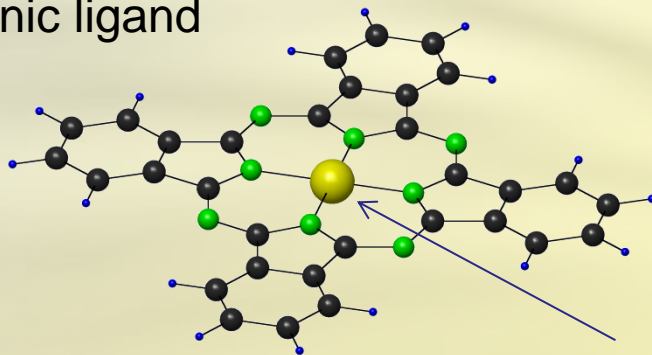


Non-equilibrium spin-crossover in Cu-Phthalocyanine

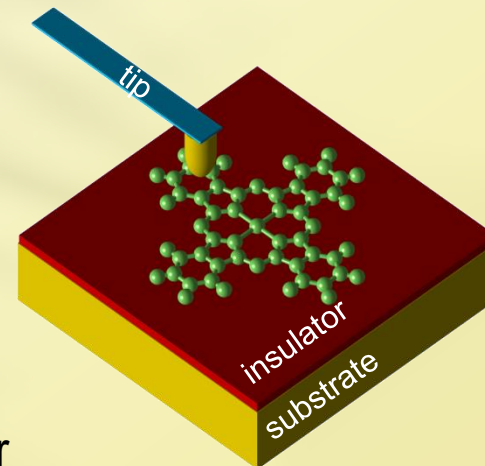
Andrea Donarini, Benjamin Siegert, Milena Grifoni

University of Regensburg (Germany)

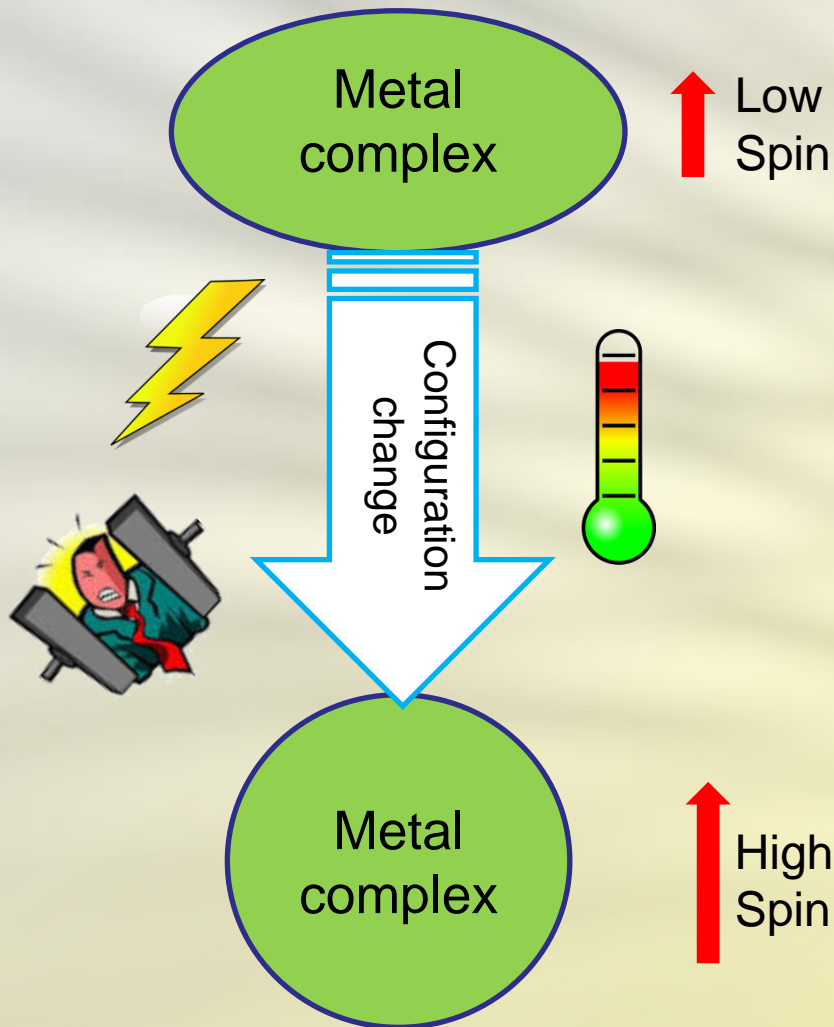
Organic ligand



Metal center



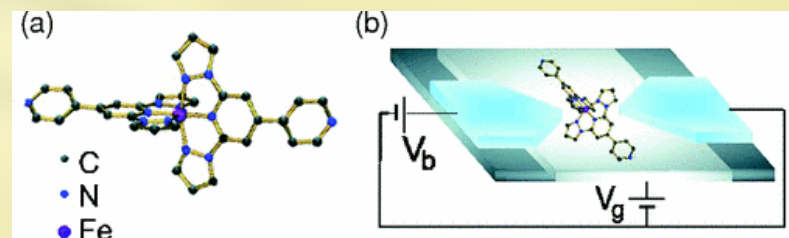
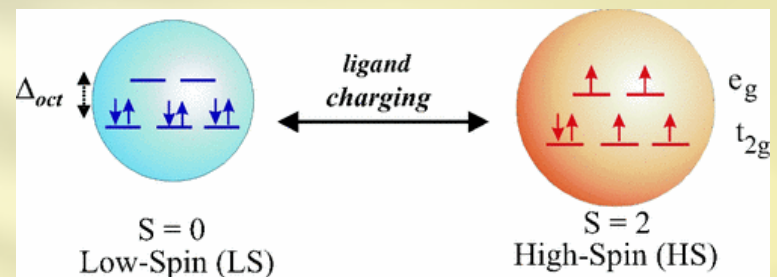
Spin crossover



Change in the occupation of the metal d -orbitals:

Interplay of:

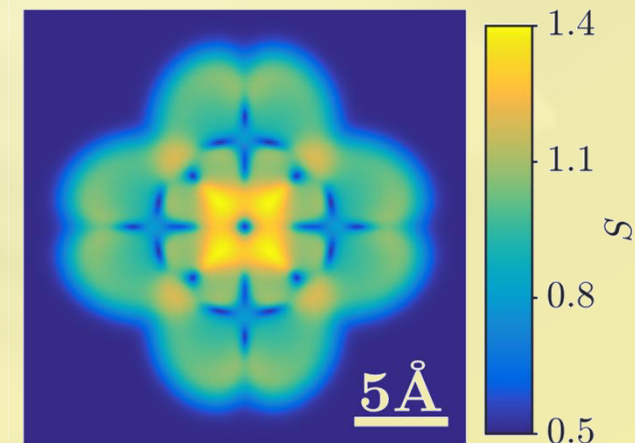
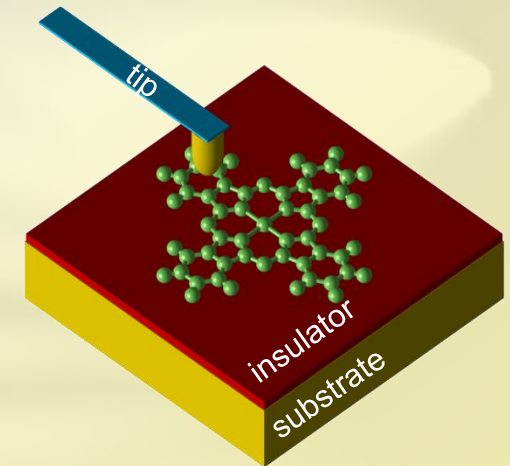
- (Octahedral) ligand field splitting
- Exchange interaction



