the matrix t

$$t = \Gamma_{\mathrm{U}}^{1/2} G^{(+)} \Gamma_{\mathrm{L}}^{1/2}$$

And the Green functions

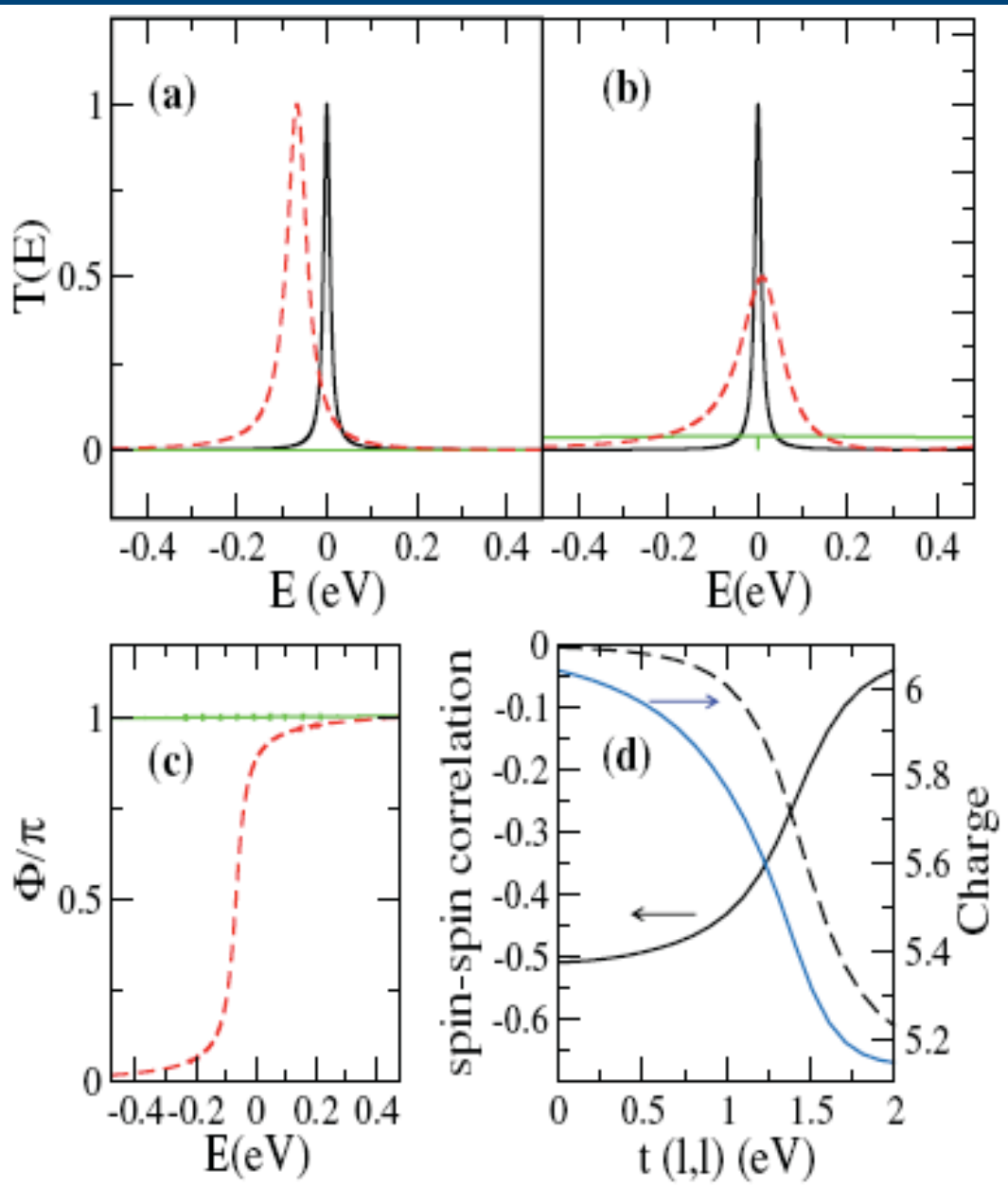
$$G^{(\pm)} = \left(\left[G_0^{(\pm)} \right]^{-1} - \left[\Sigma_U^{(\pm)} + \Sigma_L^{(\pm)} \right] \right)^{-1}$$

G_0 calculated exactly for a small cluster (Lanczos method)
OR
Slave Bosons approach

Conductance Calculations

- Lanczos (Chiappe and Anda): very versatile, ony for zero bias voltage
- Slave bosons (Anda et al, Kotliar et al): Finite bias. Requires handwork for each particular case

How Kondo peak shows up …



(Only Lanczos)

Green: no coupling between lobes

Black: standard Kondo resonance with no coupling Co/lobes

When Kondo peak shows up: an e^- leaves the molecule and there is AF correlation tip/Co (broken black line)

Quantum Interference

WHY the Kondo resonance should at all be absent in a system containing Co?

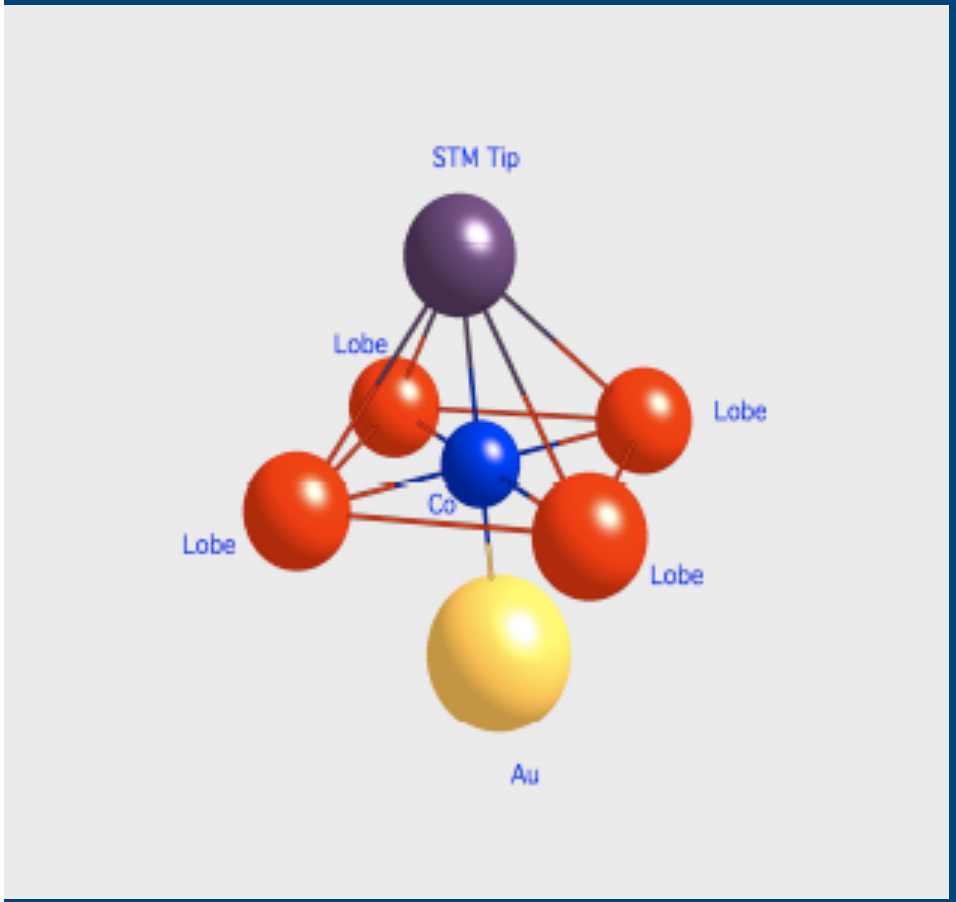
The non-existence of the Kondo peak in the UNDISTORTED molecule is the result of Quantum interference

