Spin-orbit coupling and many-body correlations in STM transport through Cu-phthalocyanine

Benjamin Siegert, Andrea Donarini and Milena Grifoni

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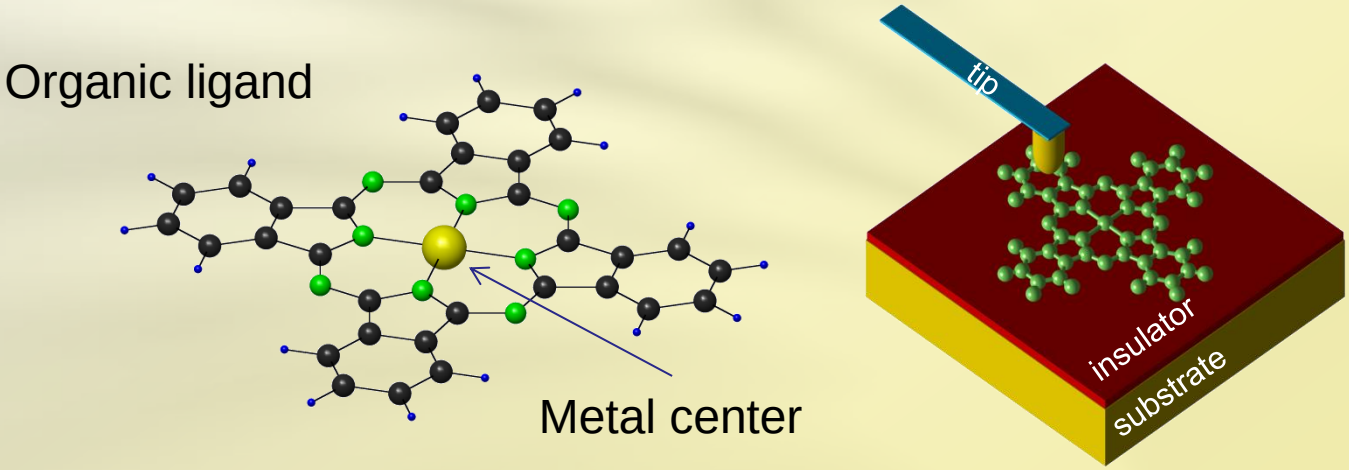
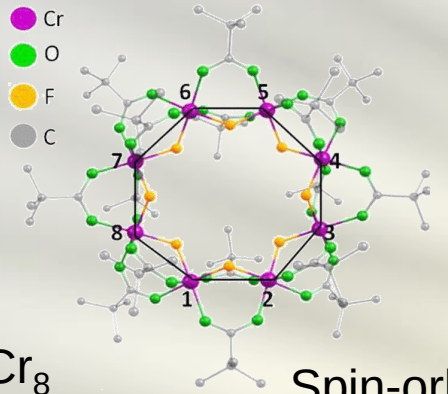


Motivation



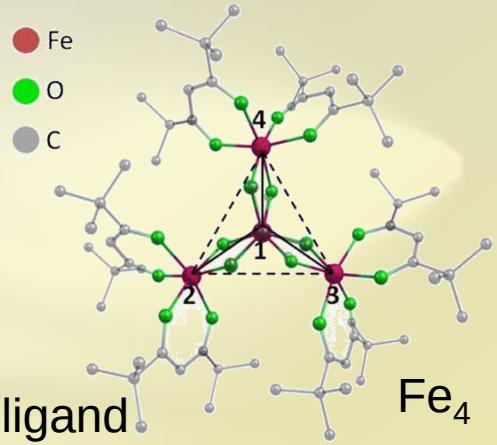
Cr_8

Metal organic complexes

Spin-orbit coupling
on the metal center(s)

+

Specific organic ligand
configuration
(ligand and crystal fields)



Fe_4

Magnetic anisotropy at the molecular scale

Single molecule magnets

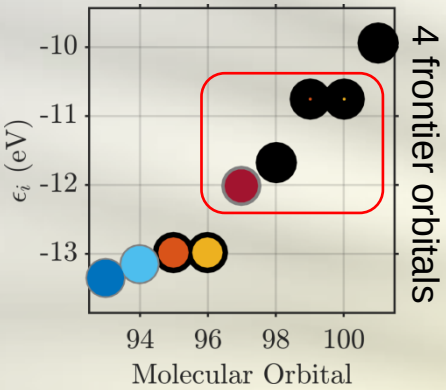
Metal-organic coordination networks

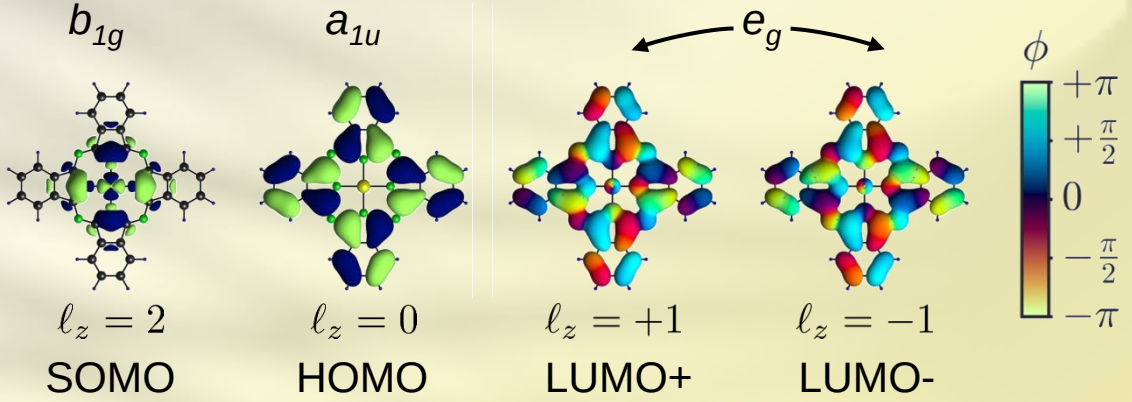
High density information storage devices

D. Gatteschi, R. Sessoli, J. Villain, *Molecular Nanomagnets,* Oxford University Press, (2006)
A. Chiesa, S. Carretta, P. Santini, G. Amoretti, E. Pavarini, *Phys. Rev. Lett.*, **110**, 157204 (2013)
J. S. Miller, *Chemical Society Reviews* **40,** 3266 (2011)

Minimal basis set

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

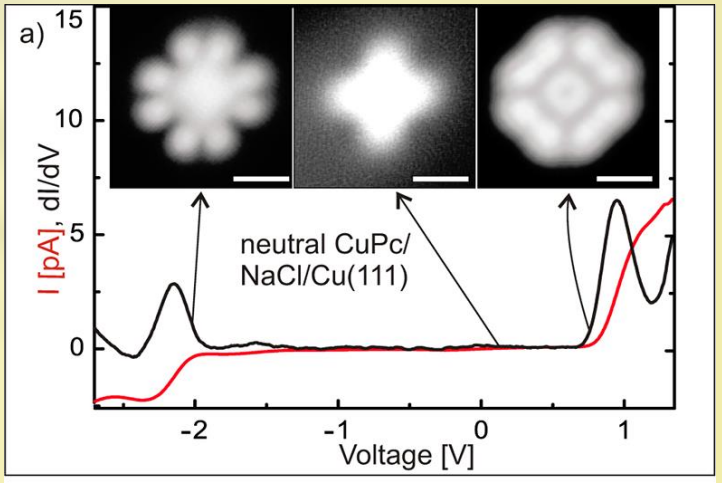




We restrict ourselves to the Fock space spanned by:

$$|\Psi\rangle \approx |\underbrace{11\ldots11}_{2N_f}\underbrace{n_{k\uparrow}n_{k\downarrow}\ldots n_{l\uparrow}n_{l\downarrow}}_{2N_d}\underbrace{00\ldots00}_{2N_e}\rangle$$

Frozen | Dynamical | Empty



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)

Many-body Hamiltonian

The many-body Hamiltonian for the molecule reads

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

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

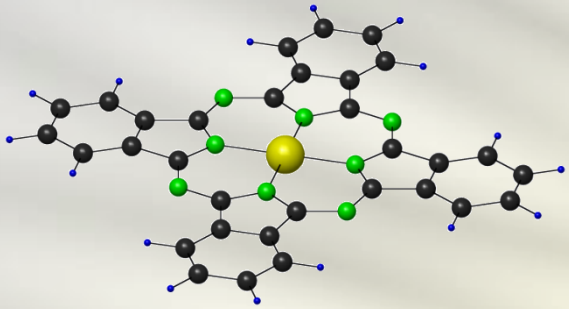
V_{ijkl} are ALL Coulomb integrals among the dynamical orbitals

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

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		

B. Siegert, A. Donarini, and M. Grifoni arXiv:1507.05504. Accepted in *PRB Rapid Comm*.

SOI in the frontier orbitals basis

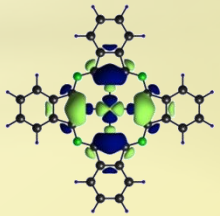


$$\hat{V}_{\mathrm{SO}} = \sum_{\alpha,\ell_\alpha} \xi_{\ell_\alpha}\, \hat{\boldsymbol{\ell}}_\alpha \cdot \hat{\mathbf{s}}_\alpha$$

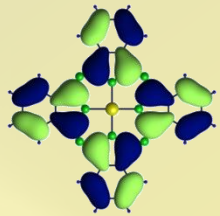
The dominant contribution is given by the *d*-orbitals of Cu

Projection onto the frontier orbital basis yields

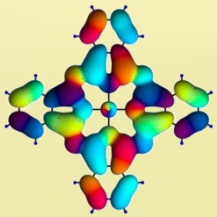
$$\hat{V}_{\mathrm{SO}} = \lambda_1 \sum_{\tau=\pm} \tau \left(\hat{d}^\dagger_{L\tau\uparrow} \hat{d}_{L\tau\uparrow} - \hat{d}^\dagger_{L\tau\downarrow} \hat{d}_{L\tau\downarrow} \right)$$
$$+ \lambda_2 \left(\hat{d}^\dagger_{S\uparrow} \hat{d}_{L-\downarrow} + \hat{d}^\dagger_{L+\uparrow} \hat{d}_{S\downarrow} + \mathrm{h.c.} \right)$$



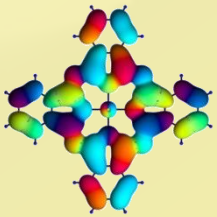
SOMO



HOMO



LUMO+

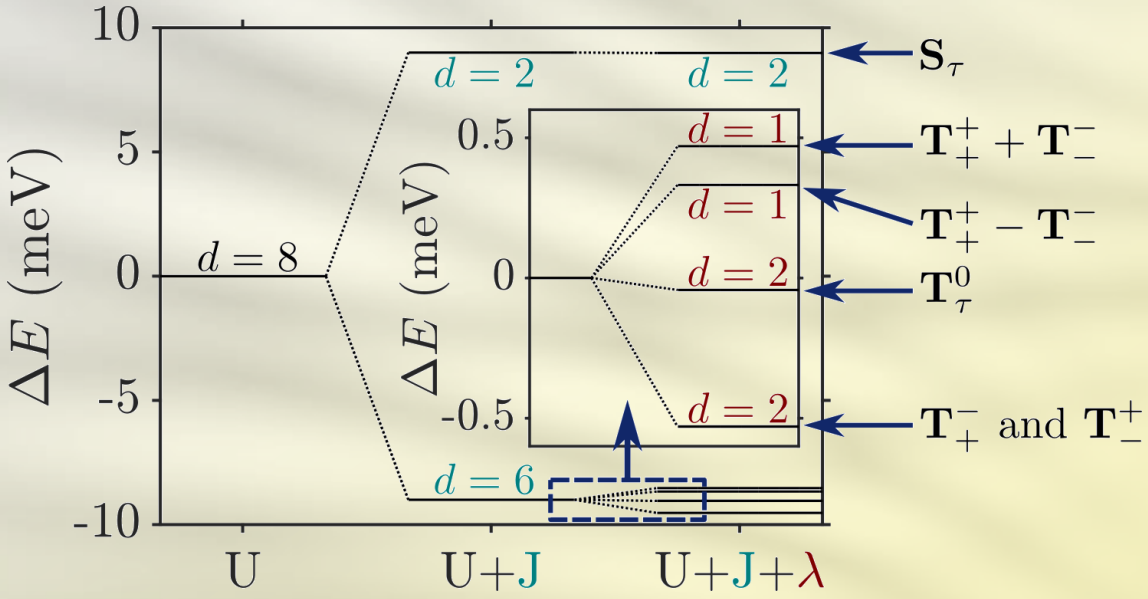


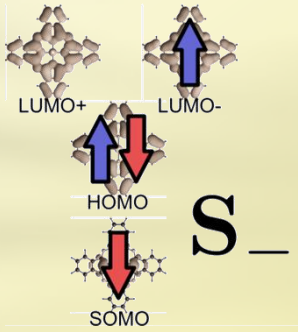
LUMO-

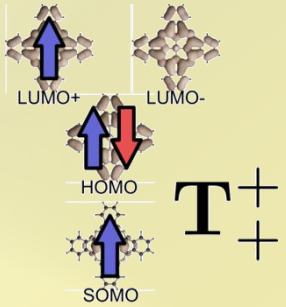
where $\lambda_1 = \frac{1}{2}\xi_{\mathrm{Cu}} |c_L|^2 = 0.47$ meV and $\lambda_2 = \xi_{\mathrm{Cu}} \frac{c_S c_L}{\sqrt{2}} = 6.16$ meV