V. Meded, *et al.* *PRB* **83**, 245415 (2011)

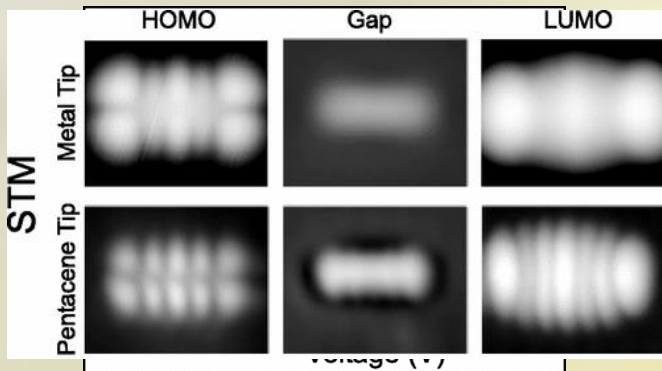
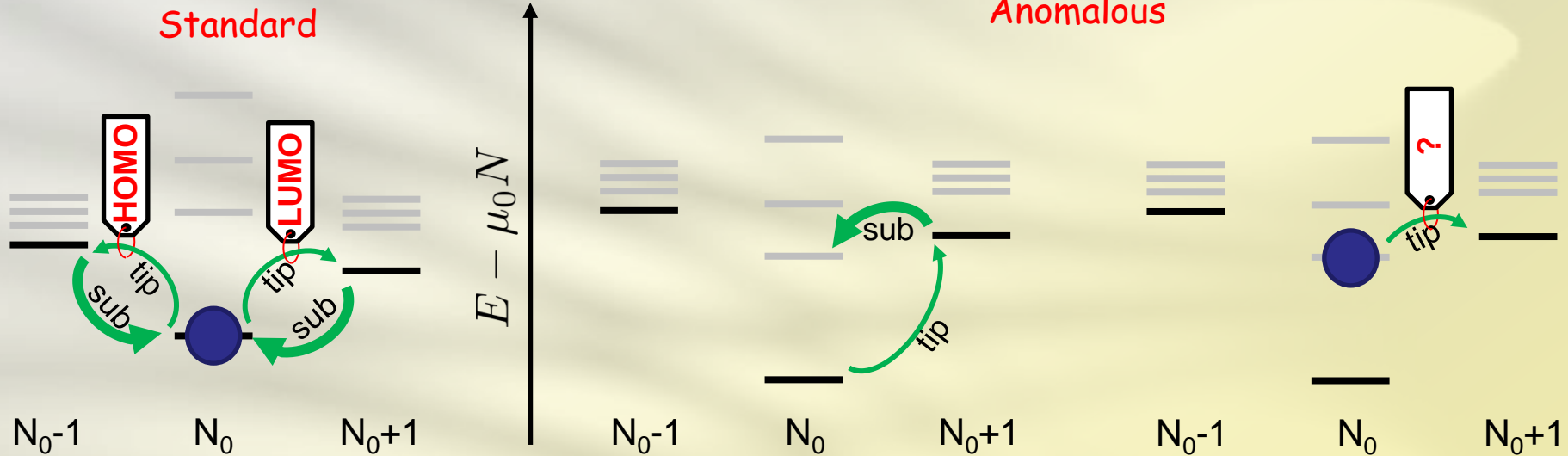
Non equilibrium spin-crossover

	$R_{\text{tip},1}$	$R_{\text{tip},2}$
$V_b = 0$	Low Spin	Low Spin
$V_b > V_{\text{th}}$	Low Spin	High Spin



$V_b = 1.72 \text{ V}$

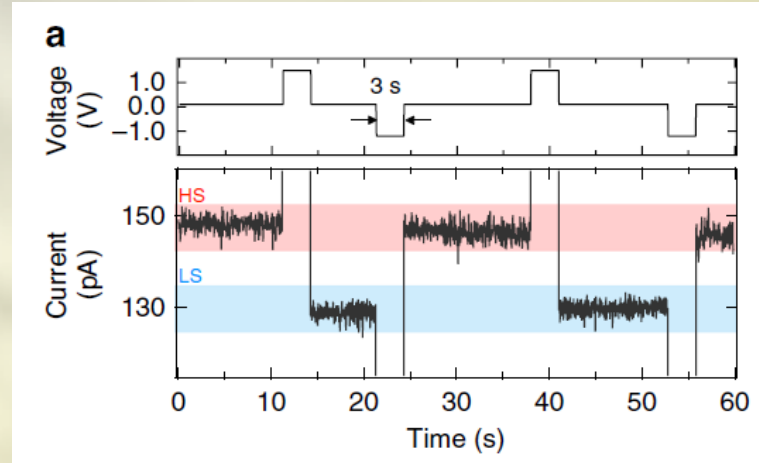
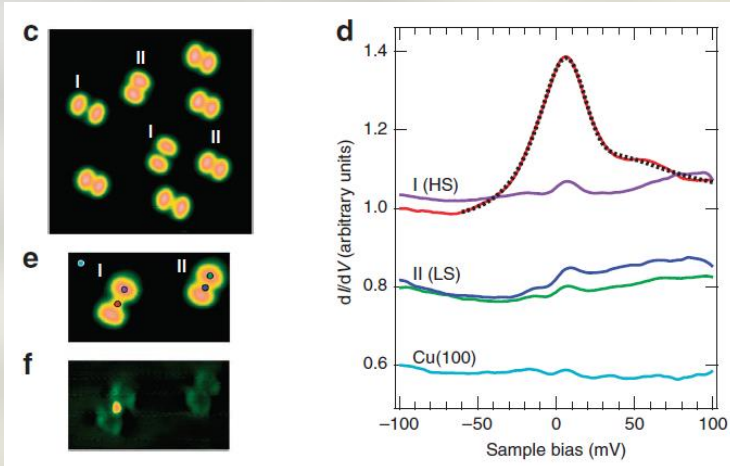
Anomalous current maps