Direct path Au-Co-STM tip interferes with Au-Co-lobes-STM tip

$$G^{(+)}(\mathrm{Au}, t) = g^{(+)}(\mathrm{Au}, t) + 4g^{(+)}(\mathrm{Au}, \mathrm{Co})\Sigma(\mathrm{Co}, l)G^{(+)}(l, t),$$

Lower case g:
no Co/lobe hopping

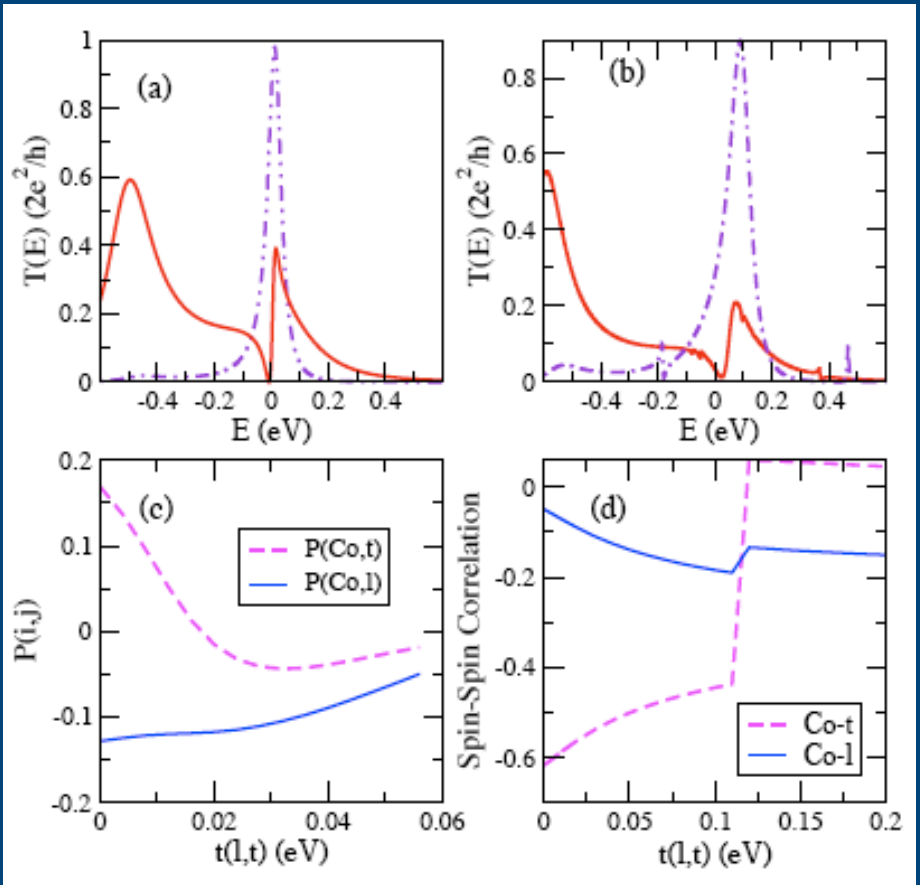
TBrPP-Co/Cu(111)



- d_{z2} orbital deeper than in CoPc
- Direct coupling STM tip/ lobes comparable to STM tip/Co

  Fano-like interference may act
- Both Lanczos and slave bosons

From dips to peaks



- Red: $t_{l,t}$ = 0.08 eV
- Magenta: $t_{l,t}$ = 0

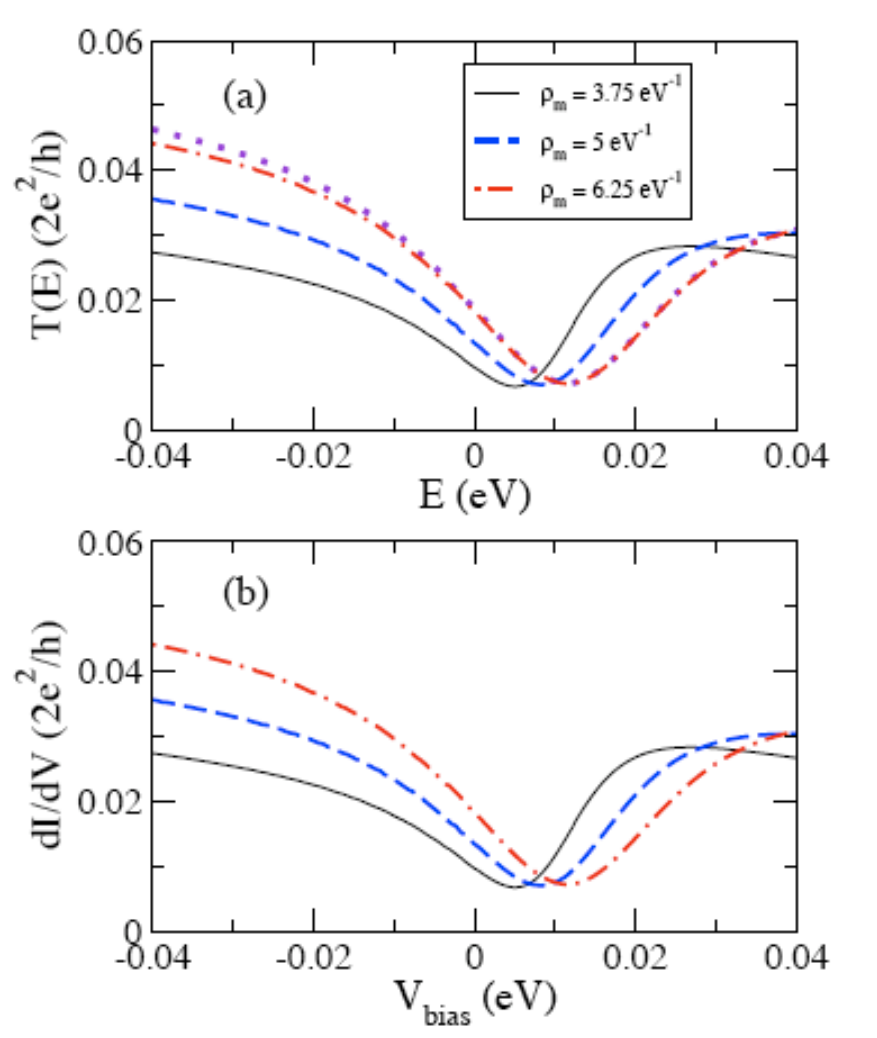
- Fano dip: Kondo regime driven by AF Co/lobes correlation

