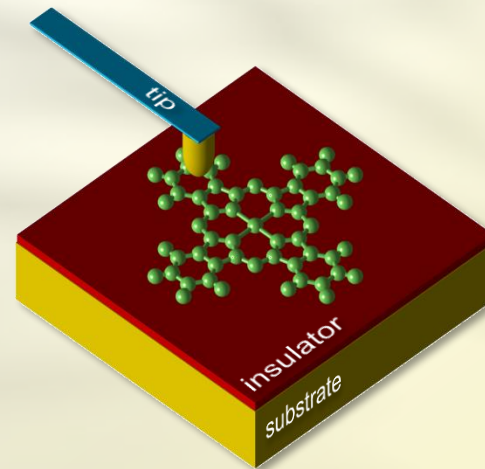


Many-body correlations in STM single molecule junctions

Andrea Donarini

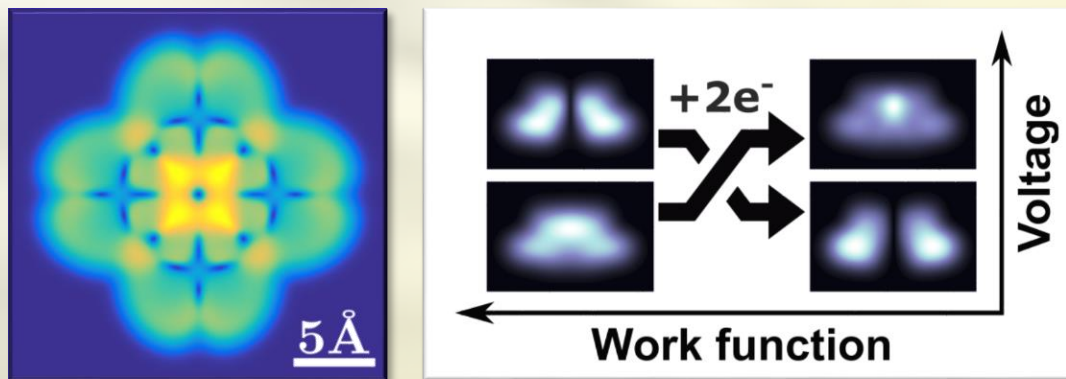
Institute of Theoretical Physics, University of Regensburg, Germany

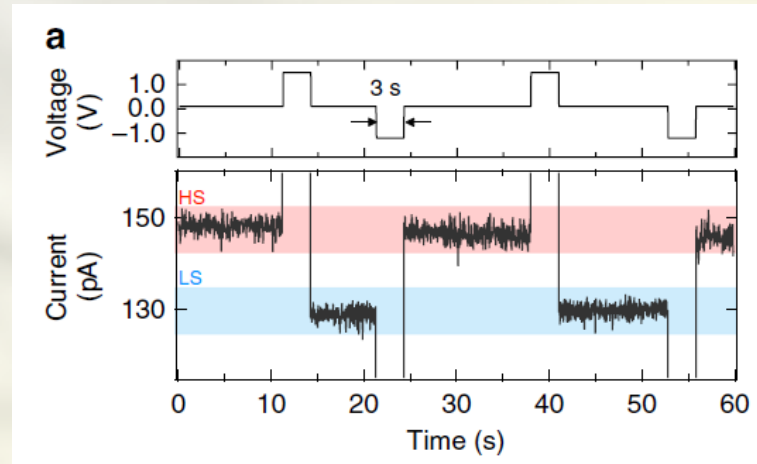
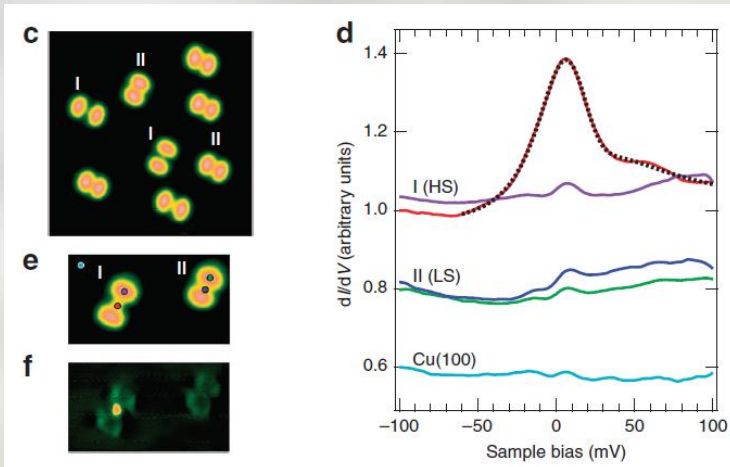


Many-body correlations in STM single molecule junctions

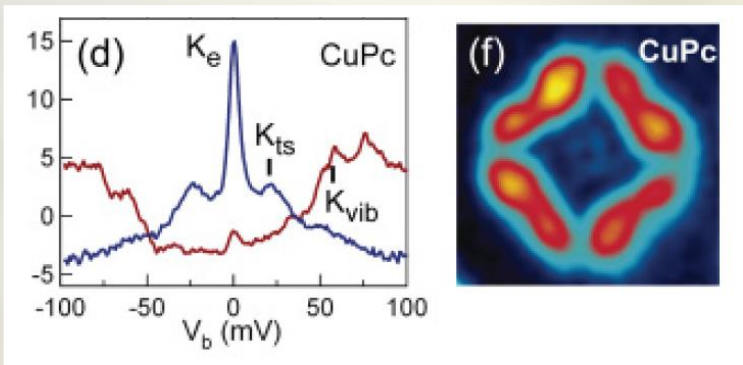
Andrea Donarini

Institute of Theoretical Physics, University of Regensburg, Germany



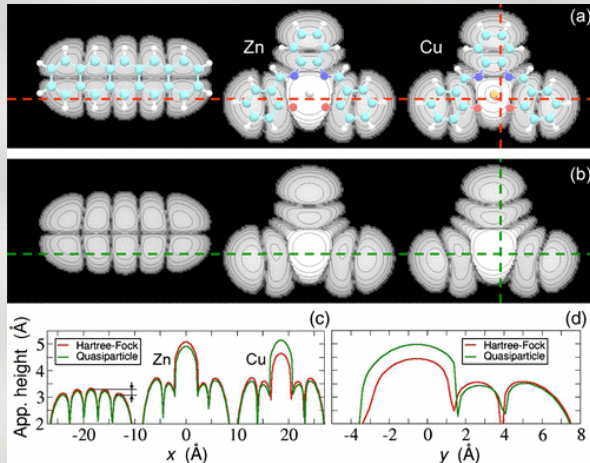


T. Miyamachi *et al.* *Nature comm.* **3**, 993 (2012)



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

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

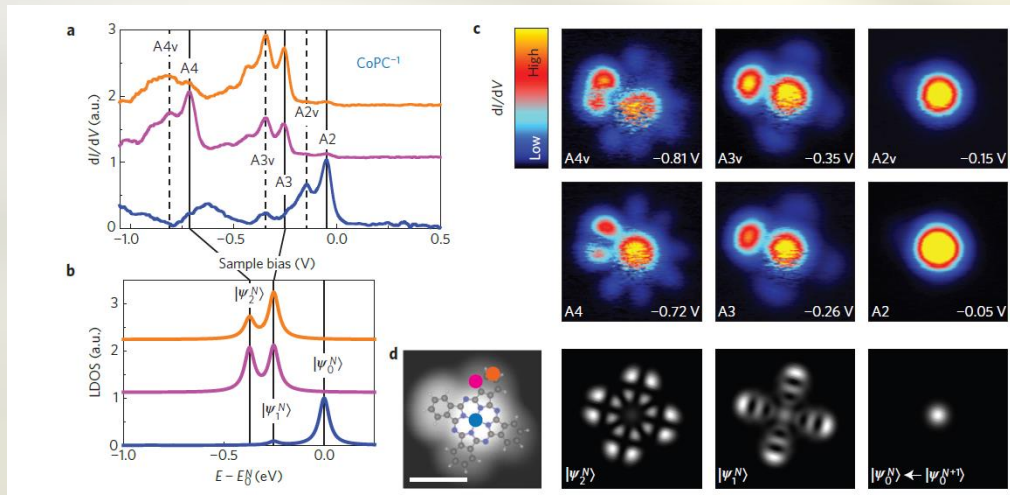


Alteration of the molecular orbitals due electronic correlation

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

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

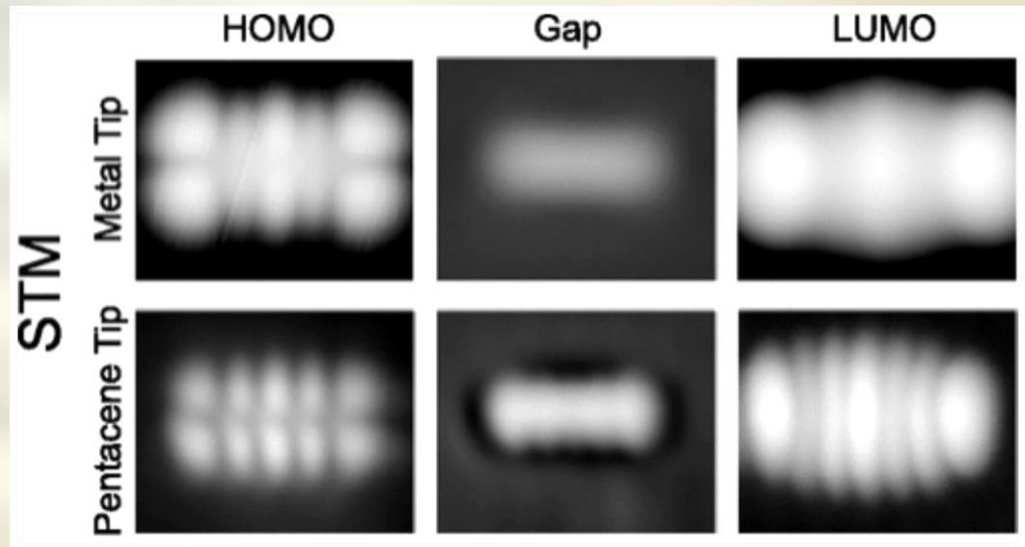
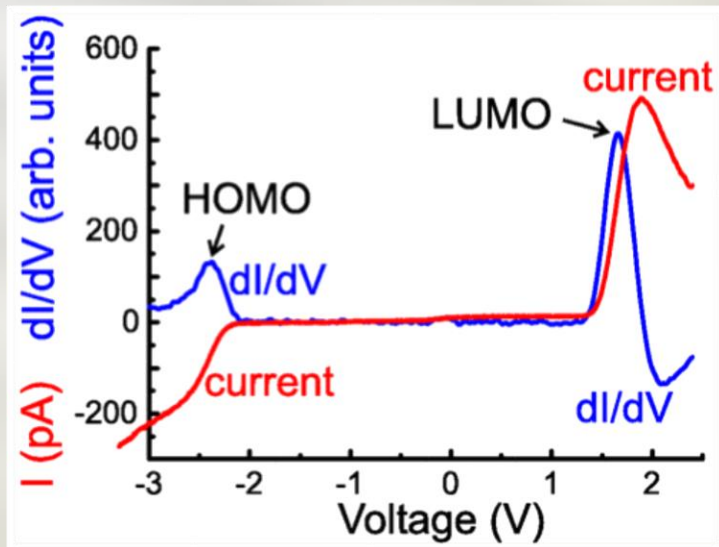
D. Toroz, et al. *PRL* **110**, 018305 (2013)