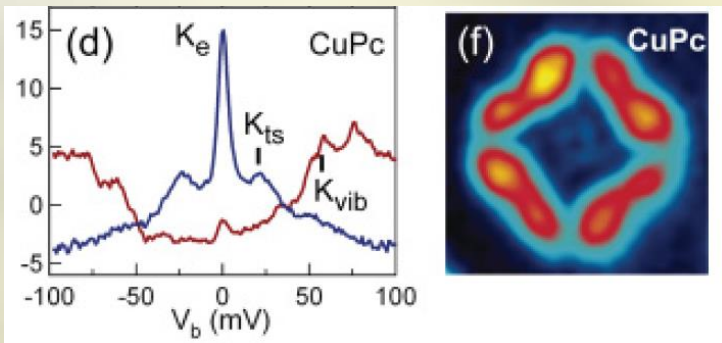
The **anomalous current map** depends on the nature of the excited state

The **population inversion** relies on the strong asymmetry between substrate and tip tunneling rates and on the weak relaxation rate

Motivation



T. Miyamachi *et al.* *Nature comm.* **3**, 993 (2012)



- CuPc on Ag(100) is **anionic** (CuPc^-)
- The ground state is a **triplet**
- Triplet-singlet splitting: **21 meV**

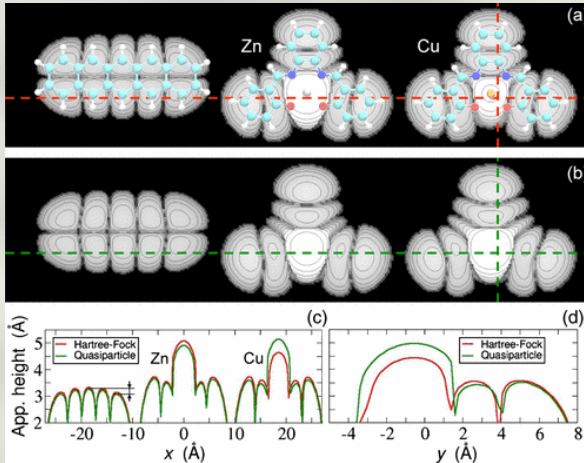
A. Mugarza, *et al.* *PRB* **85**, 155437 (2012)

Motivation

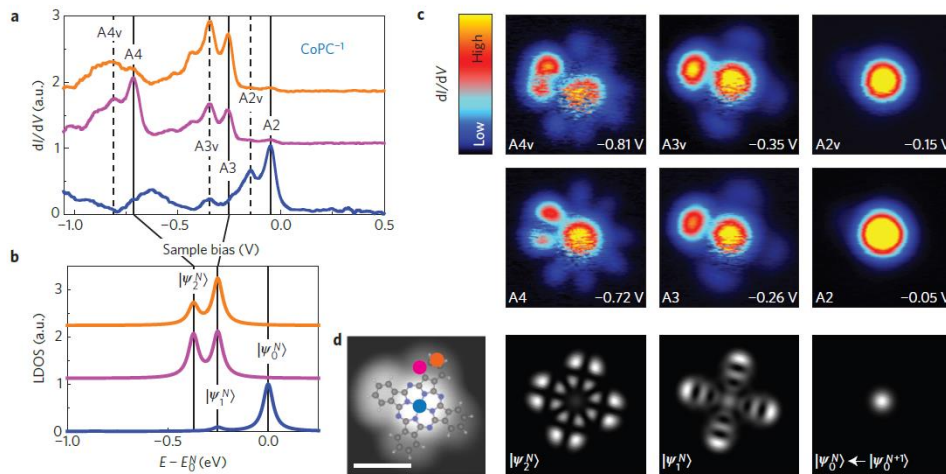
Alteration of the molecular orbitals due electronic correlation

$$\varphi(\mathbf{r}) = \sum_{i,j} (C_j^{N-1})^* C_i^N \sum_{\alpha} \phi_{\alpha}(\mathbf{r}) \langle \Phi_j^{N-1} | \hat{c}_{\alpha} | \Phi_i^N \rangle.$$

STM experiments probe quasiparticle wavefunctions which differ from the single particle molecular orbitals



D. Toroz, et al. *PRL* **110**, 018305 (2013)



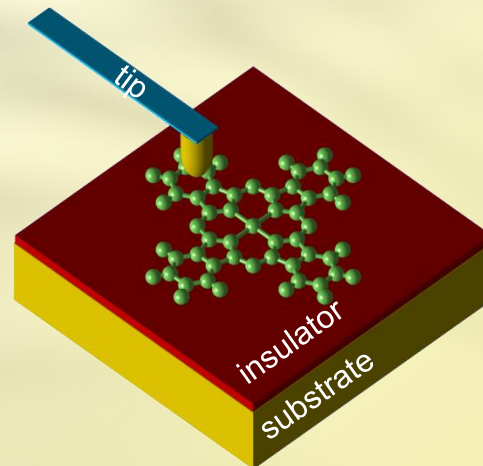
Visualization of many-body transitions in STM experiments

F. Schulz et al. *Nat. Physics* **11**, 229 (2015)

The Hamiltonian

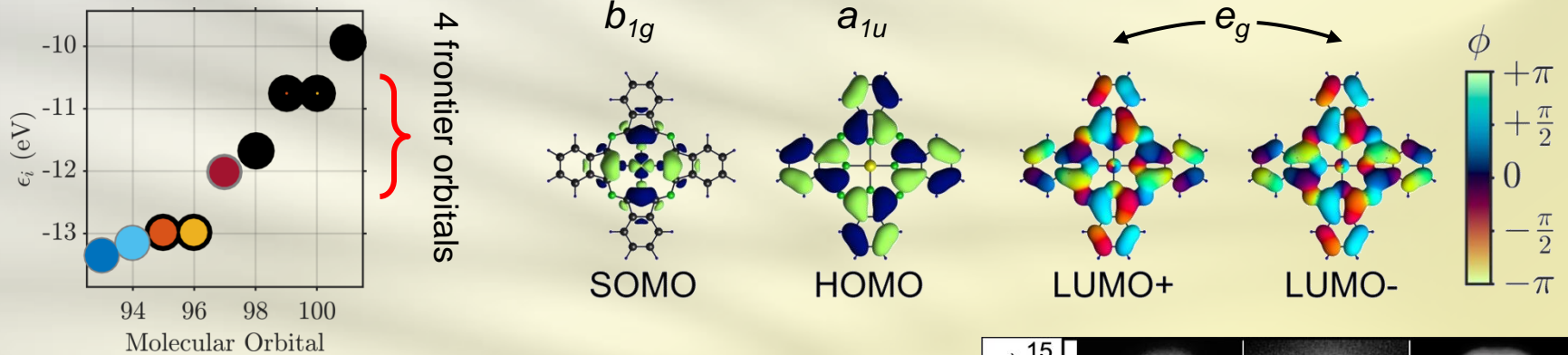
The STM single molecule junction is described by the Hamiltonian

$$\hat{H} = \hat{H}_{\text{mol}} + \hat{H}_{\text{mol-env}} + \hat{H}_{\text{S}} + \hat{H}_{\text{T}} + \hat{H}_{\text{tun}}$$



Minimal basis set

The single particle Hamiltonian is constructed following LCAO schemes of Harrison [1] and Slater-Koster [2].



