Correlations effects
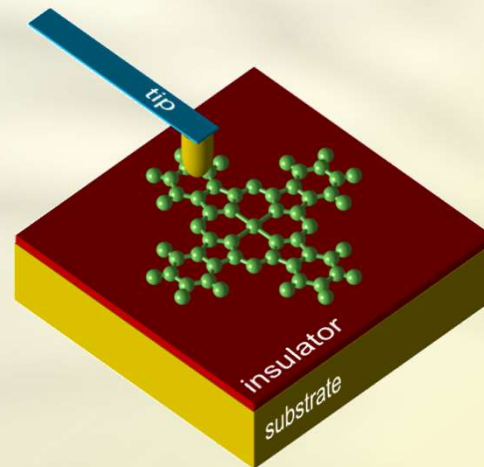# STM single molecule junctions

Andrea Donarini
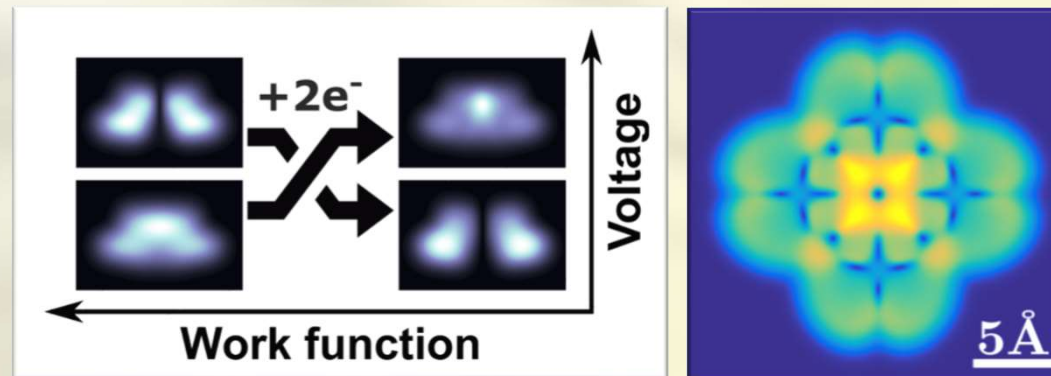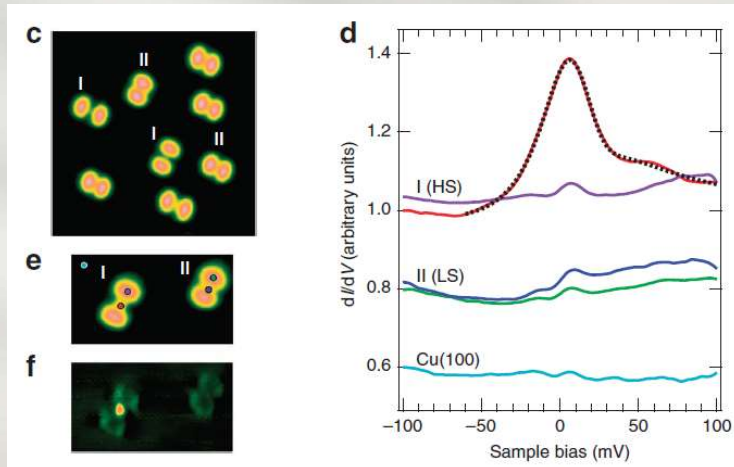
Institute of Theoretical Physics, University of Regensburg, Germany

Defects in Solids – Zürich

Correlations effects
STM single molecule junctions

Andrea Donarini

Institute of Theoretical Physics, University of Regensburg, Germany

Defects in Solids – Zürich

Motivation

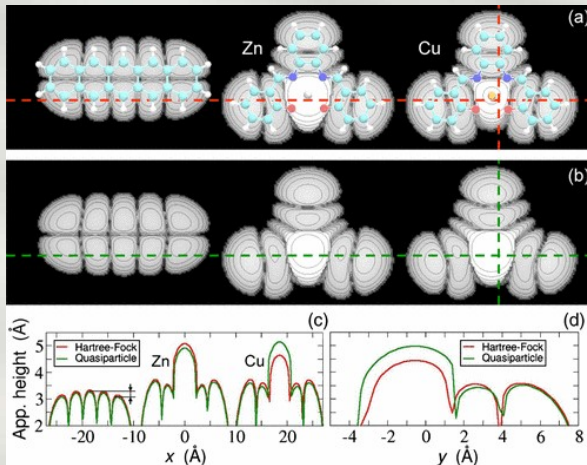T. Miyamachi *et al. Nature comm.* **3**, 993 (2012)
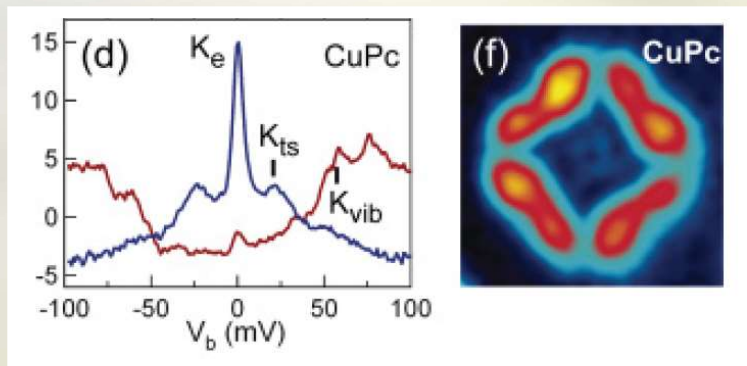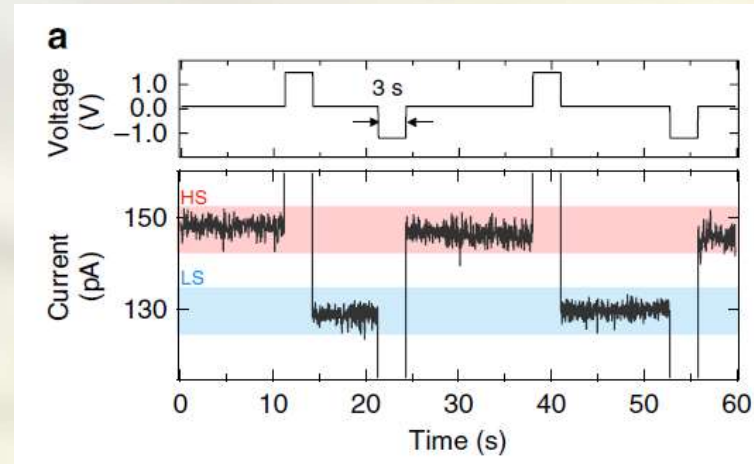
A. Mugarza, *et al.* PRB **85**, 155437 (2012)

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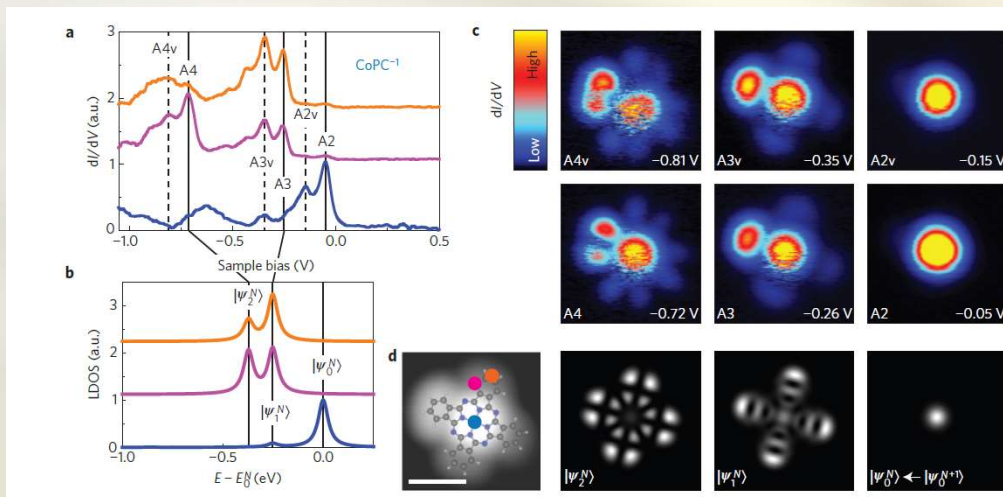- Triplet-singlet splitting: **21 meV**

Motivation

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

Alteration of the molecular orbitals due electronic correlation

$$\varphi(\mathbf{r}) = \sum_{i,j} (C_j^{N-1})^* C_i^N \sum_\alpha \phi_\alpha(\mathbf{r}) \langle \Phi_j^{N-1} | \hat{c}_\alpha | \Phi_i^N \rangle.$$
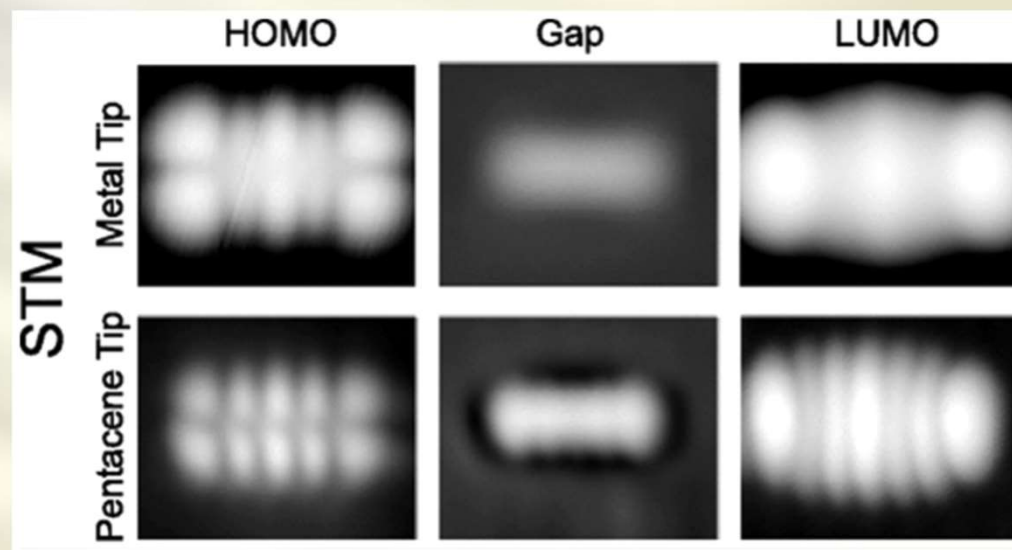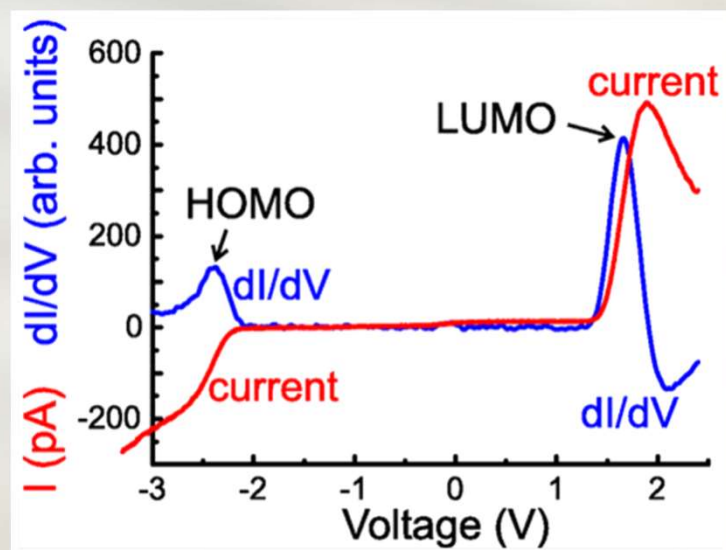
STM experiments probe quasiparticle wavefunctions which differ from the single particle molecular orbitals

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)

