Many-body correlations in STM single molecule junctions

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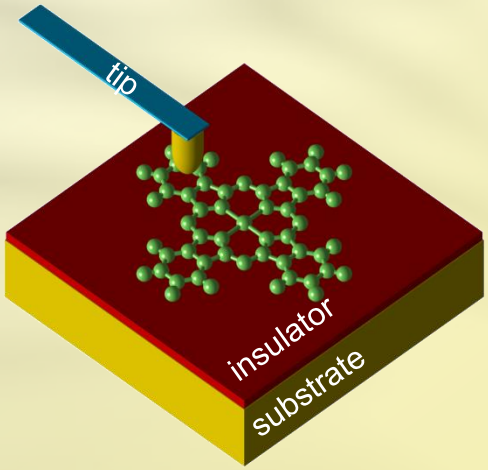
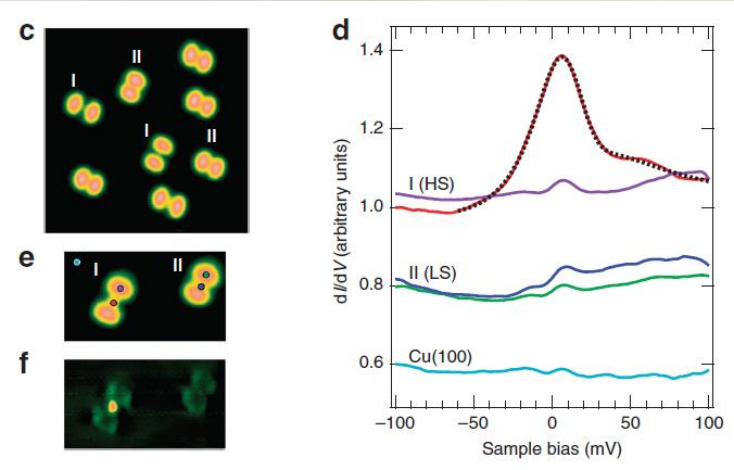
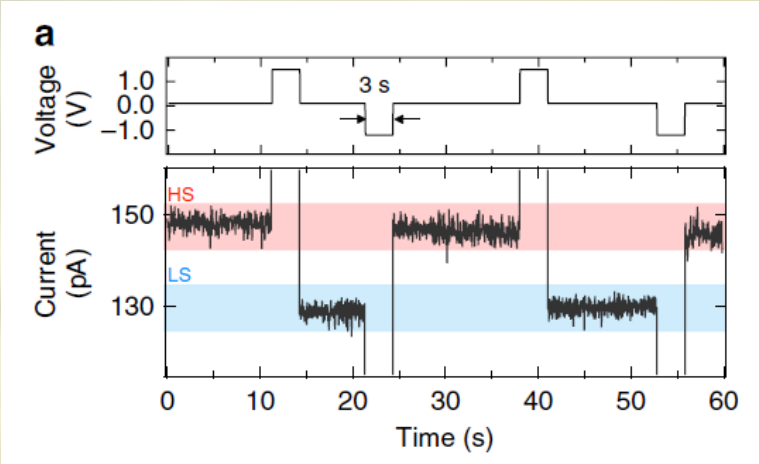


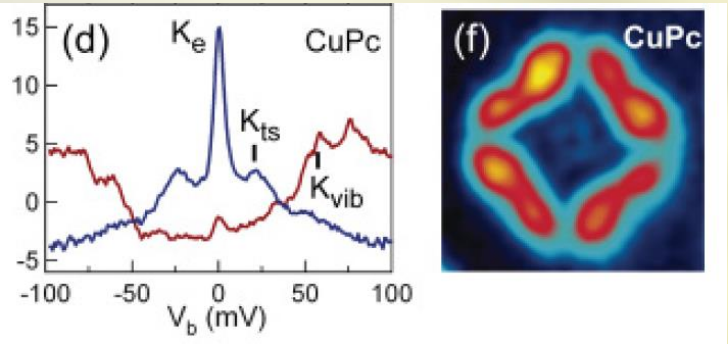
TRMME, Donostia 17.06.2016

Motivation





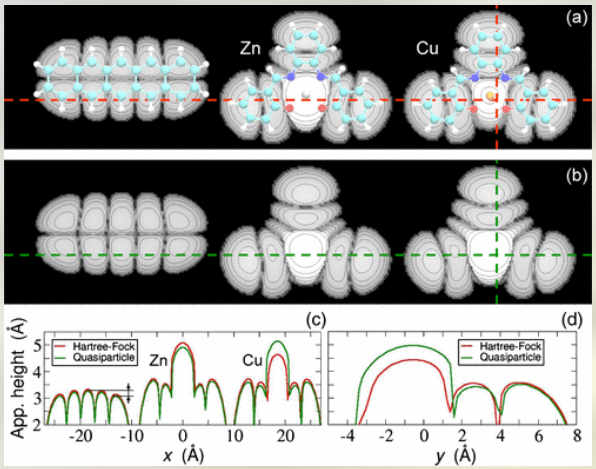
T. Miyamachi *et al. Nature comm.* **3**, 993 (2012)