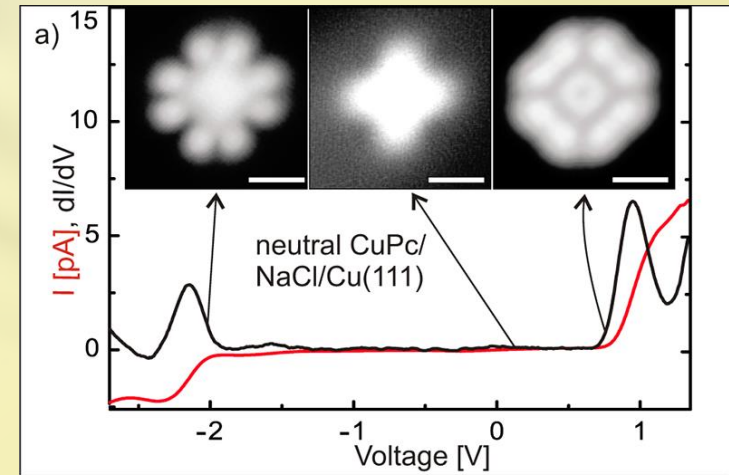
We restrict ourselves to the Fock space spanned by:

$$|\Psi\rangle \approx \underbrace{|11\dots 11\rangle}_{2N_f} \underbrace{|n_{k\uparrow}n_{k\downarrow}\dots n_{l\uparrow}n_{l\downarrow}\rangle}_{2N_d} \underbrace{|00\dots 00\rangle}_{2N_e}$$

Frozen

Dynamical

Empty



C.Uhlmann et al., *NanoLett.* **13**, 777 (2013)

[1] S. Froyen and W.A. Harrison, *PRB* **20**, 2420 (1979)

[2] J. C. Slater and G. F. Koster, *Phys. Rev.* **94**, 1498 (1954)

Many-body Hamiltonian

The many-body Hamiltonian for the molecule reads

$$\hat{H}_{\text{mol}} = \sum_i (\epsilon_i + \Delta) \hat{n}_i + \frac{1}{2} \sum_{ijkl} \sum_{\sigma\sigma'} V_{ijkl} \hat{d}_{i\sigma}^\dagger \hat{d}_{k\sigma'}^\dagger \hat{d}_{l\sigma'} \hat{d}_{j\sigma}$$

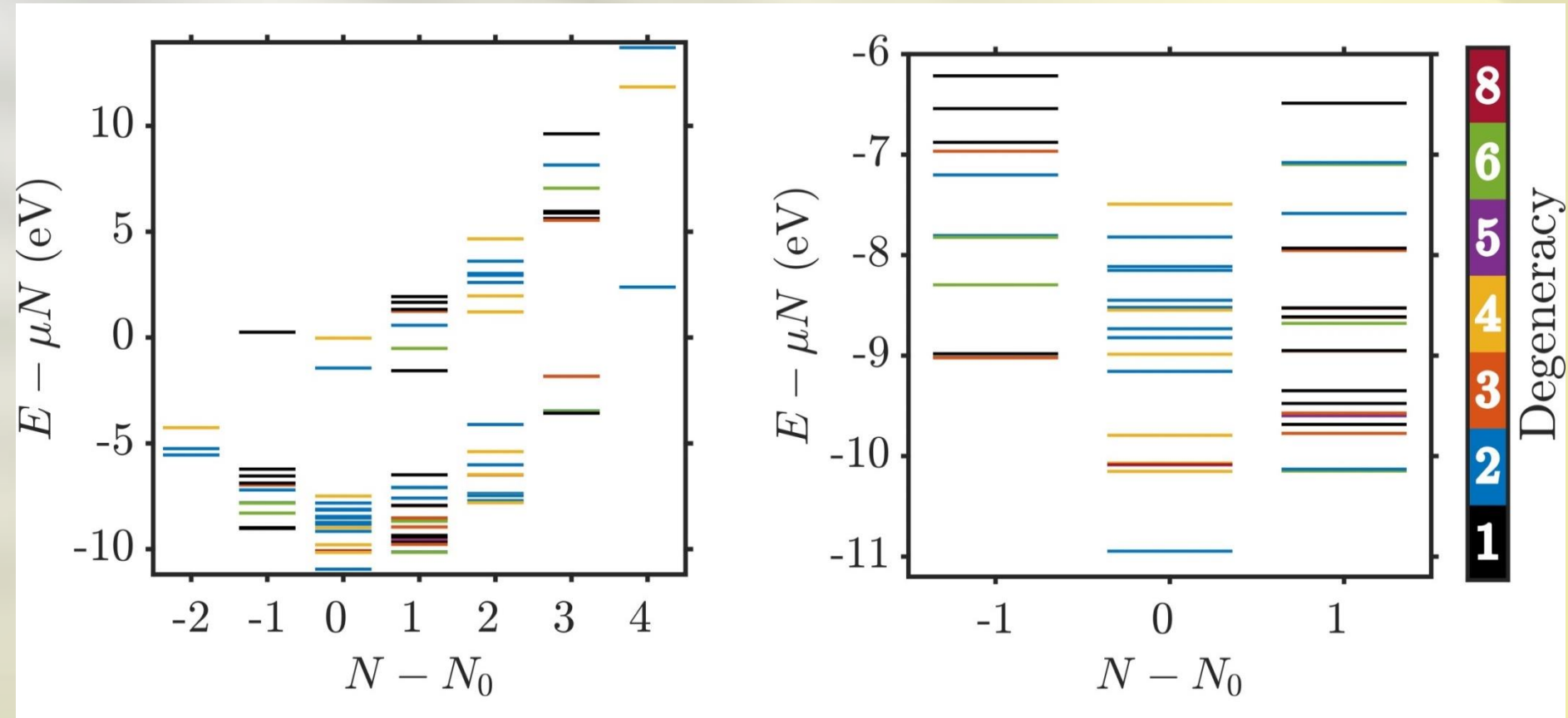
Δ is a free parameter accounting for the crystal field of the protons and frozen electrons

V_{ijkl} are ALL Coulomb integrals among the dynamical orbitals

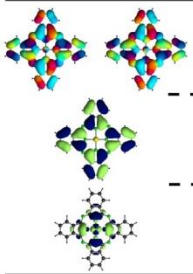
The Coulomb integrals are calculated with the relative dielectric constant $\epsilon_{\text{mol}} = 2.2$.
The atomic orbitals are of Slater type.