Single particle vs. Many-body

Substrate   Tip

μ_{sub} LUMO   HOMO μ_{tip}

$E + \phi_0 N$

HOMO   LUMO

tip   sub   tip   sub

$N_0 - 1$ N_0 $N_0 + 1$
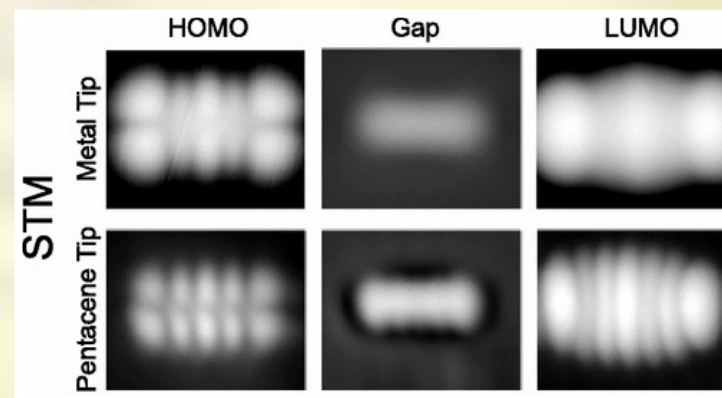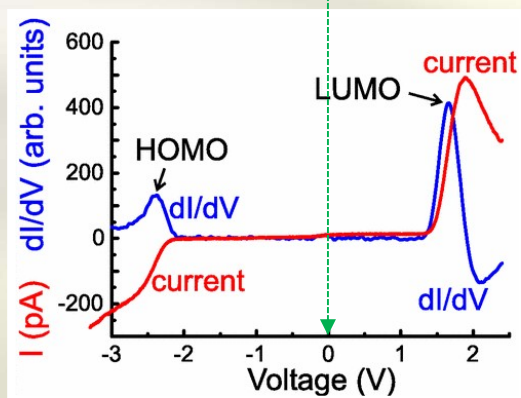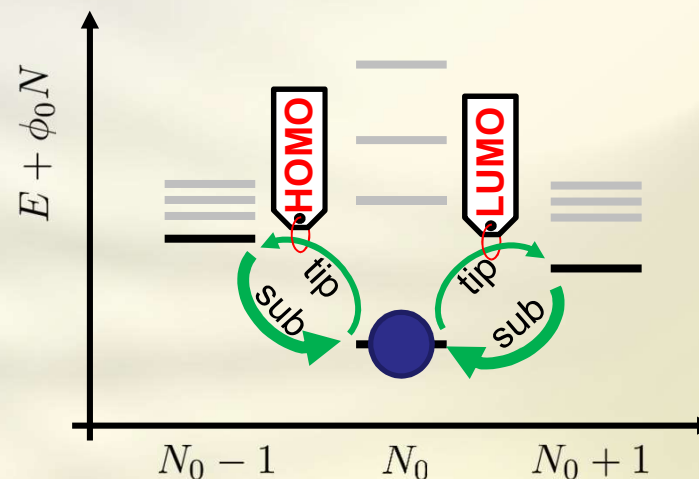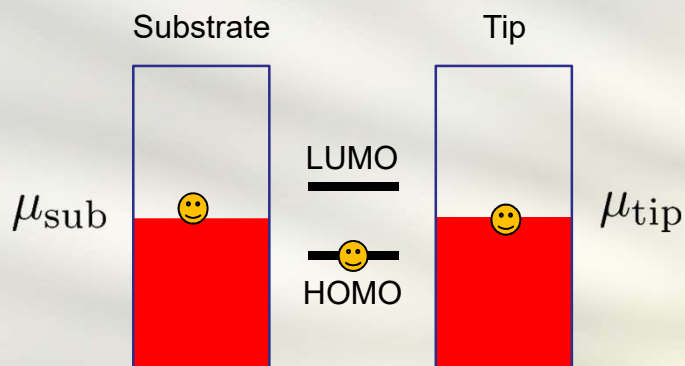
The two approaches only agree for **uncorrelated** systems close to **equilibrium**

Zürich 15.06.2022

Non-equilibrium and correlation

N_0 $N_0 + 1$

Non-equilibrium

LUMO

HOMO

tunnelling

HOMO topography

Correlated system

α + β

tunnelling

Superposition of HOMO & LUMO topography
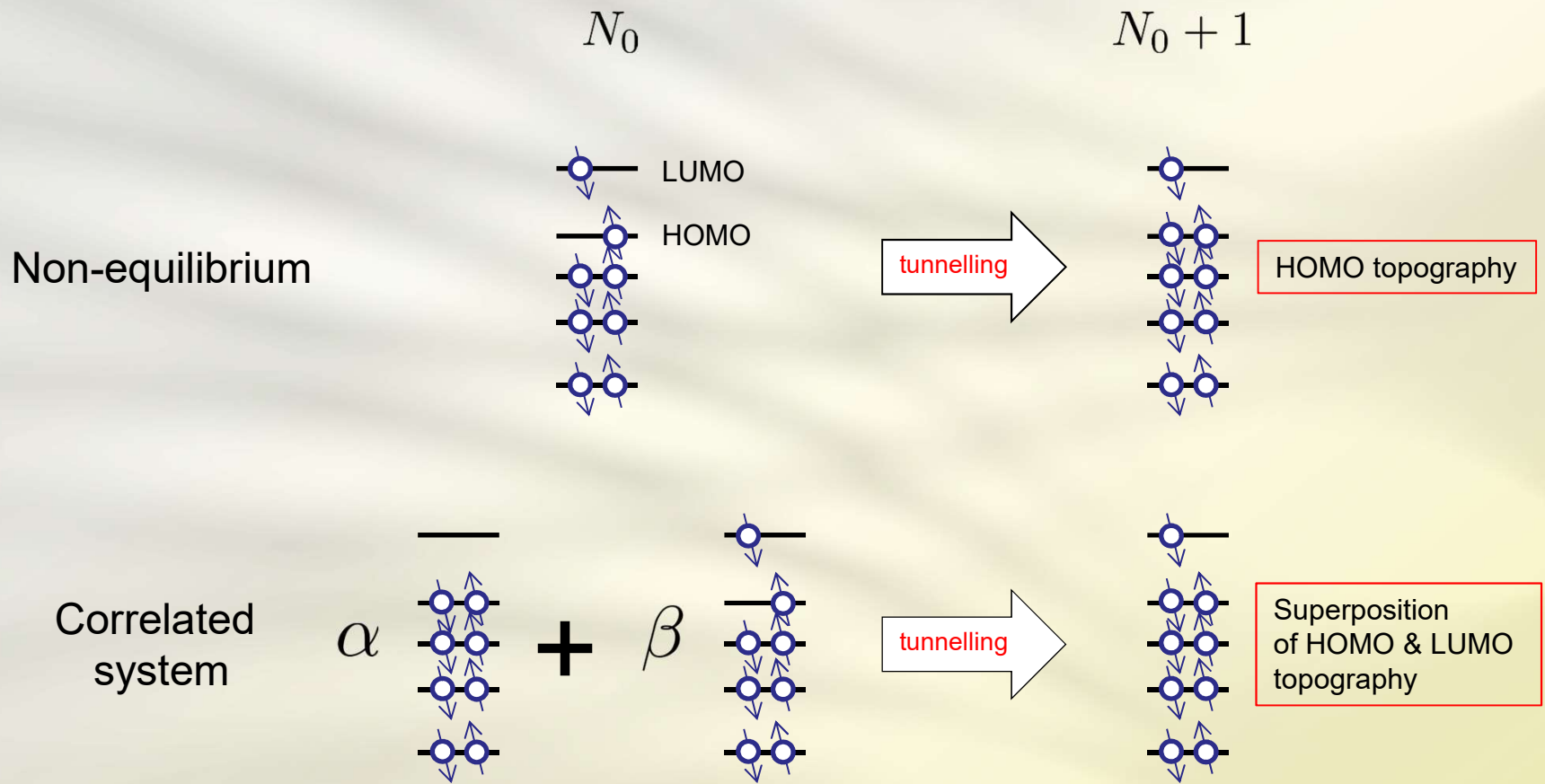
The Hamiltonian

The STM single molecule junction is described by the Hamiltonian

$$\hat{H} = \hat{H}_{\mathrm{mol}} + \hat{H}_{\mathrm{mol-env}} + \hat{H}_{\mathrm{S}} + \hat{H}_{\mathrm{T}} + \hat{H}_{\mathrm{tun}}$$
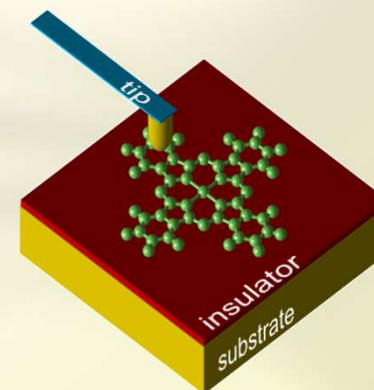
The molecule: **interacting** Hamiltonian for a small set of **frontier orbitals**

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

ϵ_i

Frontier orbitals

Image charge effects
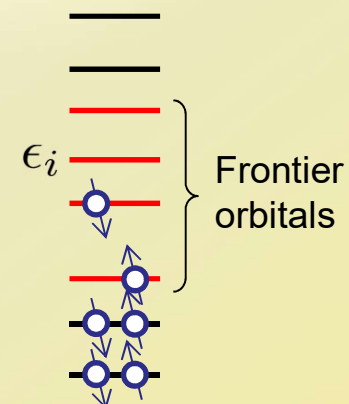
$$\hat{H}_{\mathrm{mol-env}} = -\delta_{\mathrm{ic}}(\hat{N} - N_0)^2$$

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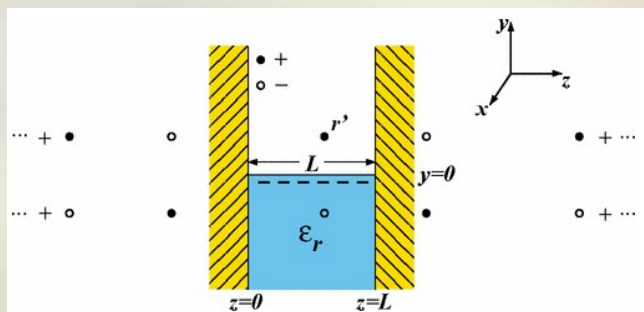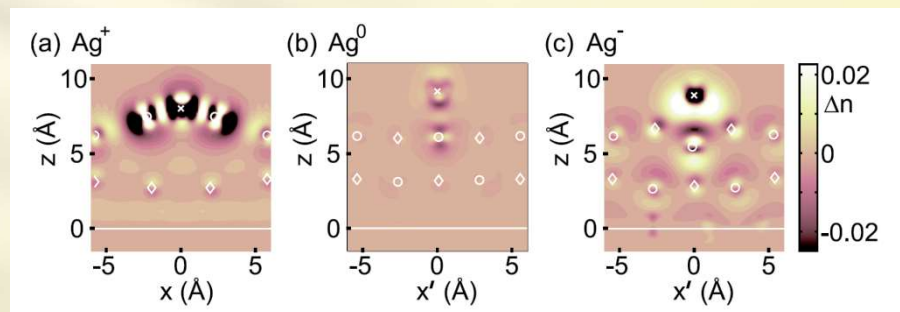
Image charge effect

Polaron formation

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

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**.