- 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

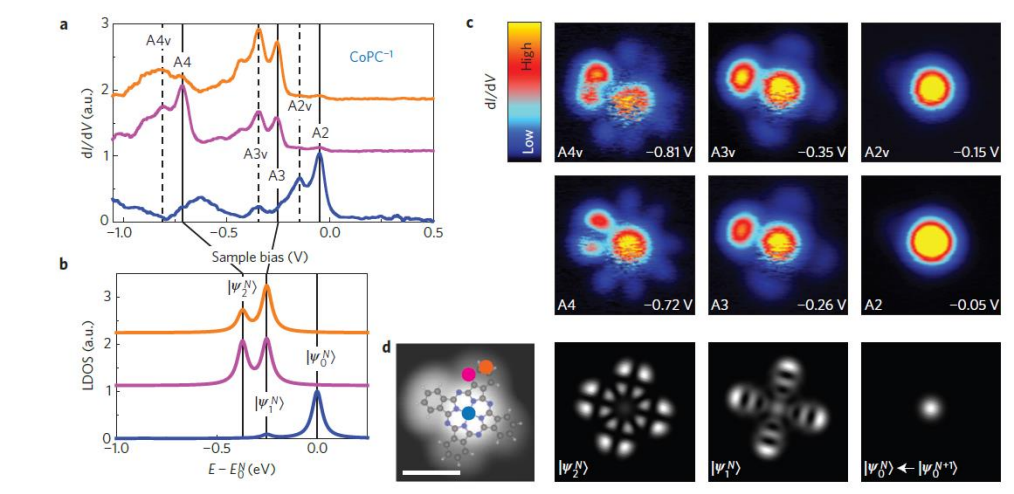


D. Toroz, et al. *PRL* **110**, 018305 (2013)

Alteration of the molecular orbitals due electronic correlation

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

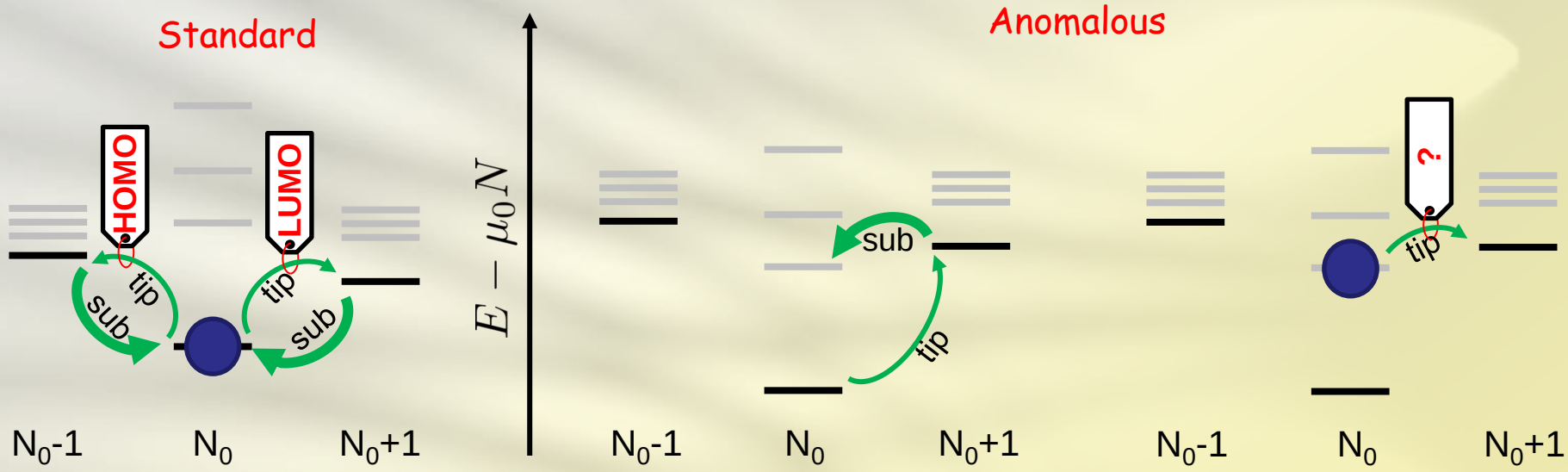
STM experiments probe quasiparticle wavefunctions which differ from the single particle molecular orbitals

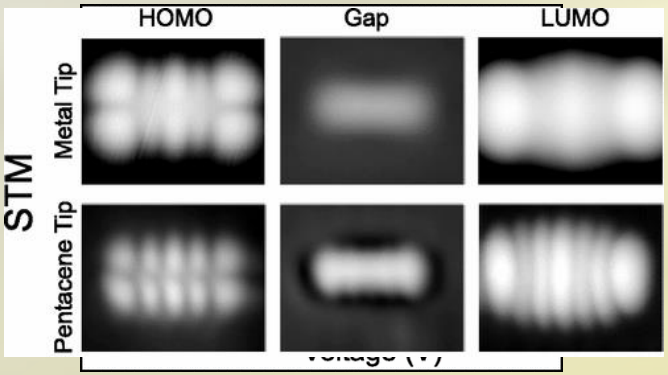


F. Schulz et al. Nat. Physics **11**, 229 (2015)

Visualization of many-body transitions in STM experiments

Anomalous microscopy



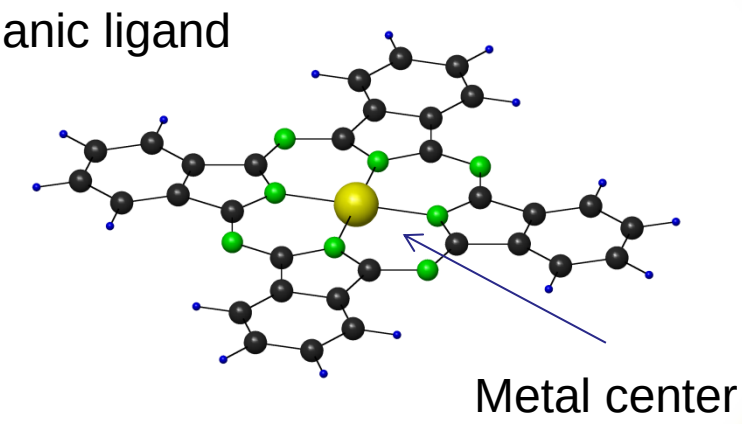


J.Repp et al. *PRL* **94**, 026803 (2005)