U_S	11.352 eV	$J_{HL}^{\text{ex}} = -\tilde{J}_{H+-}^{\text{p}}$	548 meV
U_H	1.752 eV	J_{+-}^{ex}	258 meV
$U_L = U_{+-}$	1.808 eV	J_{+-}^{p}	168 meV
U_{SH}	1.777 eV	$J_{SL}^{\text{ex}} = -\tilde{J}_{S+-}^{\text{p}}$	9 meV
U_{SL}	1.993 eV	$J_{SH}^{\text{ex}} = J_{SH}^{\text{p}}$	2 meV
U_{HL}	1.758 eV		

Many-body spectrum



Low energy eigenstates

	cation			neutral			anion		
									
LUMO±					↑	↑	↑	↓	↑ ⁺ ↑ ⁻
HOMO	↑	↑	↑ ↓	↑ ↓	↑ ↓	↑	↑ ↓	↑ ↓	↑ ↓
SOMO	↑	↓		↑		↑	↑	↑	
$E_{Nm} - E_{N0}$ (meV)	0	4	40	0	794	860	0	18	374
S	1	0	0	1/2	1/2	3/2	1	0	1
degeneracy	3	1	1	2	4	8	6	2	3

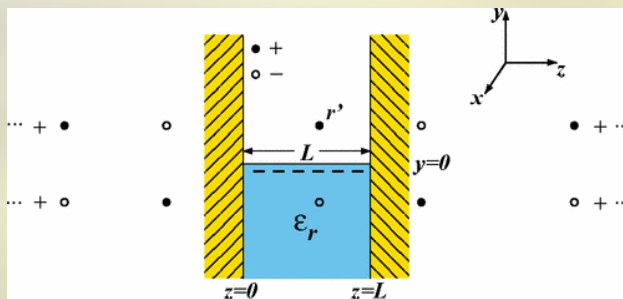
+ LUMO
+ SOMO
+ HOMO

Image charge effects

$$\hat{H}_{\text{mol-env}} = -\delta_{\text{ic}} (\hat{N} - N_0)^2$$

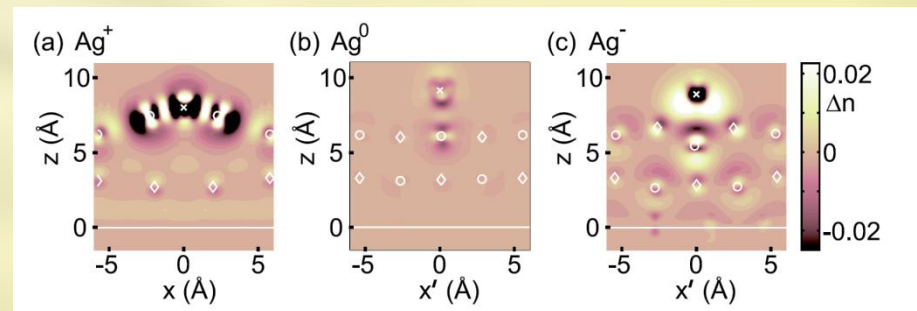
This term incorporates the two main effects which stabilize the excess charge on the molecule

Image charge effect



K. Kaasbjerg and K. Flensberg
PRB **84**, 115457 (2011)

Polaron formation



F. E. Olsson *et al.*,
PRL **98**, 176803 (2007)

Leads and tunnelling

The tip and substrate are modeled as **reservoirs of non interacting fermions**

$$\hat{H}_{S/T} = \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}}^{S/T} \hat{c}_{S/T\mathbf{k}\sigma}^\dagger \hat{c}_{S/T\mathbf{k}\sigma}$$

The tunnelling Hamiltonian is calculated following **the tunnelling theory of Bardeen.**

$$\hat{H}_{\text{tun}} = \sum_{\eta\mathbf{k}i\sigma} t_{\mathbf{k}i}^\eta \hat{c}_{\eta\mathbf{k}\sigma}^\dagger \hat{d}_{i\sigma} + \text{h.c.}$$

The tip tunnelling amplitudes follow the **Chen's derivative rule.**

The substrate tunnelling amplitudes are proportional to the **overlap** of the molecule and substrate wavefunctions.

S. Sobczyk, AD, and M. Grifoni, *PRB* **85**, 205408 (2012)

Transport calculations

The dynamics is calculated via a generalized master equation for the reduced density matrix

$$\rho_{\text{red}} = \text{Tr}_{\text{S,T}}(\rho)$$

$$\begin{aligned} \dot{\rho}_{\text{red}} = & \underbrace{-\frac{i}{\hbar} [\hat{H}_{\text{mol}} + \hat{H}_{\text{mol-env}}, \rho_{\text{red}}]}_{\text{Coherent dynamics}} \underbrace{-\frac{i}{\hbar} [\hat{H}_{\text{eff}}, \rho_{\text{red}}]}_{\text{Effective internal dynamics}} \\ & + \underbrace{\mathcal{L}_{\text{tun}}[\rho_{\text{red}}]}_{\text{Tunnelling dynamics}} + \underbrace{\mathcal{L}_{\text{rel}}[\rho_{\text{red}}]}_{\text{Phenom. relaxation}} := \mathcal{L}[\rho_{\text{red}}] \end{aligned}$$

$$\mathcal{L}_{\text{rel}}[\rho] = -\frac{1}{\tau} \left(\rho - \sum_{Nm} \rho_{mm}^{\text{th},N} |Nm\rangle \langle Nm| \sum_n \rho_{nn}^N \right)$$

$\mathcal{L}[\rho_{\text{red}}^\infty] \equiv 0$ defines the stationary reduced density matrix.

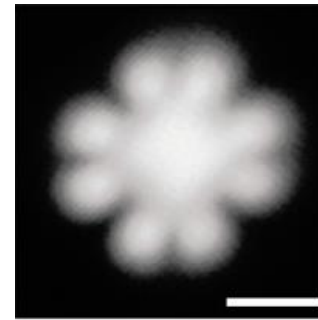
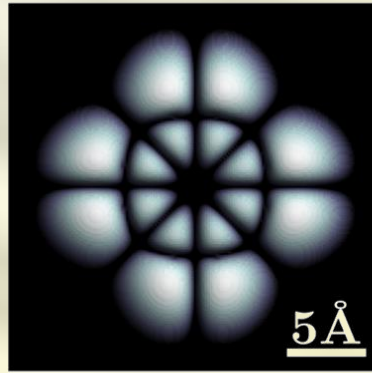
Topography of CuPc



$$I_{\eta}(\mathbf{r}_T, V_b) = \text{Tr}_{\text{mol}} \left(\hat{N} \mathcal{L}_{\eta}[\rho_{\text{red}}^{\infty}(\mathbf{r}_T, V_b)] \right)$$