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

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

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

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

Transport calculations

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

Coherent dynamics

Effective **internal** dynamics

$$\dot{\sigma} = -\frac{i}{\hbar}[\hat{H}_{\mathrm{mol}} + \hat{H}_{\mathrm{mol-env}}, \sigma] - \frac{i}{\hbar}[\hat{H}_{\mathrm{eff}}, \sigma]$$
$$+ \mathcal{L}_{\mathrm{tun}}[\sigma] + \mathcal{L}_{\mathrm{rel}}[\sigma] := \mathcal{L}[\sigma]$$

Tunnelling dynamics   **Phenom.** relaxation

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

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

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

Tunnelling Liouvillean

$$\mathcal{L}_{\text{tun}}\sigma^{NE} = -\frac{1}{2}\sum_{\chi\tau}\sum_{ij}\left\{\mathcal{P}_{NE}\left[d_{i\tau}^{\dagger}\Gamma_{ij}^{\chi}(E-H_{\text{m}})f_{\chi}^{-}(E-H_{\text{m}})d_{j\tau}+\right.\right.$$

$$\left.\left.+d_{j\tau}\Gamma_{ij}^{\chi}(H_{\text{m}}-E)f_{\chi}^{+}(H_{\text{m}}-E)d_{i\tau}^{\dagger}\right]\sigma^{NE}+h.c.\right\}$$

$$+\sum_{\chi\tau}\sum_{ijE'}\mathcal{P}_{NE}\left[d_{i\tau}^{\dagger}\Gamma_{ij}^{\chi}(E-E')\sigma^{N-1E'}f_{\chi}^{+}(E-E')d_{j\tau}+\right.$$

$$\left.+d_{j\tau}\Gamma_{ij}^{\chi}(E'-E)\sigma^{N+1E'}f_{\chi}^{-}(E'-E)d_{i\tau}^{\dagger}\right]\mathcal{P}_{NE}$$

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

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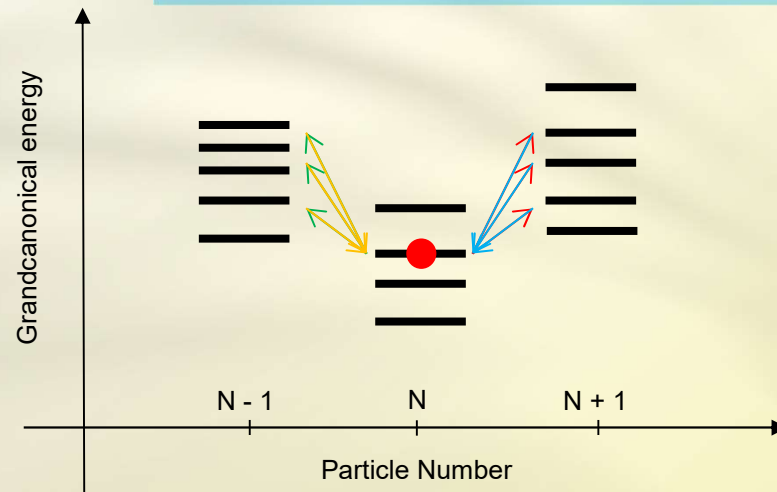
$$H_{\text{eff}} = \frac{1}{2\pi} \sum_{NE} \sum_{\chi\sigma} \sum_{ij} \mathcal{P}_{NE} \left[d_{i\sigma}^\dagger \Gamma_{ij}^\chi (E - H_{\text{m}}) p_\chi (E - H_{\text{m}}) d_{j\sigma} \right.$$
$$\left. + d_{j\sigma} \Gamma_{ij}^\chi (H_{\text{m}} - E) p_\chi (H_{\text{m}} - E) d_{i\sigma}^\dagger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

Effective
Hamiltonian

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

Current
operator

$$\Gamma_{ij}^\chi (\Delta E) = \frac{2\pi}{\hbar} \sum_{\mathbf{k}} (t_{\mathbf{k}i}^\chi)^* t_{\mathbf{k}j}^\chi \delta(\epsilon_{\mathbf{k}}^\chi - \Delta E)$$
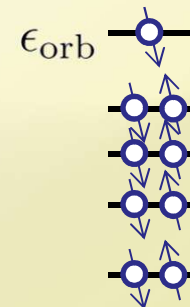
S. Sobczyk, A. Donarini, and M. Grifoni, *PRB* **85**, 205408 (2012)

Many-body rate matrix

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

$$R^{\chi\tau}_{N\,E_0 \to N+1\,E_1} = \sum_{ij} \langle N+1E_1|d^\dagger_{i\tau}|NE_0\rangle \Gamma^\chi_{ij}(E_1 - E_0) \times$$

$$\langle NE_0|d_{j\tau}|N+1E_1\rangle f^+(E_1 - E_0 - \mu_\chi)$$

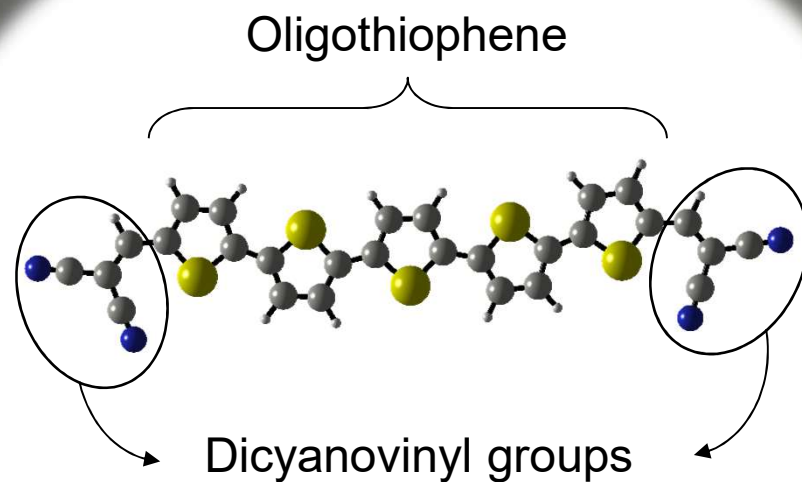For **uncorrelated** and **non-degenerate systems** the many-body rate reduces to

$$R^{\chi\tau}_{N\,E_0 \to N+1\,E_1} = \Gamma^\chi_{\mathrm{orb}}(\epsilon_{\mathrm{orb}})f^+(\epsilon_{\mathrm{orb}} - \mu_\chi)$$

ϵ_{orb}

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

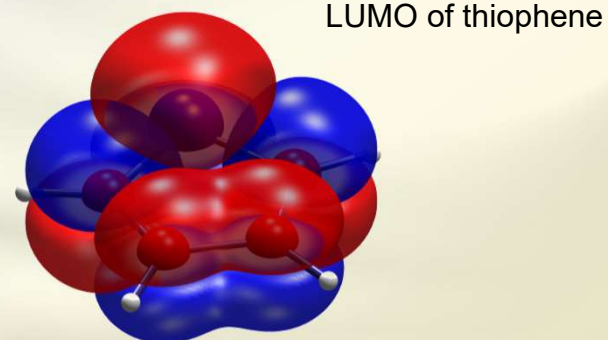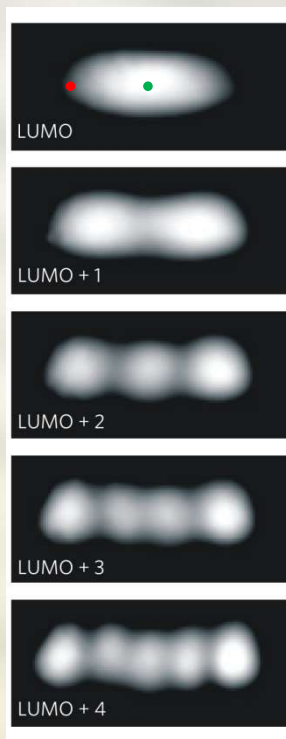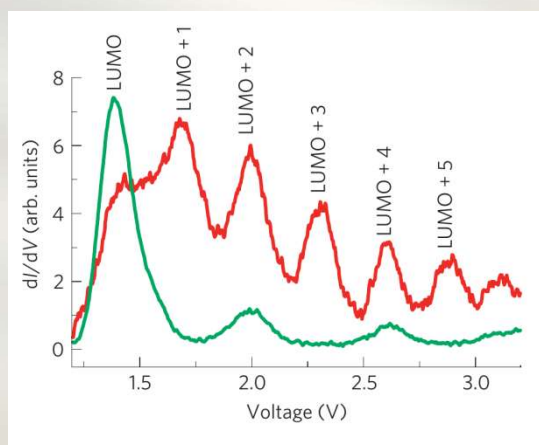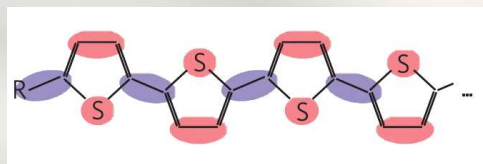S. Sobczyk, A. Donarini, and M. Grifoni, *PRB* **85**, 205408 (2012)

Dicyanovinyl-quinquethiophene

Oligothiophene

Dicyanovinyl groups

Entanglement in the two particles groundstate

Particle-in-a-box like states

In oligothiophenes

LUMO of thiophene

LUMO

LUMO + 1

LUMO + 2

LUMO + 3

LUMO + 4

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

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.
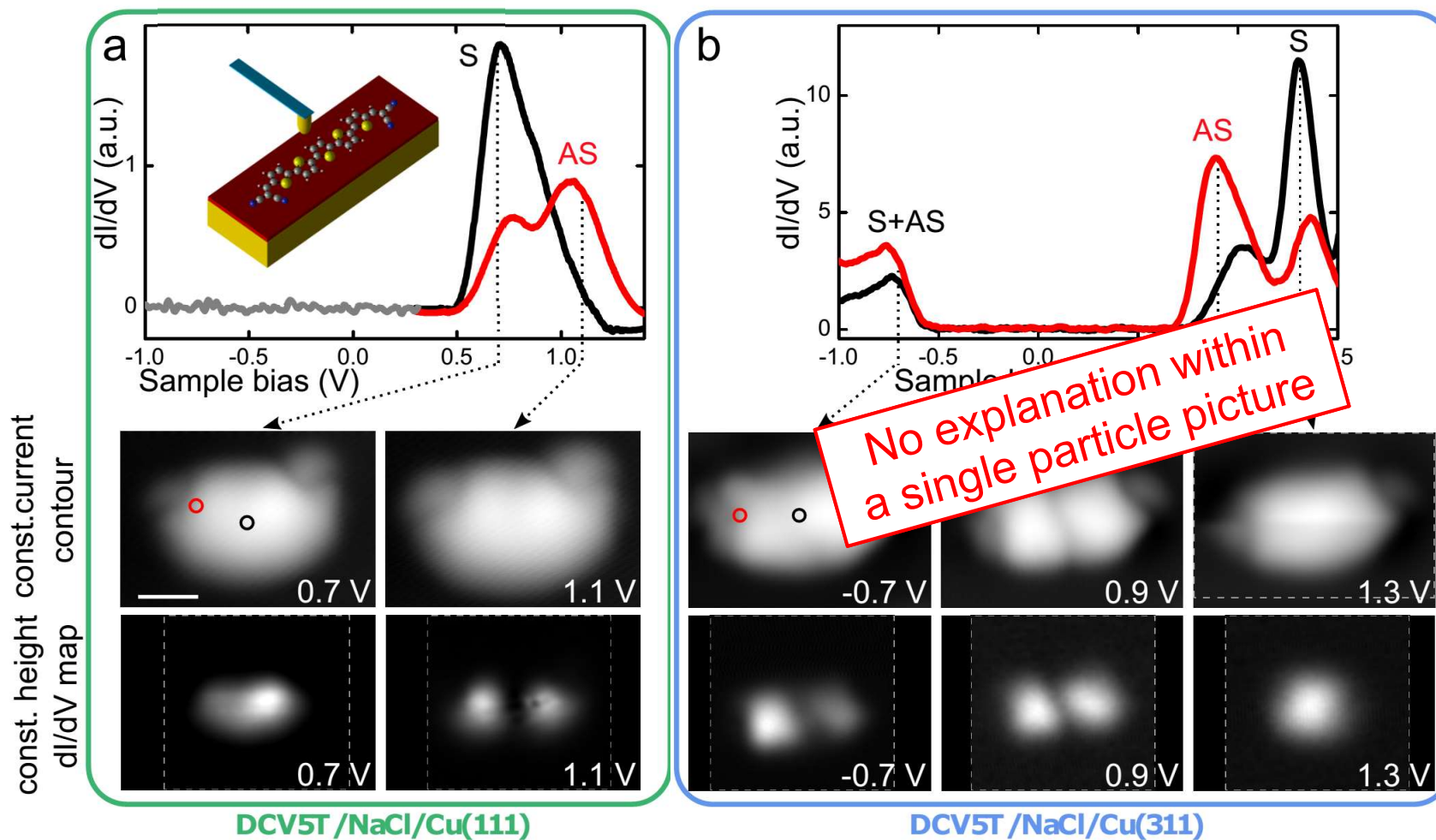
Level-spacing engineering