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

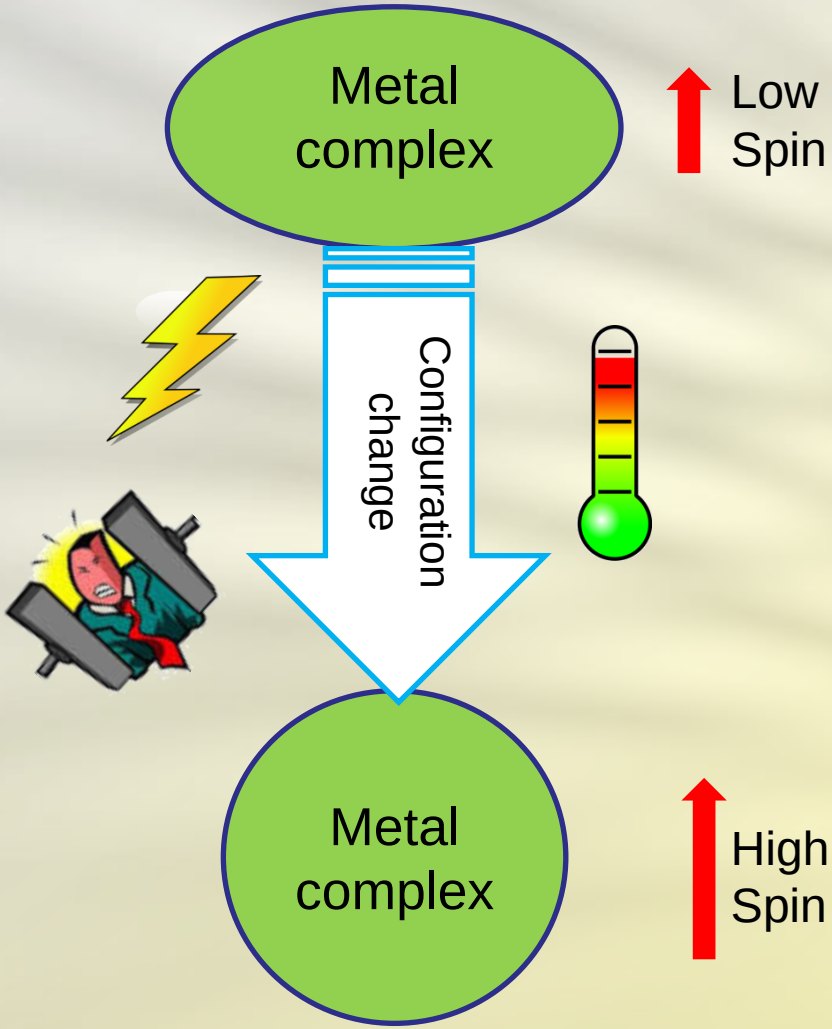
The **population inversion** relies on the strong asymmetry between substrate and tip tunneling rates and on the weak relaxation rate

Copper Phthalocyanine



Non-equilibrium spin crossover

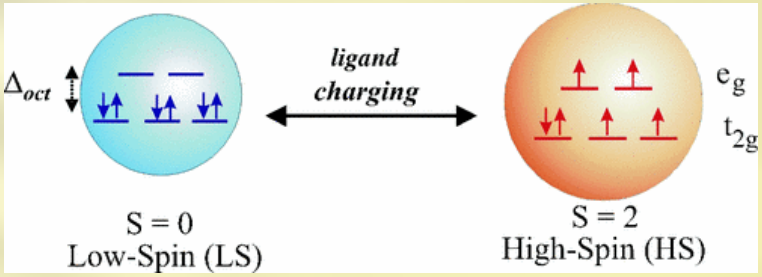
Spin crossover

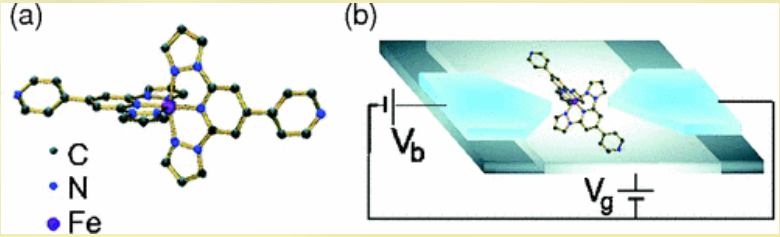


Change in the occupation of the metal *d*-orbitals:

Interplay of:

- (Octahedral) ligand field splitting
- Exchange interaction

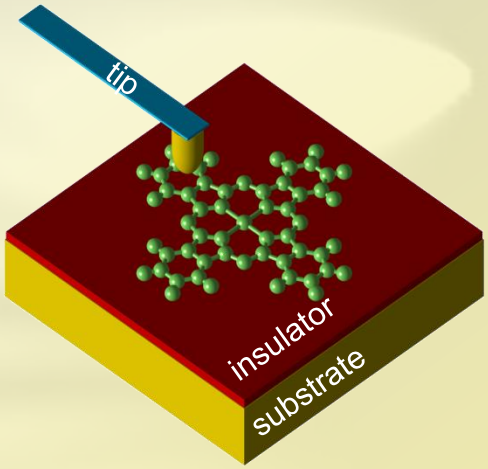


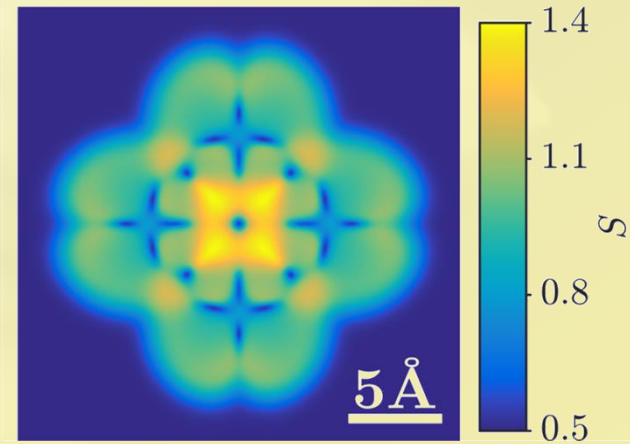


V. Meded, *et al.PRB* **83**, 245415 (2011)

Non equilibrium spin-crossover

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



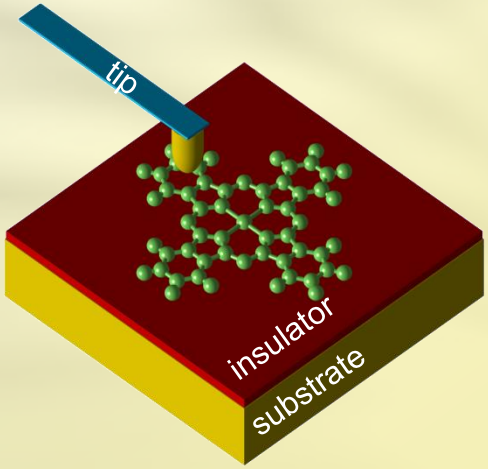


$V_{bias} = 1.38$ V

The Hamiltonian

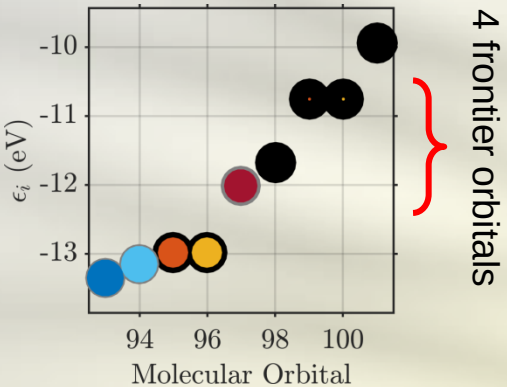
The STM single molecule junction is described by the Hamiltonian

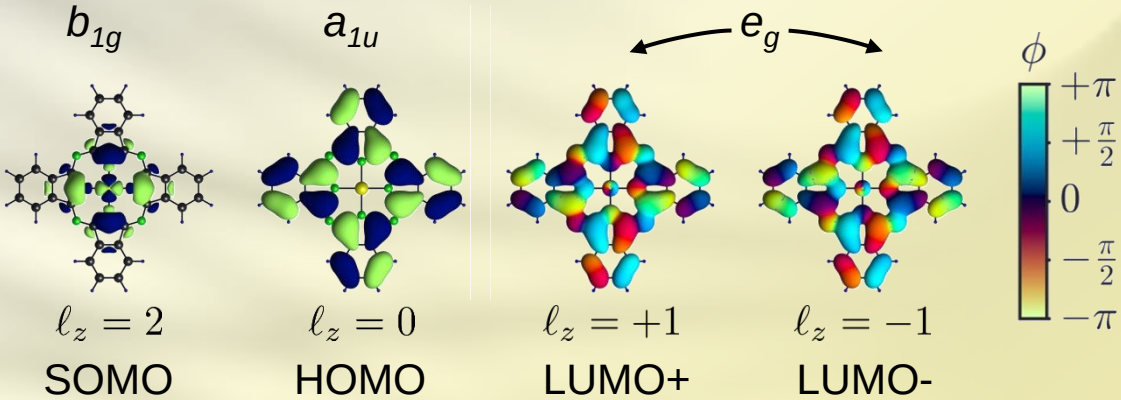
$$\hat{\mathrm{H}} = \hat{\mathrm{H}}_{\mathrm{mol}} + \hat{\mathrm{H}}_{\mathrm{mol-env}} + \hat{\mathrm{H}}_{\mathrm{S}} + \hat{\mathrm{H}}_{\mathrm{T}} + \hat{\mathrm{H}}_{\mathrm{tun}}$$



Minimal basis set

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

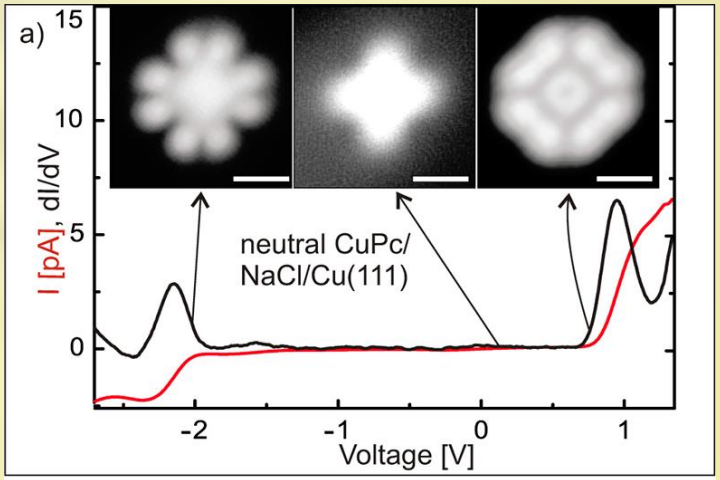




We restrict ourselves to the Fock space spanned by:

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

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

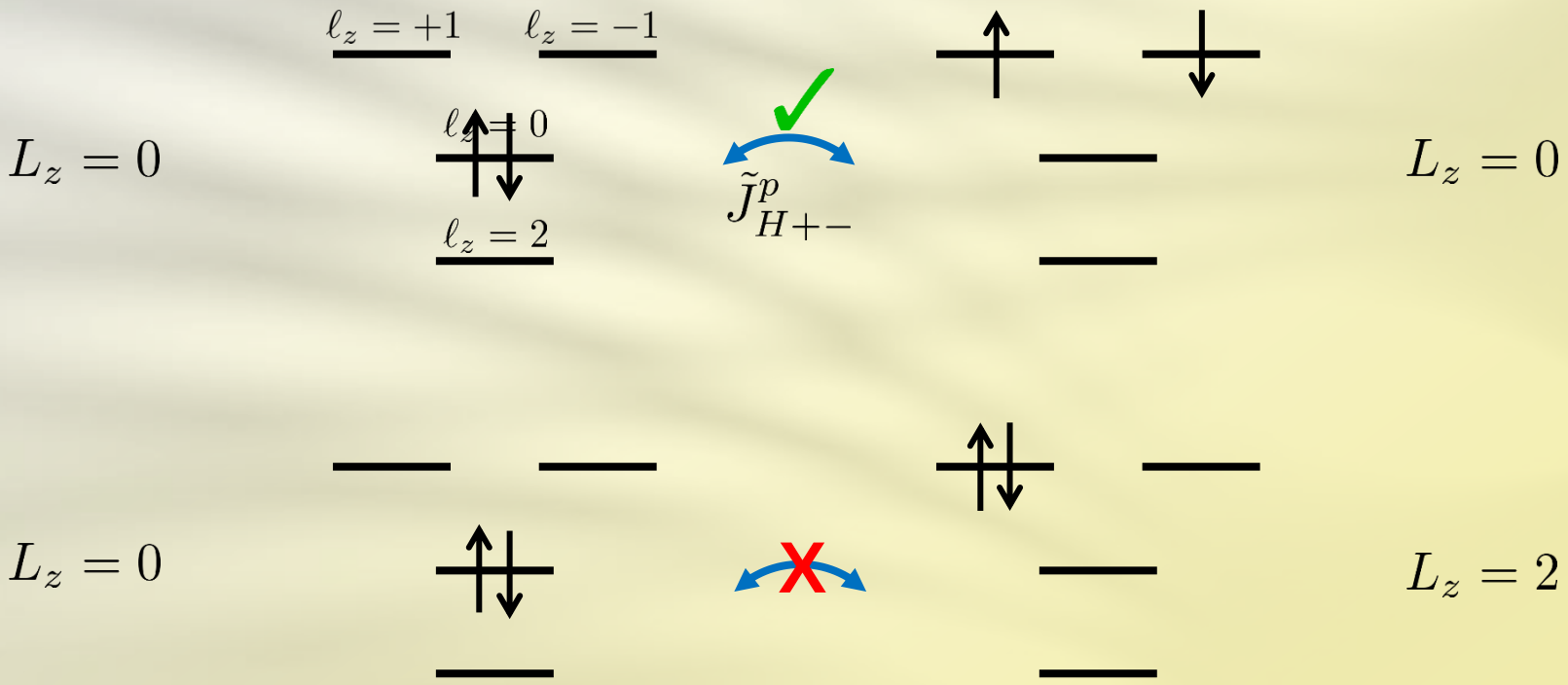
V_{ijkl} are ALL Coulomb integrals among the dynamical orbitals

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

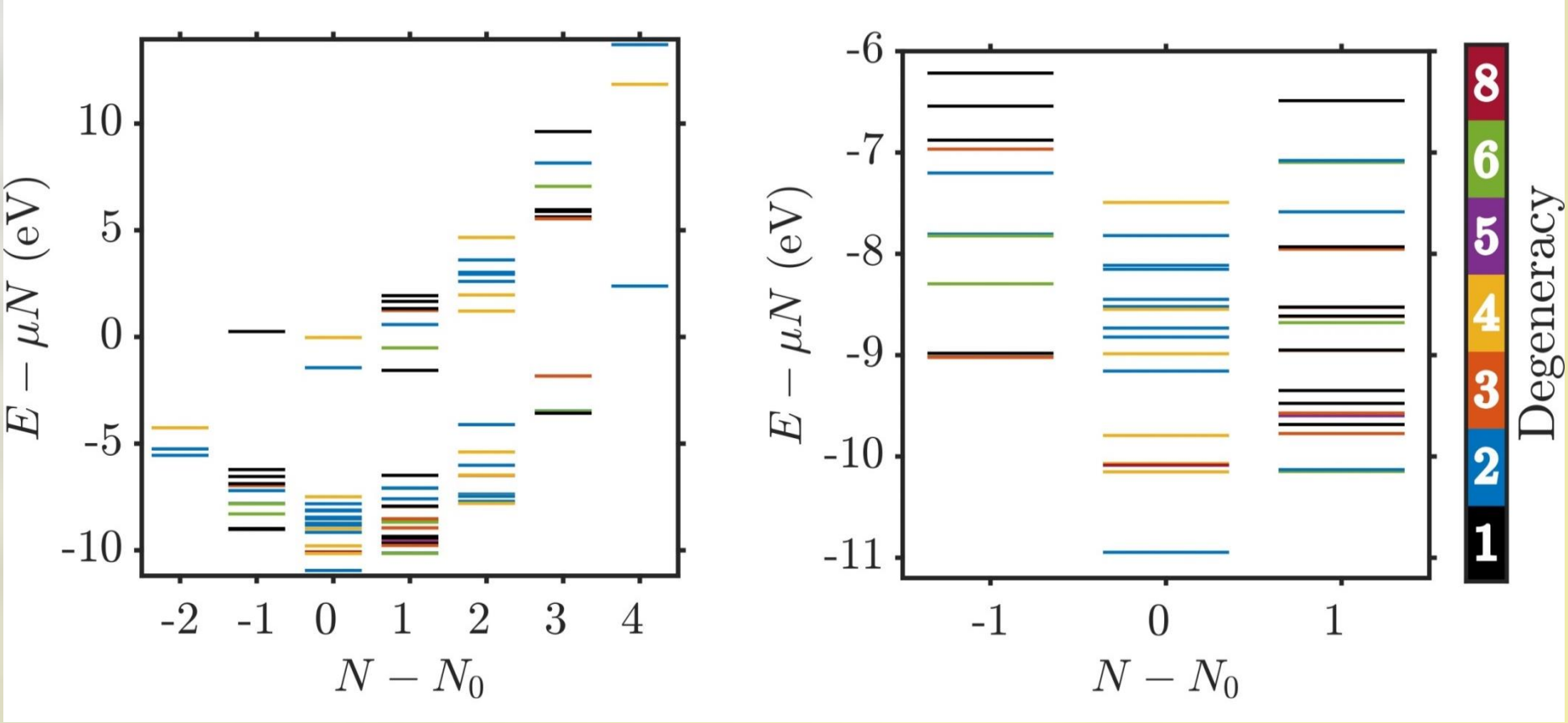
U_S	11.352 eV	$J^{\mathrm{ex}}_{HL} = -\tilde{J}^{\mathrm{p}}_{H+-}$	548 meV
U_H	1.752 eV	J^{ex}_{+-}	258 meV
$U_L = U_{+-}$	1.808 eV	J^{p}_{+-}	168 meV
U_{SH}	1.777 eV	$J^{\mathrm{ex}}_{SL} = -\tilde{J}^{\mathrm{p}}_{S+-}$	9 meV
U_{SL}	1.993 eV	$J^{\mathrm{ex}}_{SH} = J^{\mathrm{p}}_{SH}$	2 meV
U_{HL}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