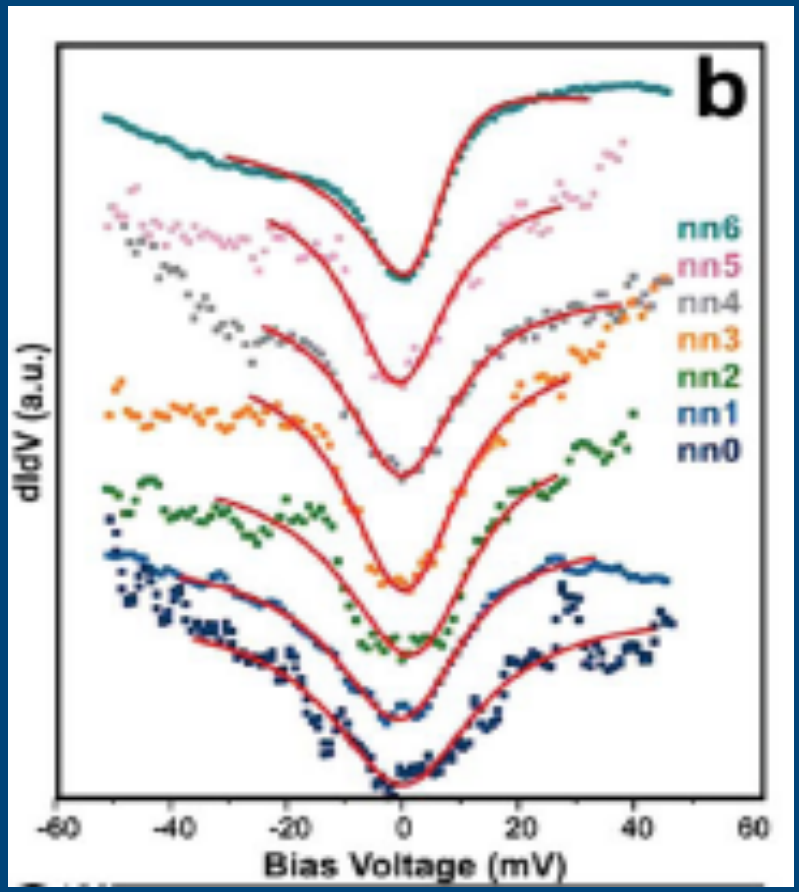
Density matrix

$$P(i,j) = \frac{1}{2\pi}\int_{-\infty}^{\infty} G^{<}(i,j;E)dE$$

Left: Slave bosons
Right: Lanczos

TBrPP-Co/Cu(111): analysis of experimental data

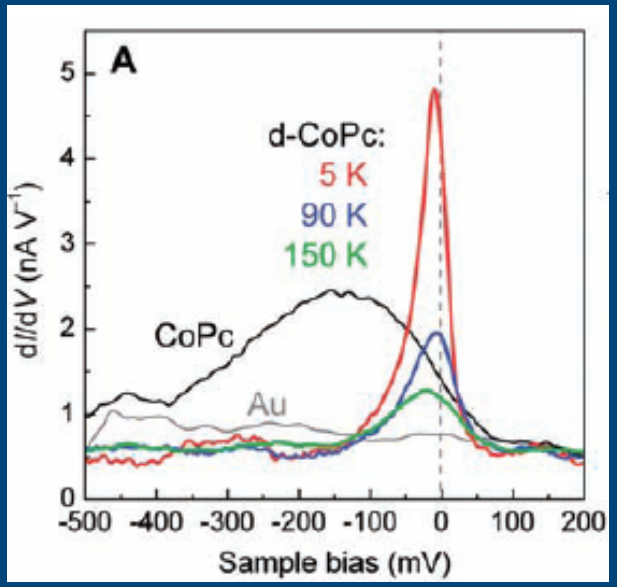


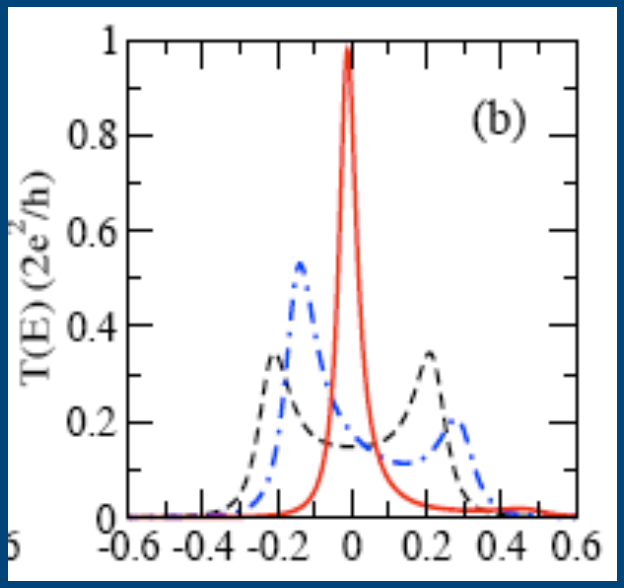


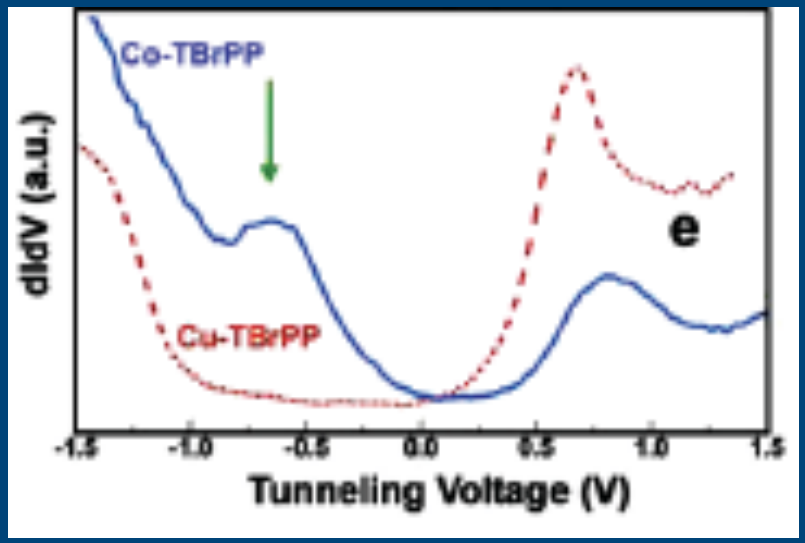
At low V_{bias}, the results for V_{bias} =0 are valid