Quinquethiophene
(5T)
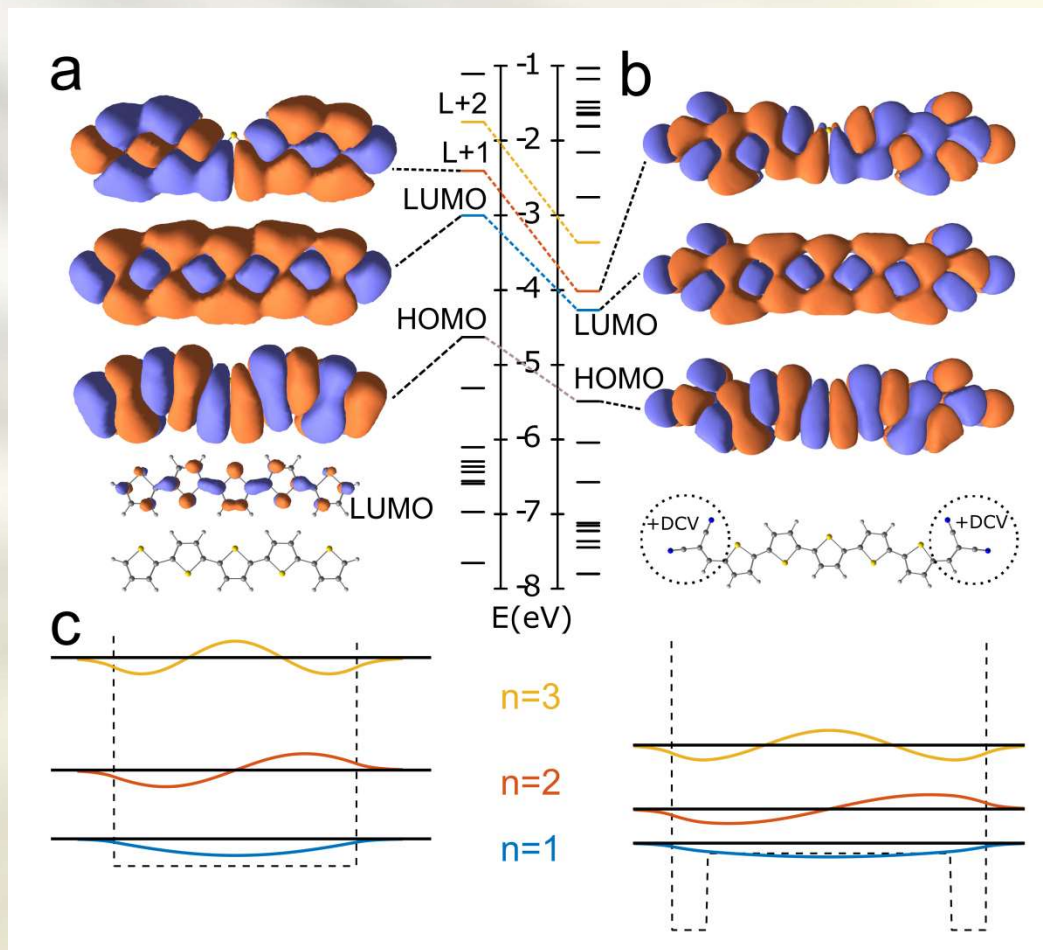
AS

S

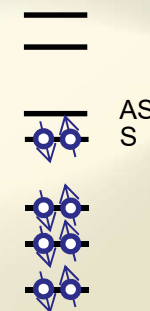Dicyanovinyl-
quinquethiophene
(DCV5T)
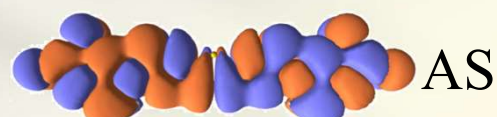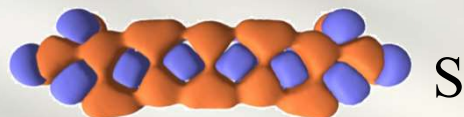
Orbital reversal

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

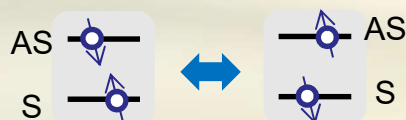# The many-body Hamiltonian

We concentrate on the dynamics of two orbitals only

 S   AS

and freeze the occupation of the other single particle states

$$\hat{H}_{\mathrm{mol}} = \epsilon_{\mathrm{S}}\,\hat{n}_{\mathrm{S}} + \epsilon_{\mathrm{AS}}\,\hat{n}_{\mathrm{AS}} + \frac{U}{2}\,\hat{N}\left(\hat{N}-1\right)$$

$$+ J \sum_{\sigma\sigma'} \hat{d}^{\dagger}_{\mathrm{S}\sigma}\hat{d}^{\dagger}_{\mathrm{AS}\sigma'}\hat{d}_{\mathrm{S}\sigma'}\hat{d}_{\mathrm{AS}\sigma} + J \sum_{\sigma\sigma'} \left(\hat{d}^{\dagger}_{\mathrm{S}\sigma}\hat{d}^{\dagger}_{\mathrm{S}\sigma'}\hat{d}_{\mathrm{AS}\sigma'}\hat{d}_{\mathrm{AS}\sigma} + \mathrm{h.c.} \right)$$

exchange ↓

pair-hopping ↓

$$\Delta = \epsilon_{\mathrm{AS}} - \epsilon_{\mathrm{S}} = 0.3\ \mathrm{eV}$$

fit to the experiment

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

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

calculated from the molecular orbitals
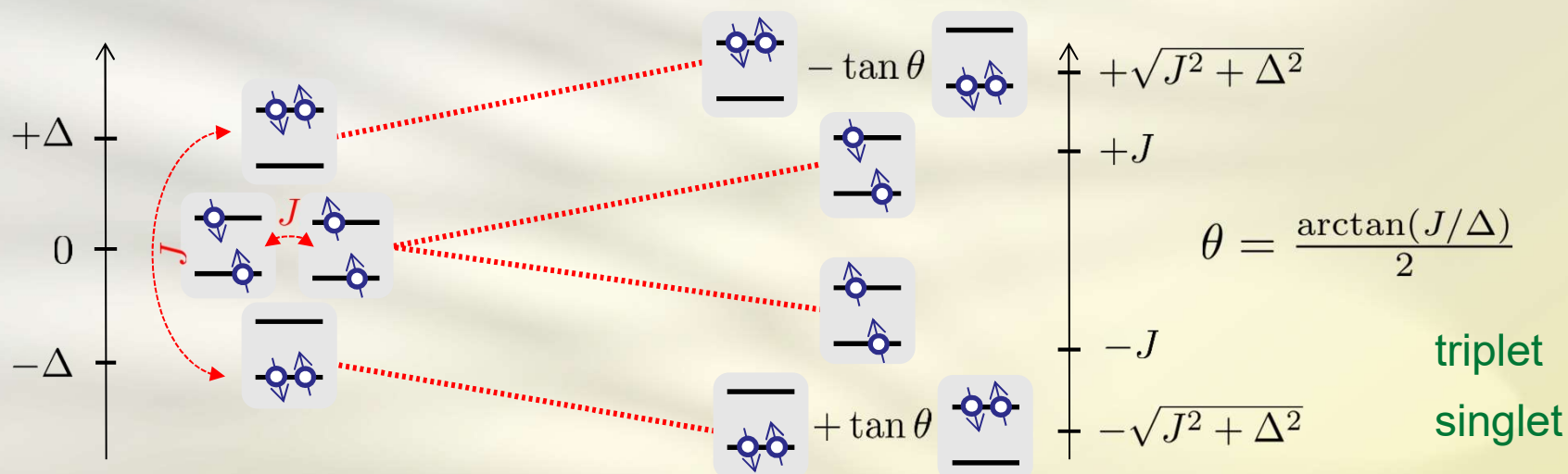
Zürich 15.06.2022

Mechanism of orbital reversal
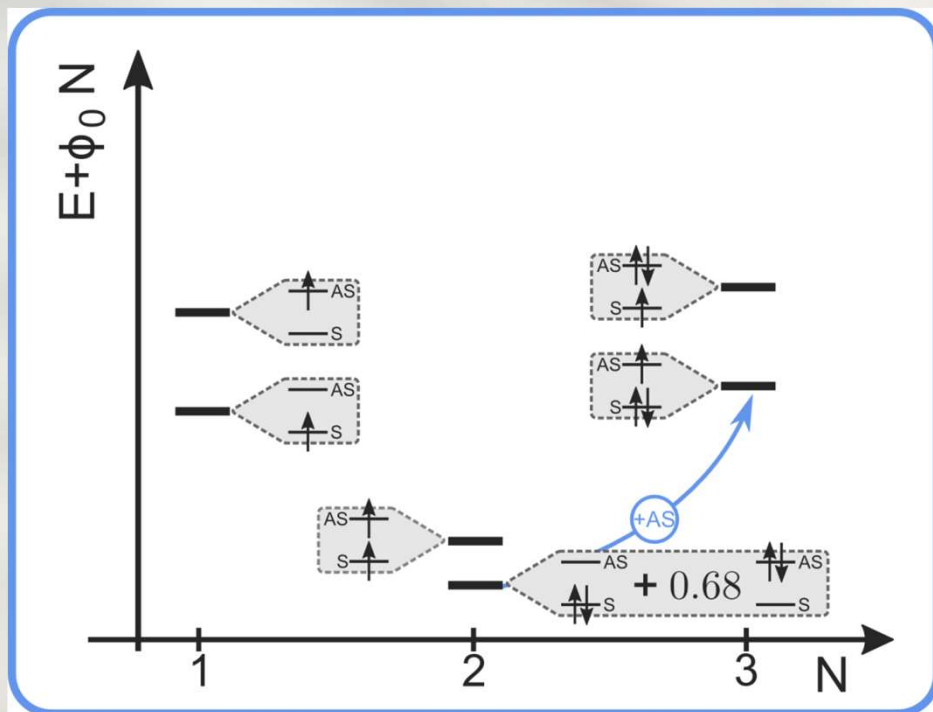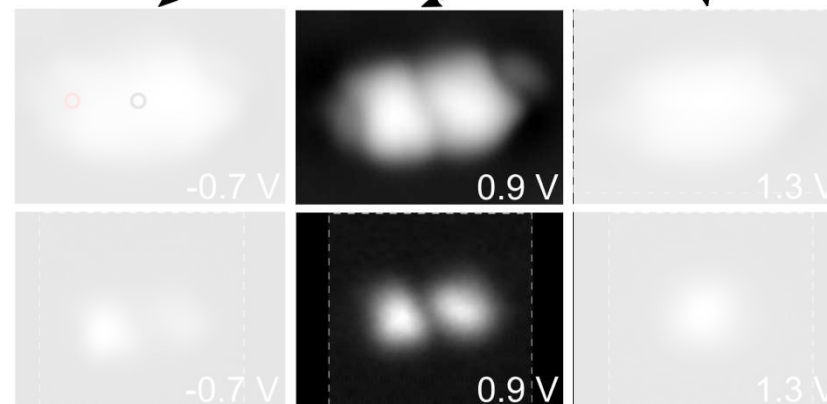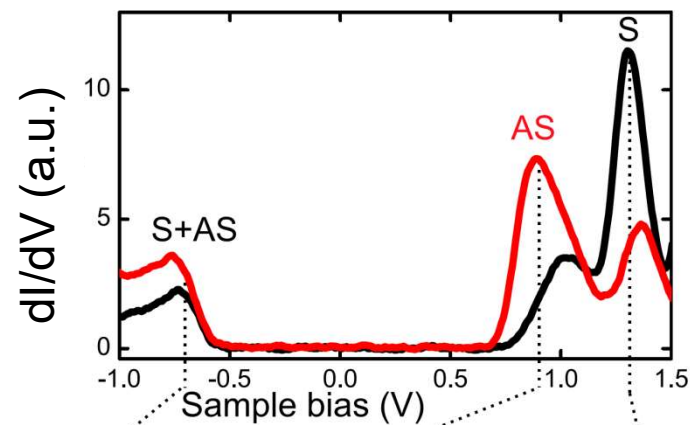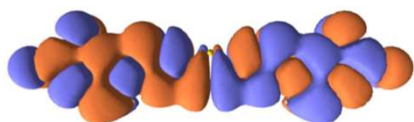
DCV5T/NaCl/Cu(311)