Angular momentum conservation

The Coulomb interaction conserves the quasi angular momentum of the molecule



Many-body spectrum



Low energy eigenstates

+ LUMO

+ SOMO

+ HOMO

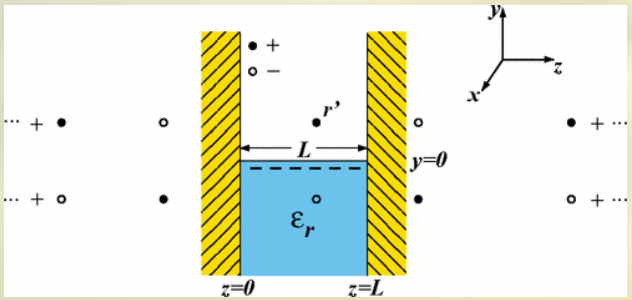
	cation			neutral			anion		
LUMO±					↑	↑	↑	↓	↑ + ↑ −
HOMO	↑	↑	↑ ↓	↑ ↓	↑ ↓	↑	↑ ↓	↑ ↓	↑ ↓
SOMO	↑	↓		↑		↑	↑	↑	
$E_{Nm} - E_{N0}$ (meV)	0	4	40	0	794	860	0	18	374
S	1	0	0	1/2	1/2	3/2	1	0	1
degeneracy	3	1	1	2	4	8	6	2	3

Image charge effects

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

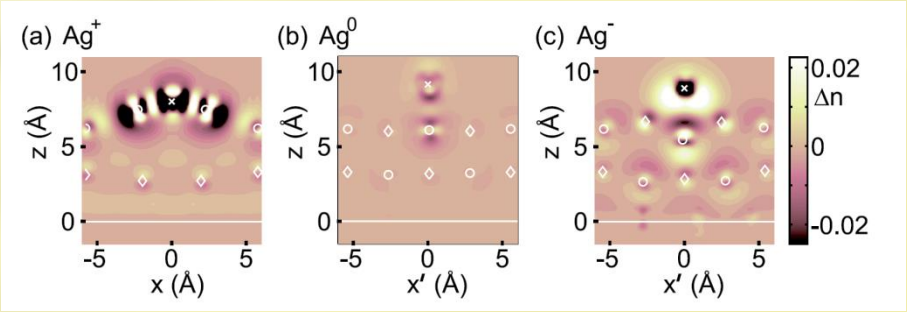
This term incorporates the two main effects which stabilize the excess charge on the molecule

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

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

$$\dot{\sigma} = -\frac{i}{\hbar}\overbrace{[\hat{\mathrm{H}}_{\mathrm{mol}} + \hat{\mathrm{H}}_{\mathrm{mol-env}}, \sigma]}^{\textbf{Coherent}\ \text{dynamics}} - \frac{i}{\hbar}\overbrace{[\hat{\mathrm{H}}_{\mathrm{eff}}, \sigma]}^{\text{Effective}\ \textbf{internal}\ \text{dynamics}}$$
$$+ \underbrace{\mathcal{L}_{\mathrm{tun}}[\sigma]}_{\textbf{Tunnelling}\ \text{dynamics}} + \underbrace{\mathcal{L}_{\mathrm{rel}}[\sigma]}_{\textbf{Phenom.}\ \text{relaxation}} := \mathcal{L}[\sigma]$$

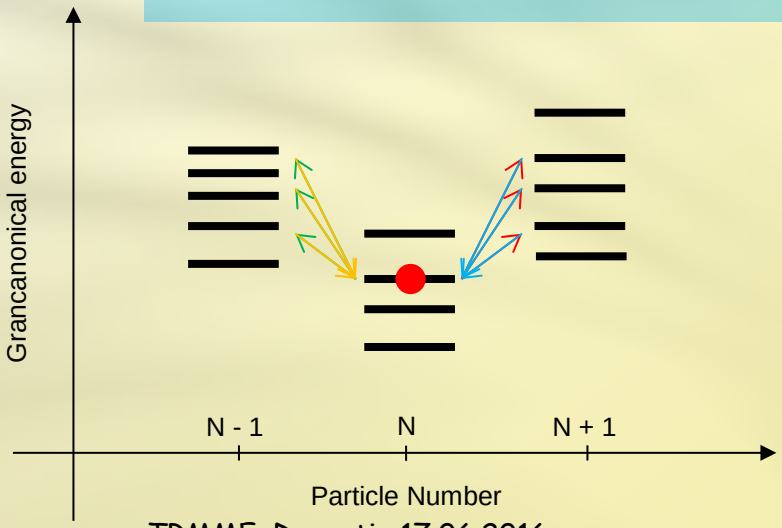
$$\mathcal{L}_{\mathrm{rel}}[\sigma] = -\frac{1}{\tau}\left(\sigma - \sum_{NFm} \sigma_{mm}^{\mathrm{th},NF} |NFm\rangle\langle NFm| \sum_{En} \sigma_{nn}^{NE}\right)$$