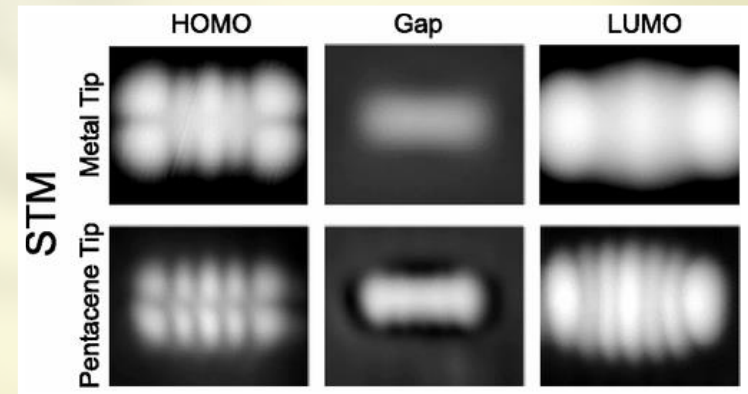
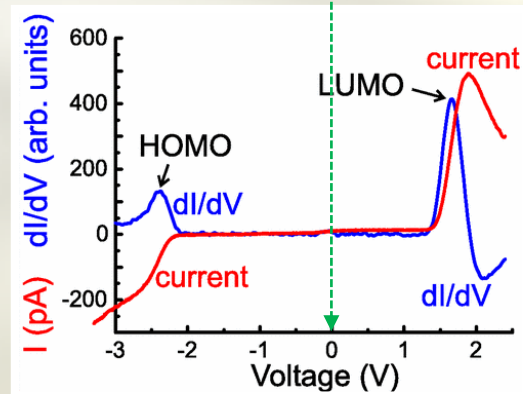
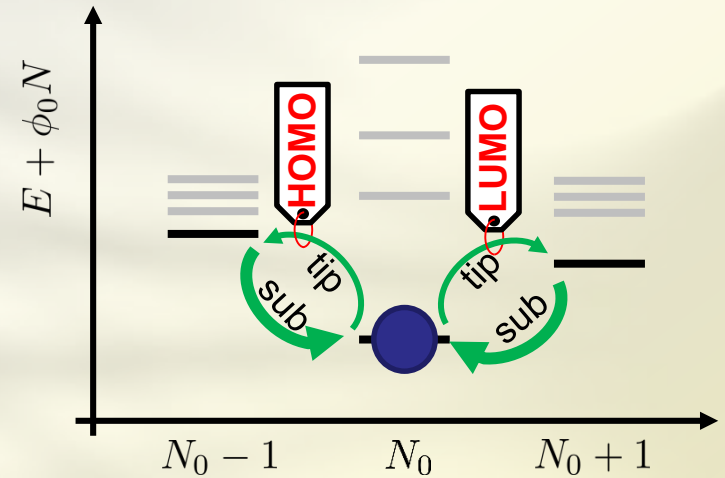
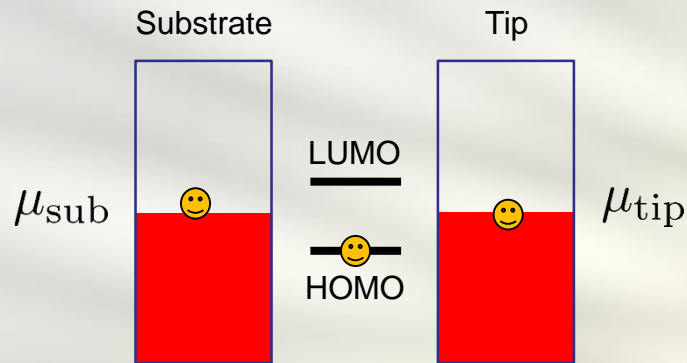
F. Schulz et al. *Nat. Physics* **11**, 229 (2015)

Visualization of many-body transitions in STM experiments

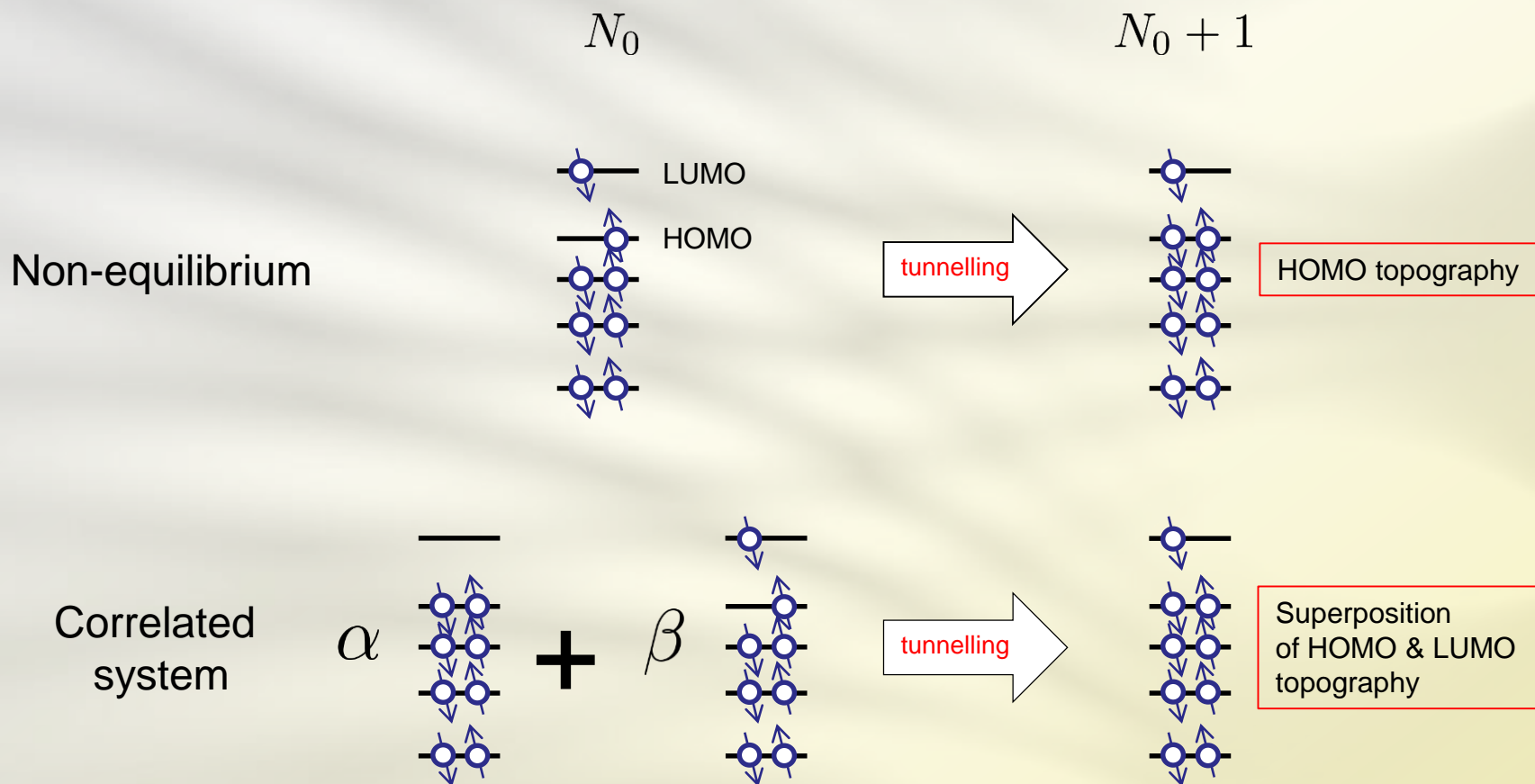
Spectroscopy & Topography



J.Repp et al. *PRL* **94**, 026803 (2005)



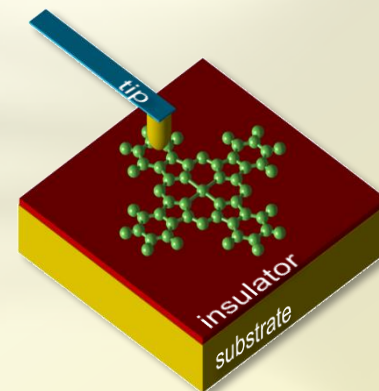
The two approaches only agree for **uncorrelated** systems close to **equilibrium**





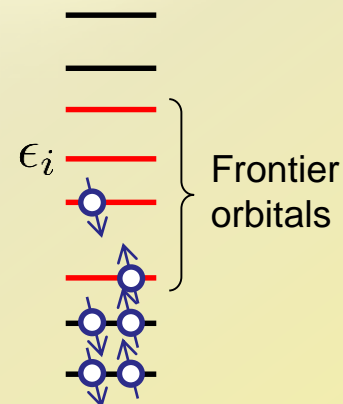
The STM single molecule junction is described by the Hamiltonian

$$\hat{H} = \hat{H}_{\text{mol}} + \hat{H}_{\text{mol-env}} + \hat{H}_S + \hat{H}_T + \hat{H}_{\text{tun}}$$



The molecule: **interacting** Hamiltonian for a small set of **frontier orbitals**

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

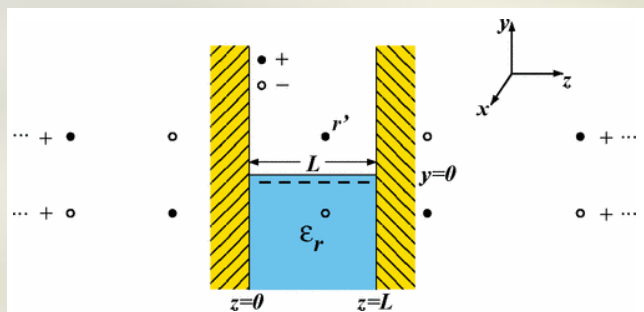




$$\hat{H}_{\text{mol-env}} = -\delta_{\text{ic}} (\hat{N} - N_0)^2$$

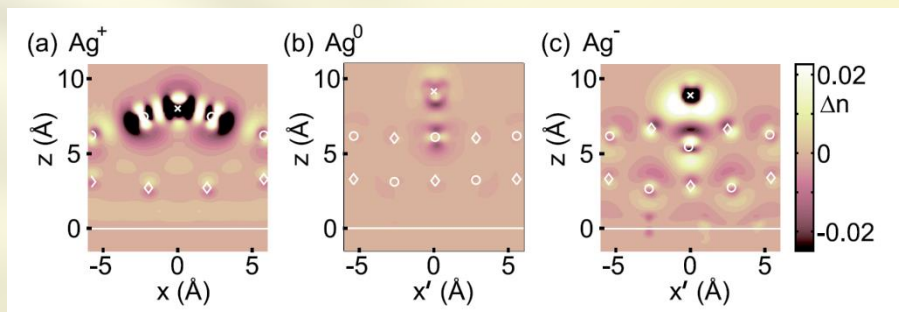
This term incorporates the two main effects which stabilize the excess charge on the molecule

Image charge effect



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

Polaron formation



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



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**.

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

Tip tunnelling amplitudes follow the **Chen's derivative rule**.

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



The system dynamics is obtained by solving a **generalized master equation** for the **reduced density matrix** $\sigma = \text{Tr}_{S,T}(\rho)$

$$\dot{\sigma} = - \frac{i}{\hbar} \underbrace{[\hat{H}_{\text{mol}} + \hat{H}_{\text{mol-env}}, \sigma]}_{\text{Coherent dynamics}} - \frac{i}{\hbar} \underbrace{[\hat{H}_{\text{eff}}, \sigma]}_{\text{Effective internal dynamics}}$$

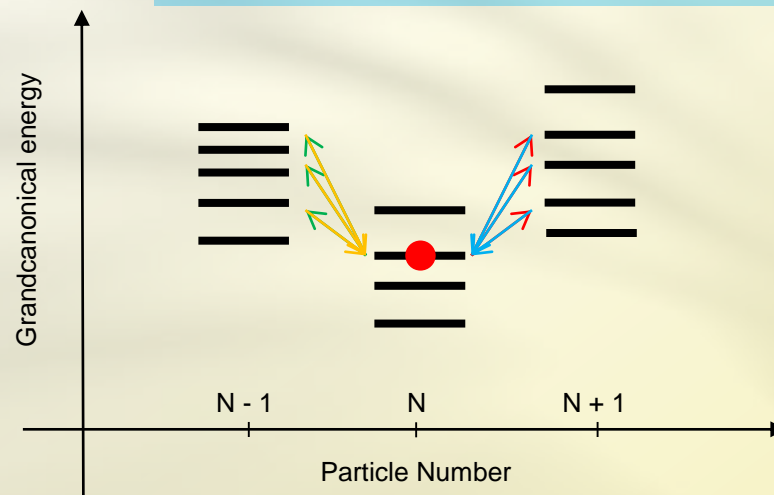
$$+ \underbrace{\mathcal{L}_{\text{tun}}[\sigma]}_{\text{Tunnelling dynamics}} + \underbrace{\mathcal{L}_{\text{rel}}[\sigma]}_{\text{Phenom. relaxation}} := \mathcal{L}[\sigma]$$

$$\mathcal{L}_{\text{rel}}[\sigma] = -\frac{1}{\tau} \left(\sigma - \sum_{NFm} \sigma_{mm}^{\text{th}, NF} |NFm\rangle \langle NFm| \sum_{En} \sigma_{nn}^{NE} \right)$$