Low energy spectrum of $CuPc^-$

H_{mol} contains three different energy scales $U > J > \lambda$







To first order in the spin orbit coupling

$$\hat{H}_0^{N_0+1} = E^{\mathrm{g}}_{N_0+1} - J^{\mathrm{ex}}_{SL}\left(\hat{S}^2 - 1\right) + \lambda_1\,\hat{\tau}_z\hat{S}_z$$

$$\hat{\tau}_z = \hat{n}_{\mathrm{L}+} - \hat{n}_{\mathrm{L}-}$$

B. Siegert, A. Donarini and M. Grifoni, *Beilstein J. of Nanotech.* **6**, 2452 (2015)

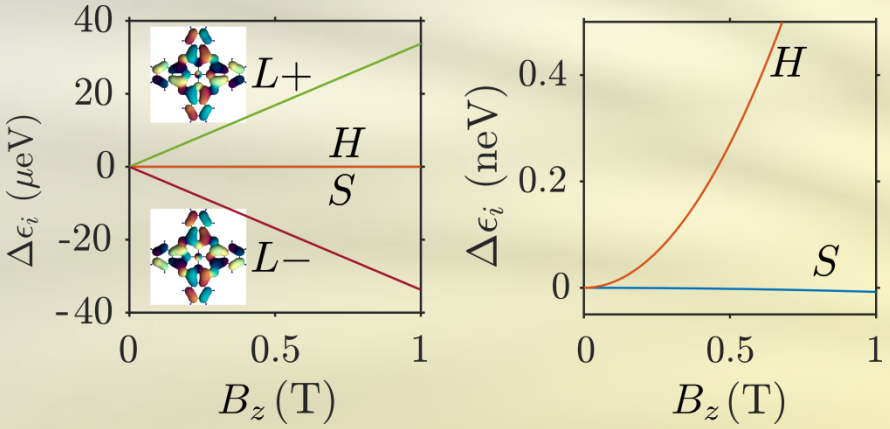
External magnetic field

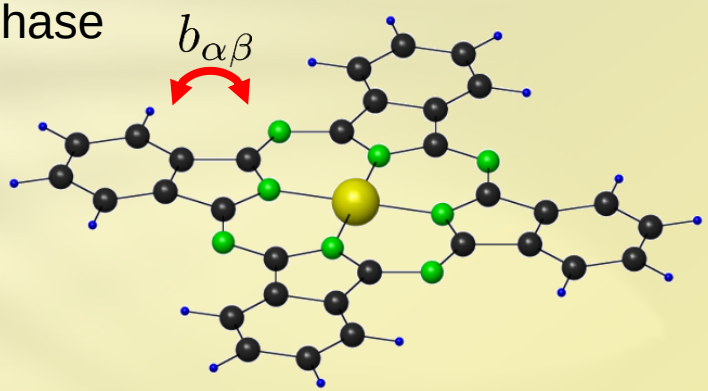
The effective Hamiltonian shows both **orbital** and **spin** components

$$\hat{H}^N_{\text{eff}} = \hat{H}^N_0 + \mu_{\text{orb}}\,\hat{\tau}_z B_z + g_S \mu_{\text{B}}\,\hat{\mathbf{S}}\cdot\mathbf{B}$$

where $\mu_{\text{orb}} = 33.7\mu\text{eVT}^{-1}$, $\mu_{\text{B}} = 57.9\mu\text{eVT}^{-1}$ and $\hat{\tau}_z = \hat{n}_{\text{L}+} - \hat{n}_{\text{L}-}$.

The orbital component is described by the Peierls phase



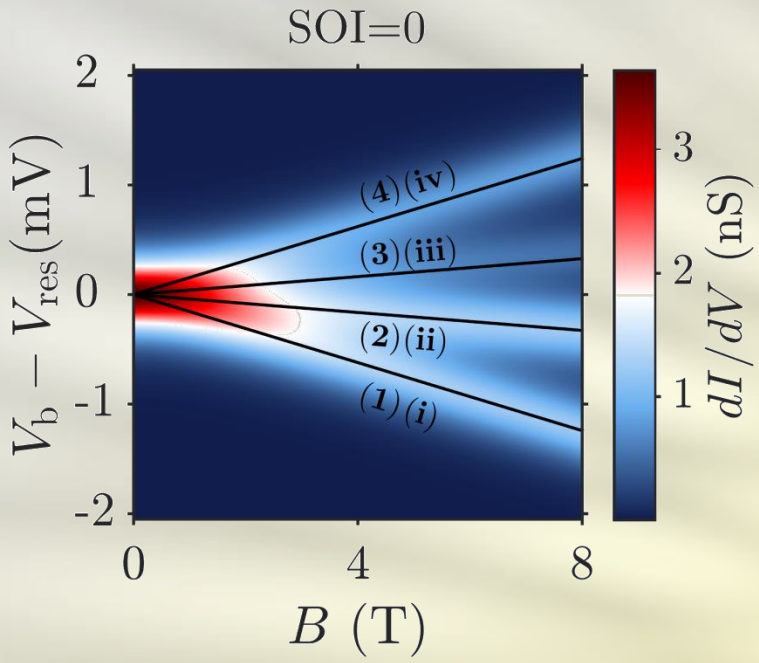


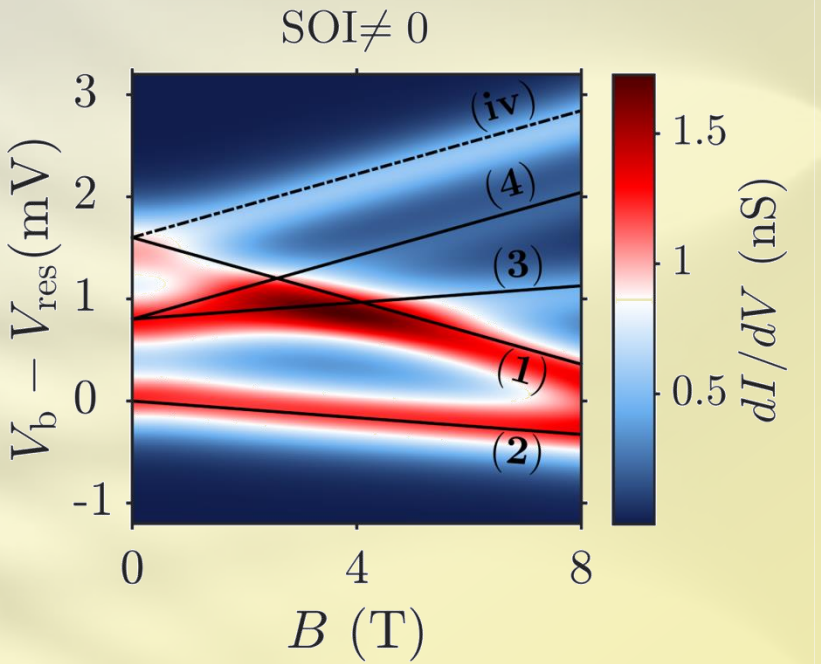
$$b_{\alpha\beta} \to b_{\alpha\beta}\,\mathrm{e}^{i\phi_{\alpha\beta}}$$

$$\phi_{\alpha\beta} = \frac{eB_z}{2\hbar}\,(y_\alpha + y_\beta)\,(x_\alpha - x_\beta)$$

B. Siegert, A. Donarini and M. Grifoni, *Beilstein J. of Nanotech.* **6**, 2452 (2015)

Magnetotransport





$$(1): \quad |\mathbf{D}_0^{\downarrow}\rangle \rightarrow |\mathbf{T}_-^{-}\rangle \qquad (\mathrm{i}): \quad |\mathbf{D}_0^{\uparrow}\rangle \rightarrow |\mathbf{T}_-^{0}\rangle$$

$$(2): \quad |\mathbf{D}_0^{\downarrow}\rangle \rightarrow |\mathbf{T}_+^{-}\rangle \qquad (\mathrm{ii}): \quad |\mathbf{D}_0^{\uparrow}\rangle \rightarrow |\mathbf{T}_+^{0}\rangle$$

$$(3): \quad |\mathbf{D}_0^{\downarrow}\rangle \rightarrow |\mathbf{T}_-^{0}\rangle \qquad (\mathrm{iii}): \quad |\mathbf{D}_0^{\uparrow}\rangle \rightarrow |\mathbf{T}_-^{+}\rangle$$

$$(4): \quad |\mathbf{D}_0^{\downarrow}\rangle \rightarrow |\mathbf{T}_+^{0}\rangle \qquad (\mathrm{iv}): \quad |\mathbf{D}_0^{\uparrow}\rangle \rightarrow |\mathbf{T}_+^{+}\rangle$$

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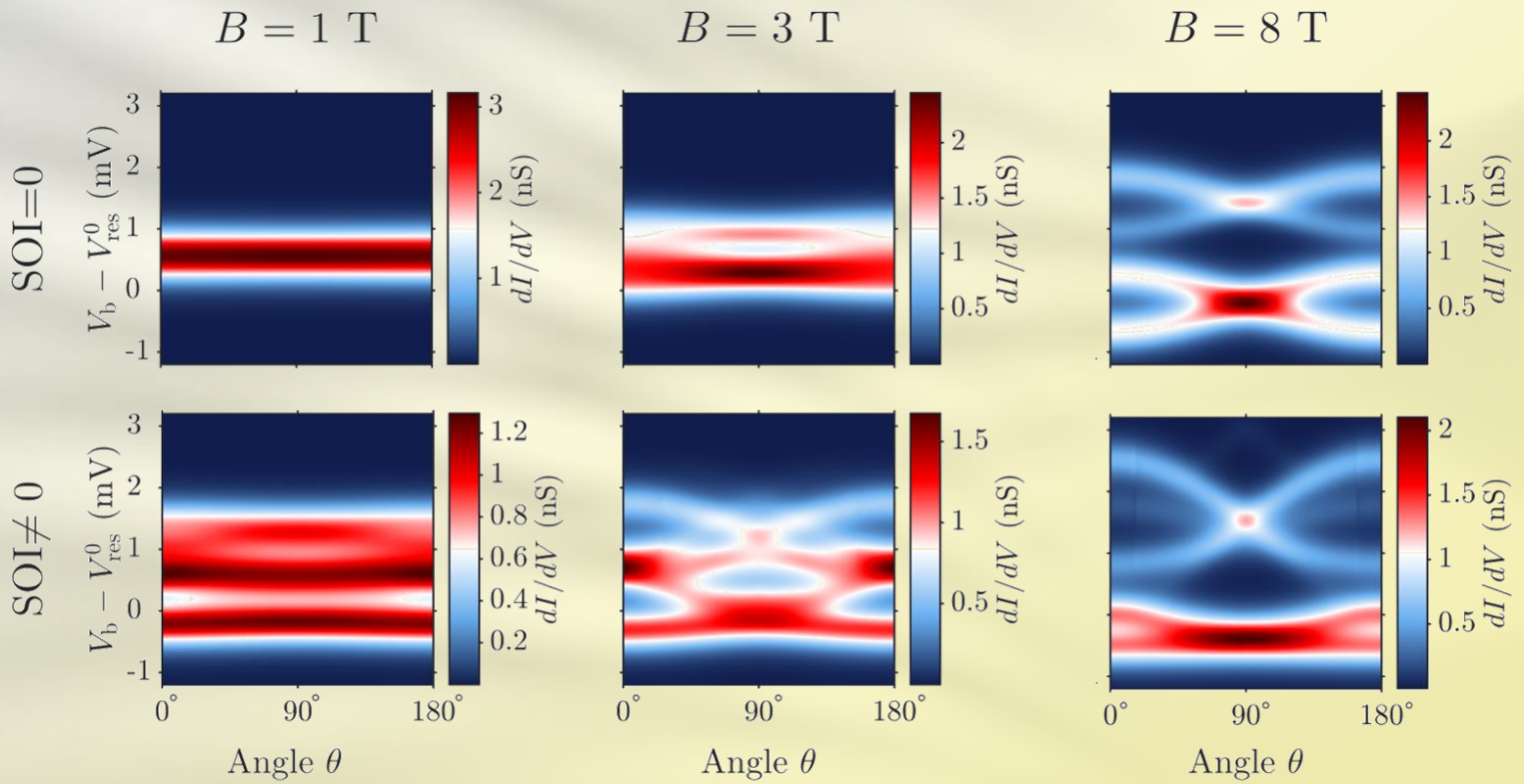
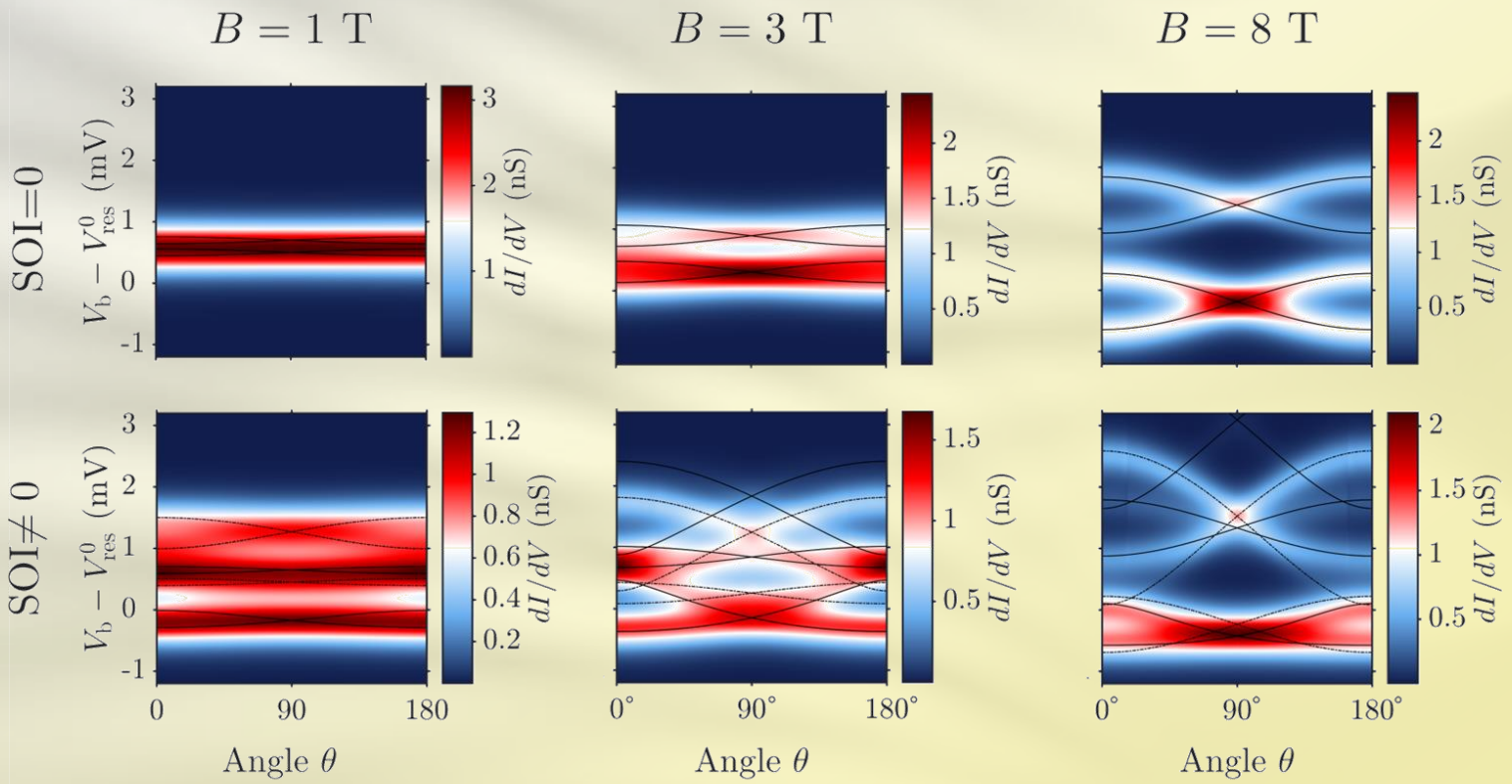
Magnetic anisotropy