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

Tunnelling Liouvillean

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

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



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

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

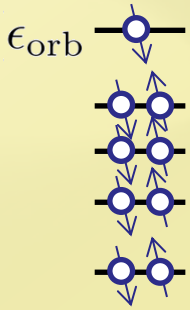
Many-body rate matrix

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

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

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

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



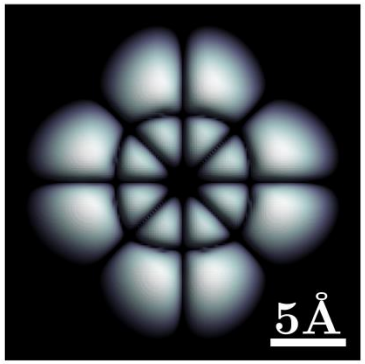
Close to equilibrium, the **constant current map** is the **isosurface** of a **specific molecular orbital** (Tersoff-Hamann theory of STM)

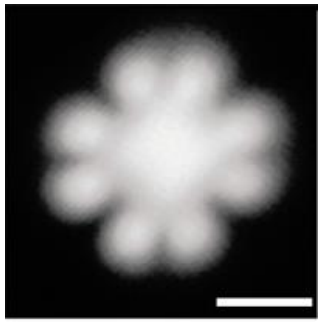
Topography of CuPc

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

cationic resonance: $\phi_0 = 4.65$ eV

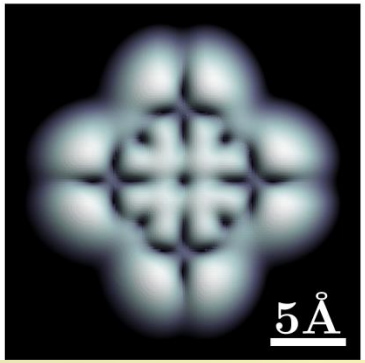
$I_\chi(\mathbf{r}_\mathrm{T}, V_\mathrm{res}) = 0.5\,\mathrm{pA}$