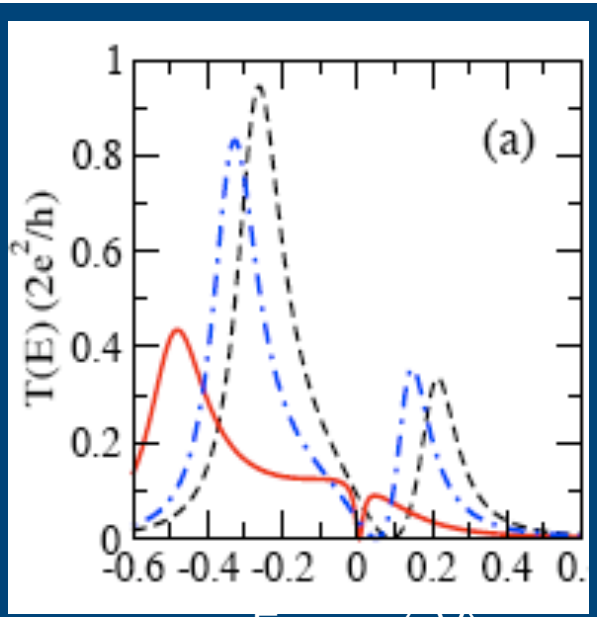
Analysis of experiments: well below E_F

(varying the lobe-lobe hopping)









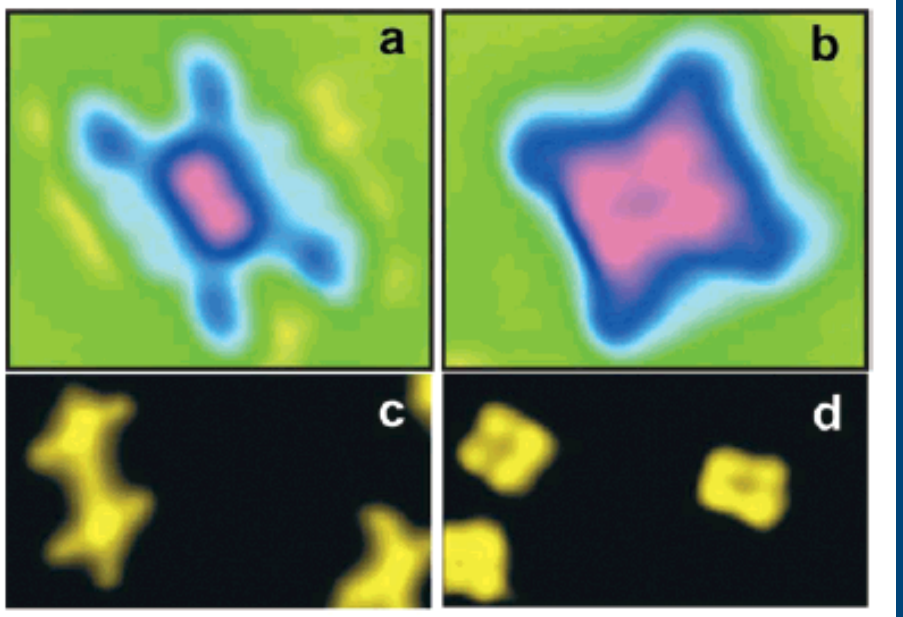
TBrPP-Co/Cu(111): analysis of experimental data. *A technical point*

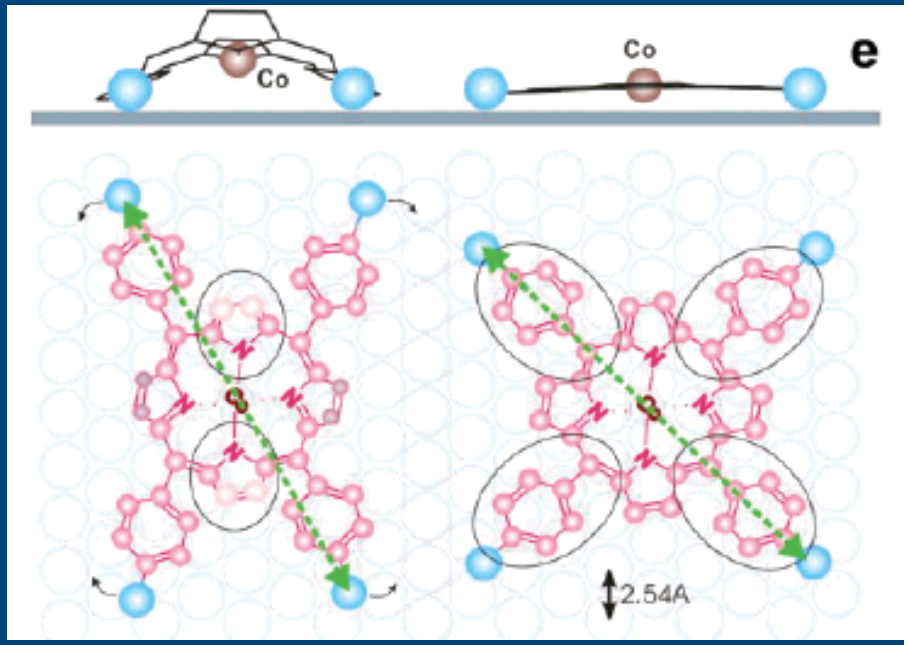
- All results (but one) in previous Fig. obtained with hoppings between STM tips and molecule similar to hoppings metal surface with molecule orbitals WHILE they should be much smaller
- The shape does not change if the ratio of $t_{Co,t}$ to $t_{l,t}$ is kept constant
- As hopping to STM tip decreases, T_K decreases down to a constant, while G decreases to zero.

Experiments: TBrPP-Co/Cu(111)

(Iancu et al, Nanoletters, 6, 820 (2006))