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



$$\begin{aligned}
 \mathcal{L}_{\text{tun}} \sigma^{NE} = & -\frac{1}{2} \sum_{\chi\tau} \sum_{ij} \left\{ \mathcal{P}_{NE} \left[d_{i\tau}^\dagger \Gamma_{ij}^\chi (E - H_m) f_\chi^- (E - H_m) d_{j\tau} + \right. \right. \\
 & \left. \left. + d_{j\tau} \Gamma_{ij}^\chi (H_m - E) f_\chi^+ (H_m - E) d_{i\tau}^\dagger \right] \sigma^{NE} + h.c. \right\} \\
 & + \sum_{\chi\tau} \sum_{ijE'} \mathcal{P}_{NE} \left[d_{i\tau}^\dagger \Gamma_{ij}^\chi (E - E') \sigma^{N-1E'} f_\chi^+ (E - E') d_{j\tau} + \right. \\
 & \left. + d_{j\tau} \Gamma_{ij}^\chi (E' - E) \sigma^{N+1E'} f_\chi^- (E' - E) d_{i\tau}^\dagger \right] \mathcal{P}_{NE}
 \end{aligned}$$





$$H_{\text{eff}} = \frac{1}{2\pi} \sum_{NE} \sum_{\chi\sigma} \sum_{ij} \mathcal{P}_{NE} \left[d_{i\sigma}^\dagger \Gamma_{ij}^\chi (E - H_m) p_\chi (E - H_m) d_{j\sigma} \right. \\ \left. + d_{j\sigma} \Gamma_{ij}^\chi (H_m - E) p_\chi (H_m - E) d_{i\sigma}^\dagger \right] \mathcal{P}_{NE}$$

Effective
Hamiltonian

$$I_\chi = \sum_{NE\sigma ij} \mathcal{P}_{NE} \left[d_{j\sigma} \Gamma_{ij}^\chi (H_m - E) f_\chi^+ (H_m - E) d_{i\sigma}^\dagger \right. \\ \left. - d_{i\sigma}^\dagger \Gamma_{ij}^\chi (E - H_m) f_\chi^- (E - H_m) d_{j\sigma} \right] \mathcal{P}_{NE}$$

Current
operator

$$\Gamma_{ij}^\chi(\Delta E) = \frac{2\pi}{\hbar} \sum_{\mathbf{k}} (t_{\mathbf{k}i}^\chi)^* t_{\mathbf{k}j}^\chi \delta(\epsilon_{\mathbf{k}}^\chi - \Delta E)$$

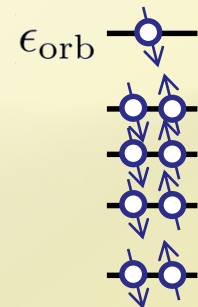


The **current** is proportional to the **transition rate** between **many-body states**

$$R_{N E_0 \rightarrow N+1 E_1}^{\chi\tau} = \sum_{ij} \langle N+1 E_1 | d_{i\tau}^\dagger | N E_0 \rangle \Gamma_{ij}^\chi (E_1 - E_0) \times \\ \langle N E_0 | d_{j\tau} | N+1 E_1 \rangle f^+(E_1 - E_0 - \mu_\chi)$$

For **uncorrelated** and **non-degenerate systems** the many-body rate reduces to

$$R_{N E_0 \rightarrow N+1 E_1}^{\chi\tau} = \Gamma_{\text{orb}}^\chi(\epsilon_{\text{orb}}) f^+(\epsilon_{\text{orb}} - \mu_\chi)$$

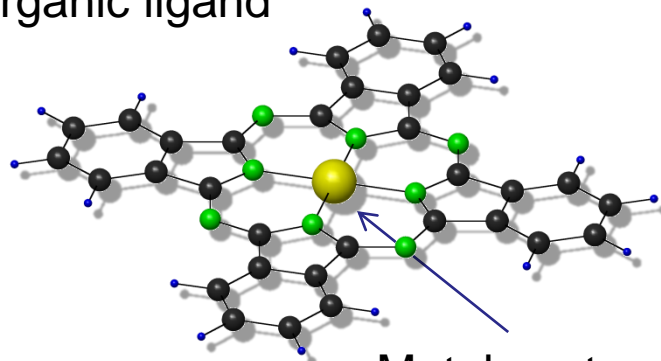


Close to equilibrium, the **constant current map** is the **isosurface** of a **specific molecular orbital** (Tersoff-Hamann theory of STM)

Copper-Phthalocyanine

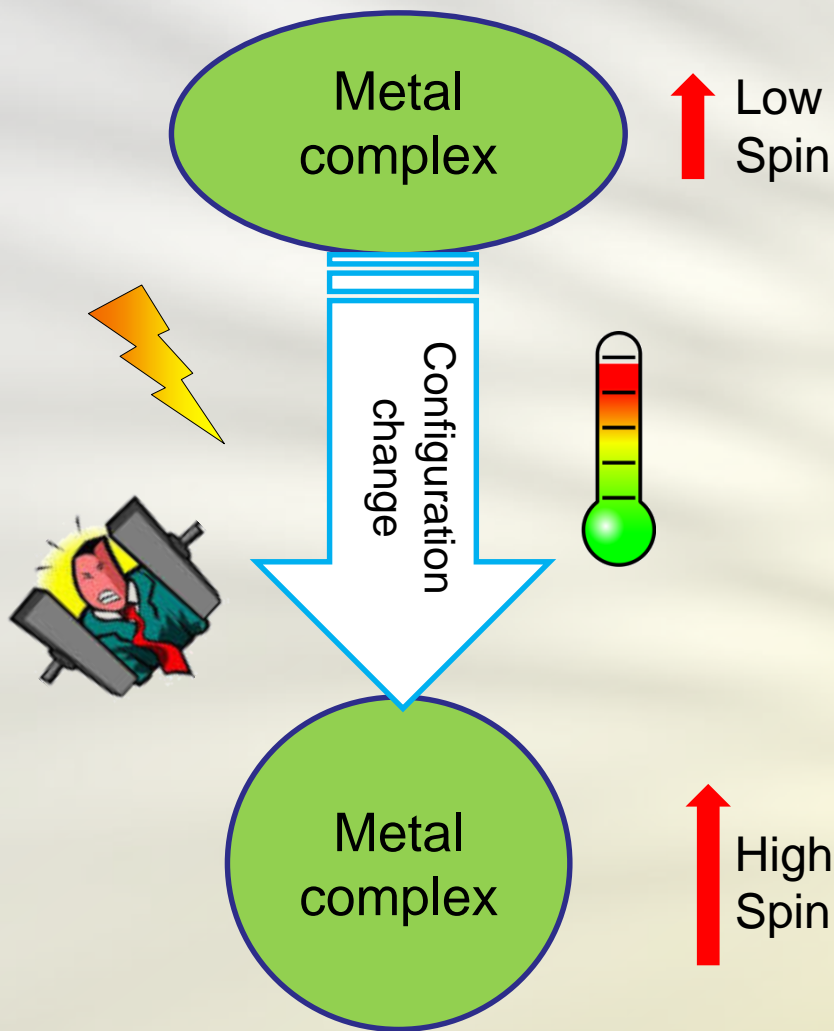


Organic ligand



Metal center

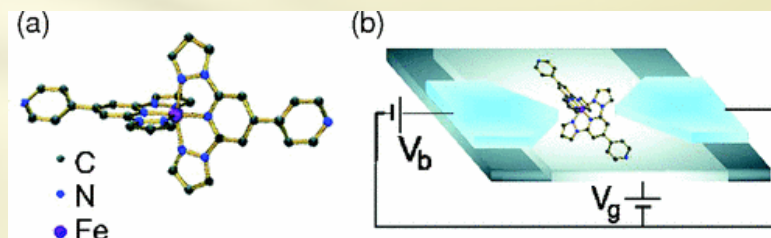
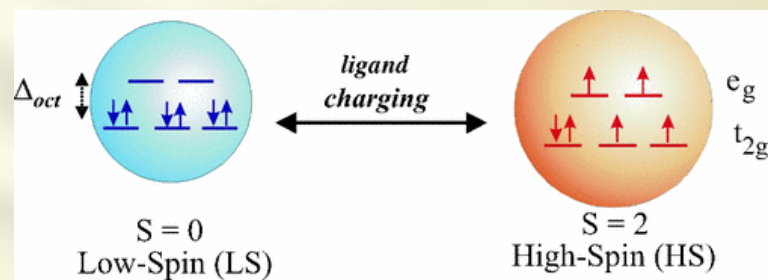
Non-equilibrium spin crossover



Change in the occupation of the metal d -orbitals:

Interplay of:

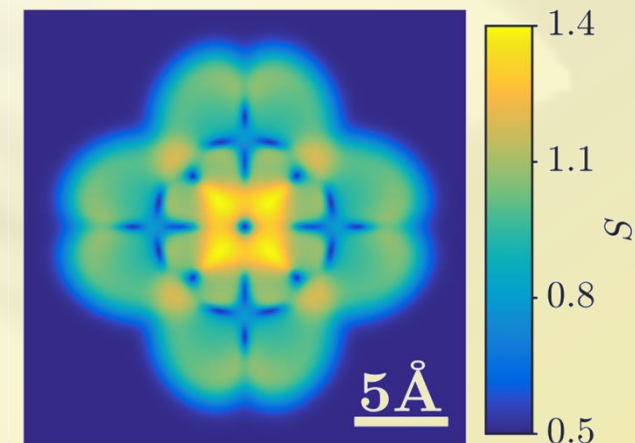
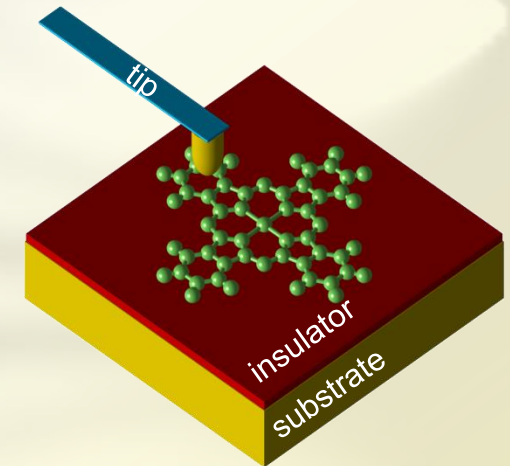
- (Octahedral) ligand field splitting
- Exchange interaction



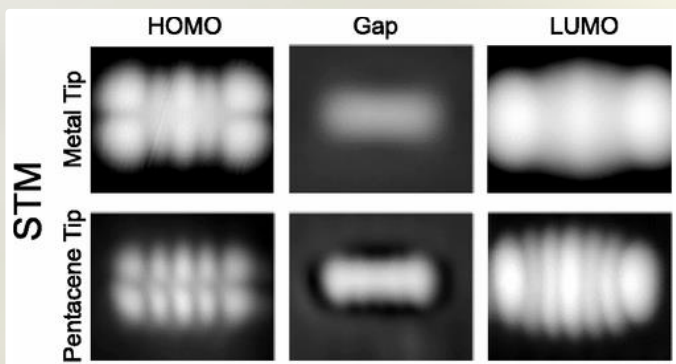
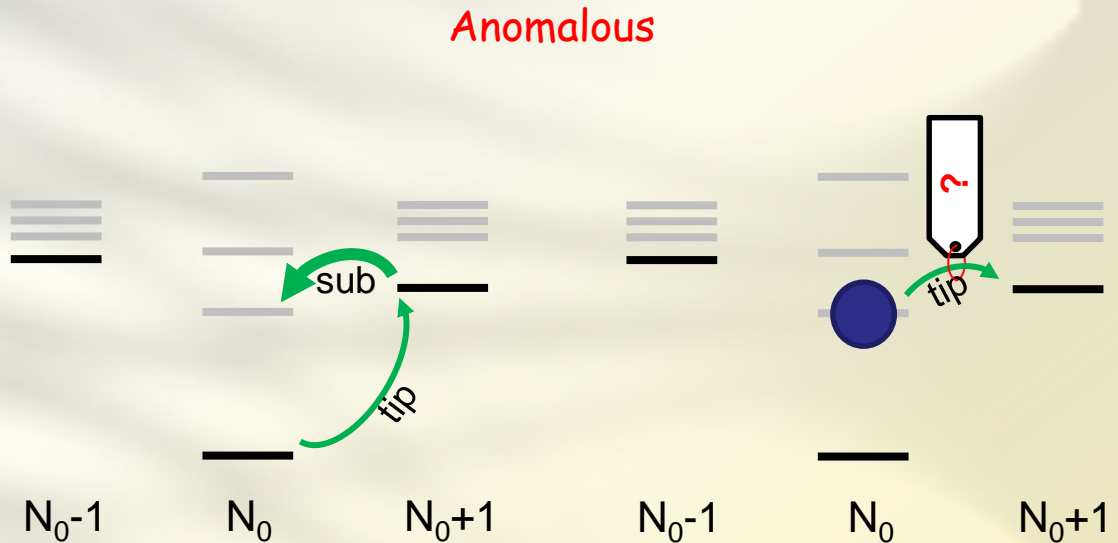
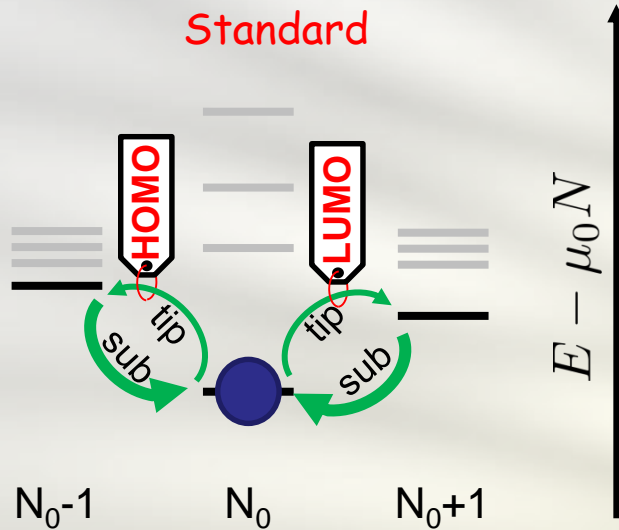
V. Meded, *et al. PRB* **83**, 245415 (2011)