B. Siegert, A. Donarini and M. Grifoni, *Beilstein J. of Nanotech.* **6**, 2452 (2015)

Magnetic anisotropy



B. Siegert, A. Donarini and M. Grifoni, *Beilstein J. of Nanotech.* **6**, 2452 (2015)

Conclusions

- We developed a minimal model which captures the interplay of organic **ligand configuration** and **spin orbit interaction** in CuPc

- The low energy spectrum is characterized in terms of **spin** and **pseudo-spin** quantum numbers

- The calculated **transport characteristics** of an STM single molecule junction show signatures of sizeable **magnetic anisotropy**

Aknowledgments

Milena Grifoni

Benjamin Siegert

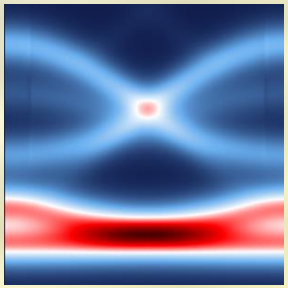
J. Repp

T. Niehaus

D. Ryndyk

R. Korytar

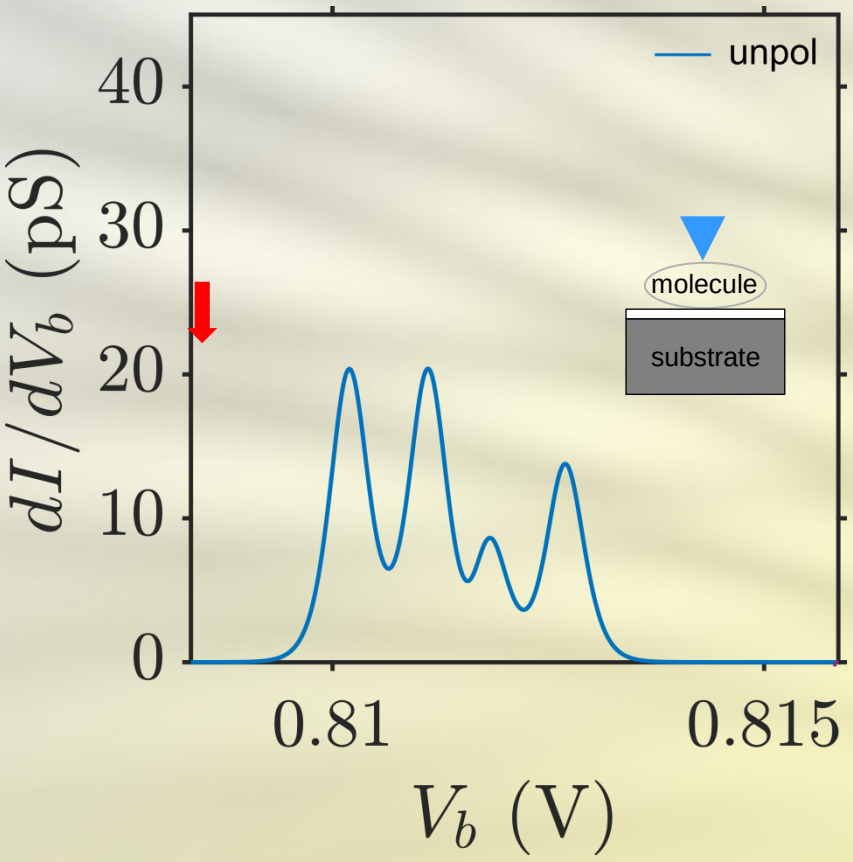
Thank you for your attention!