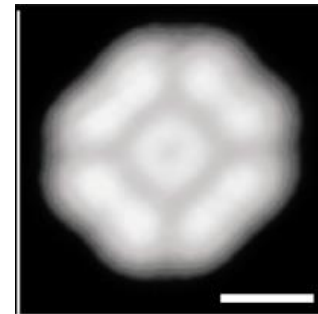
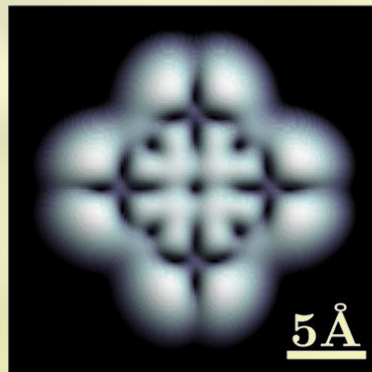
cationic resonance: $\phi_0 = 4.65$ eV

$$I_{\eta}(\mathbf{r}_T, V_{\text{res}}) = 0.5 \text{ pA}$$



anionic resonance: $\phi_0 = 4.65$ eV

$$I_{\eta}(\mathbf{r}_T, V_{\text{res}}) = 0.75 \text{ pA}$$

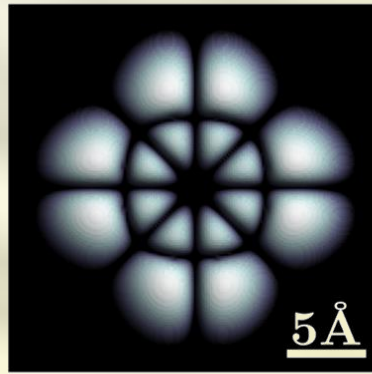


B. Siegert, A. Donarini, and M. Grifoni, arXiv:1508.04647

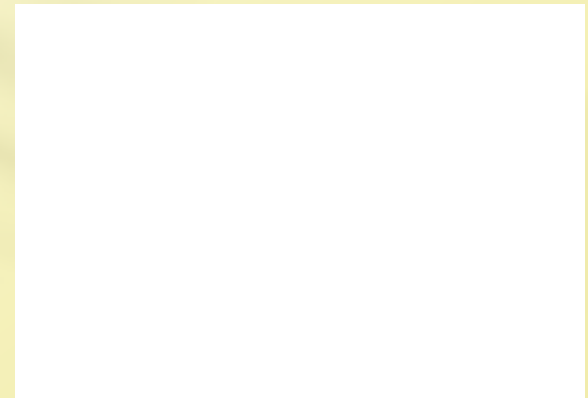
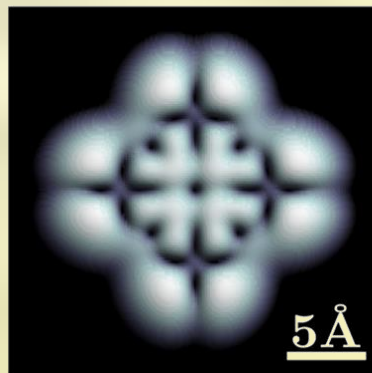
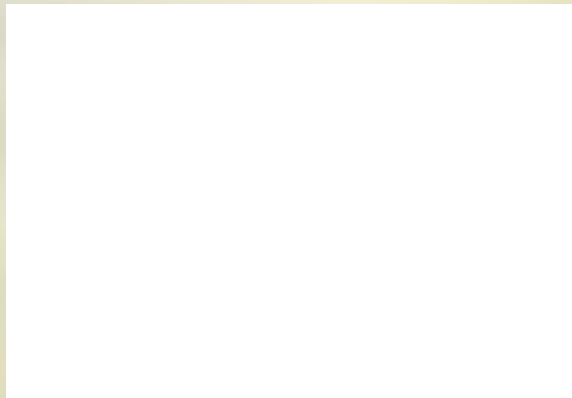


$$S(\mathbf{r}_T, V_b) = \sqrt{\langle \hat{S}^2 \rangle(\mathbf{r}_T, V_b) + \frac{1}{4}} - \frac{1}{2} \quad \text{with} \quad \langle \hat{S}^2 \rangle(\mathbf{r}_T, V_b) = \text{Tr}_{\text{mol}} \left(\hat{S}^2 \rho_{\text{red}}^\infty(\mathbf{r}_T, V_b) \right)$$