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



$V_b = 1.38 \text{ V}$

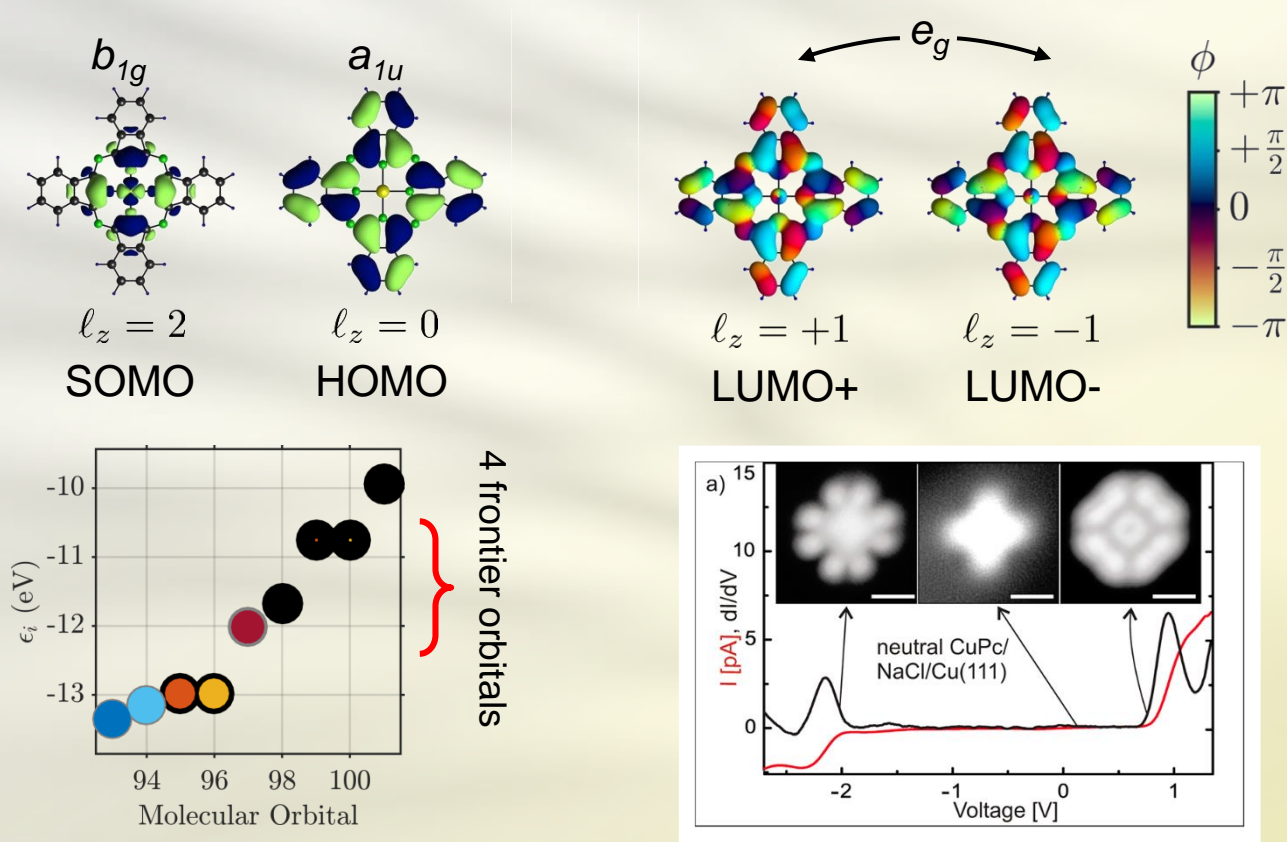


The **anomalous current map** depends on the nature of the excited state

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



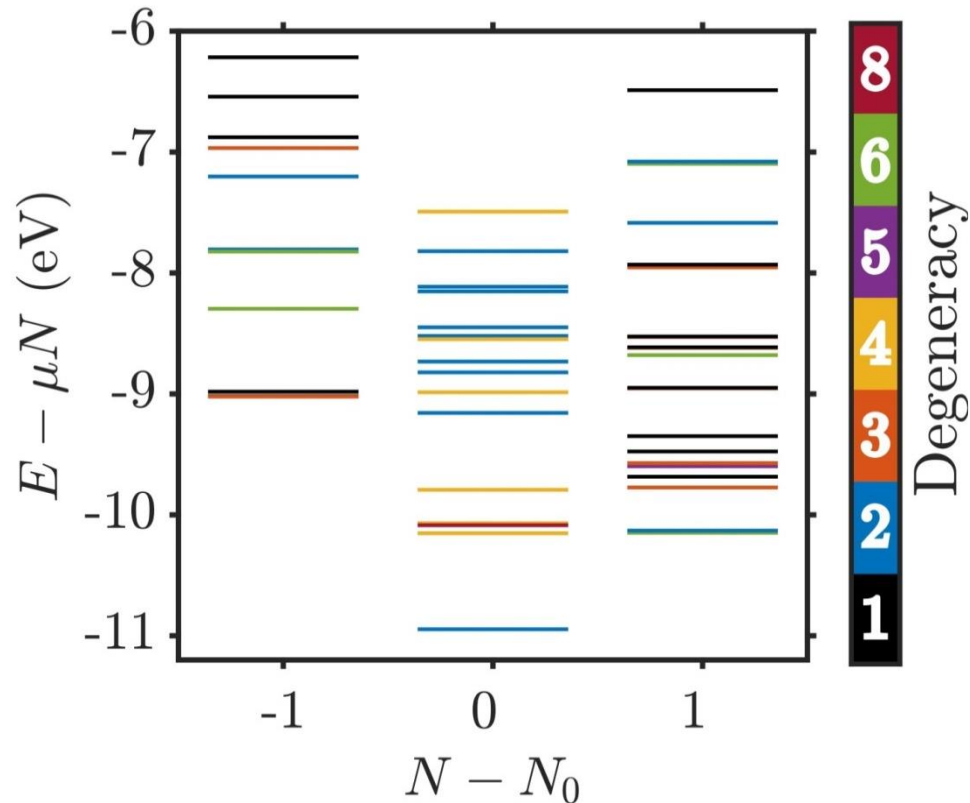
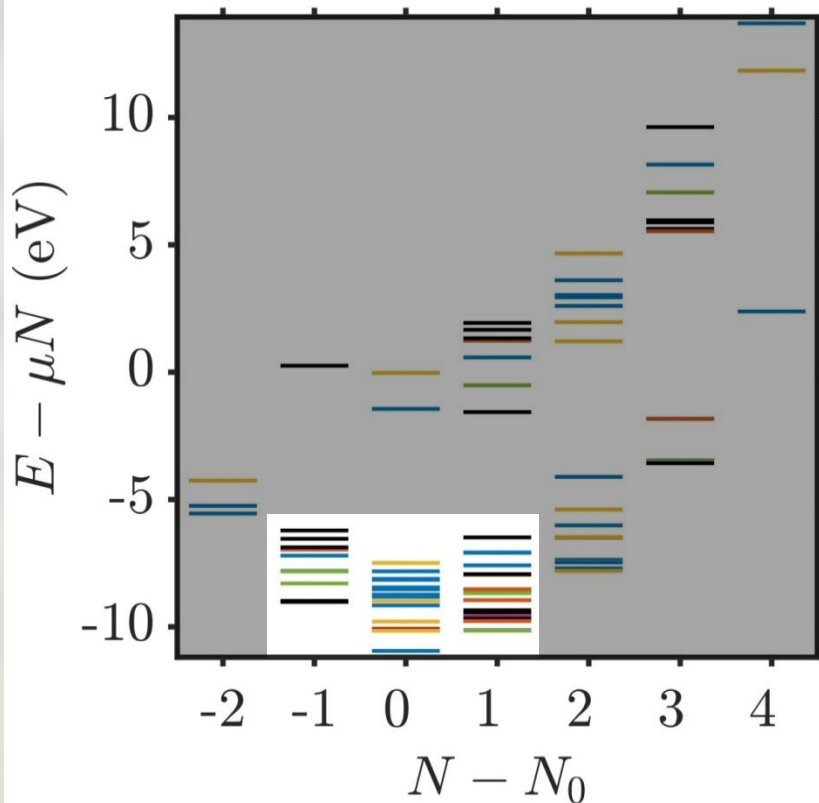
The single particle Hamiltonian is constructed following LCAO schemes of Harrison [1] and Slater-Koster [2].



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

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

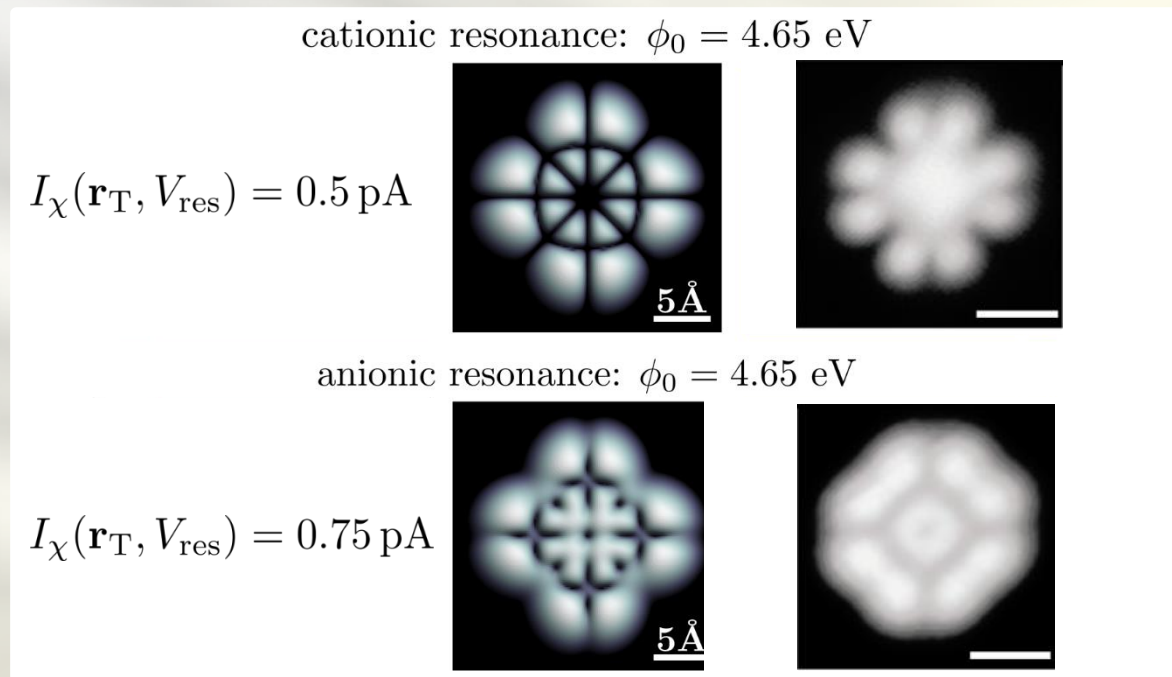
[2] J. C. Slater and G. F. Koster, *Phys. Rev.* **94**, 1498 (1954)