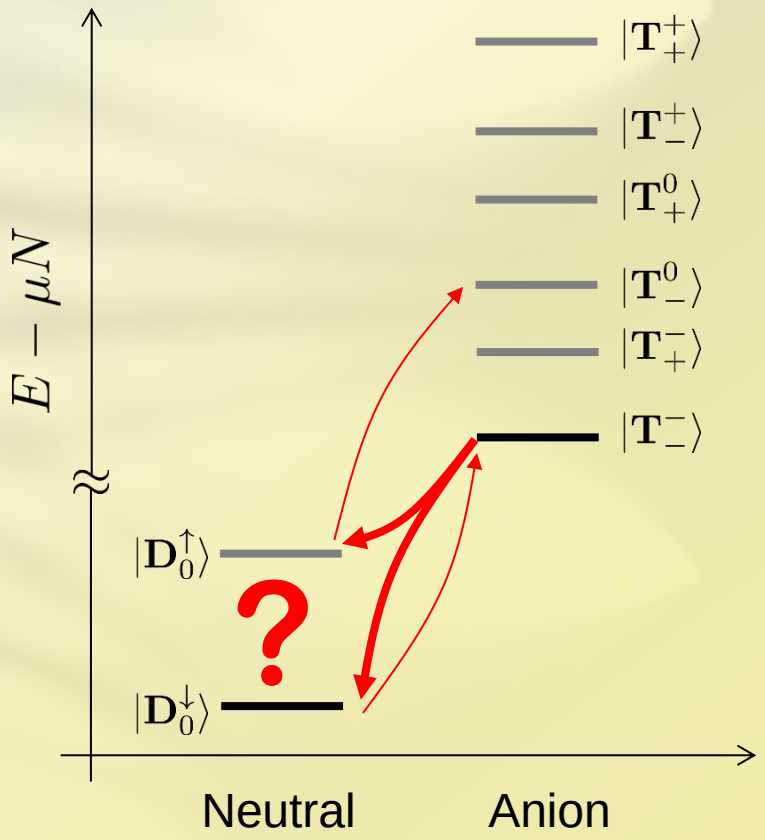


Universität Regensburg

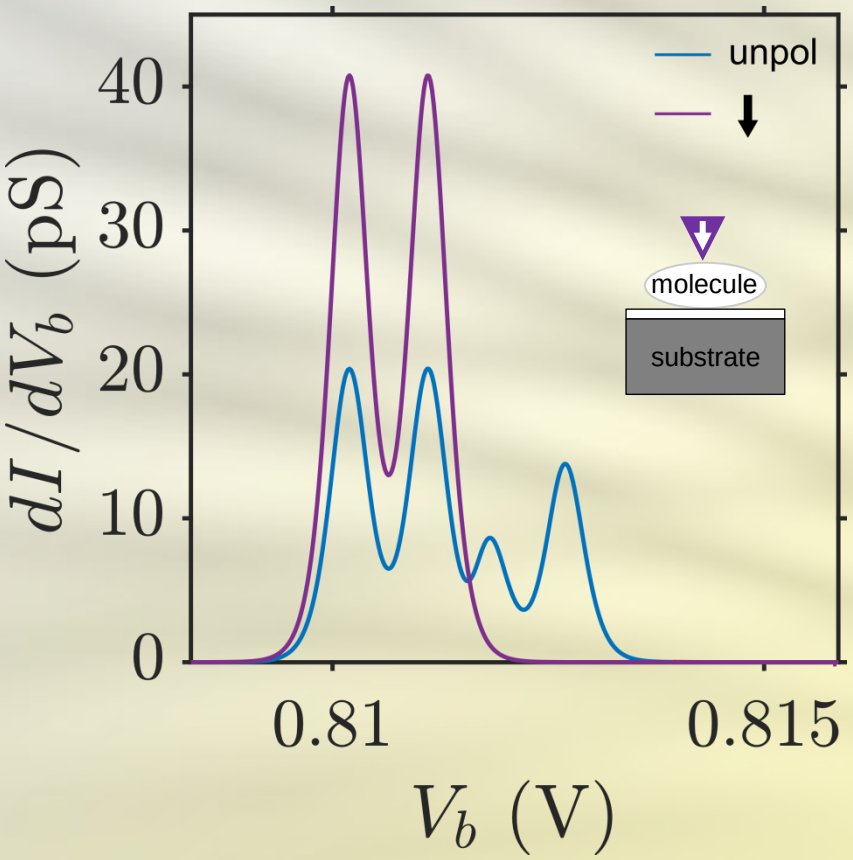
DFG Deutsche Forschungsgemeinschaft

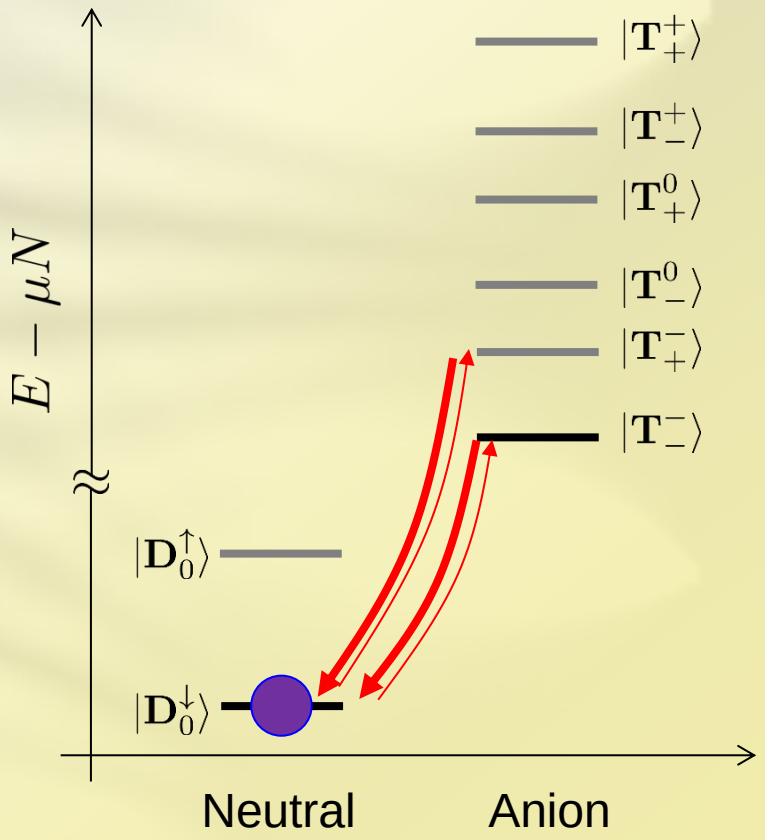
Asymmetric conductance peaks



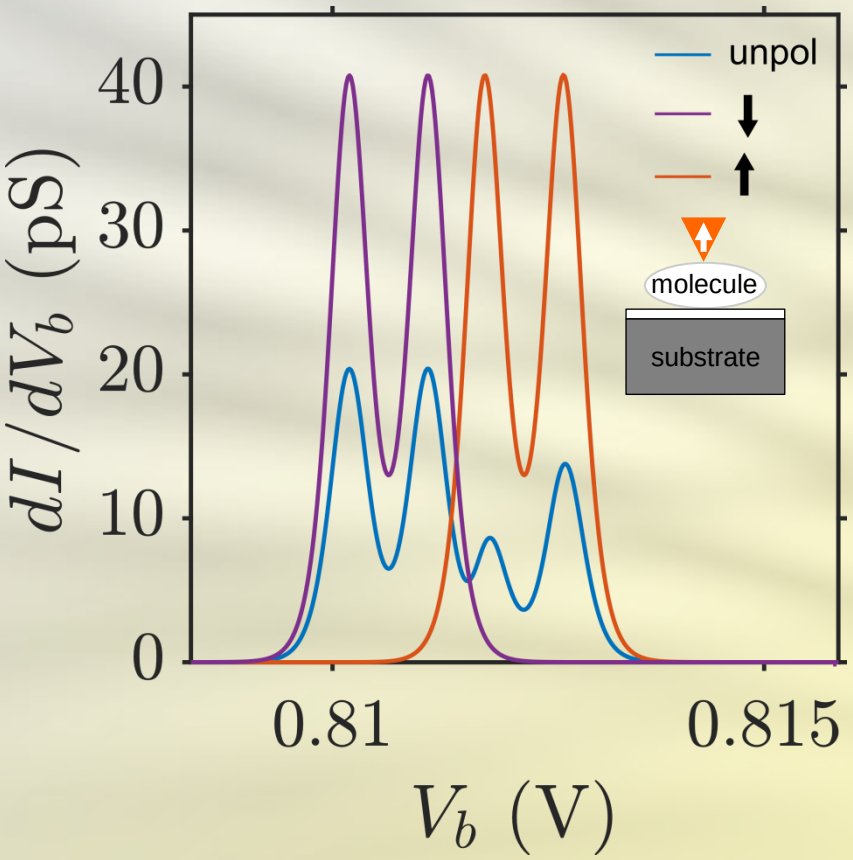


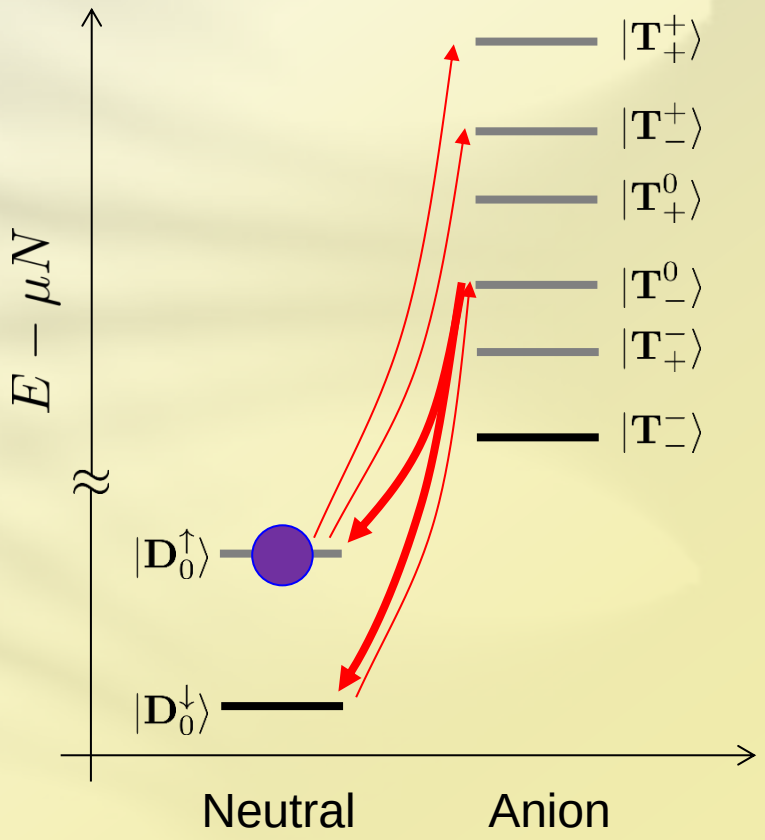
Asymmetric conductance peaks



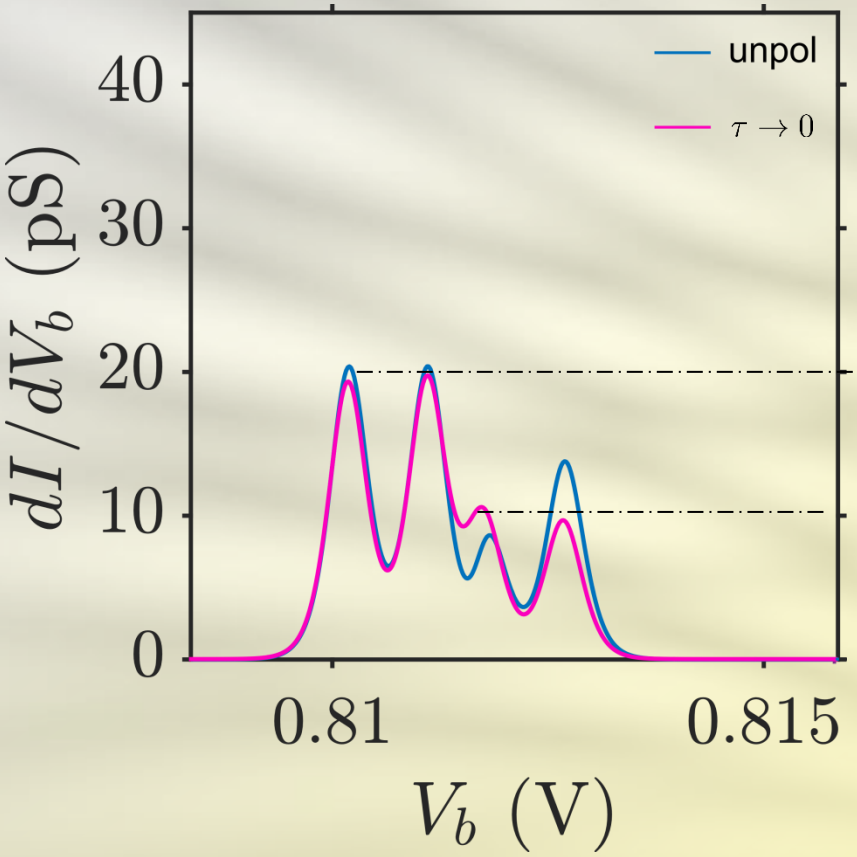


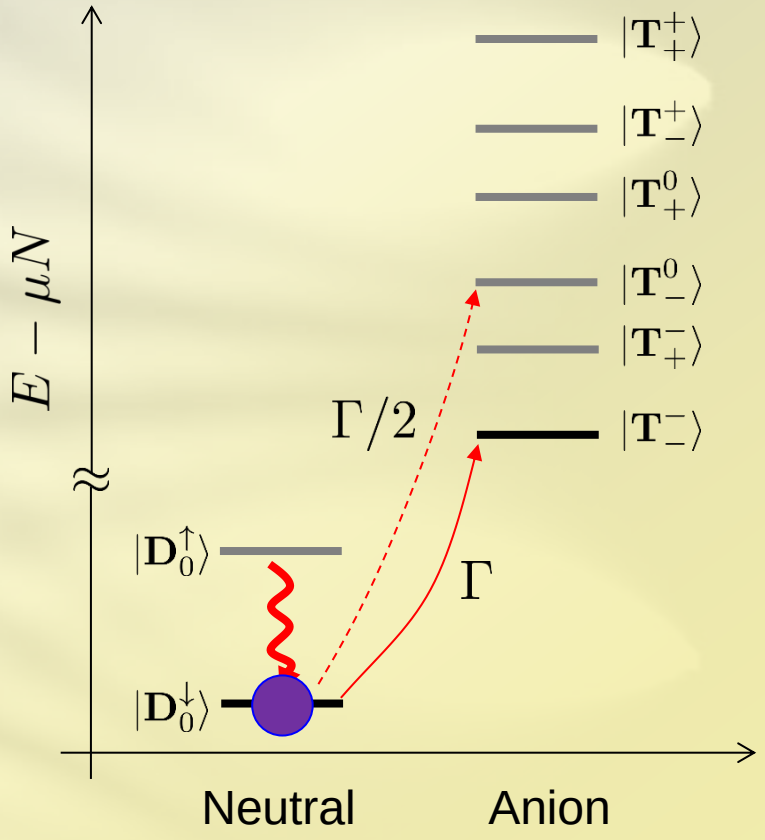
Asymmetric conductance peaks





Asymmetric conductance peaks

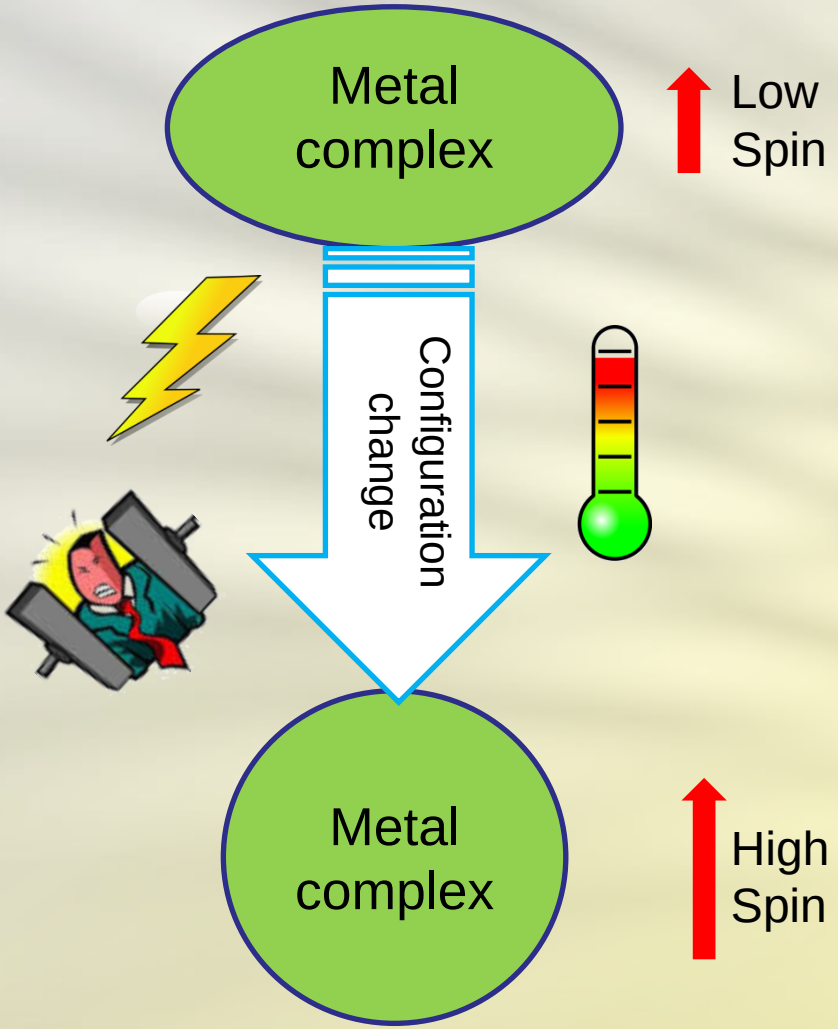




$$|\mathbf{T}_-^-\rangle = \hat{d}^\dagger_{L-\downarrow}|\mathbf{D}_0^\downarrow\rangle \qquad |\mathbf{T}_-^0\rangle = \tfrac{1}{\sqrt{2}}\left[\hat{d}^\dagger_{L-\uparrow}|\mathbf{D}_\mathbf{0}^\downarrow\rangle + \hat{d}^\dagger_{L-\downarrow}|\mathbf{D}_\mathbf{0}^\uparrow\rangle\right]$$

Non-equilibrium spin-crossover

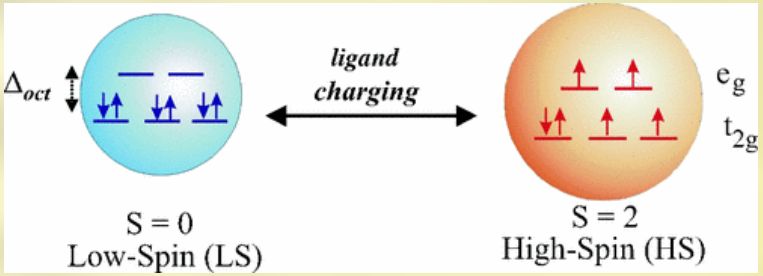
Spin crossover

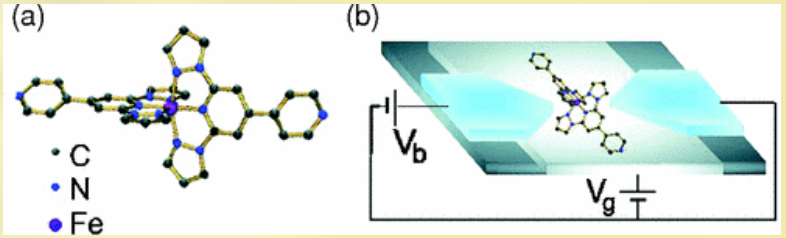


Change in the occupation of the metal *d*-orbitals:

Interplay of:

- (Octahedral) ligand field splitting
- Exchange interaction

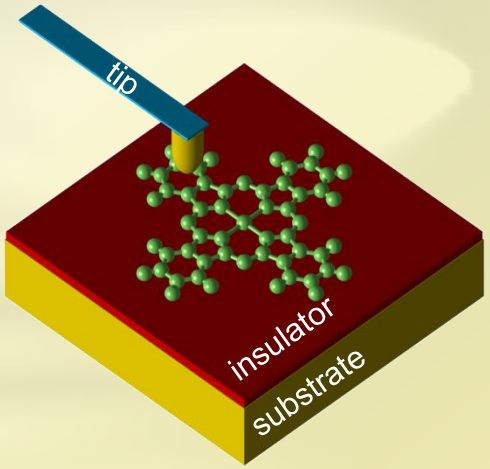


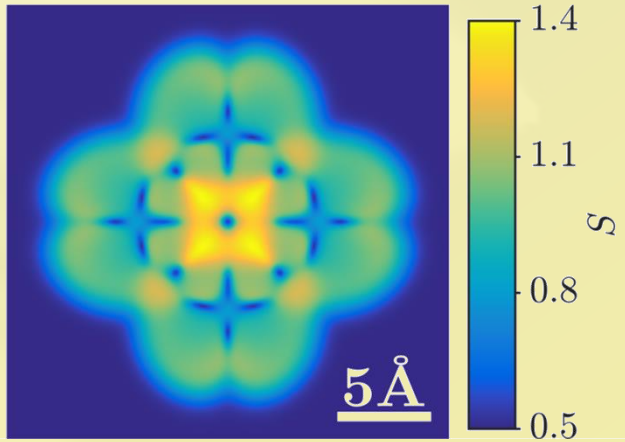


V. Meded, *et al.PRB* **83**, 245415 (2011)

Non equilibrium spin-crossover

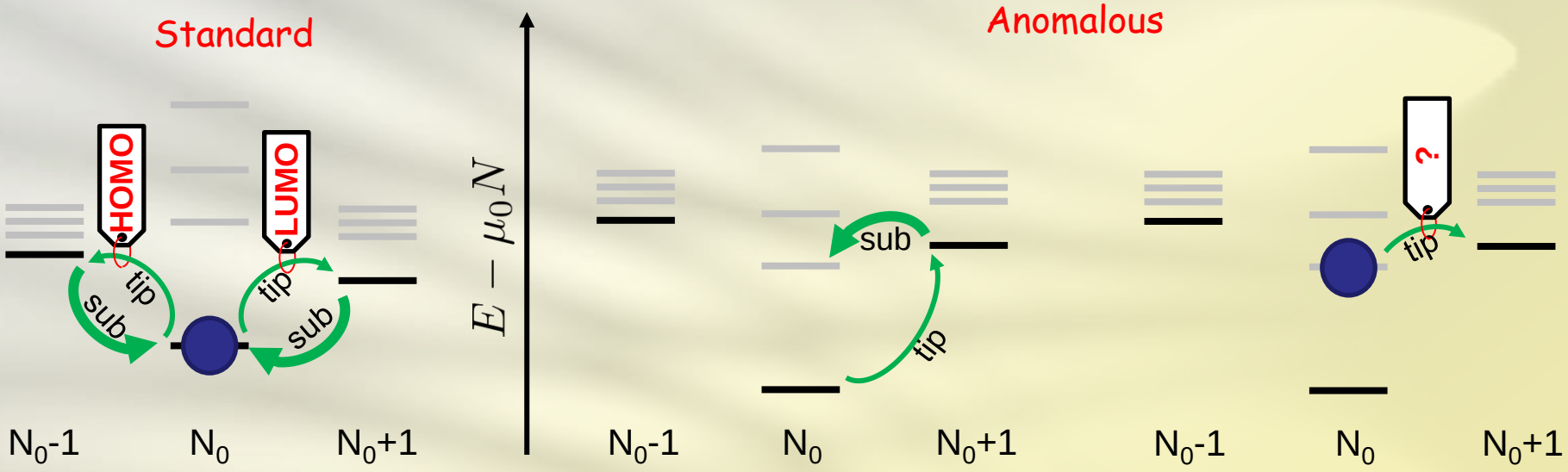
	$R_{tip,1}$	$R_{tip,2}$
$V_b = 0$	Low Spin	Low Spin
$V_b > V_{th}$	Low Spin	High Spin