cationic resonance: $\phi_0 = 4.65$ eV

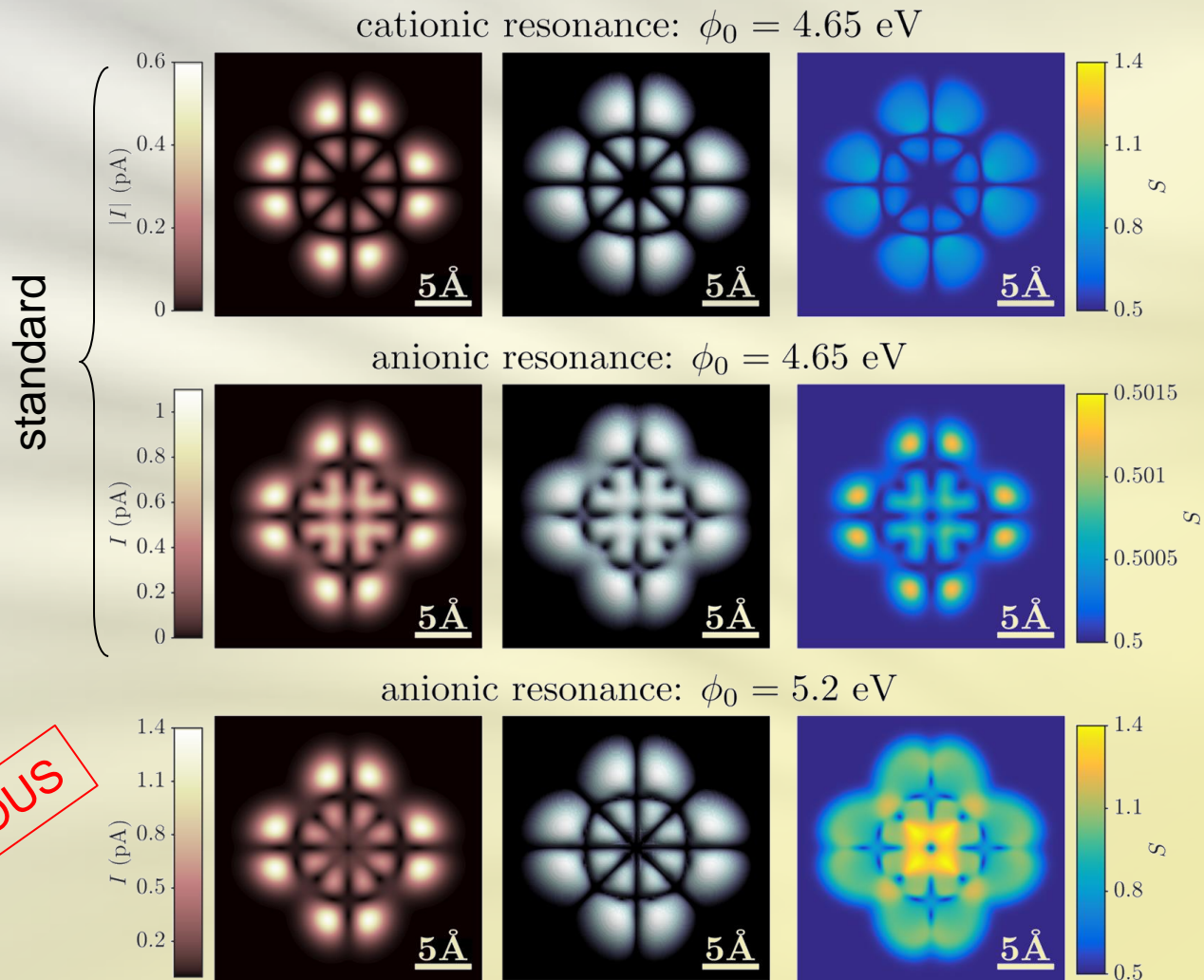


anionic resonance: $\phi_0 = 4.65$ eV



B. Siegert, A. Donarini, and M. Grifoni, arXiv:1508.04647

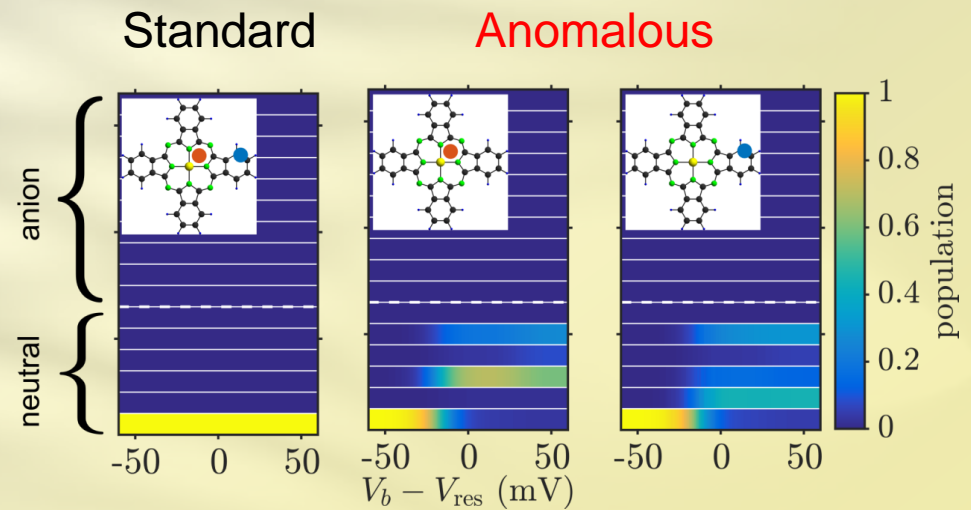
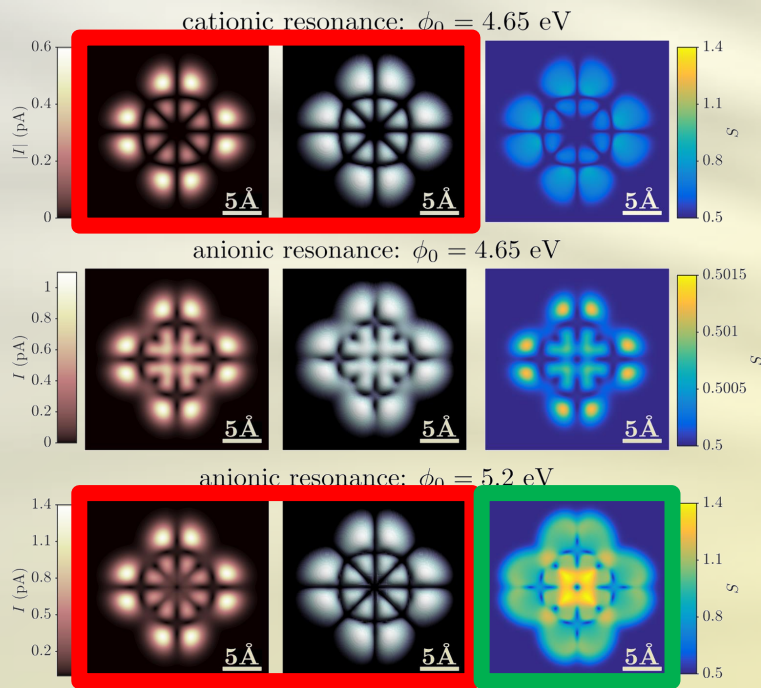
The anomalous case



Population inversion

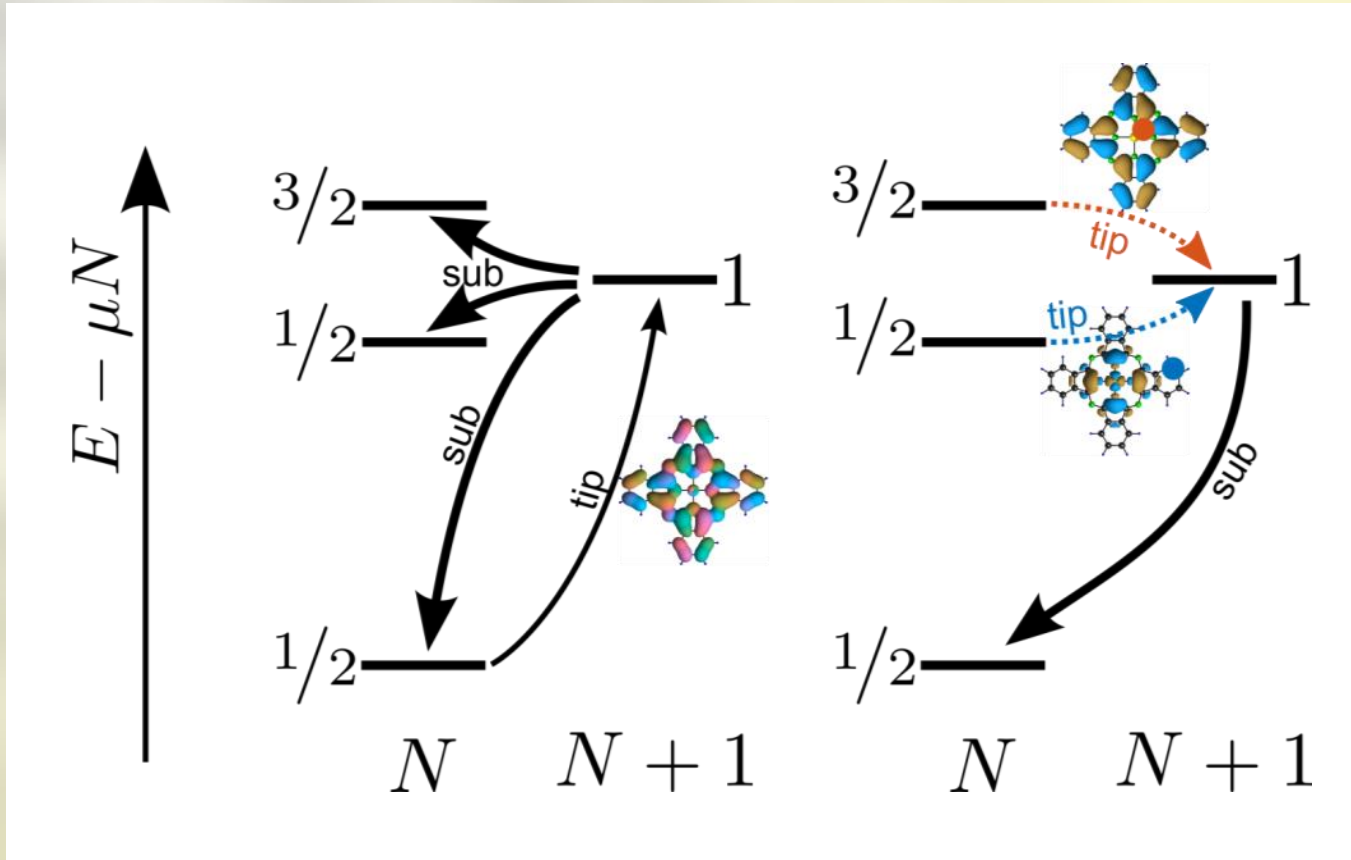
The current and topographic maps of an **anionic transition** resembles the **HOMO**