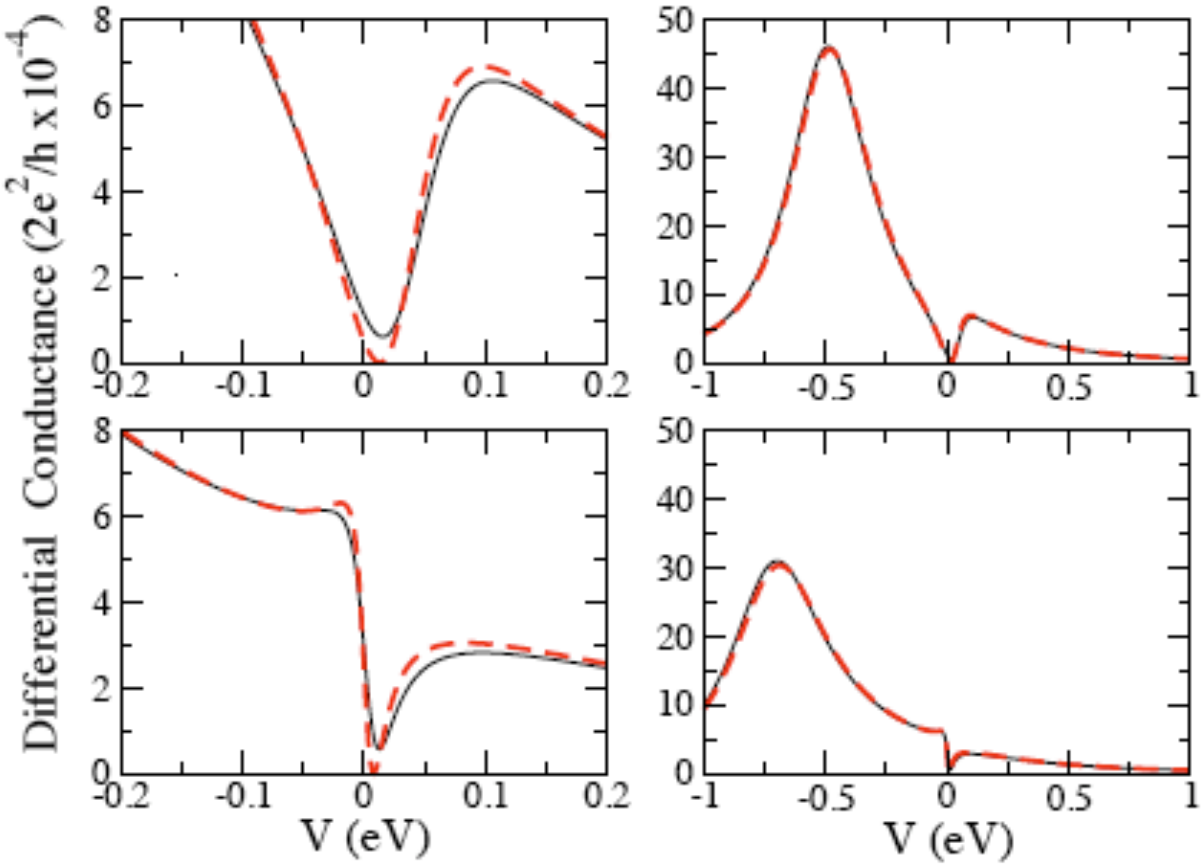
Two conformations





CAN BE switched from saddle
to planar by applying voltage pulses

Effects of Molecule Conformation



- Upper: planar.
- Lower: saddle

- Red: $t_{Co,m} = 0$
- Black: $t_{Co,m} = 0.2$ eV

- Lobe/lobe hoppings inversely proportional to a power of distance.
- Peak width decreases as average Lobe-lobe distance increases