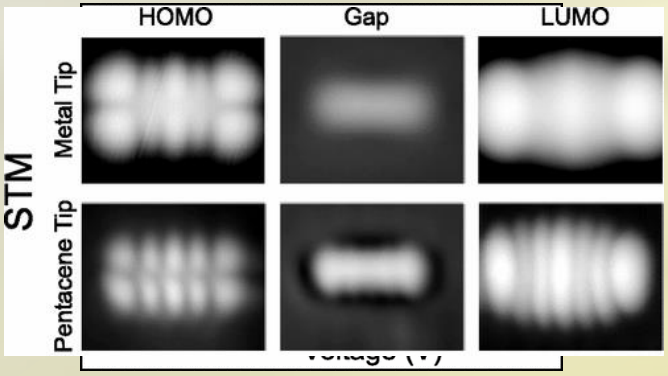




V_b = 1.38 V

Anomalous current maps



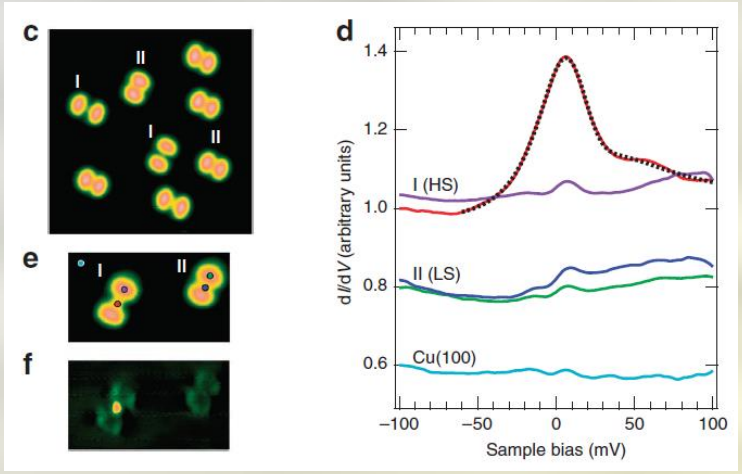


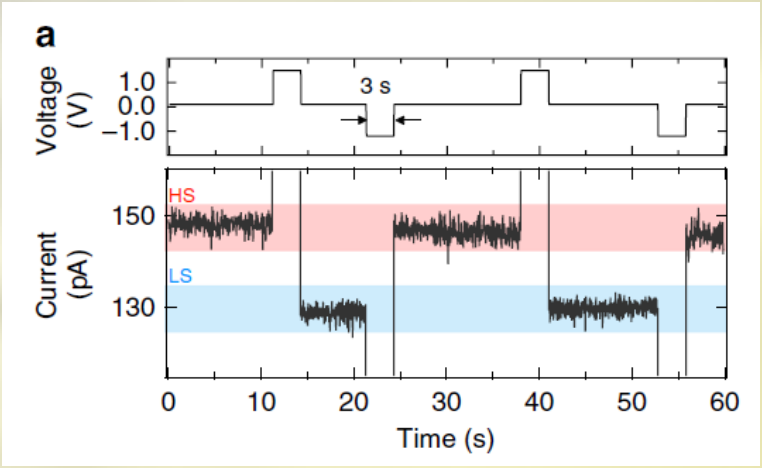
J.Repp et al. *PRL* **94**, 026803 (2005)

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

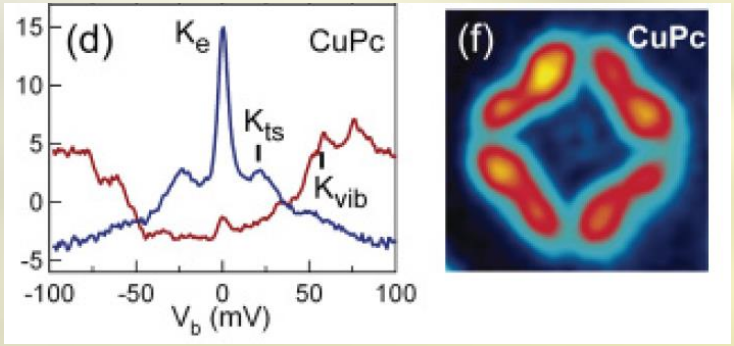
The **population inversion** relies on the strong asymmetry between substrate and tip tunneling rates and on the weak relaxation rate

Motivation





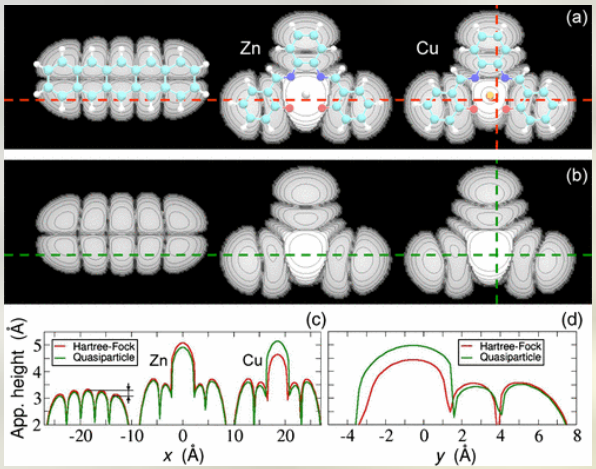
T. Miyamachi *et al. Nature comm.* **3**, 993 (2012)



- 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

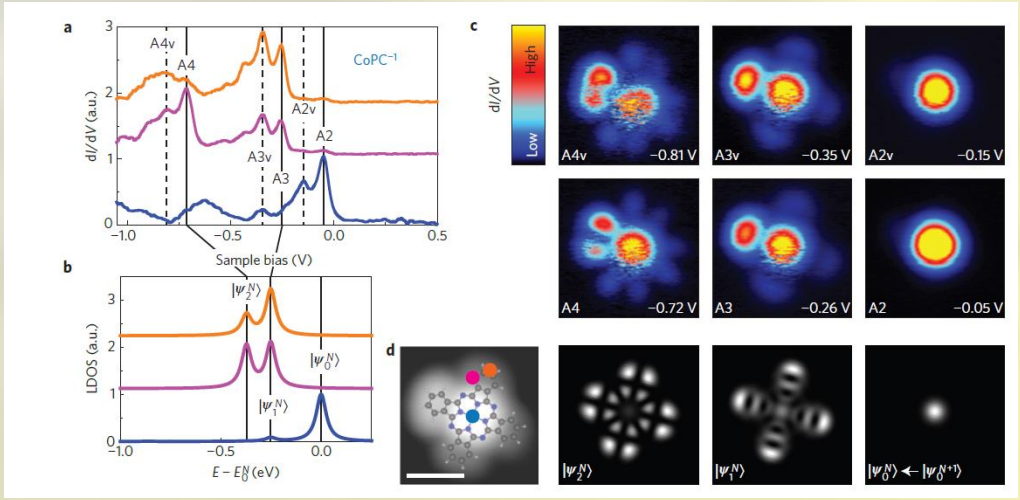


Alteration of the molecular orbitals due electronic correlation

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

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

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



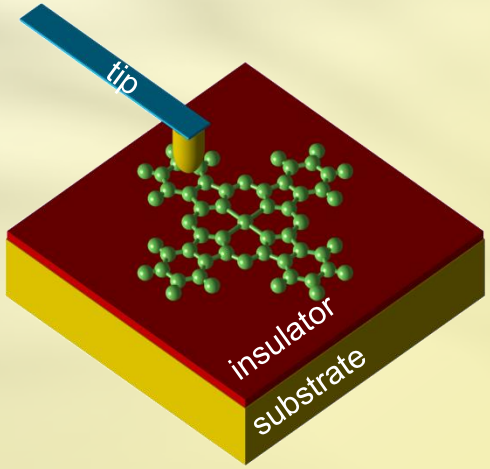
Visualization of many-body transitions in STM experiments

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

The Hamiltonian

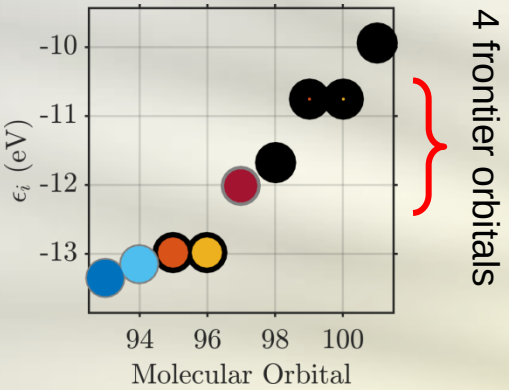
The STM single molecule junction is described by the Hamiltonian

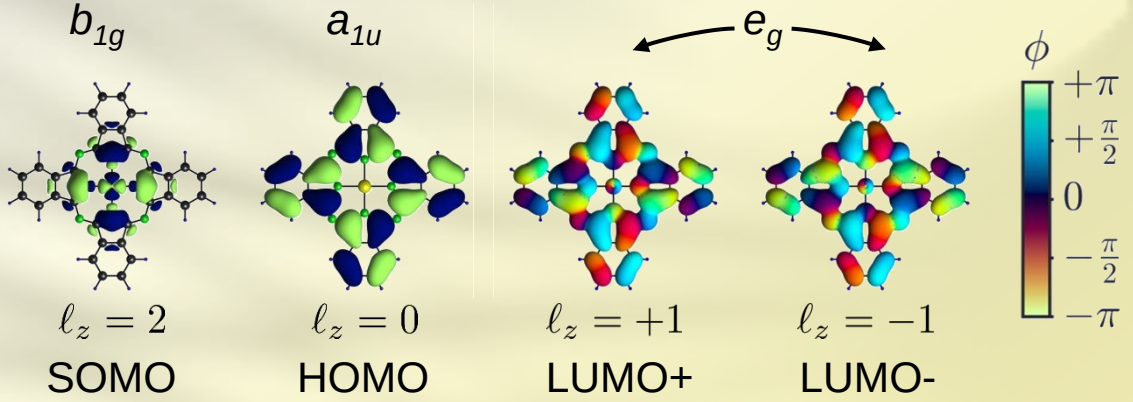
$$\hat{\mathrm{H}} = \hat{\mathrm{H}}_{\mathrm{mol}} + \hat{\mathrm{H}}_{\mathrm{mol-env}} + \hat{\mathrm{H}}_{\mathrm{S}} + \hat{\mathrm{H}}_{\mathrm{T}} + \hat{\mathrm{H}}_{\mathrm{tun}}$$



Minimal basis set

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

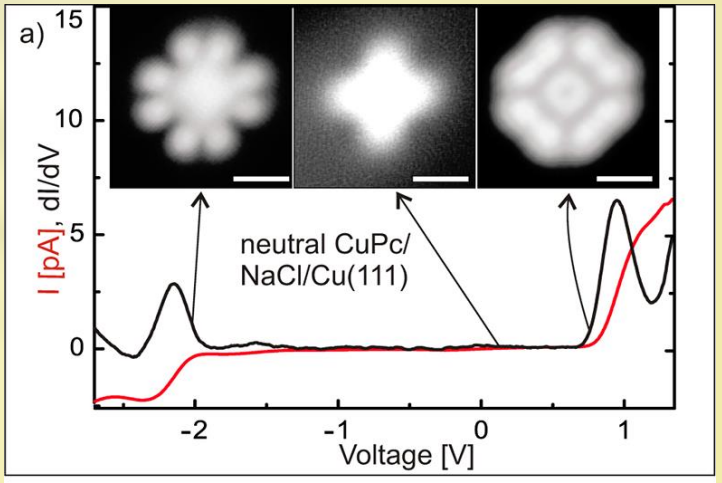




We restrict ourselves to the Fock space spanned by:

$$|\Psi\rangle \approx |\underbrace{11\ldots11}_{2N_f}\underbrace{n_{k\uparrow}n_{k\downarrow}\ldots n_{l\uparrow}n_{l\downarrow}}_{2N_d}\underbrace{00\ldots00}_{2N_e}\rangle$$