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 $J/\Delta = 0$

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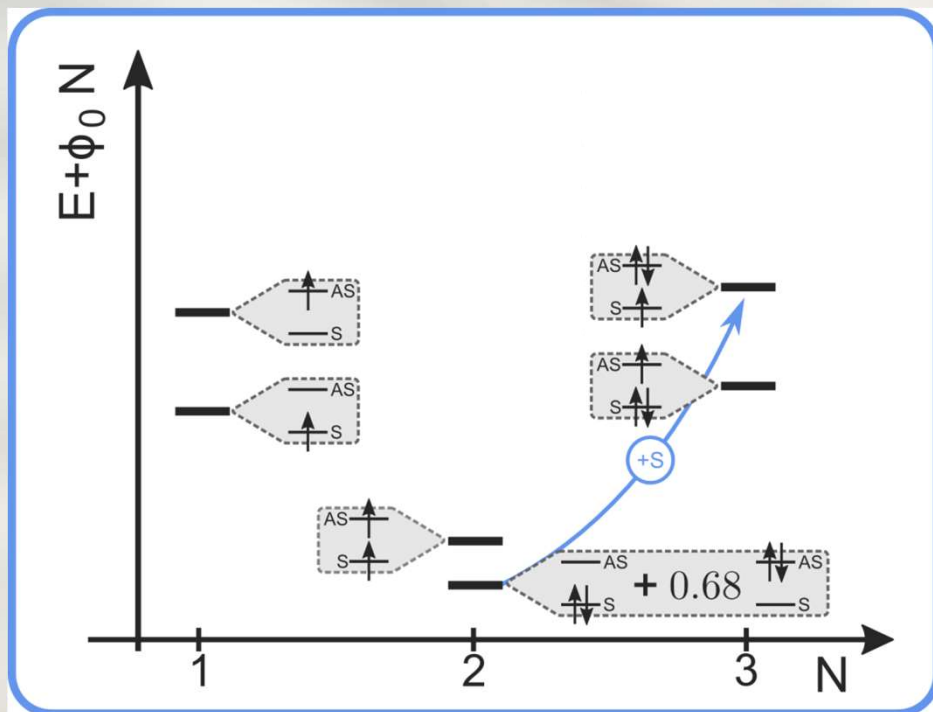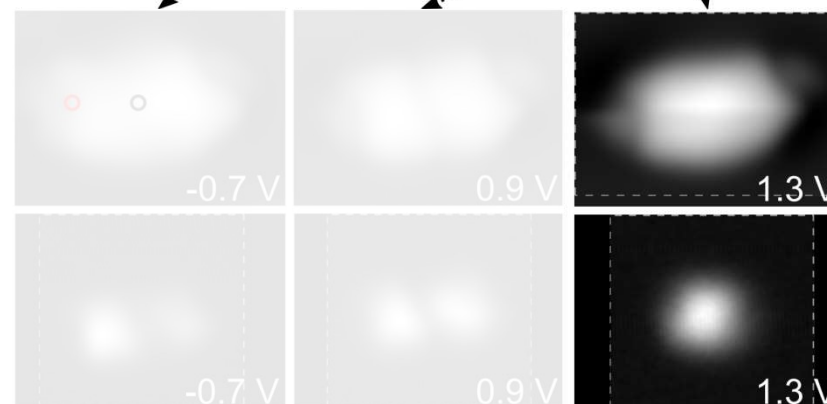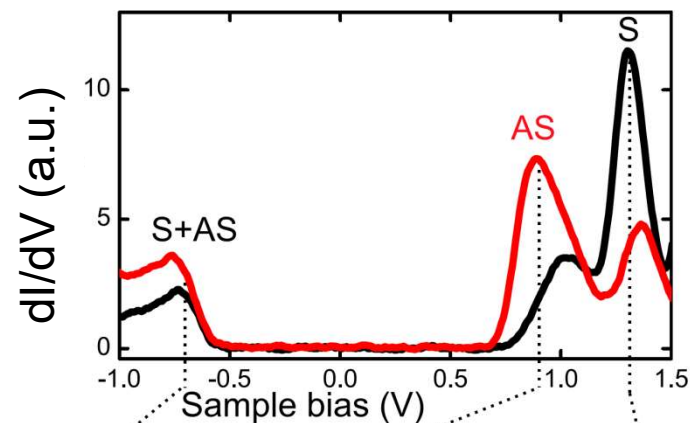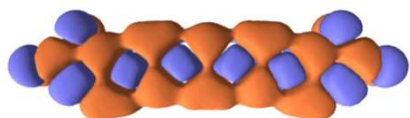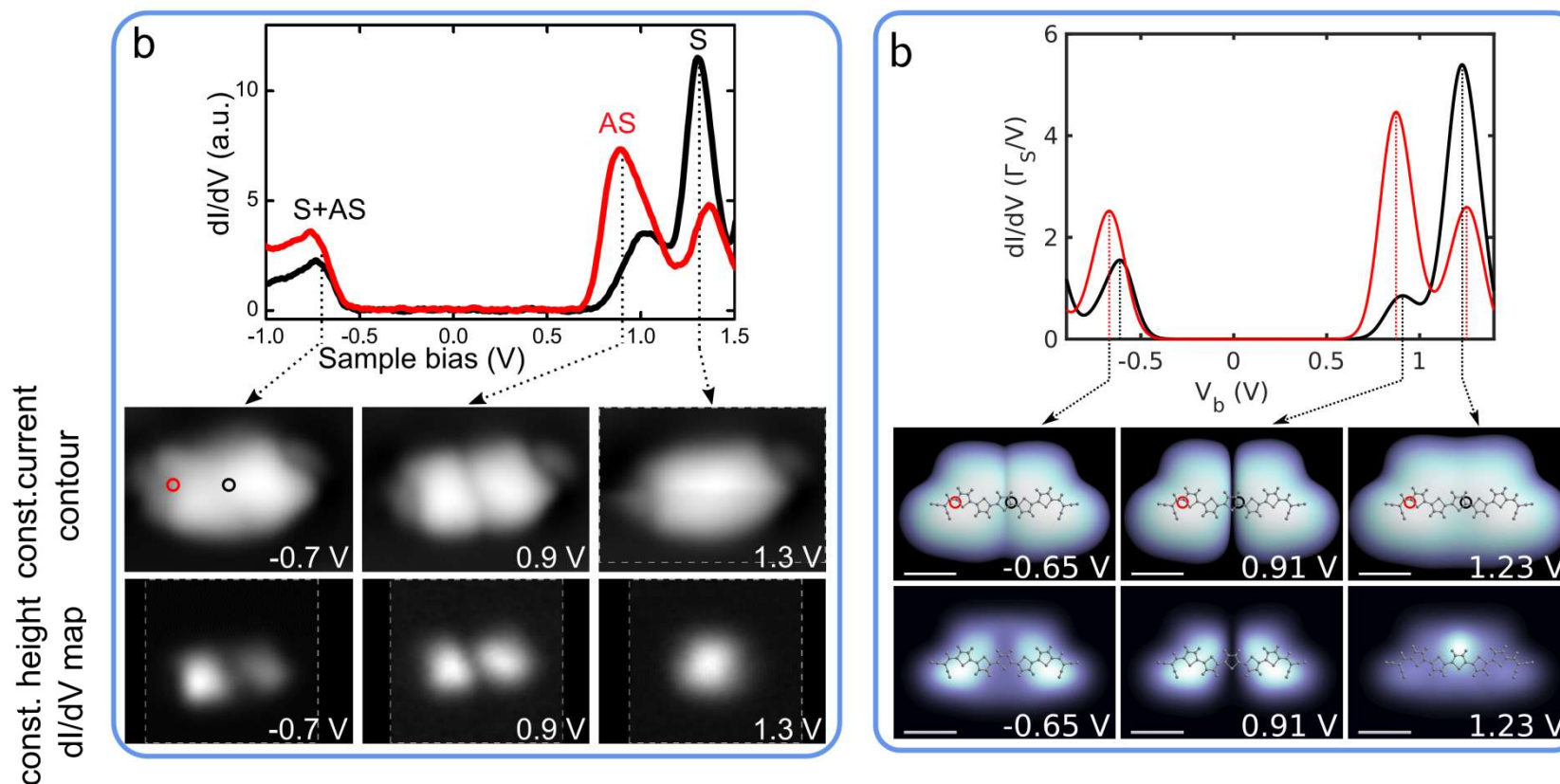
Theory vs. Experiment

DCV5T/NaCl/Cu(311)

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

Conclusions I

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
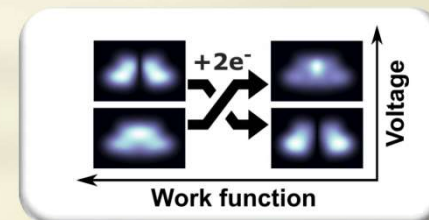
The orbital reversal is the signature of an **entangled ground state** which we understand in terms of a minimal interacting model
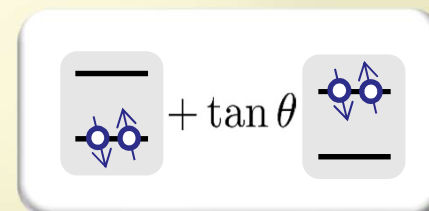
Criteria for such entanglement are clearly formulated in terms of the parameters in the **minimal model** and allow us to **predict** and **control** its occurrence for other molecules.
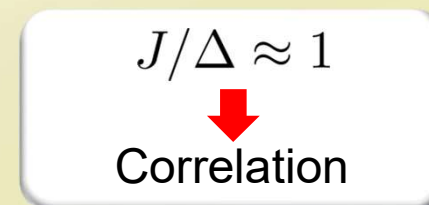
$$J/\Delta \approx 1$$

Correlation

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

Zürich 15.06.2022

Spin crossover

Metal complex

Metal complex

Configuration change
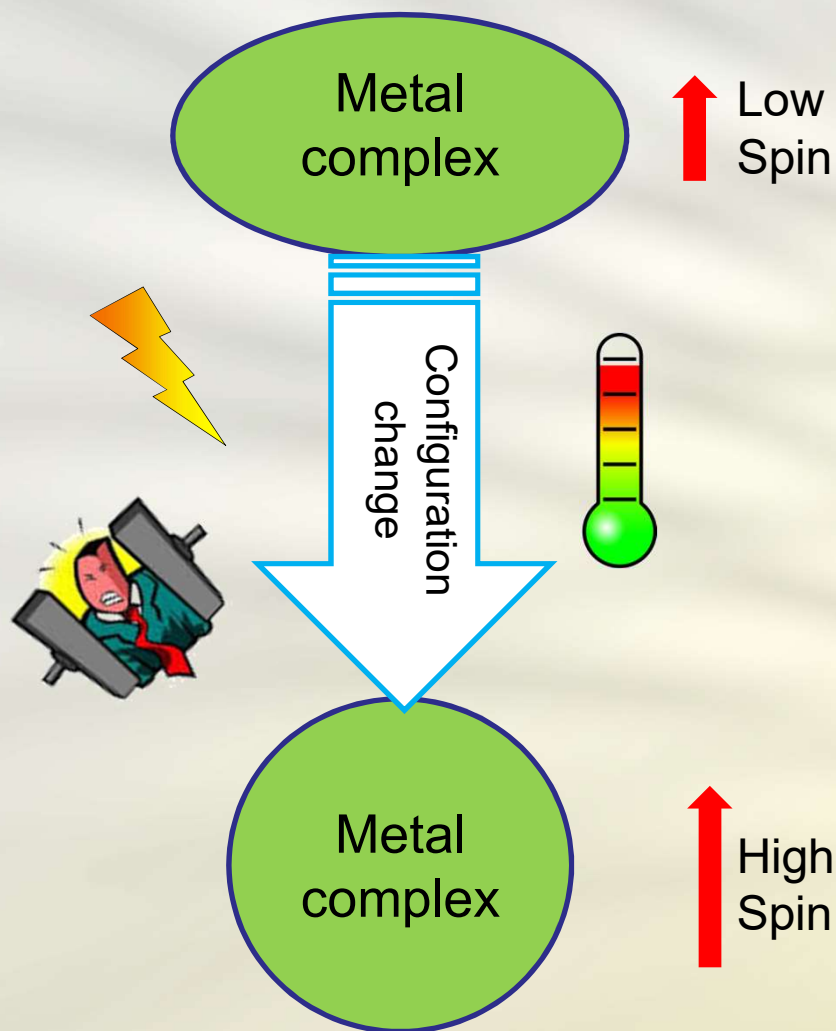
Low Spin

High Spin

Change in the occupation of the metal d-orbitals:

Interplay of:
- (Octahedral) ligand field splitting
- Exchange interaction

Δ_{oct} ligand charging

e_g

t_{2g}

$S = 0$
Low-Spin (LS)

$S = 2$
High-Spin (HS)

(a)

(b)

- C
- N
- Fe

V_b

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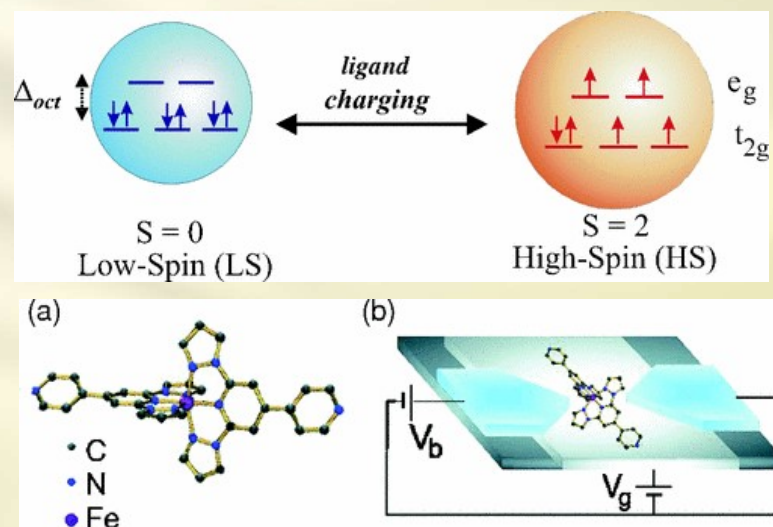
V. Meded, *et al.* PRB **83**, 245415 (2011)

Non equilibrium spin-crossover

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

$V_b = 1.38$ V

B. Siegert, A. Donarini, and M. Grifoni, *PRB* **93**, 121406(R) (2016)

Zürich 15.06.2022

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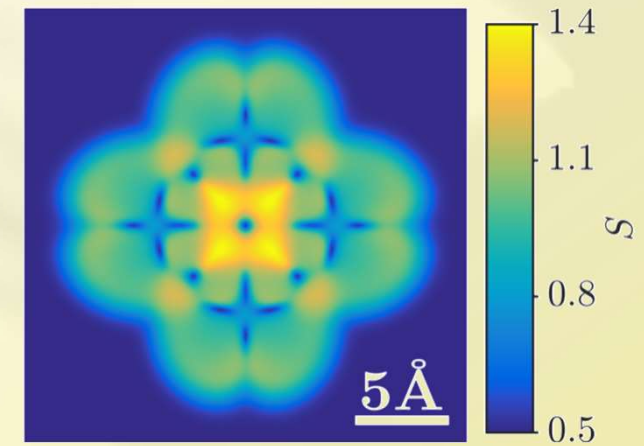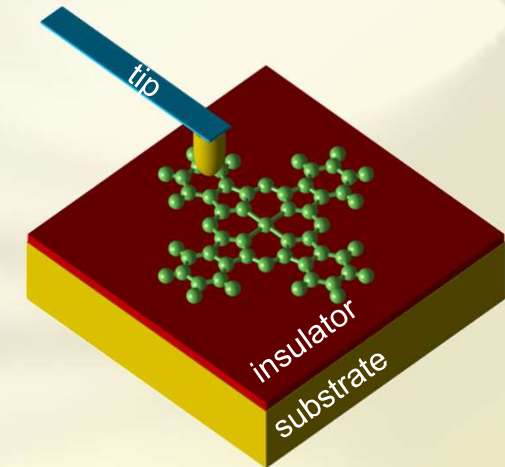
The single particle Hamiltonian is constructed following LCAO schemes of Harrison [1] and Slater-Koster [2].

b_{1g} a_{1u} e_g

$\ell_z = 2$ $\ell_z = 0$ $\ell_z = +1$ $\ell_z = -1$

SOMO   HOMO   LUMO+   LUMO-

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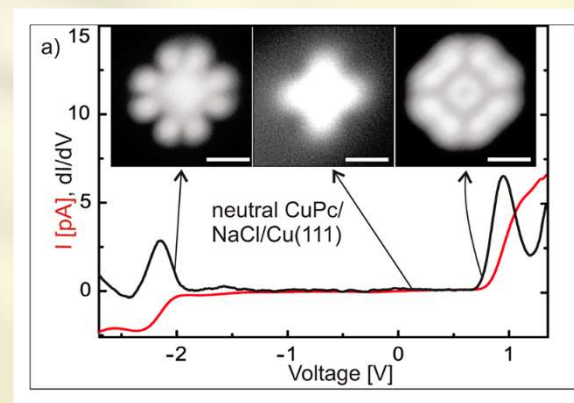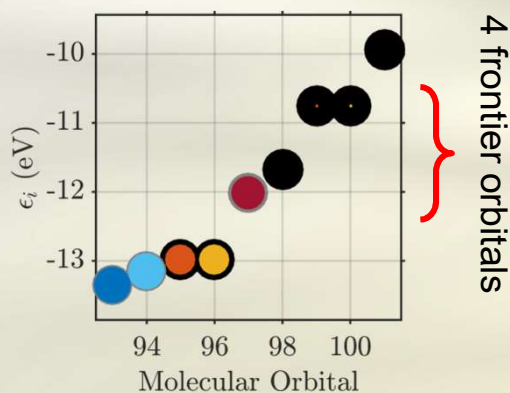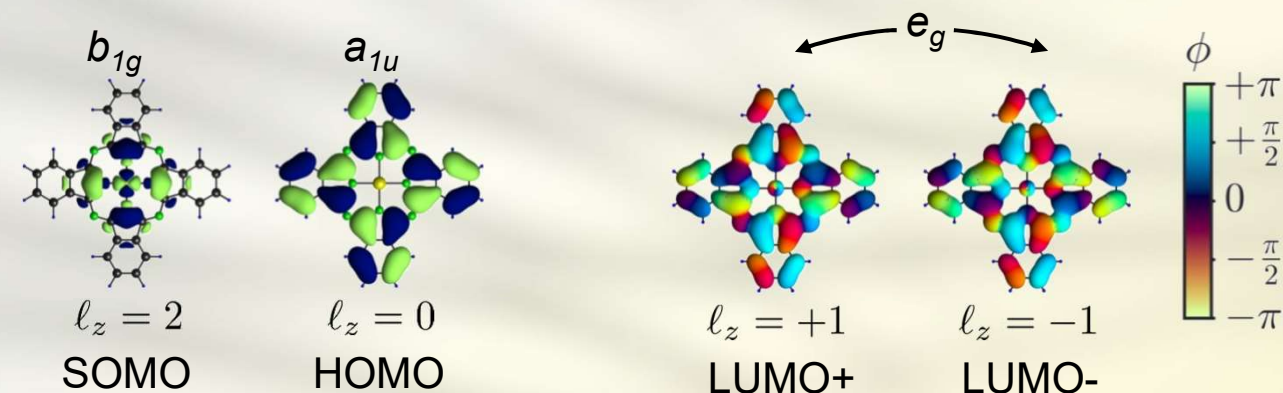
C. Uhlmann et al., *Nano Lett.* **13**, 777 (2013)

[1] S. Froyen and W.A. Harrison, *PRB* **20,** 2420 (1979)
[2] J. C. Slater and G. F. Koster, *Phys. Rev.* **94**, 1498 (1954)

Zürich 15.06.2022

Many-body Hamiltonian

The many-body Hamiltonian for the molecule reads

$$\hat{H}_{\mathrm{mol}} = \sum_{i}(\epsilon_i + \Delta)\,\hat{n}_i + \frac{1}{2}\sum_{ijkl}\sum_{\sigma\sigma'}V_{ijkl}\,\hat{d}^{\dagger}_{i\sigma}\hat{d}^{\dagger}_{k\sigma'}\hat{d}_{l\sigma'}\hat{d}_{j\sigma}$$
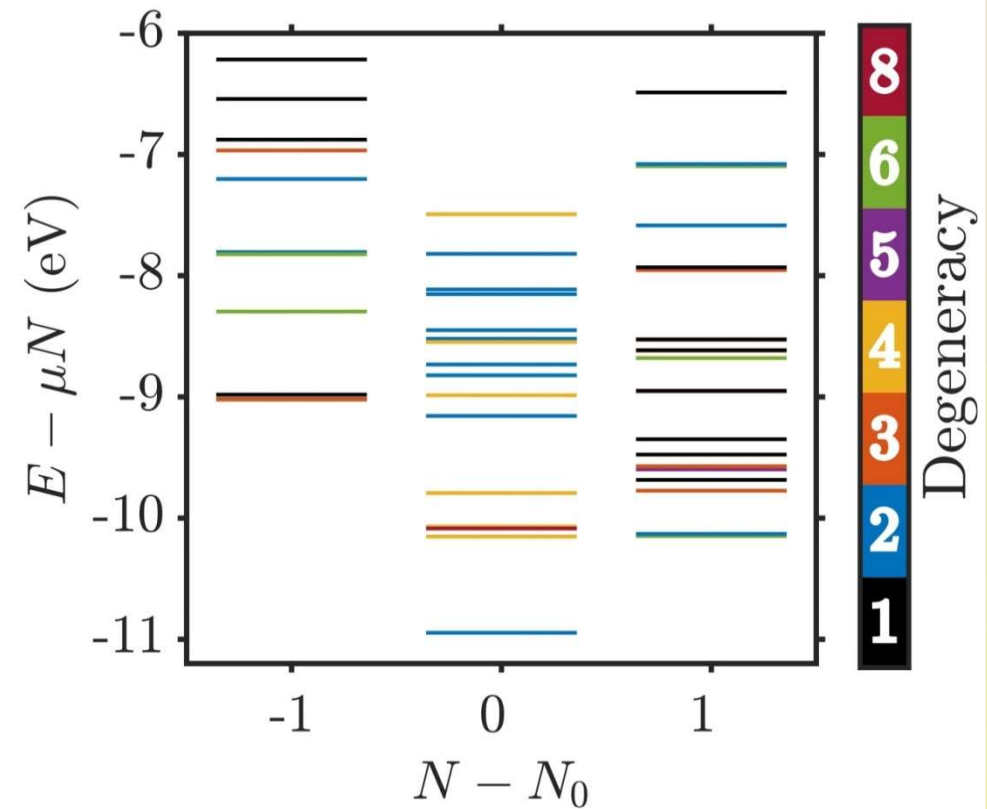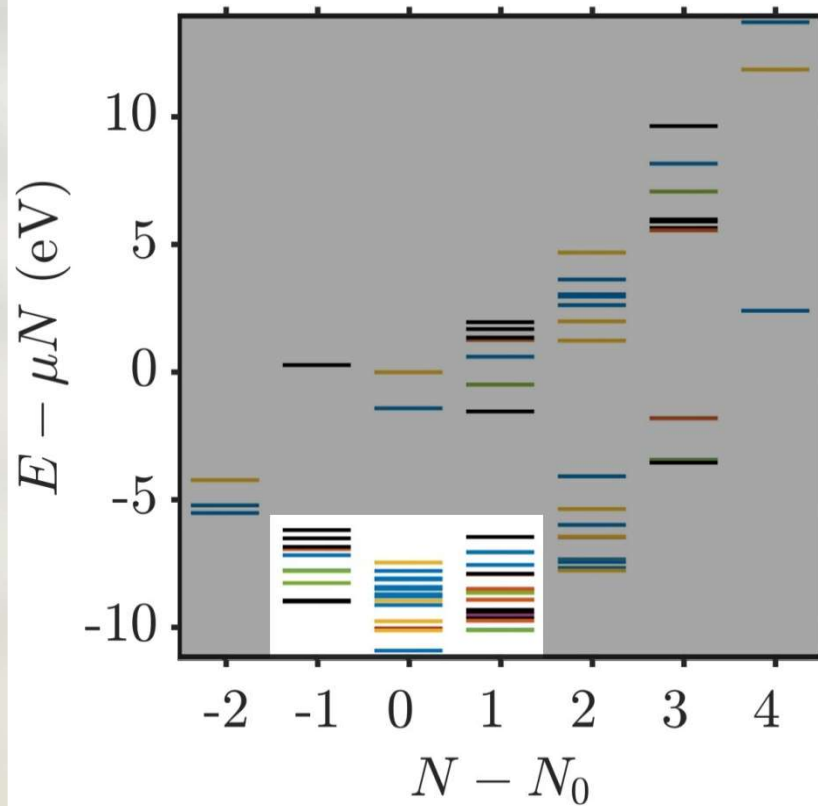
Δ is a free parameter accounting for the crystal field of the core ions and the frozen electrons