The average **spin** of the molecule varies with the tip position and does **not** correspond to the one of the **molecular ground state**



The molecule undergoes a population inversion which depends on the tip position

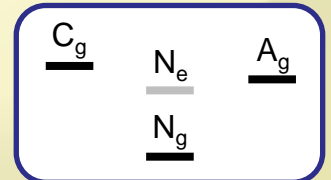
The anomalous current map



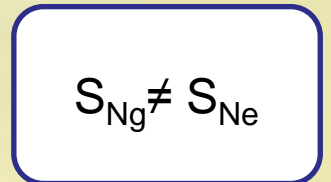
Is CuPc so special ?

Necessary and sufficient conditions for the appearance of non equilibrium spin-crossover are:

1 The energy of the excited neutral state should be lower than the ones of the cationic and anionic ground states

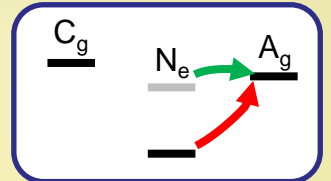


2 The spin of the ground state should be different



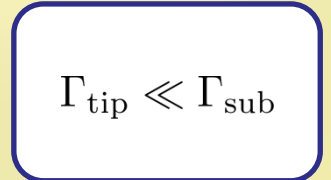
3 The (tip) transition state and the neutral ground state have different molecular orbitals

Closed shell conjugated molecules

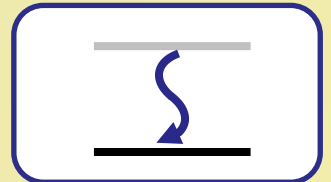


4 The tip and substrate interaction is strongly asymmetric

STM on thin insulating films



5 The (intrinsic) relaxation time of the molecule on the substrate should be low (i.e. comparable to the lifetime of the excited state)



A class of single molecule junctions

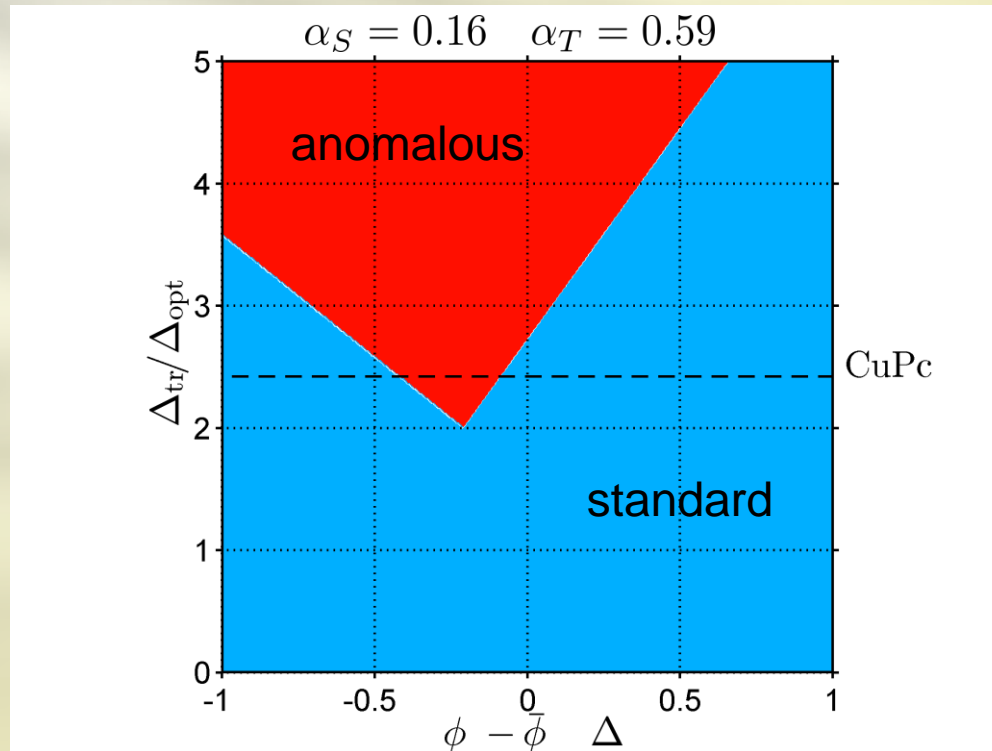


$$\Delta_{\text{tr}} = \text{IP} - \text{EA} - 2\delta_{\text{ic}}$$

$$\Delta_{\text{opt}} = E_{N_e} - E_{N_g}$$

$$\bar{\phi} = \frac{\text{IP} + \text{EA}}{2}$$

ϕ = Substrate workfunction



Predicting power

Fitting parameters

crystal field energy shift
dielectric constant of the molecule
image charge renormalization energy

$$\Delta$$

$$\epsilon_{\text{mol}}$$

$$\delta_{\text{ic}}$$

$$V_{\text{an}}$$

$$V_{\text{cat}}$$

$$n_{\text{SOMO}} = 1$$

Constraints

Experimental anionic resonance
Experimental cationic resonance
Equilibrium SOMO occupation



Confirmed Predictions

Triplet anionic ground state and triplet-singlet splitting of 18 meV (exp 21 meV)

HOMO (LUMO) like current maps for the cationic (anionic) resonance

- Both for CuPc on NaCl(3ML)/Cu(100) and CuPc on NaCl(2ML)/Cu(111) -

Open Prediction

Non equilibrium spin-crossover for CuPc on a substrate with workfunction of 5.2 eV

Conclusions

We have developed a **minimal model** for the Cu-Phthalocyanine in terms of **four interacting frontier orbitals**.

Upon fitting three free parameters to experimental constraints, the model correctly reproduces the low energy spectrum and eigenstates of the molecule

For an experimentally accessible substrate workfunction of 5.2 eV, we predict the appearance, close to the anionic resonance of **non equilibrium spin-crossover**.

Dramatic changes in the current and topographical maps with respect to standard LUMO resonances are found as fingerprints of the spin-crossover

A **class of single molecule junctions** candidates for the observation of non equilibrium spin-crossover is defined in terms of relations between transport gap, optical gap and substrate workfunction.

Aknowledgments



Milena Grifoni



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J. Repp



T. Niehaus



D. Ryndyk



R. Korytar

Thank you for your attention!