Frozen | Dynamical | Empty



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)

Many-body Hamiltonian

The many-body Hamiltonian for the molecule reads

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

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

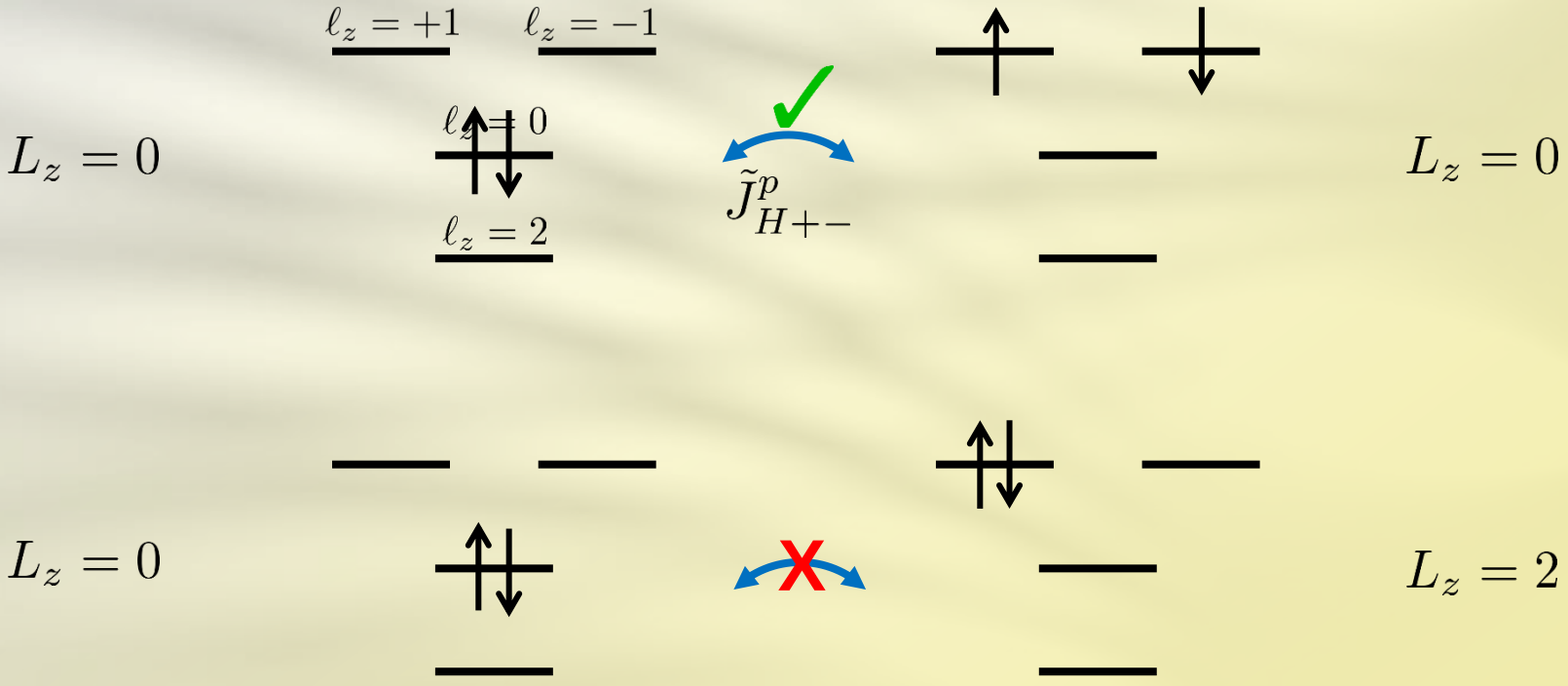
V_{ijkl} are ALL Coulomb integrals among the dynamical orbitals

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

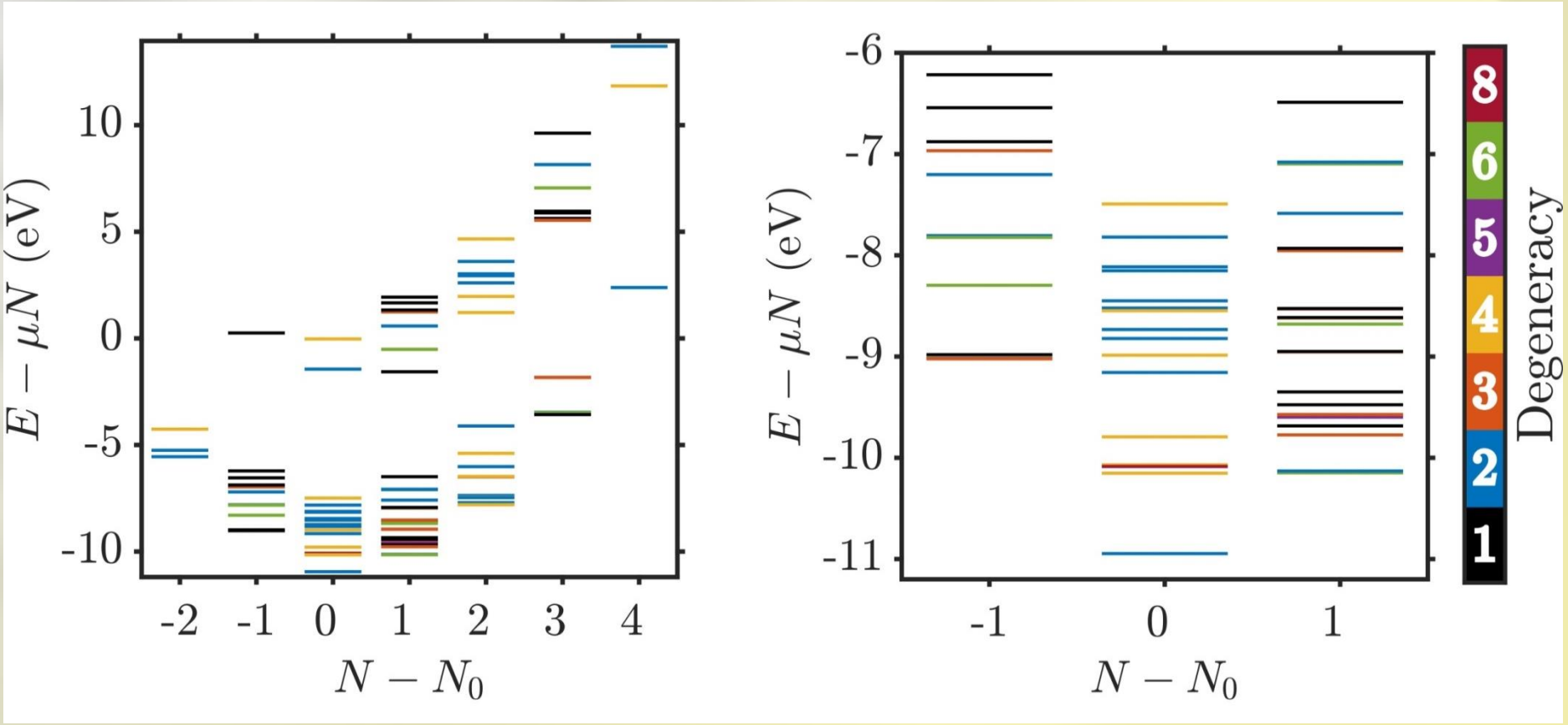
U_S	11.352 eV	$J^{\mathrm{ex}}_{HL} = -\tilde{J}^{\mathrm{p}}_{H+-}$	548 meV
U_H	1.752 eV	J^{ex}_{+-}	258 meV
$U_L = U_{+-}$	1.808 eV	J^{p}_{+-}	168 meV
U_{SH}	1.777 eV	$J^{\mathrm{ex}}_{SL} = -\tilde{J}^{\mathrm{p}}_{S+-}$	9 meV
U_{SL}	1.993 eV	$J^{\mathrm{ex}}_{SH} = J^{\mathrm{p}}_{SH}$	2 meV
U_{HL}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

Angular momentum conservation

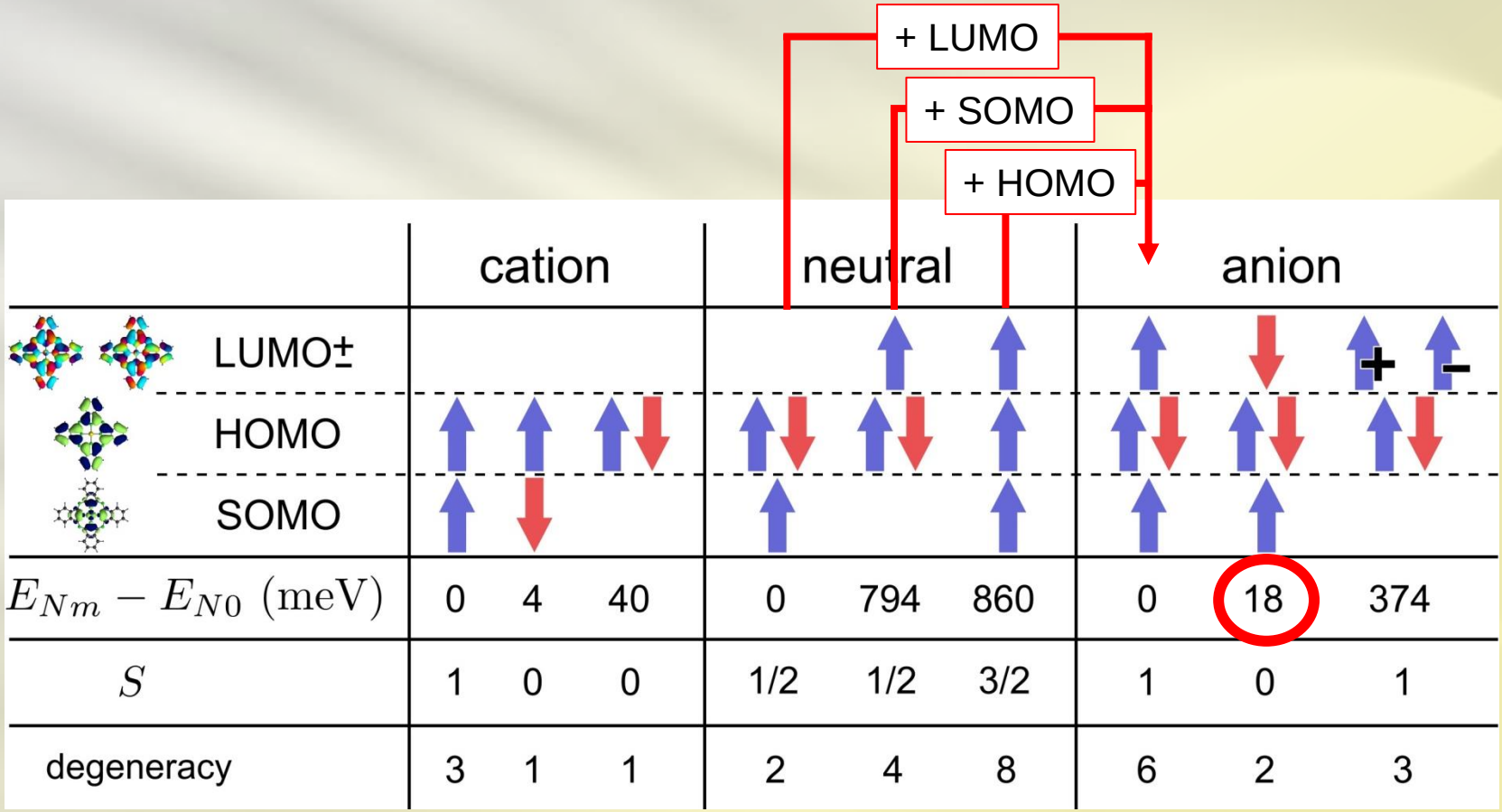
The Coulomb interaction conserves the quasi angular momentum of the molecule



Many-body spectrum



Low energy eigenstates



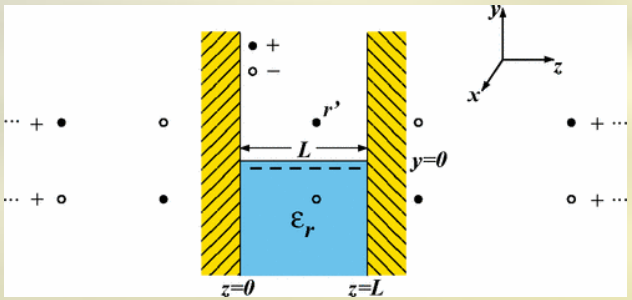
	cation			neutral			anion		
$E_{Nm} - E_{N0}$ (meV)	0	4	40	0	794	860	0	18	374
S	1	0	0	1/2	1/2	3/2	1	0	1
degeneracy	3	1	1	2	4	8	6	2	3

Image charge effects

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

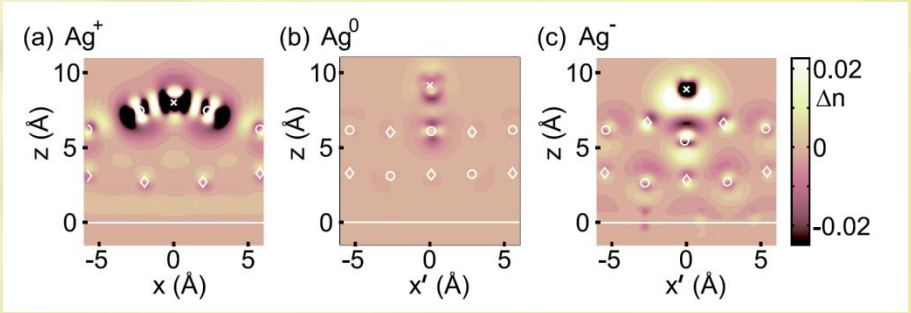
This term incorporates the two main effects which stabilize the excess charge on the molecule