Voltage fully drops at STM/ molecule contact

Local Density of States

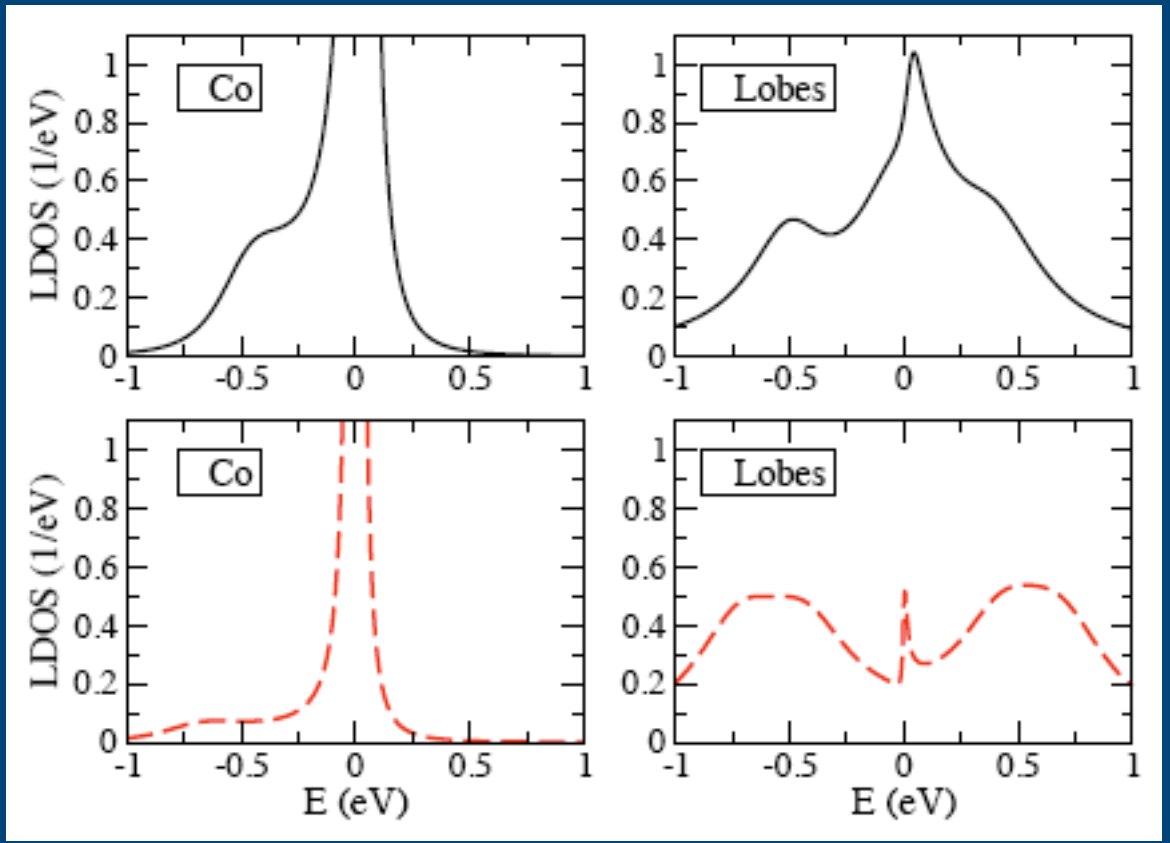
Upper: planar

Lower: saddle

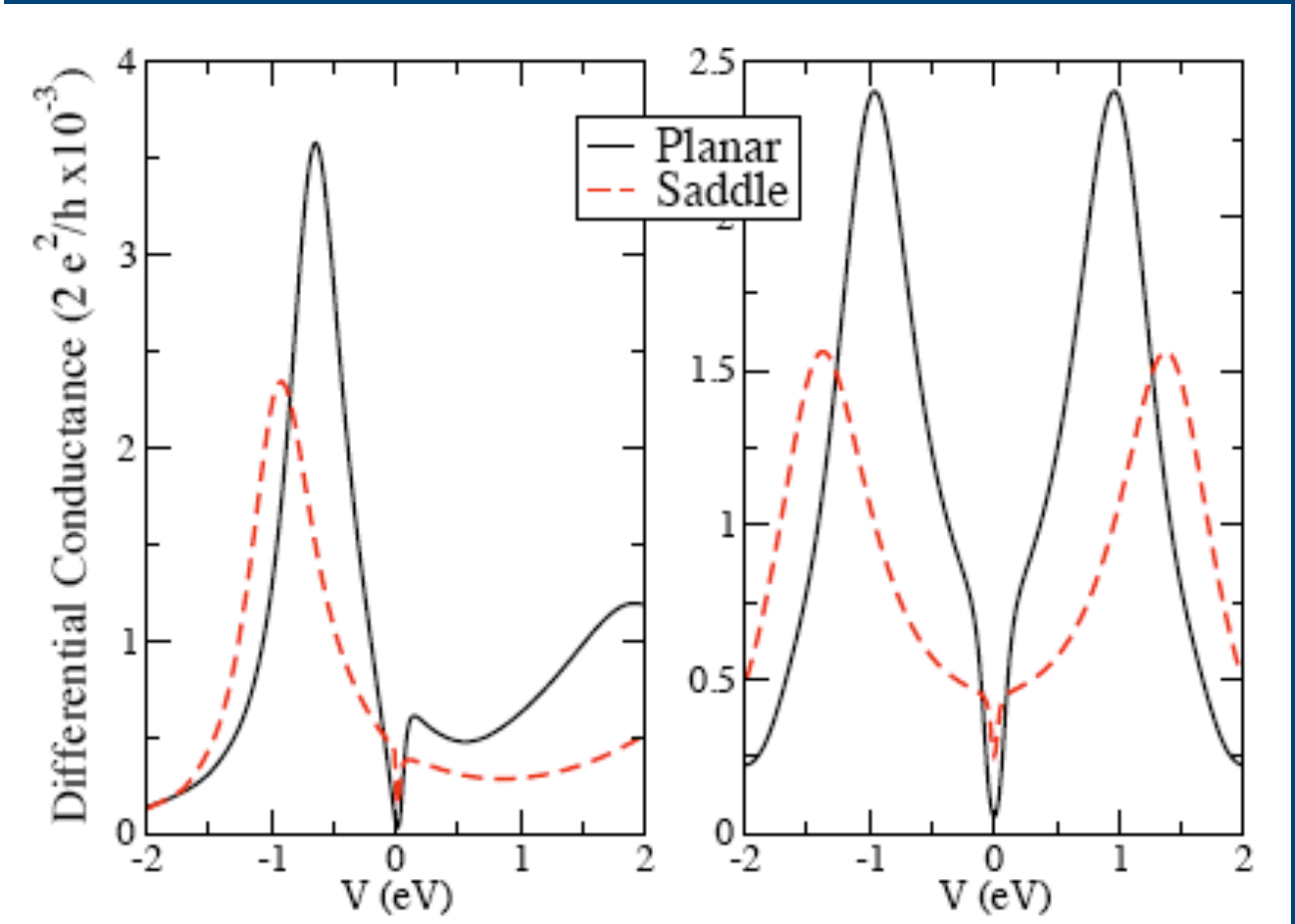
Note reduction in the -0.5 eV peak for the saddle configuration.

While both peaks has weight on the lobes, only one has on Co and, thus, in the conductance

lower peak is fully symmetric (++++) while higher is anti-symmetric (+-+-)



Effect of Potential Profile



- Left: 25/75 %
- Right: 50/50%
- Drops at Mol/metal & mol/STM
- Experiments are explained if the potential is rather symmetric

Concluding Remarks

- A model, which incorporates in a simple way the internal structure of the molecules, has allowed us to describe the Kondo effect in transport through CoPc/Au(111) and TBrPP-Co/Cu(111)

- *The molecules have a four lobed structure, to which we ascribe an essential role, the active d-orbital being deeper in CoPc*

Concluding Remarks

- We showed that, the lobe/lobe hopping, modified experimentally by distorting the molecule, controls even the entrance into the Kondo regime
- *The transition from Fano dips to Kondo peaks is controlled by the ratio of STM tip/Co to STM tip/lobes hoppings*
- TBrPP-Co/Cu(111): the model reproduces satisfactorily the differences between saddle and planar configurations
- ***The system is out of the reach of DFT approaches***

References

PRL:

PRL 97, 076806 (2006) PHYSICAL REVIEW LETTERS week ending 18 AUGUST 2006

Kondo Effect of an Adsorbed Cobalt Phthalocyanine (CoPc) Molecule: The Role of Quantum Interference

G. Chiappe[1,2] and E. Louis[1]

PRB:

PHYSICAL REVIEW B 76, 155427 (2007)

Kondo effect in transport through molecules adsorbed on metal surfaces: From Fano dips to Kondo peaks

J. M. Aguiar-Hualde,[1] G. Chiappe,[1,2] E. Louis,[2] and E. V. Anda[3]

PREPRINT:

Effect of molecule conformation on transport through TBrPP-Co adsorbed onto Cu(111)

J.M. Aguiar-Hualde,[1] G. Chiappe,[2] E. Louis,[2] and J. Simonin[3]