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

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

U_S	11.352 eV	$J^{\mathrm{ex}}_{HL} = -\tilde{J}^{\mathrm{p}}_{H+-}$	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	$J^{\mathrm{ex}}_{SL} = -\tilde{J}^{\mathrm{p}}_{S+-}$	9 meV
U_{SL}	1.993 eV	$J^{\mathrm{ex}}_{SH} = J^{\mathrm{p}}_{SH}$	2 meV
U_{HL}	1.758 eV		

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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	

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Topography of CuPc

cationic resonance: $\phi_0 = 4.65$ eV
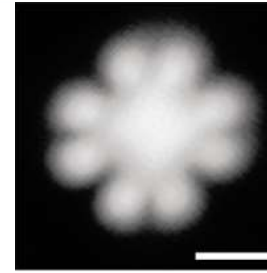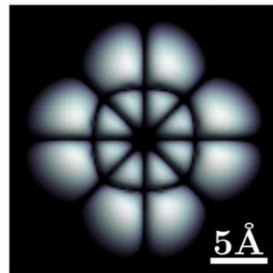
$I_\chi(\mathbf{r}_{\mathrm{T}}, V_{\mathrm{res}}) = 0.5\,\mathrm{pA}$

anionic resonance: $\phi_0 = 4.65$ eV

$I_\chi(\mathbf{r}_{\mathrm{T}}, V_{\mathrm{res}}) = 0.75\,\mathrm{pA}$

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

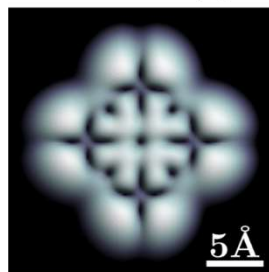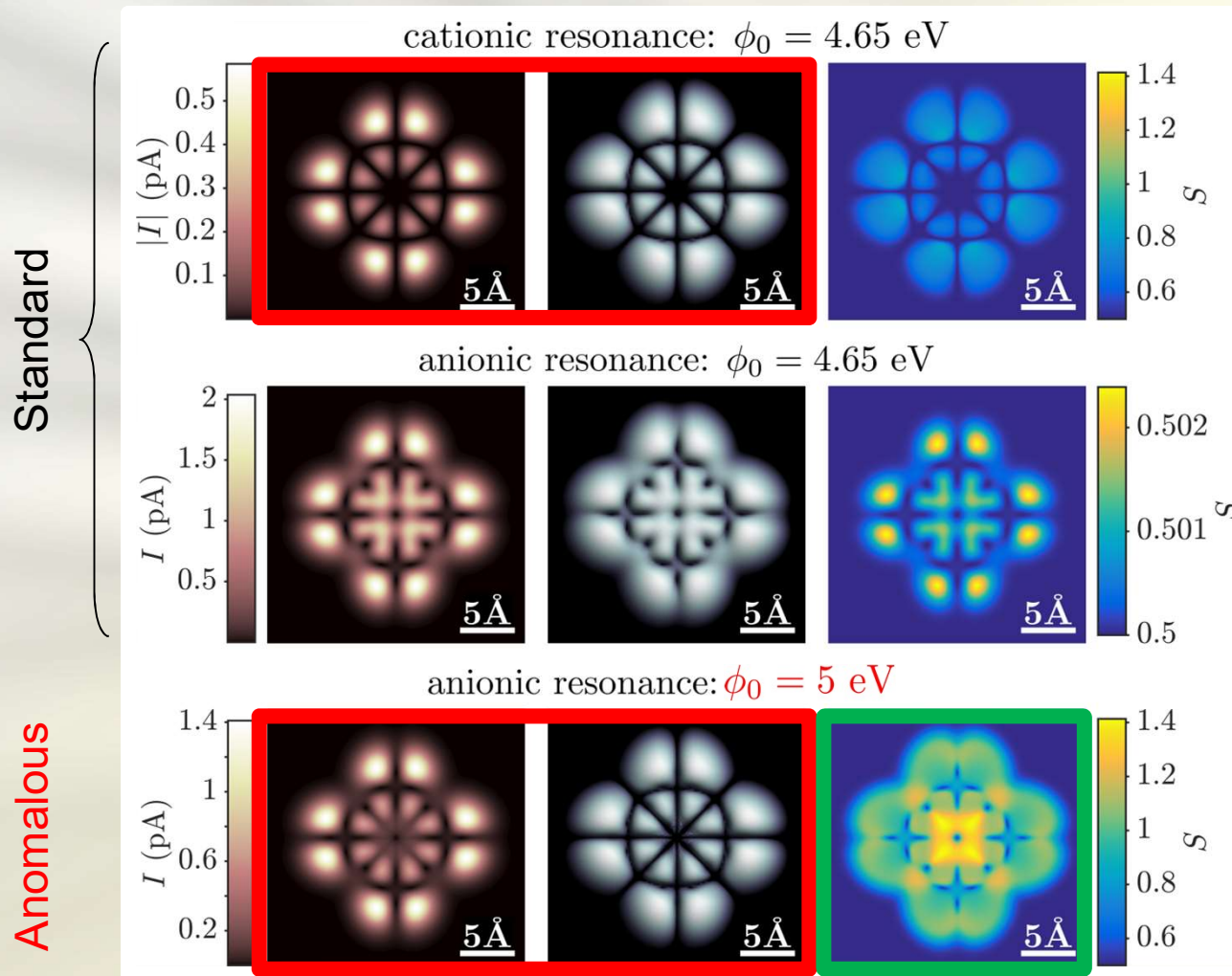B. Siegert, A. Donarini, and M. Grifoni, *PRB* **93**, 121406(R) (2016)
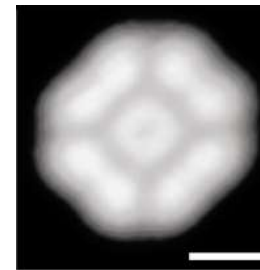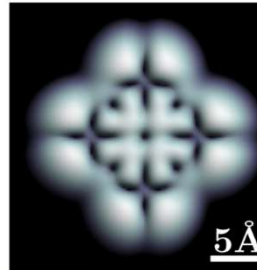
Standard

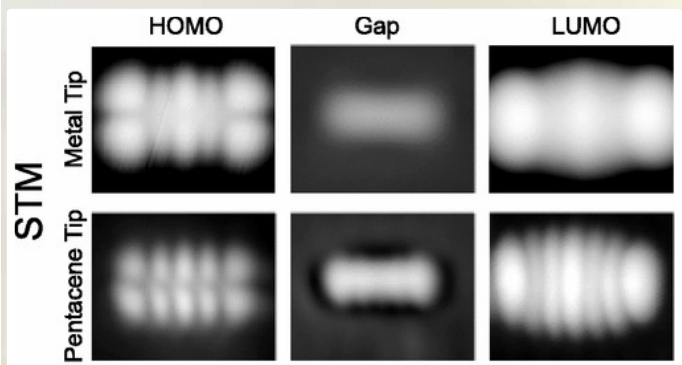cationic resonance: $\phi_0 = 4.65$ eV

5Å

anionic resonance: $\phi_0 = 4.65$ eV

5Å
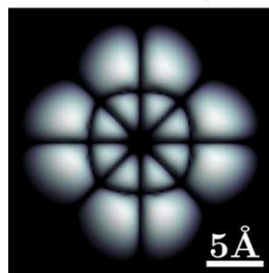
$$S(\mathbf{r}_\mathrm{T}, V_b) = \sqrt{\langle \hat{S}^2 \rangle (\mathbf{r}_\mathrm{T}, V_b) + \frac{1}{4}} - \frac{1}{2} \quad \text{with} \quad \langle \hat{S}^2 \rangle (\mathbf{r}_\mathrm{T}, V_b) = \mathrm{Tr}_\mathrm{mol} \left(\hat{S}^2 \rho_\mathrm{red}^\infty (\mathbf{r}_\mathrm{T}, V_b) \right)$$

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Standard vs. anomalous

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Anomalous current maps

Standard

Anomalous

$E - \mu_0 N$

HOMO

LUMO

tip

sub

sub

tip

?

sub

tip

tip

N_0-1 N_0 N_0+1 N_0-1 N_0 N_0+1 N_0-1 N_0 N_0+1

HOMO   Gap   LUMO

STM   Metal Tip

Pentacene Tip

J.Repp et al. *PRL* **94**, 026803 (2005)
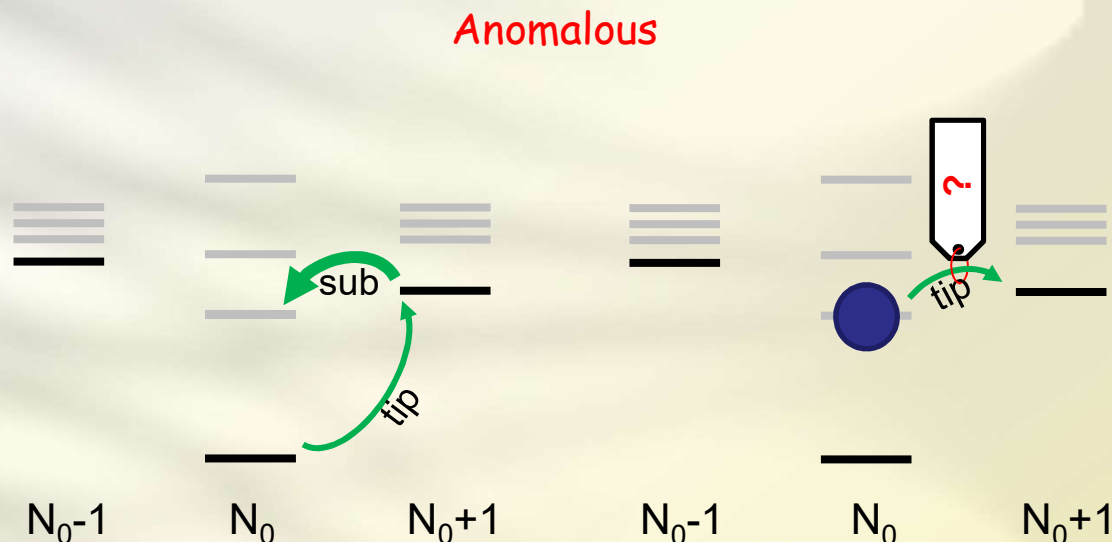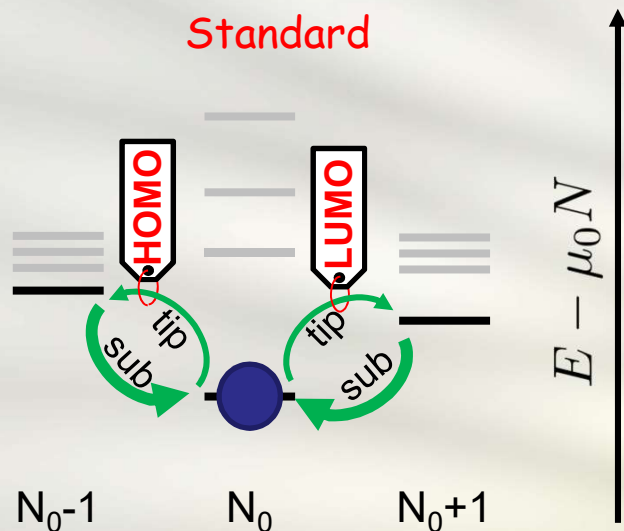
The **anomalous current map** depends on the nature of the excited state