Image charge effect



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**

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

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

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

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

$\sigma = \mathrm{Tr}_{\mathrm{S,T}}(\rho)$

Coherent dynamics

Effective **internal** dynamics

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

Tunnelling dynamics

Phenom. relaxation

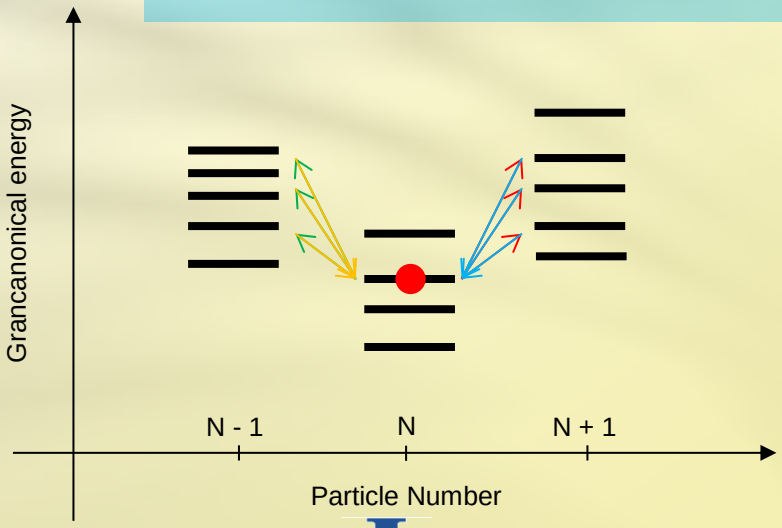
$$\mathcal{L}_{\mathrm{rel}}[\sigma] = -\frac{1}{\tau}\left(\sigma - \sum_{NFm} \sigma_{mm}^{\mathrm{th},NF} |NFm\rangle\langle NFm| \sum_{En} \sigma_{nn}^{NE}\right)$$

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

Tunnelling Liouvillean

$$\mathcal{L}_{\rm tun}\sigma^{NE} = -\frac{1}{2}\sum_{\chi\tau}\sum_{ij}\Big\{\mathcal{P}_{NE}\Big[d^\dagger_{i\tau}\Gamma^\chi_{ij}(E-H_{\rm m})f^-_\chi(E-H_{\rm m})d_{j\tau} + d_{j\tau}\Gamma^\chi_{ij}(H_{\rm m}-E)f^+_\chi(H_{\rm m}-E)d^\dagger_{i\tau}\Big]\sigma^{NE} + h.c.\Big\}$$

$$+\sum_{\chi\tau}\sum_{ijE'}\mathcal{P}_{NE}\Big[d^\dagger_{i\tau}\Gamma^\chi_{ij}(E-E')\sigma^{N-1E'}f^+_\chi(E-E')d_{j\tau} + d_{j\tau}\Gamma^\chi_{ij}(E'-E)\sigma^{N+1E'}f^-_\chi(E'-E)d^\dagger_{i\tau}\Big]\mathcal{P}_{NE}$$



Tunnelling rate matrix

$$H_{\text{eff}} = \frac{1}{2\pi}\sum_{NE}\sum_{\chi\sigma}\sum_{ij}\mathcal{P}_{NE}\Big[d^{\dagger}_{i\sigma}\Gamma^{\chi}_{ij}(E-H_{\text{m}})p_{\chi}(E-H_{\text{m}})d_{j\sigma} + d_{j\sigma}\Gamma^{\chi}_{ij}(H_{\text{m}}-E)p_{\chi}(H_{\text{m}}-E)d^{\dagger}_{i\sigma}\Big]\mathcal{P}_{NE}$$

Effective Hamiltonian

$$I_{\chi} = \sum_{NE\sigma ij}\mathcal{P}_{NE}\Big[d_{j\sigma}\Gamma^{\chi}_{ij}(H_{\text{m}}-E)f^{+}_{\chi}(H_{\text{m}}-E)d^{\dagger}_{i\sigma} - d^{\dagger}_{i\sigma}\Gamma^{\chi}_{ij}(E-H_{\text{m}})f^{-}_{\chi}(E-H_{\text{m}})d_{j\sigma}\Big]\mathcal{P}_{NE}$$

Current operator

$$\Gamma^{\chi}_{ij}(\Delta E) = \frac{2\pi}{\hbar}\sum_{\mathbf{k}}(t^{\chi}_{\mathbf{k}i})^{*}t^{\chi}_{\mathbf{k}j}\delta(\epsilon^{\chi}_{\mathbf{k}}-\Delta E)$$

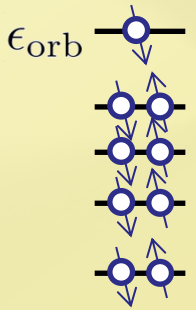
Many-body rate matrix

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

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

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

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



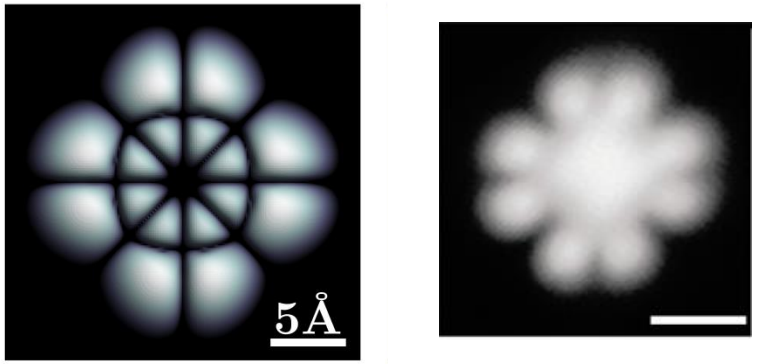
Close to equilibrium, the **constant current map** is the **isosurface** of a **specific molecular orbital** (Tersoff-Hamann theory of STM)

Topography of CuPc

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

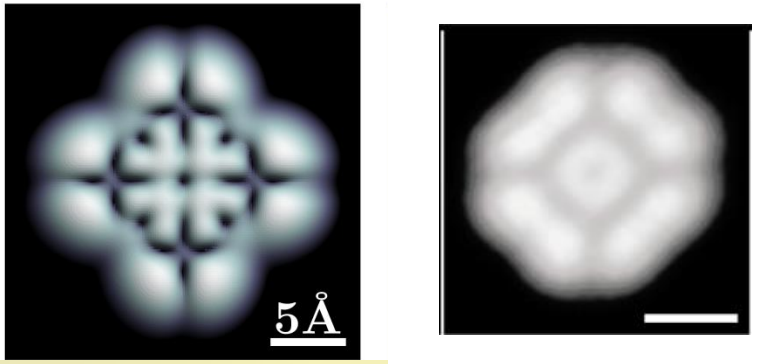
cationic resonance: $\phi_0 = 4.65$ eV

$I_\chi(\mathbf{r}_\mathrm{T}, V_\mathrm{res}) = 0.5\,\mathrm{pA}$



anionic resonance: $\phi_0 = 4.65$ eV

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

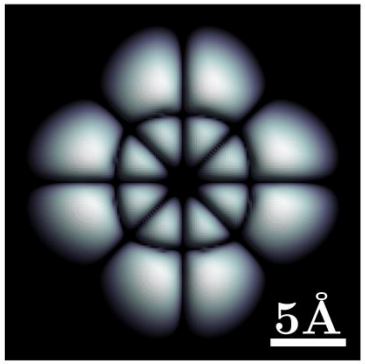


B. Siegert, A. Donarini, and M. Grifoni arXiv:1507.05504

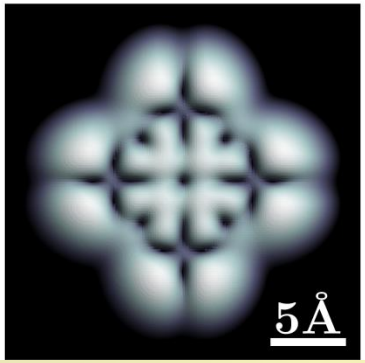
Current and spin maps

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

cationic resonance: $\phi_0 = 4.65$ eV

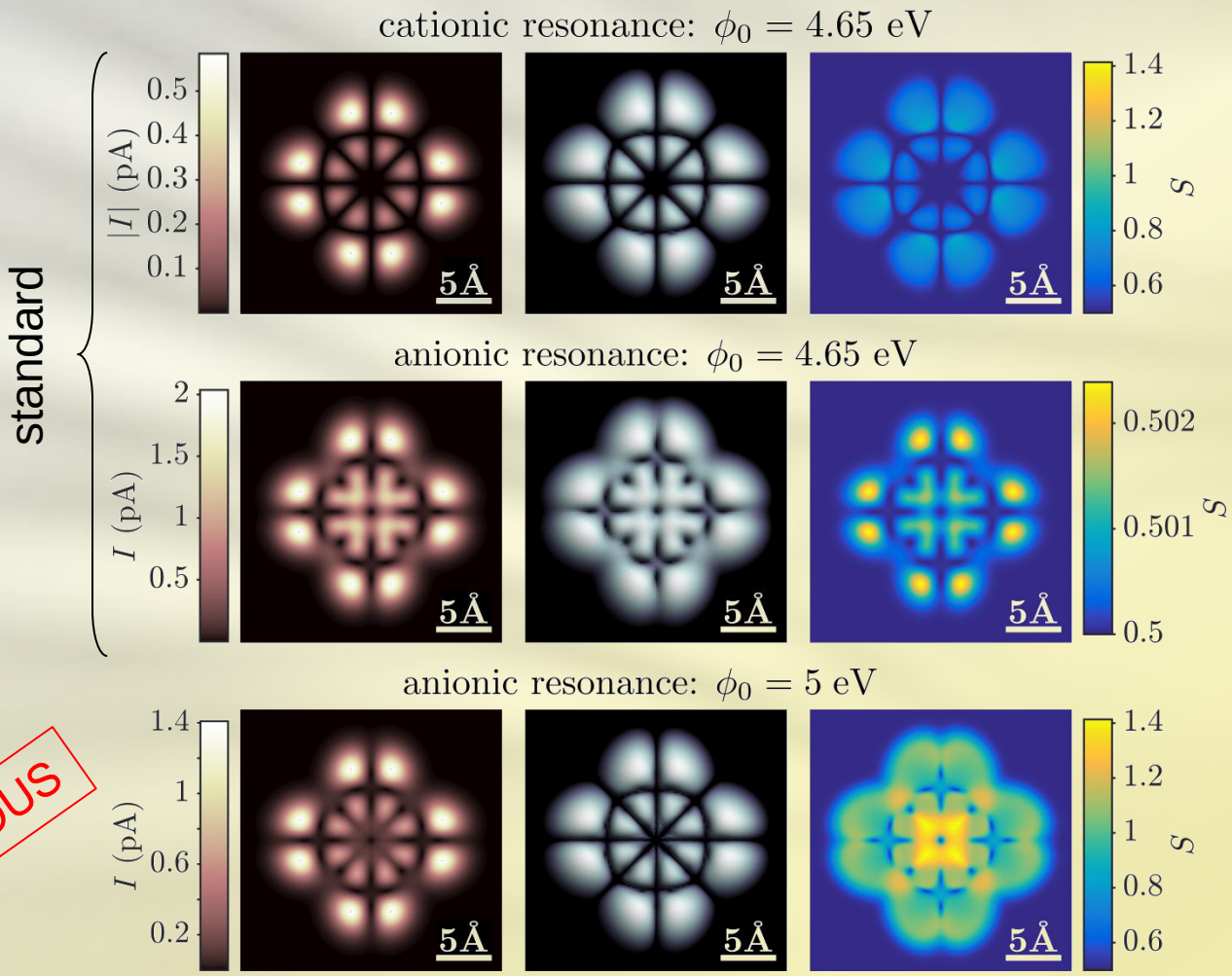


anionic resonance: $\phi_0 = 4.65$ eV



B. Siegert, A. Donarini, and M. Grifoni arXiv:1507.05504

The anomalous case



B. Siegert, A. Donarini, and M. Grifoni arXiv:1507.05504

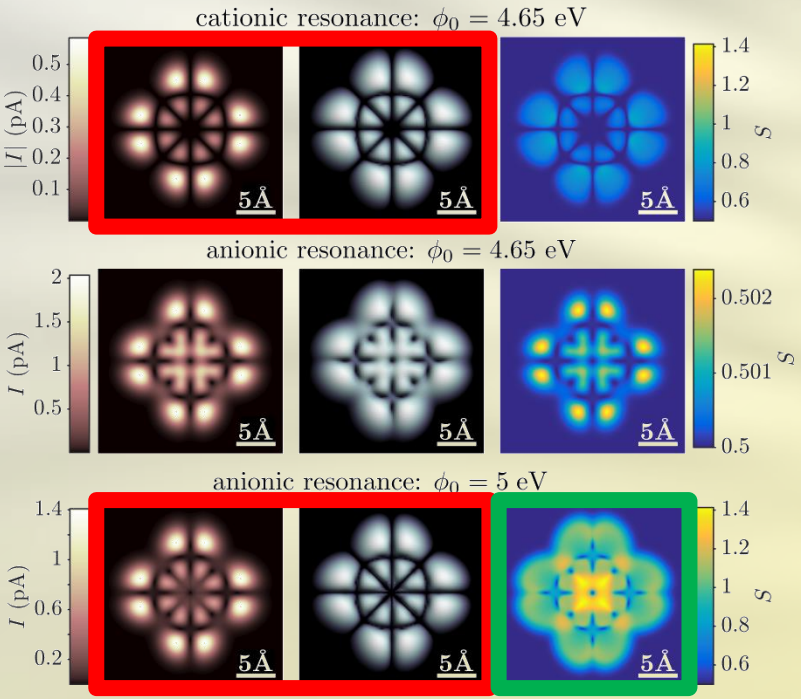
Population inversion

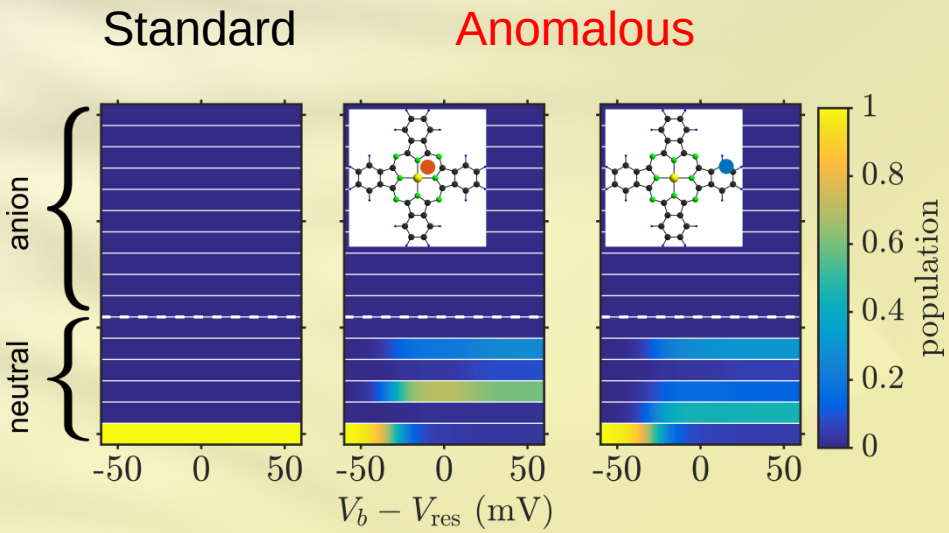
The current and topographic maps of an **anionic transition** resembles the **HOMO**