	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

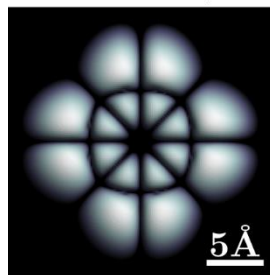


$$I_{\chi}(\mathbf{r}_T, V_b) = \text{Tr}_{\text{mol}} \left(\hat{N} \mathcal{L}_{\chi}[\sigma^{\infty}(\mathbf{r}_T, V_b)] \right)$$

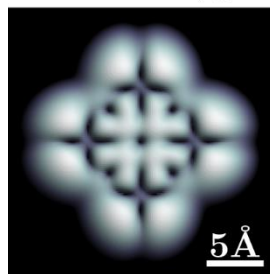


Standard

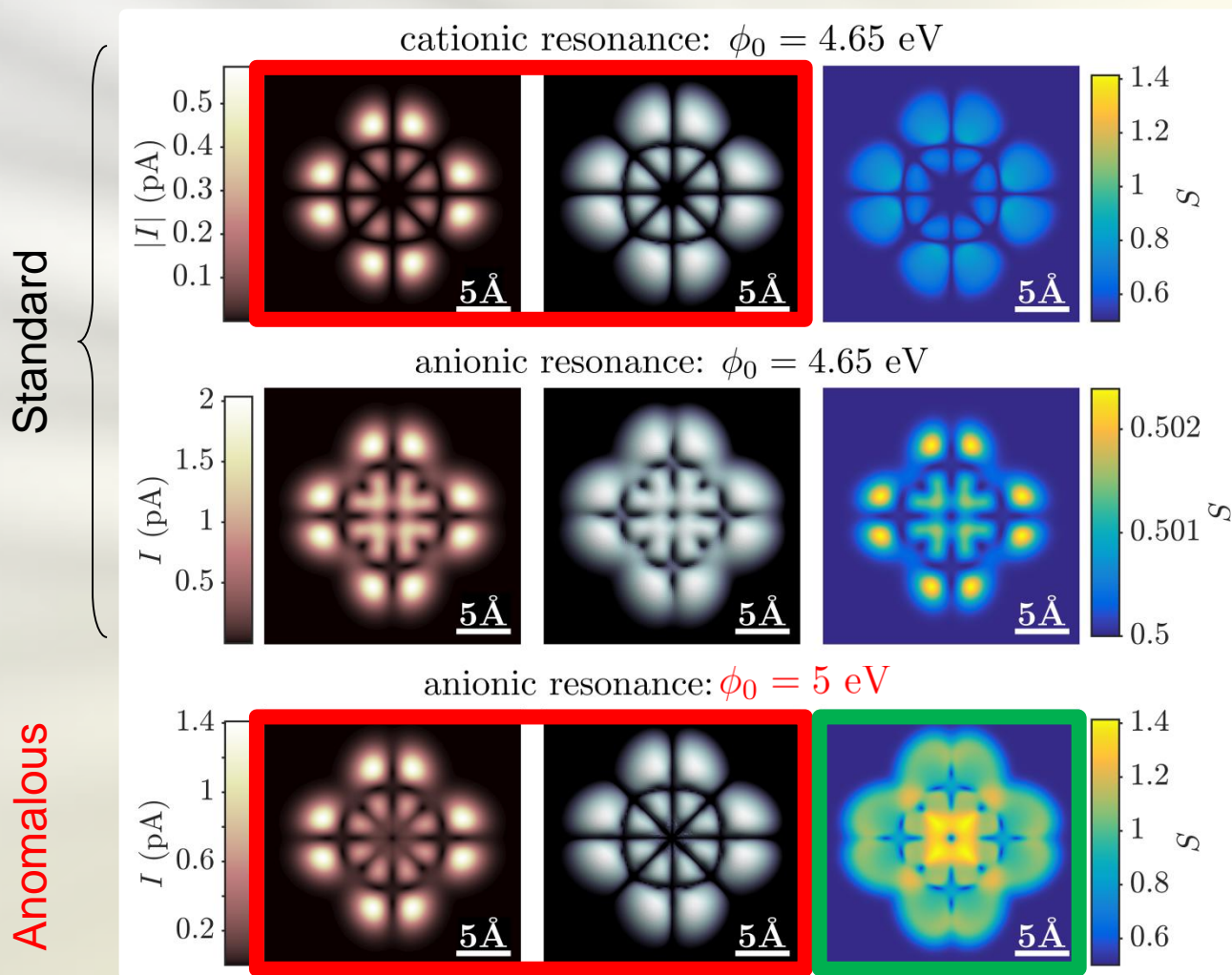
cationic resonance: $\phi_0 = 4.65$ eV



anionic resonance: $\phi_0 = 4.65$ eV



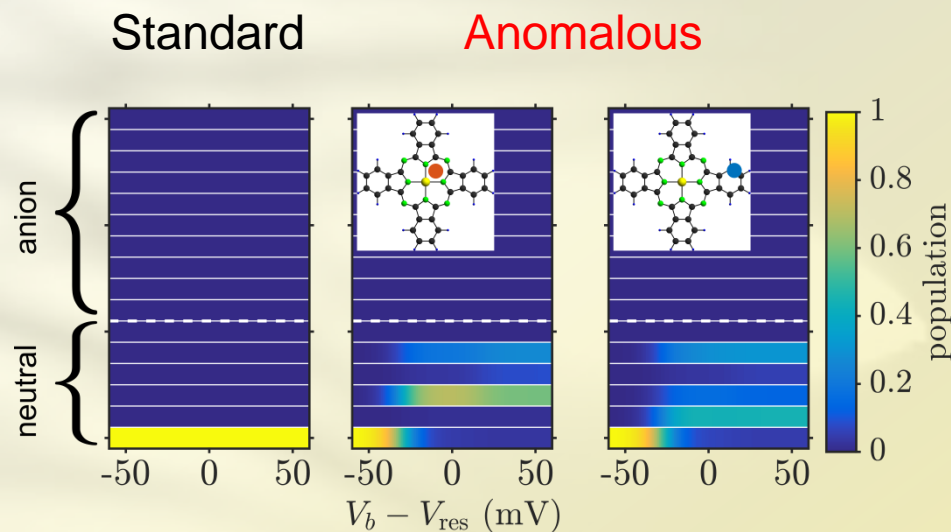
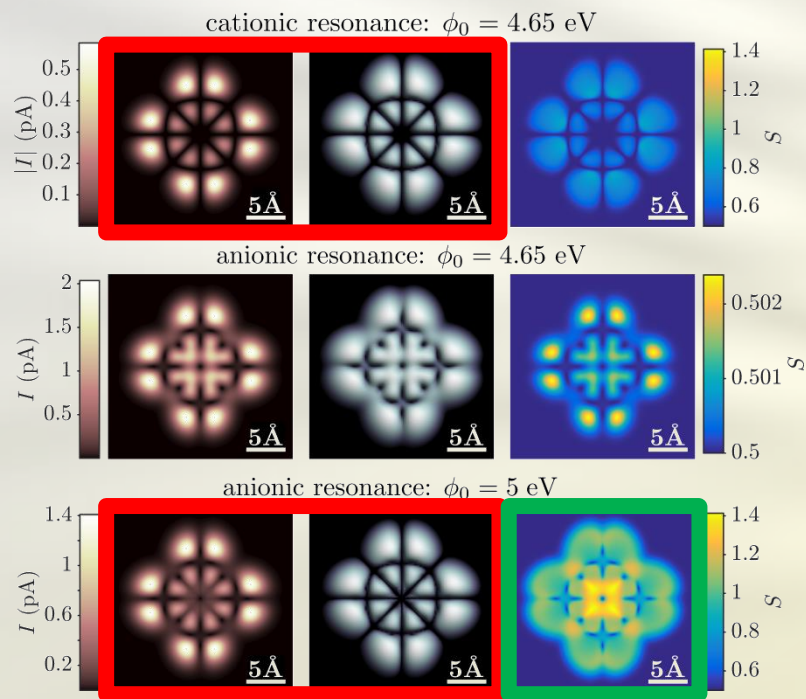
$$S(\mathbf{r}_T, V_b) = \sqrt{\langle \hat{S}^2 \rangle(\mathbf{r}_T, V_b) + \frac{1}{4}} - \frac{1}{2} \quad \text{with} \quad \langle \hat{S}^2 \rangle(\mathbf{r}_T, V_b) = \text{Tr}_{\text{mol}} \left(\hat{S}^2 \rho_{\text{red}}^\infty(\mathbf{r}_T, V_b) \right)$$



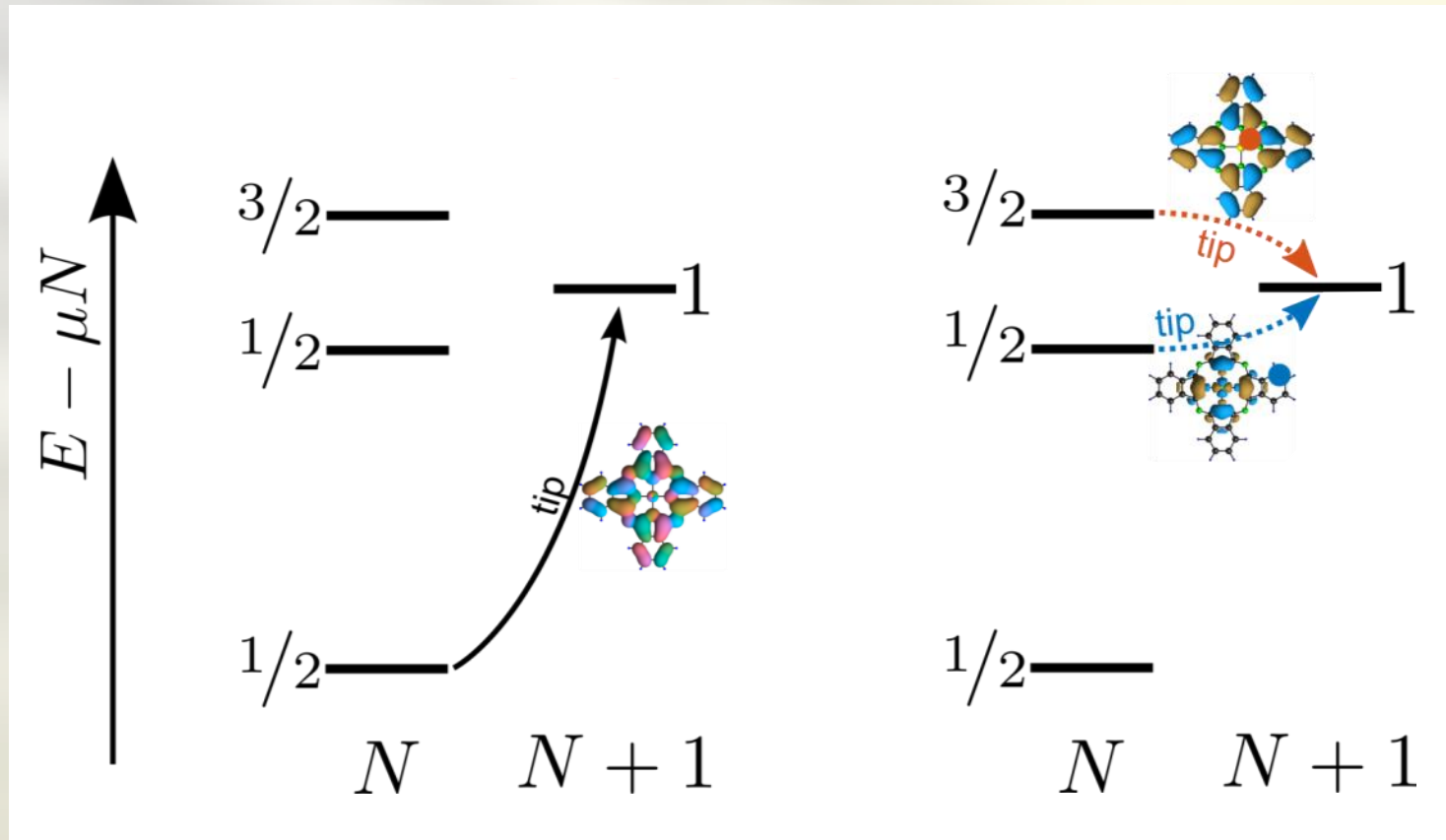


Current and topographic maps of an **anionic transition** resembles the **HOMO**

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



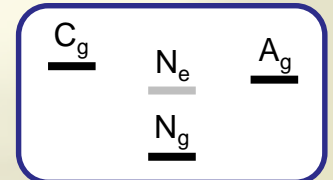
The molecule undergoes a **population inversion** which depends on the tip position



Is CuPc so special ?