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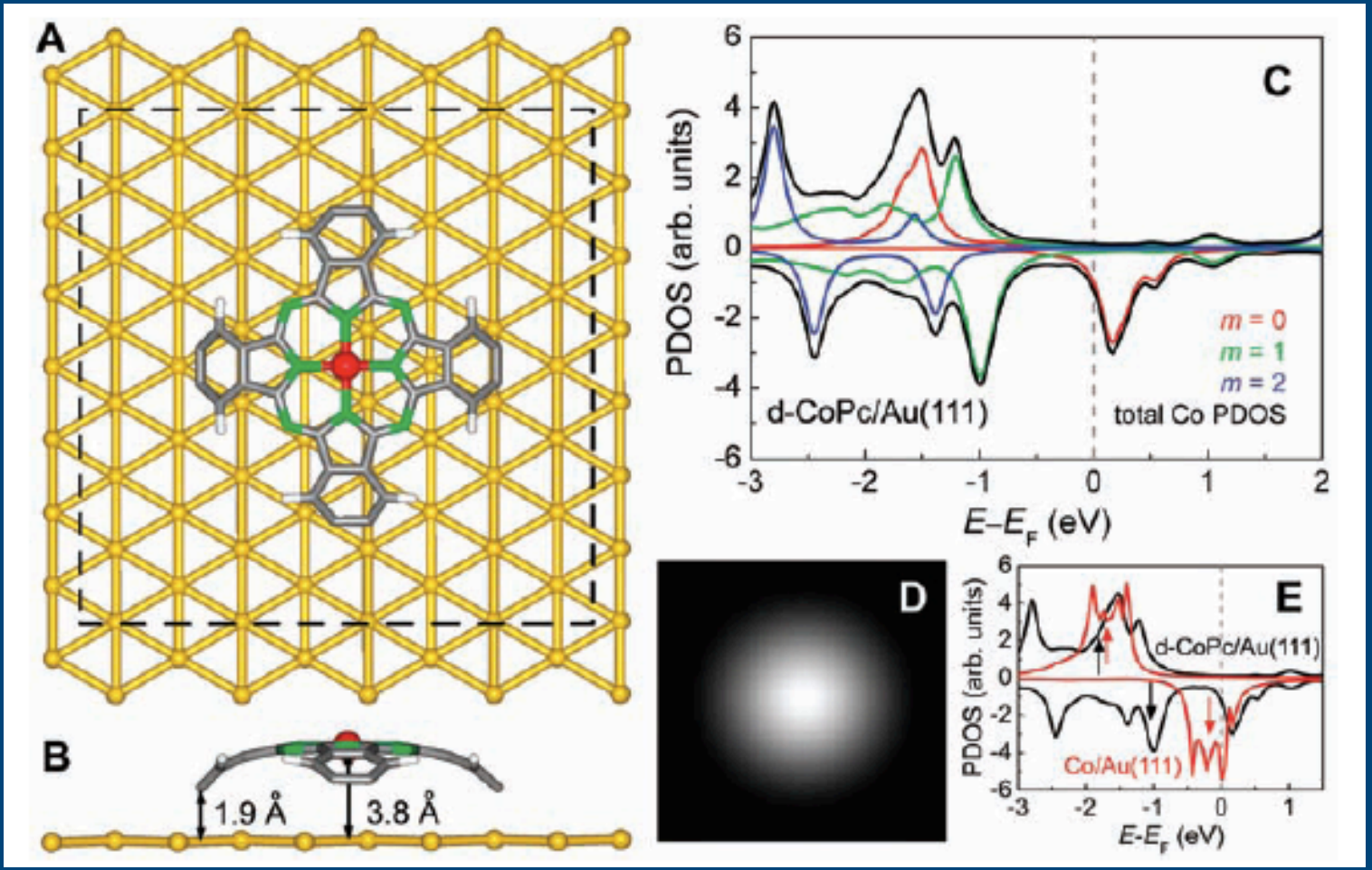
Universidad de Alicante

INSTITUTO UNIVERSITARIO DE MATERIALES DE ALICANTE

THANK YOU

Experiments: CoPc/Au(111)



$T_K = D_0 e^{-(\pi U/8M\Delta)}$

U larger in Co than in CoPc
Thus, T_K is smaller in Co

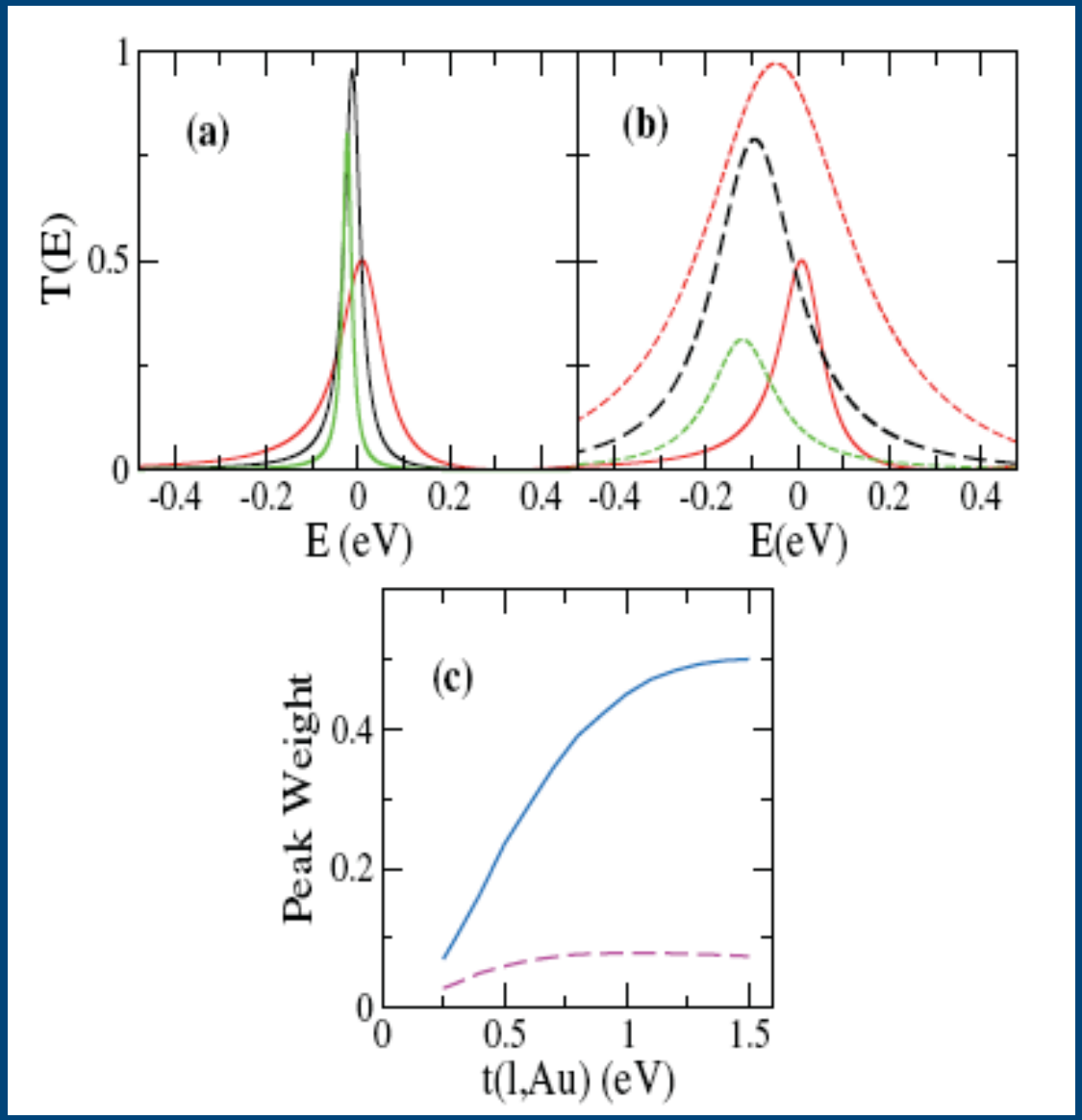
Slave Bosons

- Introduce new boson operators that create (or destroy) empty, singly or doubly occupied sites
- Constraints: 1) a site can only be empty, singly or doubly occupied, 2) if there is a fermion on a site, then it is singly or doubly occupied

- Transform fermion operators to acount for those constraints
- Rewrite Hamiltonian and introduce constraints through Lagrange multipliers
- Mean field approx. and minimize energy with respect multipliers and boson expectation values