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

Standard

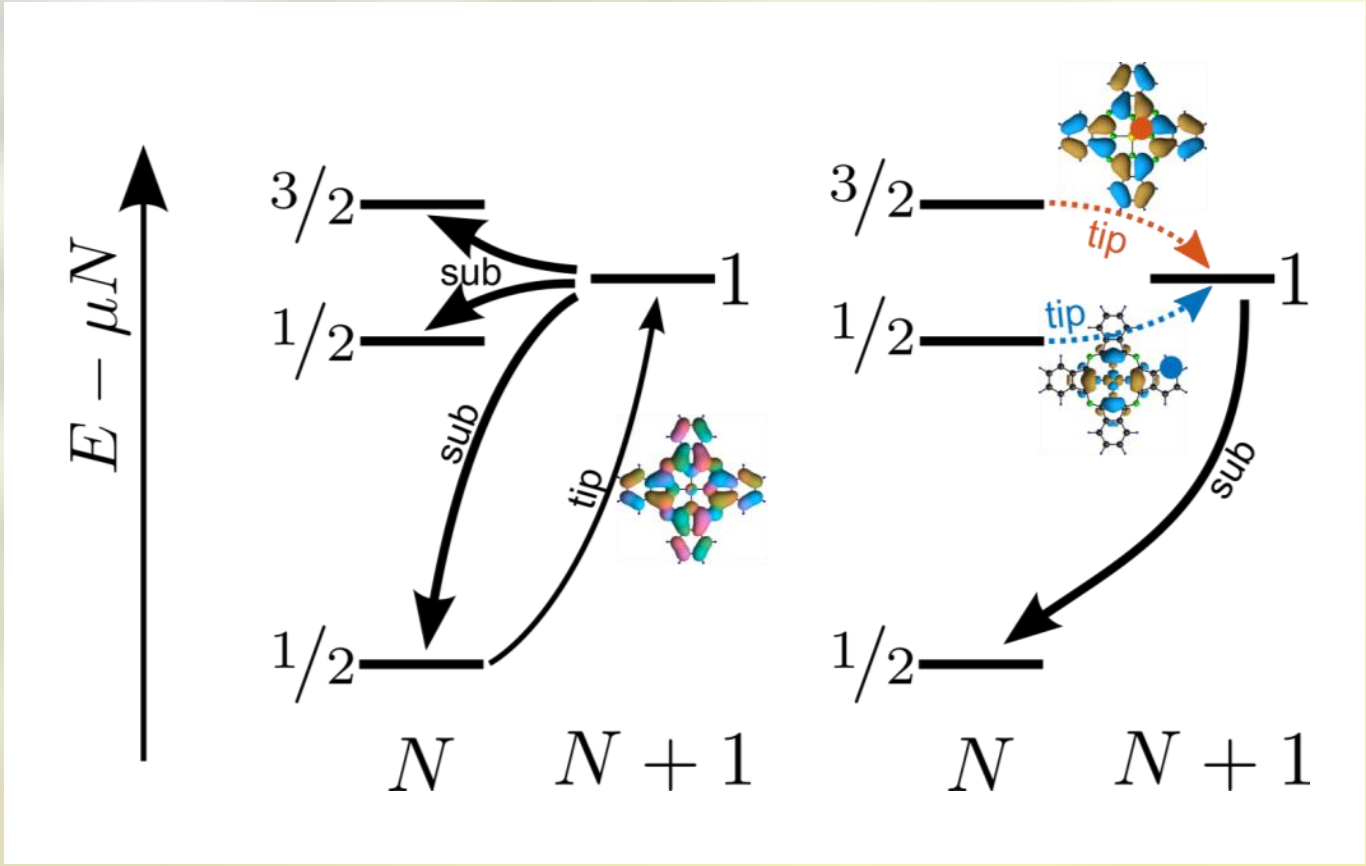
Anomalous



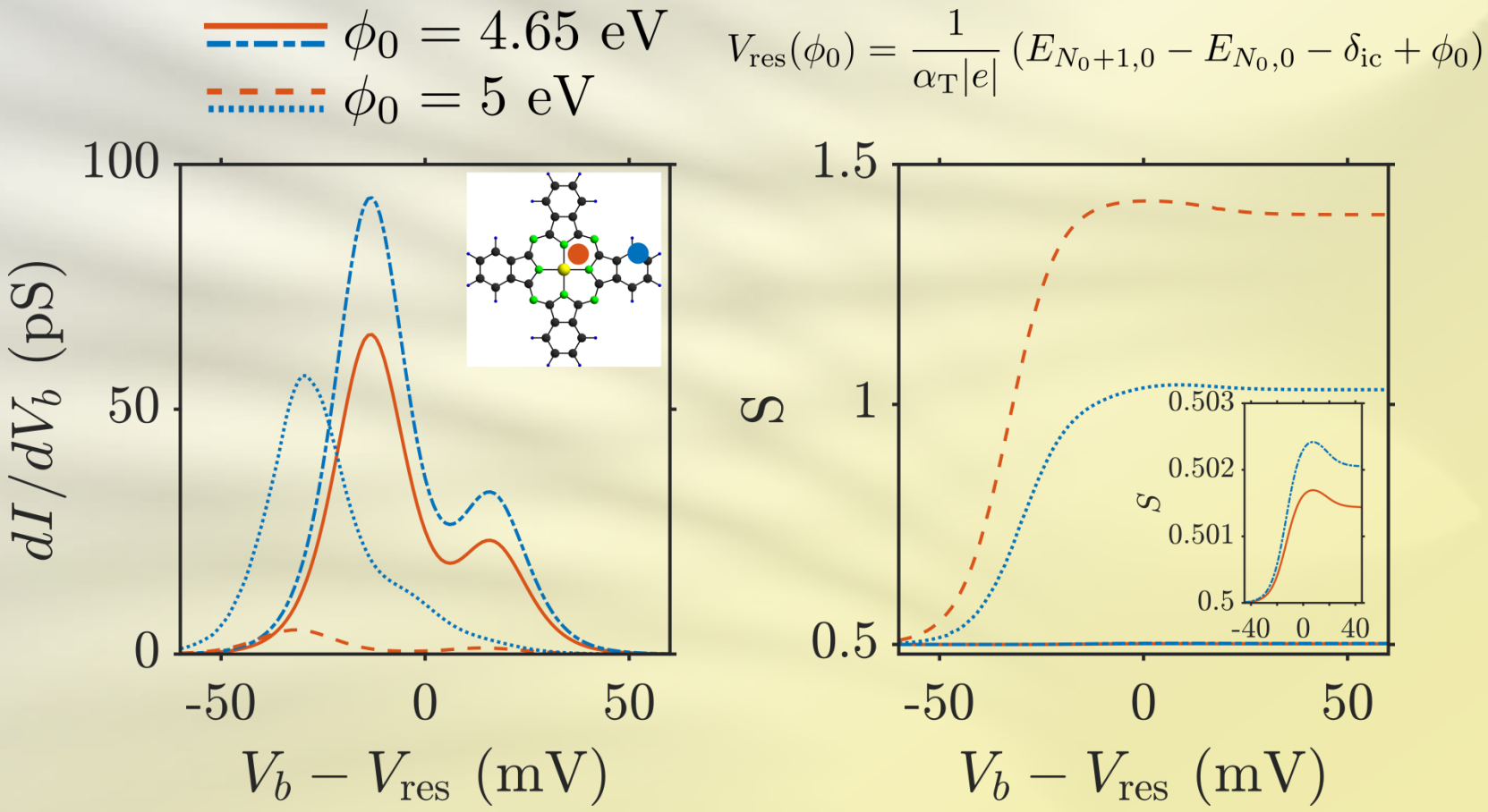


The molecule undergoes a **population inversion** which depends on the tip position

The anomalous current map



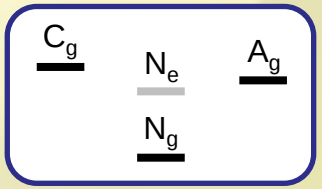
Spectroscopic anomalies



Is CuPc so special ?

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

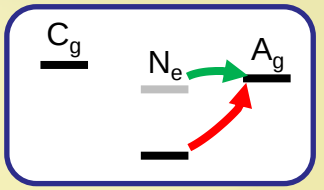
1. The energy of the excited neutral state should be lower than the ones of the cationic and anionic ground states



2. The spin of the gr… te should be different

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

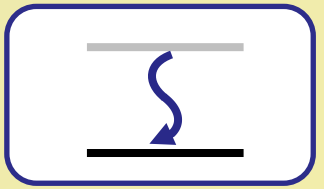
3. The (tip) transitio… tate and the the neutral groun… ve different molecular orbitals



4. The tip and substrat… gly asymmetric

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

5. The (intrinsic) relaxa… ubstrate should be low (i.e. comparable … ate)



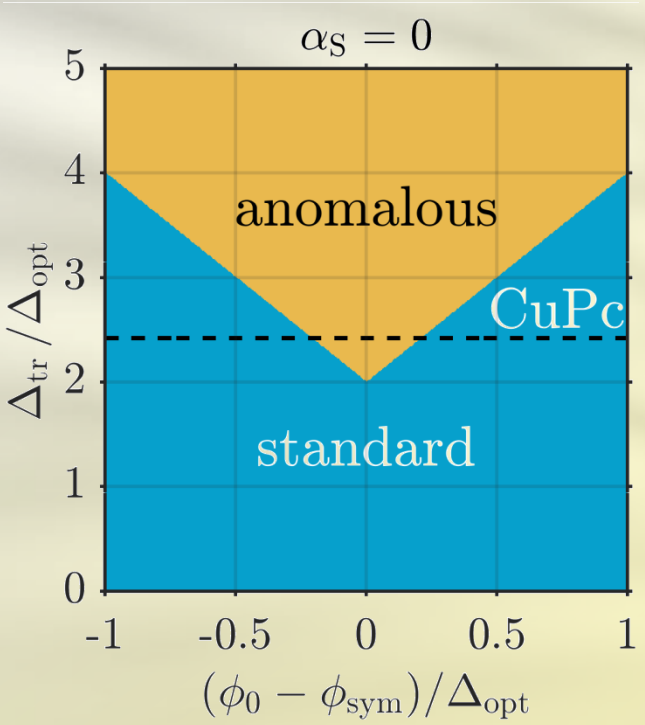
Closed shell conjugated molecules

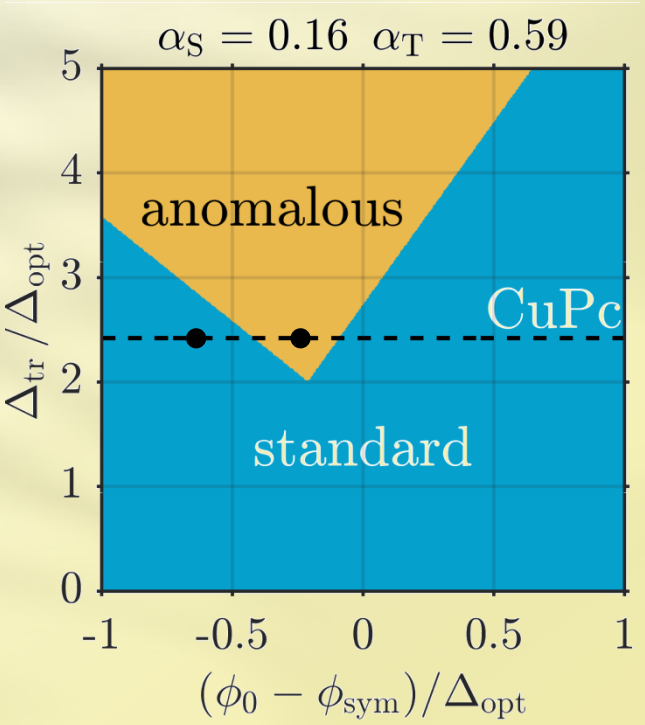
STM on thin insulating films

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





Predicting power

Fitting parameters		Contraints	
crystal field energy shift	Δ	V_{an}	Experimental anionic resonance
dielectric constant of the molecule	ϵ_{mol}	V_{cat}	Experimental cationic resonance
image charge renormalization energy	δ_{ic}	$n_{\mathrm{SOMO}} = 1$	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 eV

Conclusions I

- 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 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.

Spin-orbit interaction (SOI) and Magnetic anisotropy