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

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

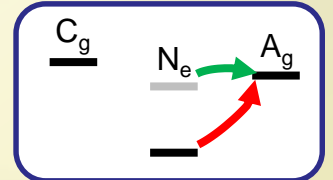


2 The spin of the ground state should be different

$$S_{N_g} \neq S_{N_e}$$

3 The (tip) transition rate to the excited state and the transition rate to the neutral ground state should be different

Closed shell
conjugated molecules

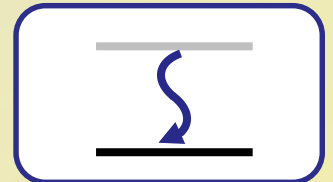


4 The tip and substrate transition rates should be strongly asymmetric

$$\Gamma_{\text{tip}} \ll \Gamma_{\text{sub}}$$

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

STM
on thin insulating films



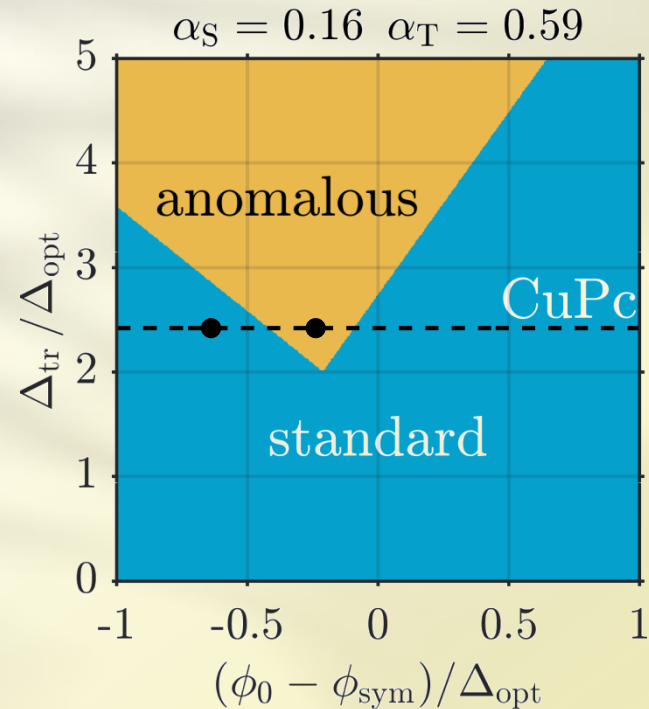
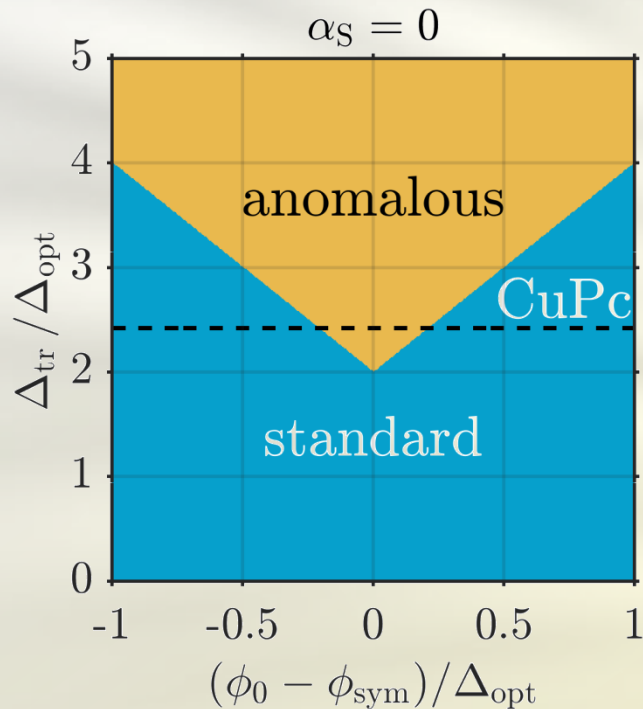
URA class of single molecule junctions

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

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

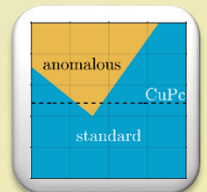
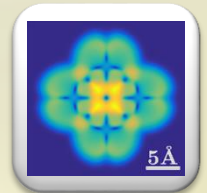
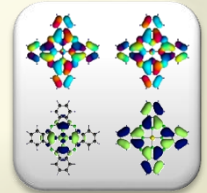
$$\phi_{\text{sym}} = \frac{\text{IP} + \text{EA}}{2}$$

ϕ_0 = Substrate workfunction

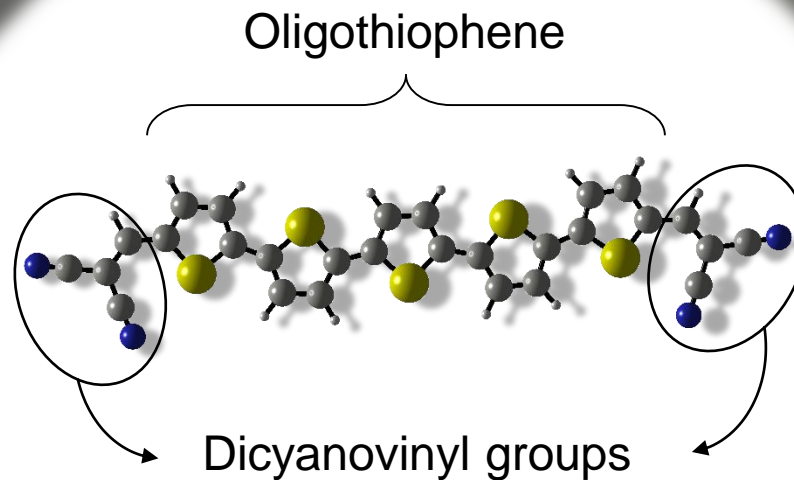




- We developed a **minimal model** for the Cu-Phthalocyanine in terms of **four interacting frontier orbitals**.
- For an experimentally accessible substrate workfunction of 5 eV, we predict the appearance, close to the anionic resonance of **non equilibrium spin-crossover**.
- **Dramatic changes in 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.



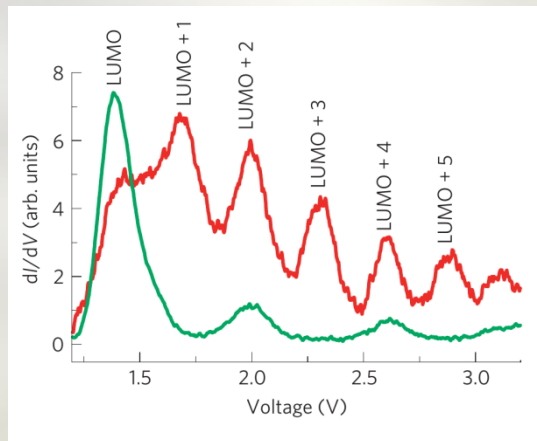
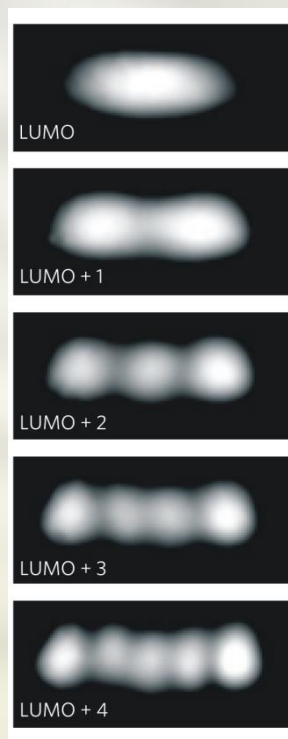
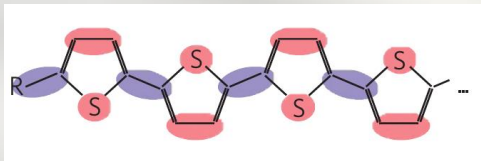
Dicyanovinyl-quinquethiophene



Entanglement in the two particles groundstate

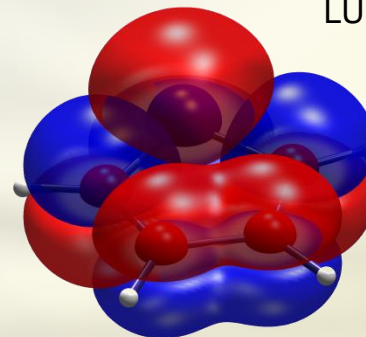


In oligothiophenes



J. Repp *et al.*, *Nat. Phys.* **6**, 975 (2010)

LUMO of thiophene

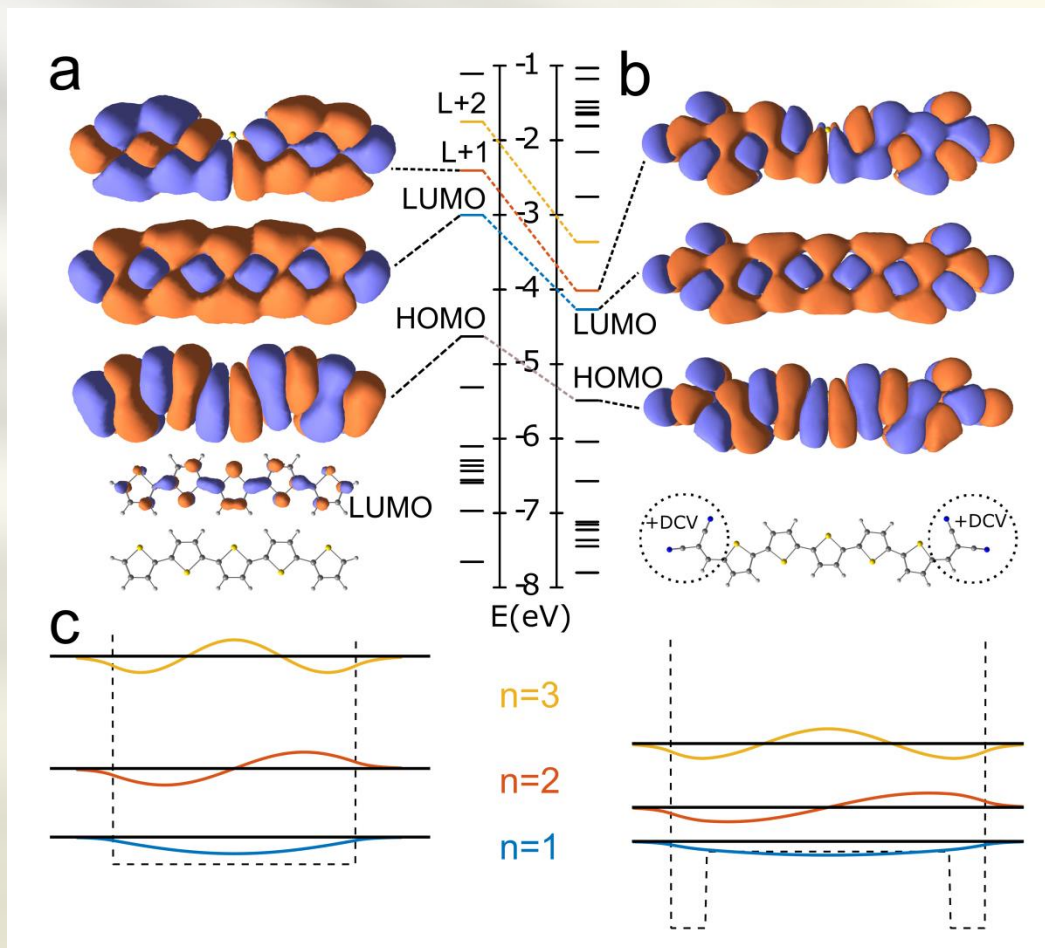


General statement of the **Sturm-Liouville theory** for differential equations:

In a one dimensional system the eigenfunction of the **n -th** excited state has **n** nodes.