- Result: model parameters are renormalized

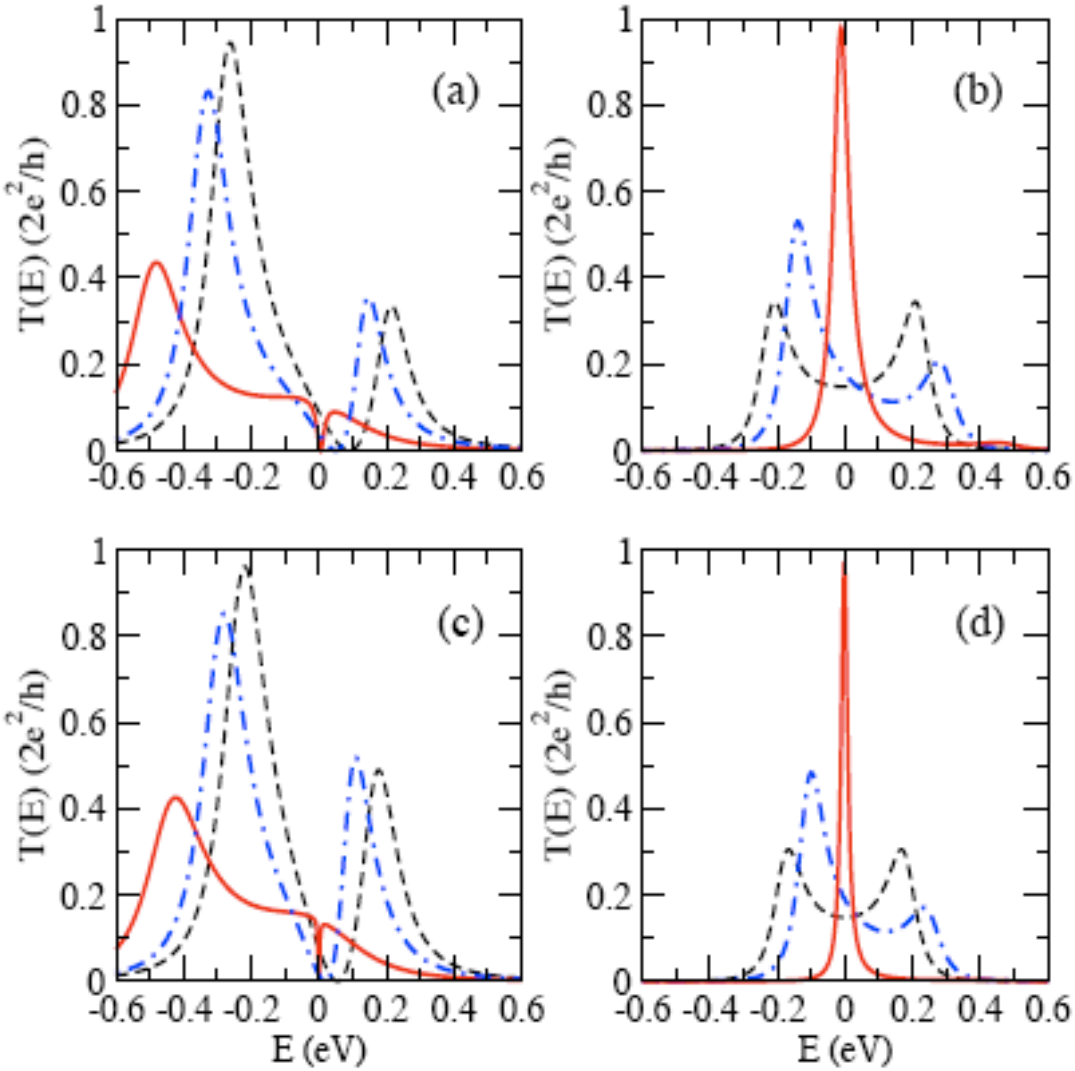
Weight of the Kondo peak ….



Blue and magenta: two values of Co/tip hopping

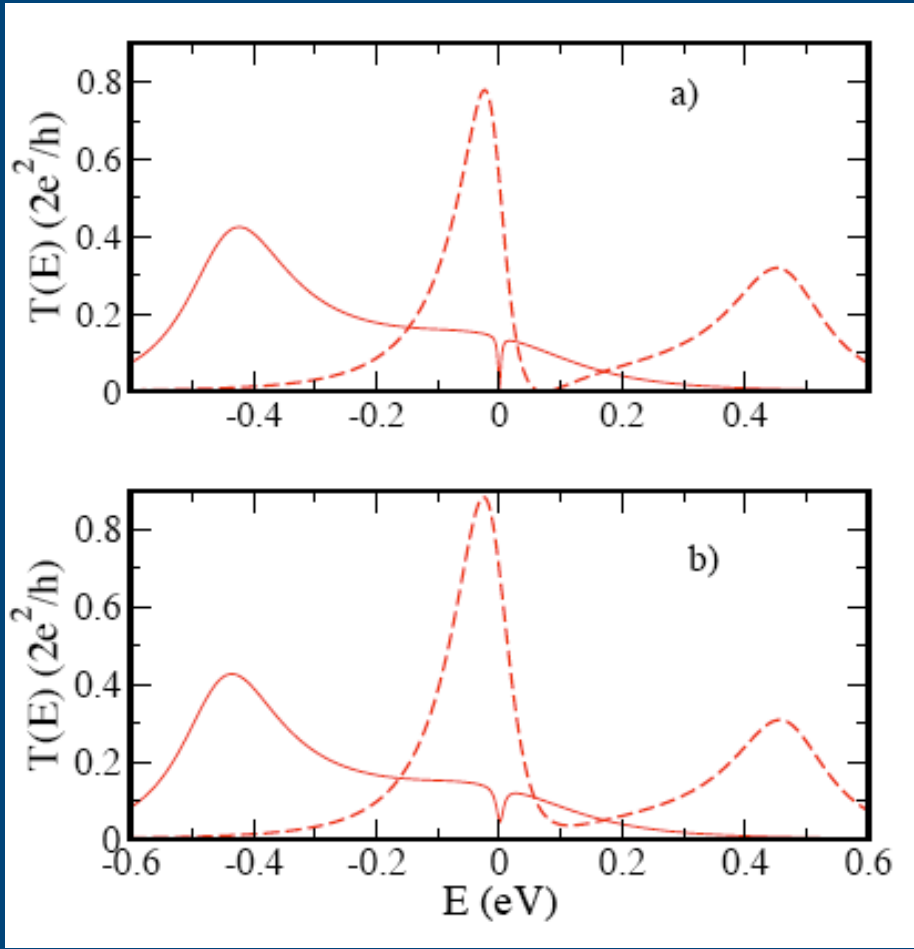
The result of an interplay of several parameters

More on the effects of the internal structure of the molecule



- Varying the lobe/ lobe coupling
- For $t_{l,l}$ =0 the system is out the Kondo regime (revealed, for example, by the dependence on U)

More on the effects of the internal structure of the molecule



- Just changing sign of the lobe/lobe coupling
- The hopping Co/ metal substrate does not matter much