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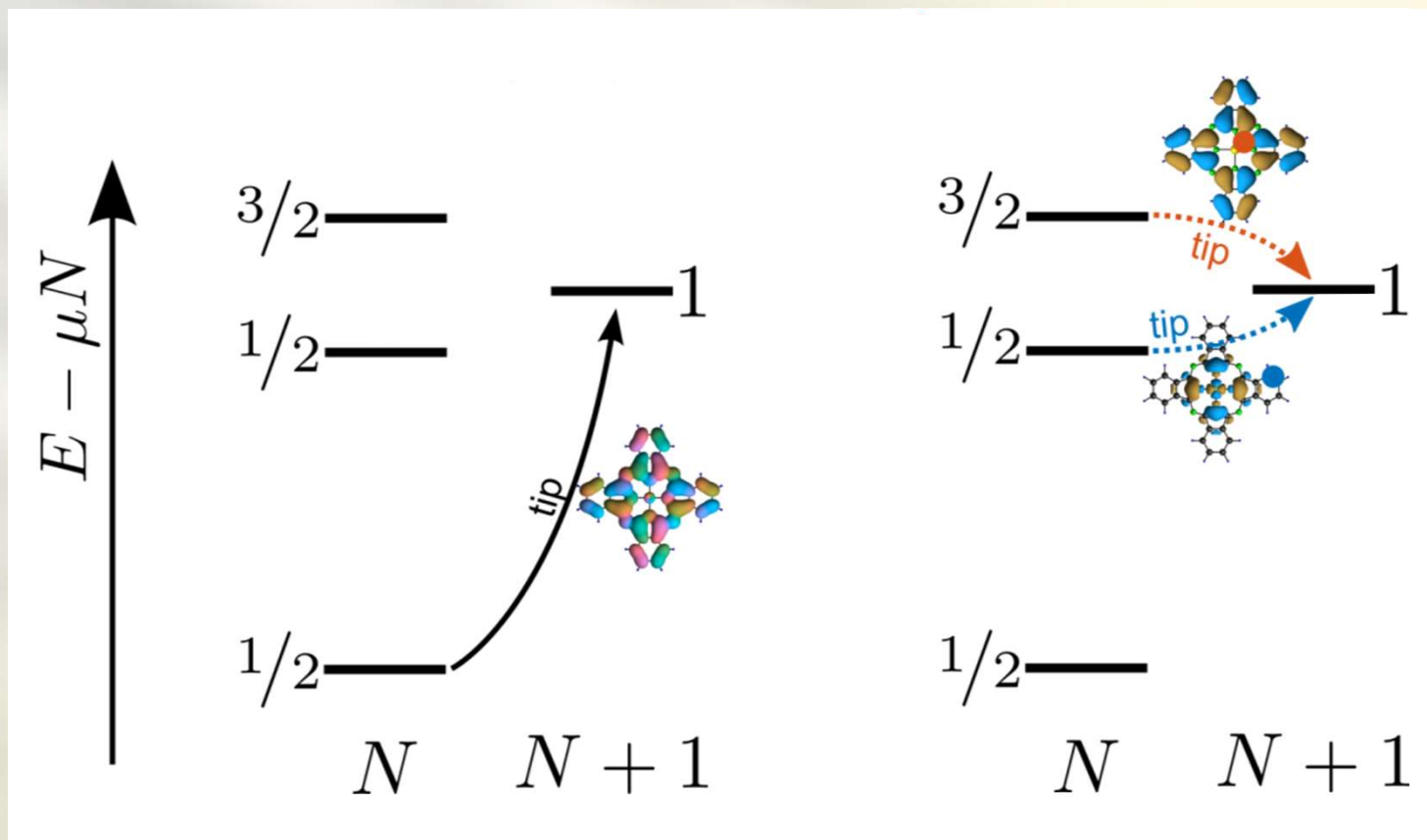
Population inversion

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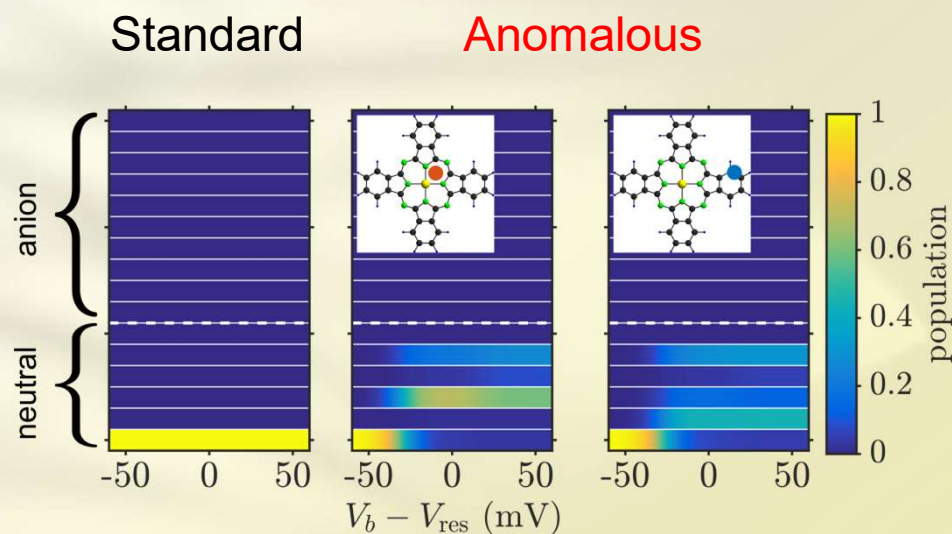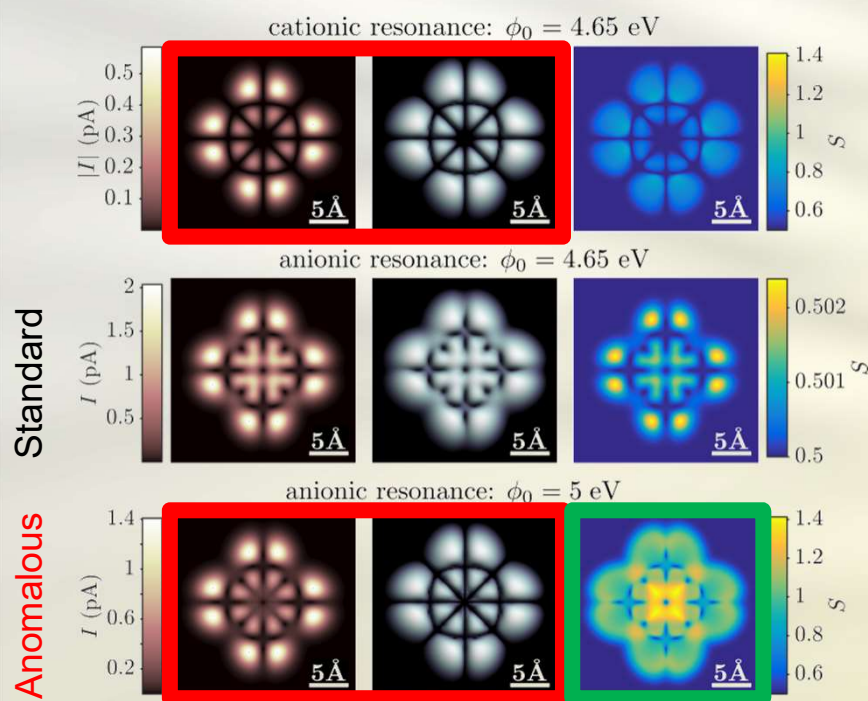
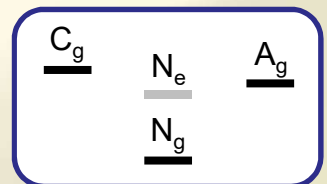The molecule undergoes a **population inversion** which depends on the tip position

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Is CuPc so special ?

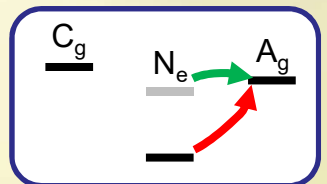Necessary and sufficient conditions for the appearance of non equilibrium spin-crossover:

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

$$C_g \qquad N_e \qquad A_g$$
$$N_g$$

2 The spin of the gr~~ound~~ ~~sta~~te should be different

$$S_{Ng} \neq S_{Ne}$$

> Closed shell conjugated molecules

3 The (tip) transiti~~on~~ ~~st~~ate and the neutral grou~~nd~~ ~~ha~~ve different molecular orbital~~s~~

$$C_g \qquad N_e \longrightarrow A_g$$

4 The tip and substrat~~e~~ ~~stro~~ngly asymmetric

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

> STM on thin insulating films

5 The (intrinsic) relaxa~~tion~~ ~~su~~bstrate should be low (i.e. comparable ~~ate)~~

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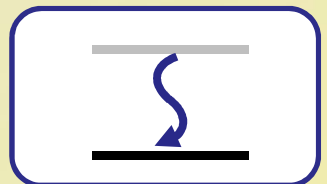
A class of single molecule junctions

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

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

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

$\phi_0 =$ Substrate workfunction

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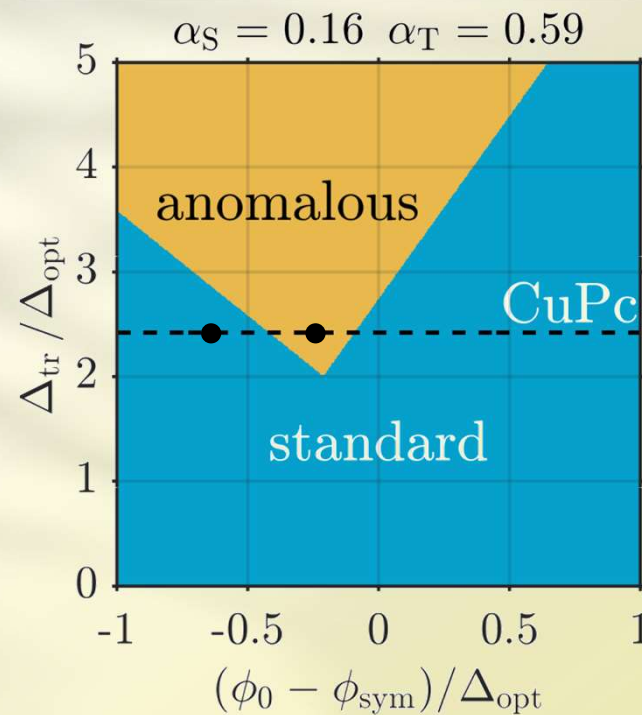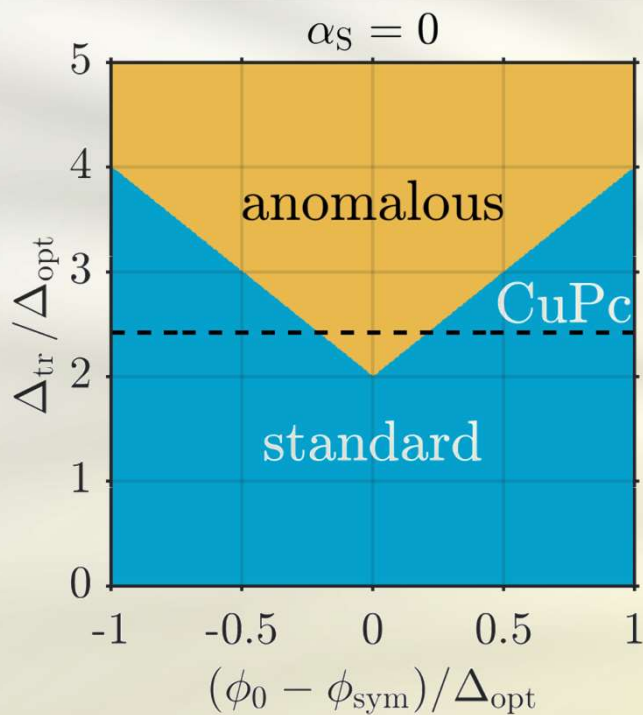
- We developed a **minimal model** for the Cu-Phthalocyanine in terms of **four interacting frontier orbitals**.

- 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.

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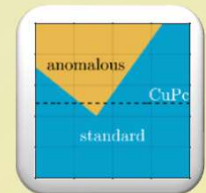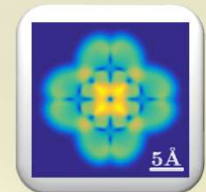
Aknowledgments

Theory

Milena Grifoni   Benjamin Siegert   Sandra Sobczyk

Experiment

Nemania Kocić   Ping Yu   Jascha Repp
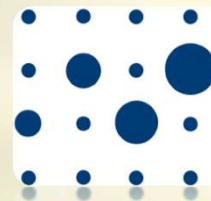
GRK 1570   SFB 689   VolkswagenStiftung

Lichtenberg Programm

Thank you for your attention