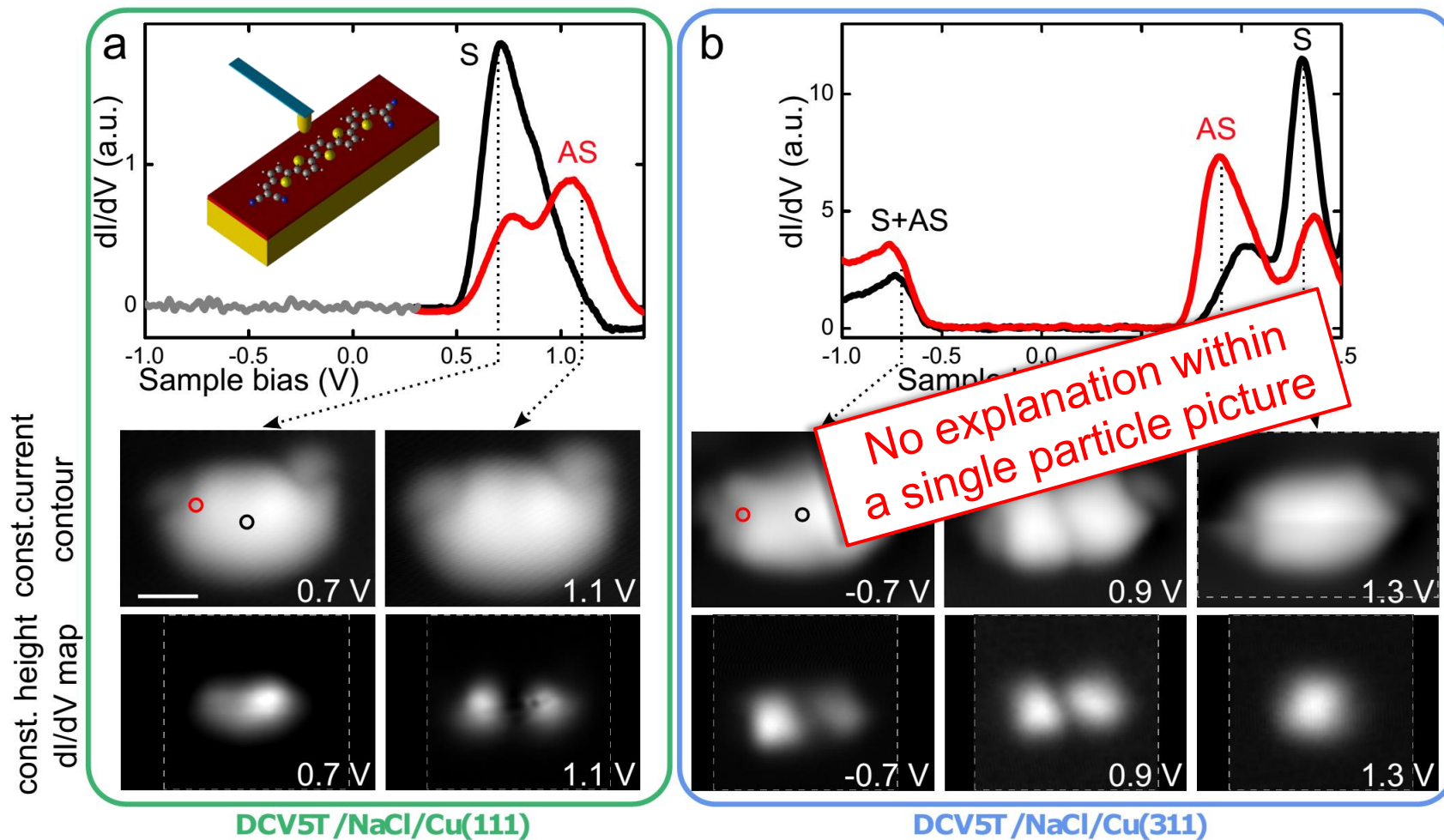
Quinquethiophene
(5T)



AS

S

Dicyanovinyl-
quinquethiophene
(DCV5T)

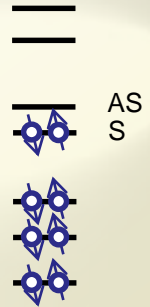


P. Yu, N. Kocić, J. Repp, B. Siegert, and A. Donarini, *PRL* **119**, 056801 (2017)

The many-body Hamiltonian



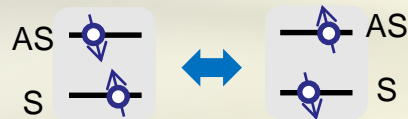
We concentrate on the dynamics of two orbitals only



and freeze the occupation of the other single particle states

$$\hat{H}_{\text{mol}} = \epsilon_S \hat{n}_S + \epsilon_{AS} \hat{n}_{AS} + \frac{U}{2} \hat{N} (\hat{N} - 1) + J \sum_{\sigma\sigma'} \hat{d}_{S\sigma}^\dagger \hat{d}_{AS\sigma'}^\dagger \hat{d}_{S\sigma} \hat{d}_{AS\sigma'} + J \sum_{\sigma\sigma'} \left(\hat{d}_{S\sigma}^\dagger \hat{d}_{S\sigma'}^\dagger \hat{d}_{AS\sigma} \hat{d}_{AS\sigma'} + \text{h.c.} \right)$$

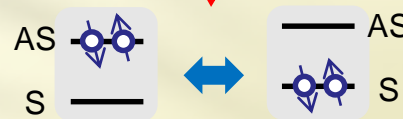
exchange



$$\Delta = \epsilon_{AS} - \epsilon_S = 0.3 \text{ eV}$$

fit to the experiment

pair-hopping

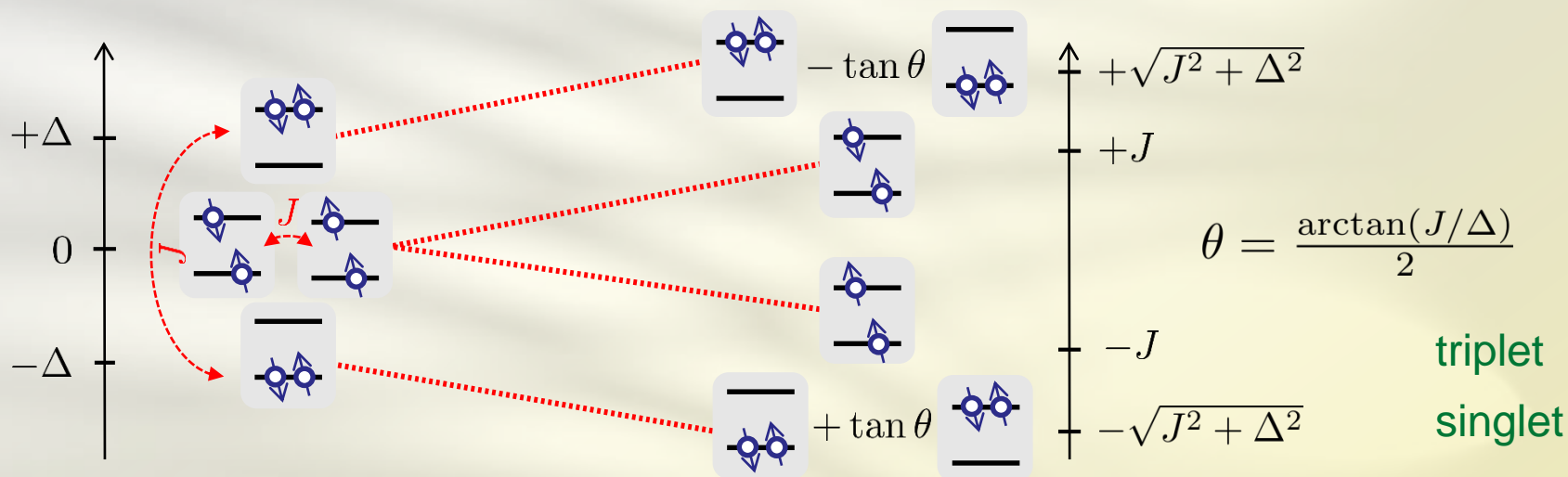
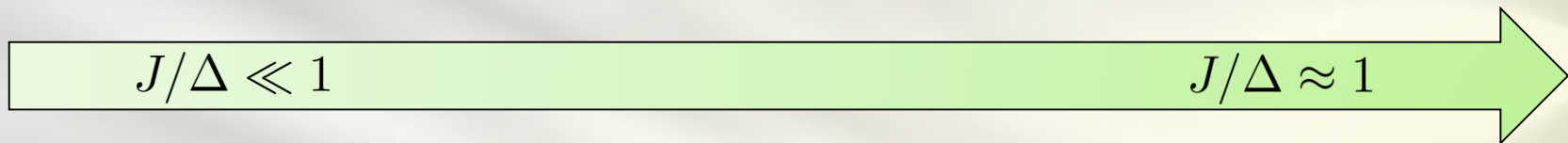


$$U = 1.4 \text{ eV}$$

calculated from the molecular orbitals

$$J = 0.75 \text{ eV}$$

The two-particle spectrum



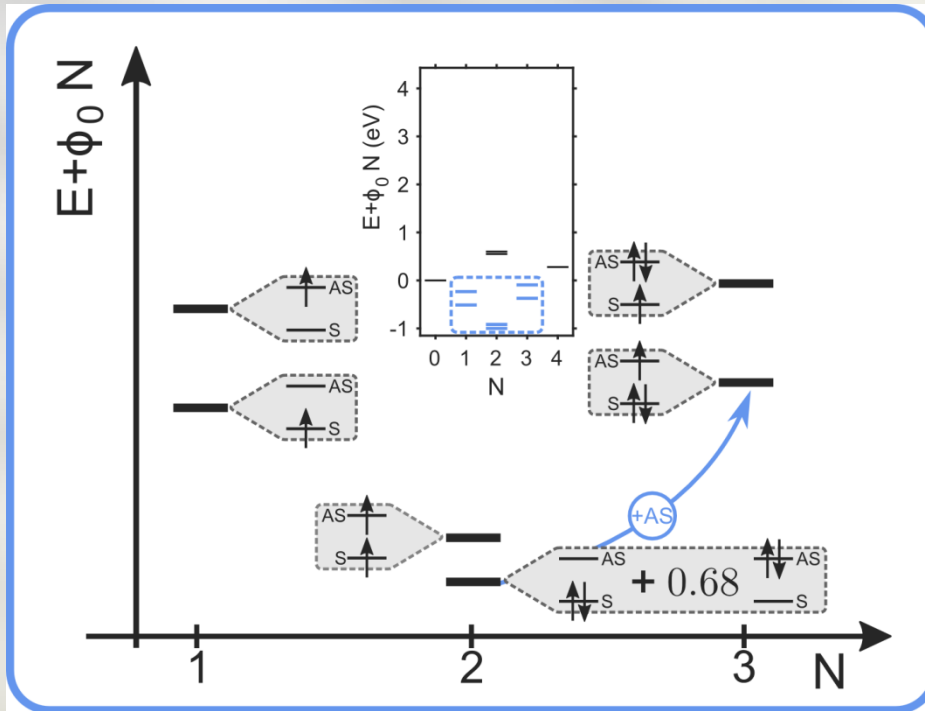
In DCV5T
 $J/\Delta \approx 3$



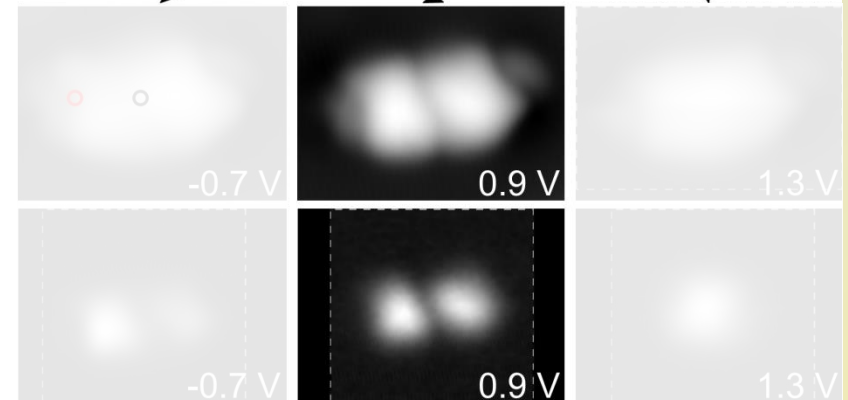
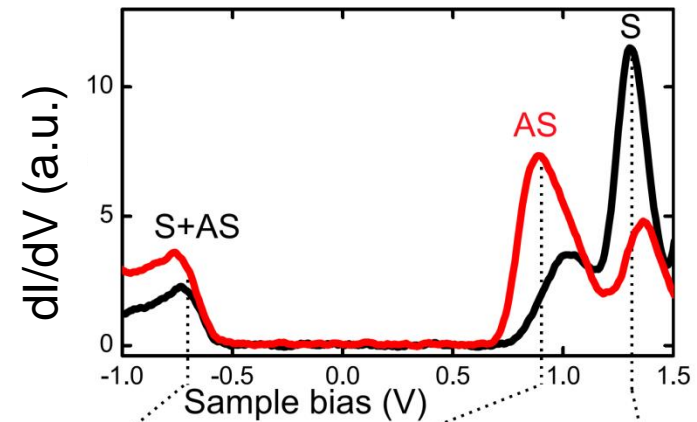
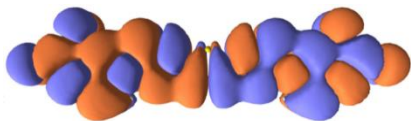
$\tan \theta \approx 0.68$
 $\Delta_{\text{ST}} \approx 58 \text{ meV}$

Strongly entangled
ground state

Mechanism of orbital reversal

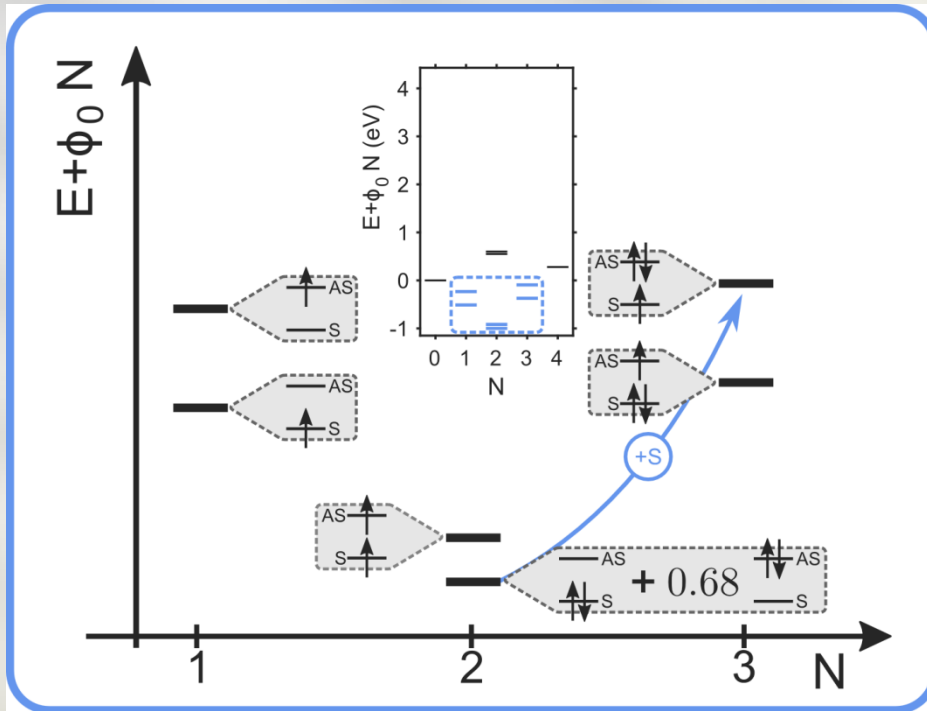


DCV5T/NaCl/Cu(311)

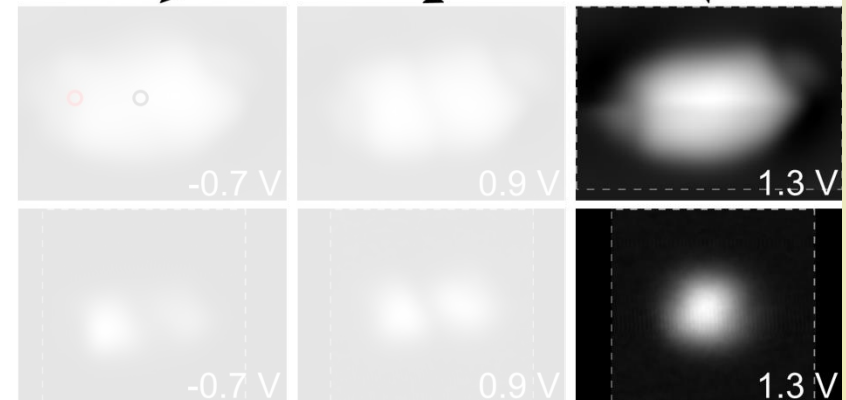
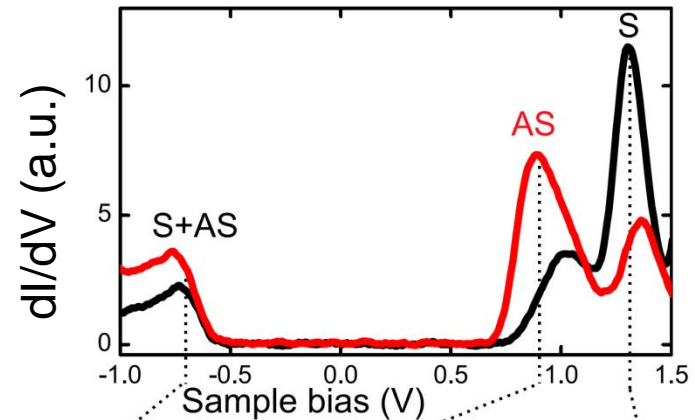
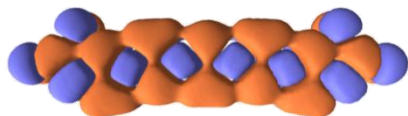


P. Yu, N. Kocić, J. Repp, B. Siegert, and A. Donarini, *PRL* **119**, 056801 (2017)

Mechanism of orbital reversal



DCV5T/NaCl/Cu(311)

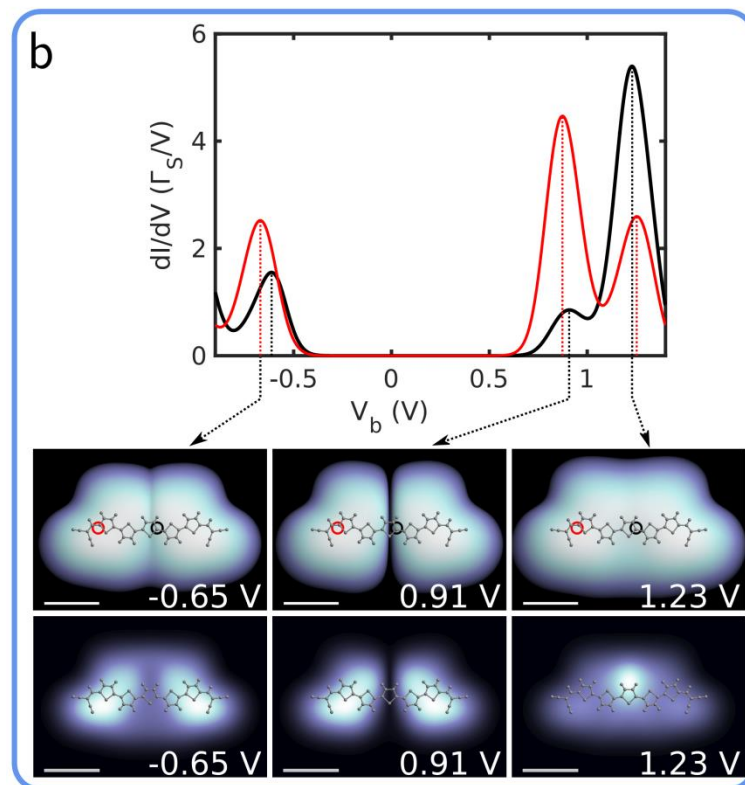
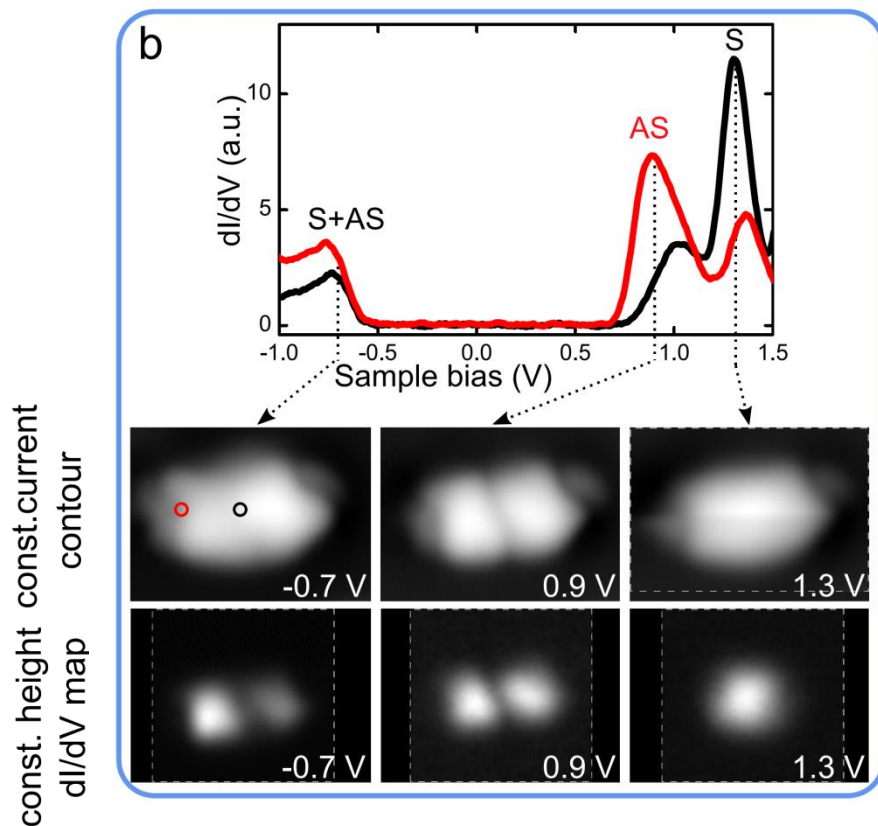


This transition would be forbidden if $J/\Delta = 0$

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DCV5T/NaCl/Cu(311)

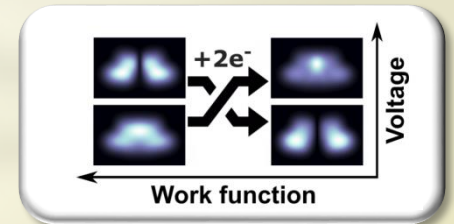




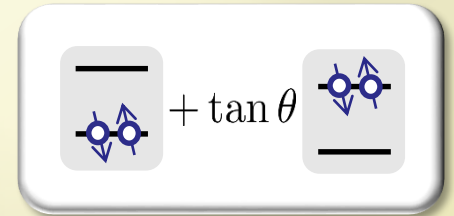
By **chemical engineering** of the single-particle level spacing between two frontier orbitals we **control** the degree of **electronic-correlation** in single molecule junctions



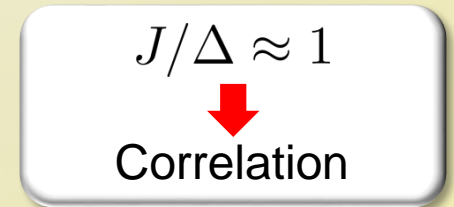
We observe the **apparent reversal** in the orbital sequence of a dicyanovinyl-quinquethiophene (DCV5T) in STM upon changing the crystallographic orientation of the insulator-coated copper substrate



The orbital reversal is the signature of an **entangled ground state** which we understand in terms of a minimal interacting model



Criteria for such entanglement are clearly formulated in terms of the parameters in the **minimal model** and allow us to **predict** and **control** its occurrence for other molecules.



Aknowledgments

Theory



Milena Grifoni



Benjamin Siegert



Sandra Sobczyk

Experiment



Nemanja Kocić



Ping Yu



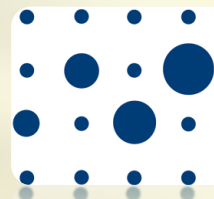
Jascha Repp



GRK 1570



SFB 689



VolkswagenStiftung

Lichtenberg Programm

Thank you for your attention