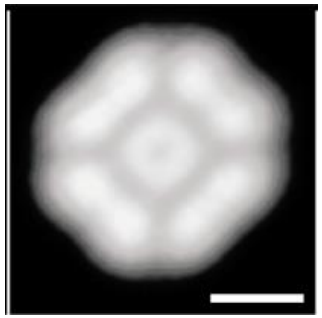




anionic resonance: $\phi_0 = 4.65$ eV

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



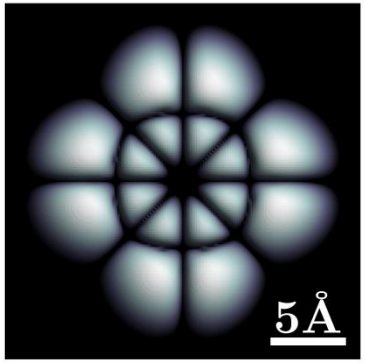


B. Siegert, A. Donarini, and M. Grifoni PRB **93** 121406(R) (2016)

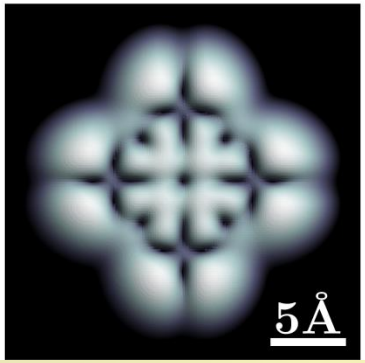
Current and spin maps

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

cationic resonance: $\phi_0 = 4.65$ eV

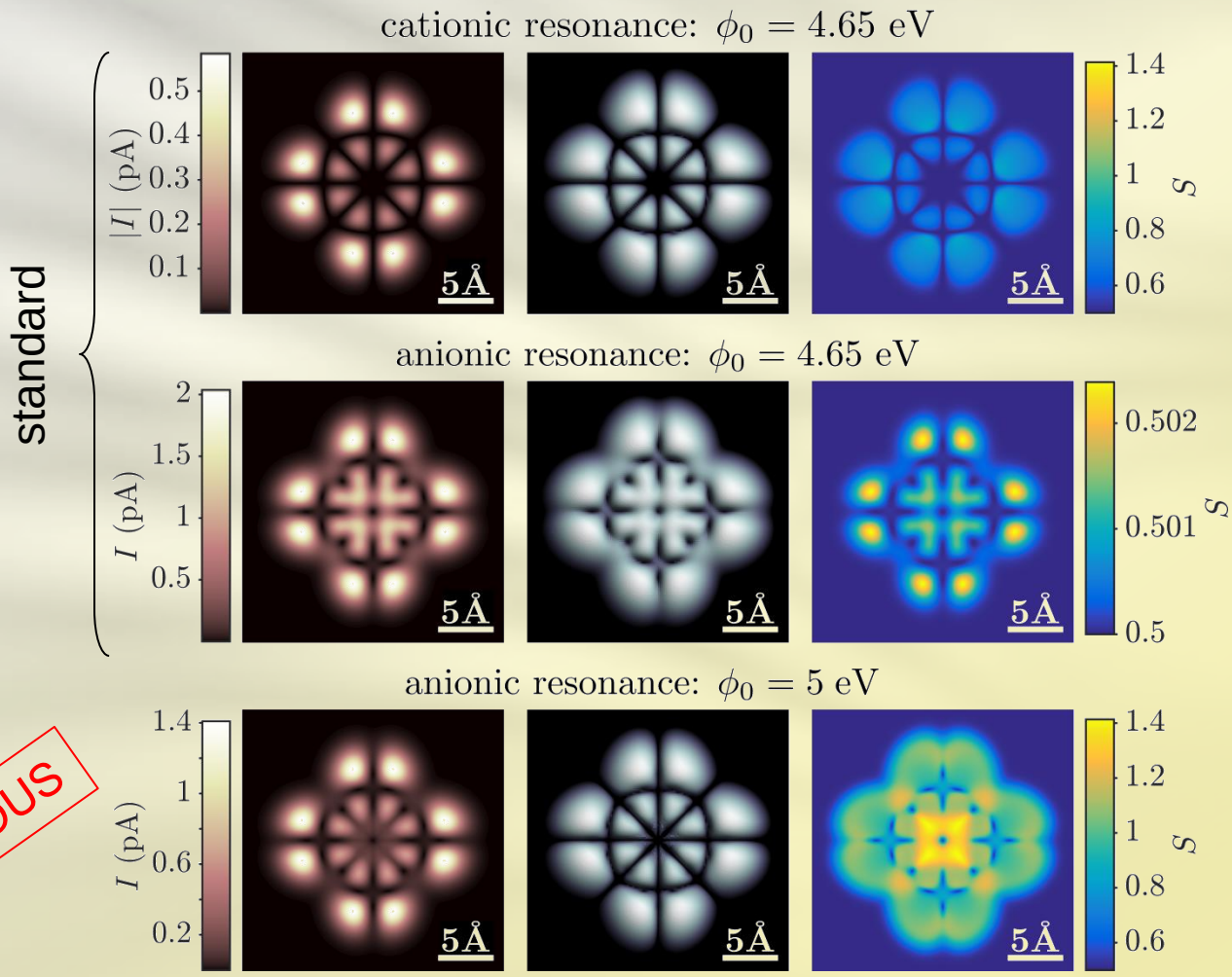


anionic resonance: $\phi_0 = 4.65$ eV



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

The anomalous case

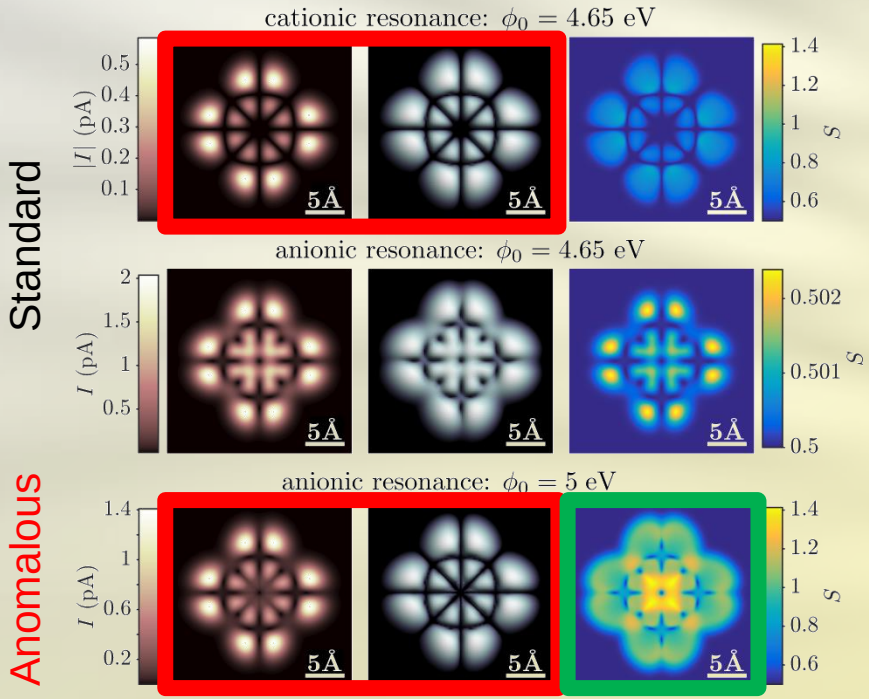


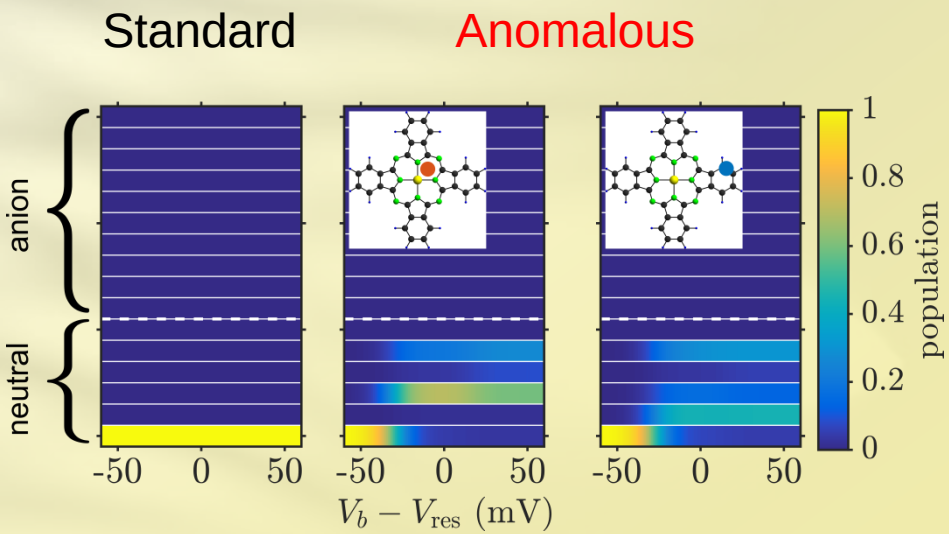
ANOMALOUS

Population inversion

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

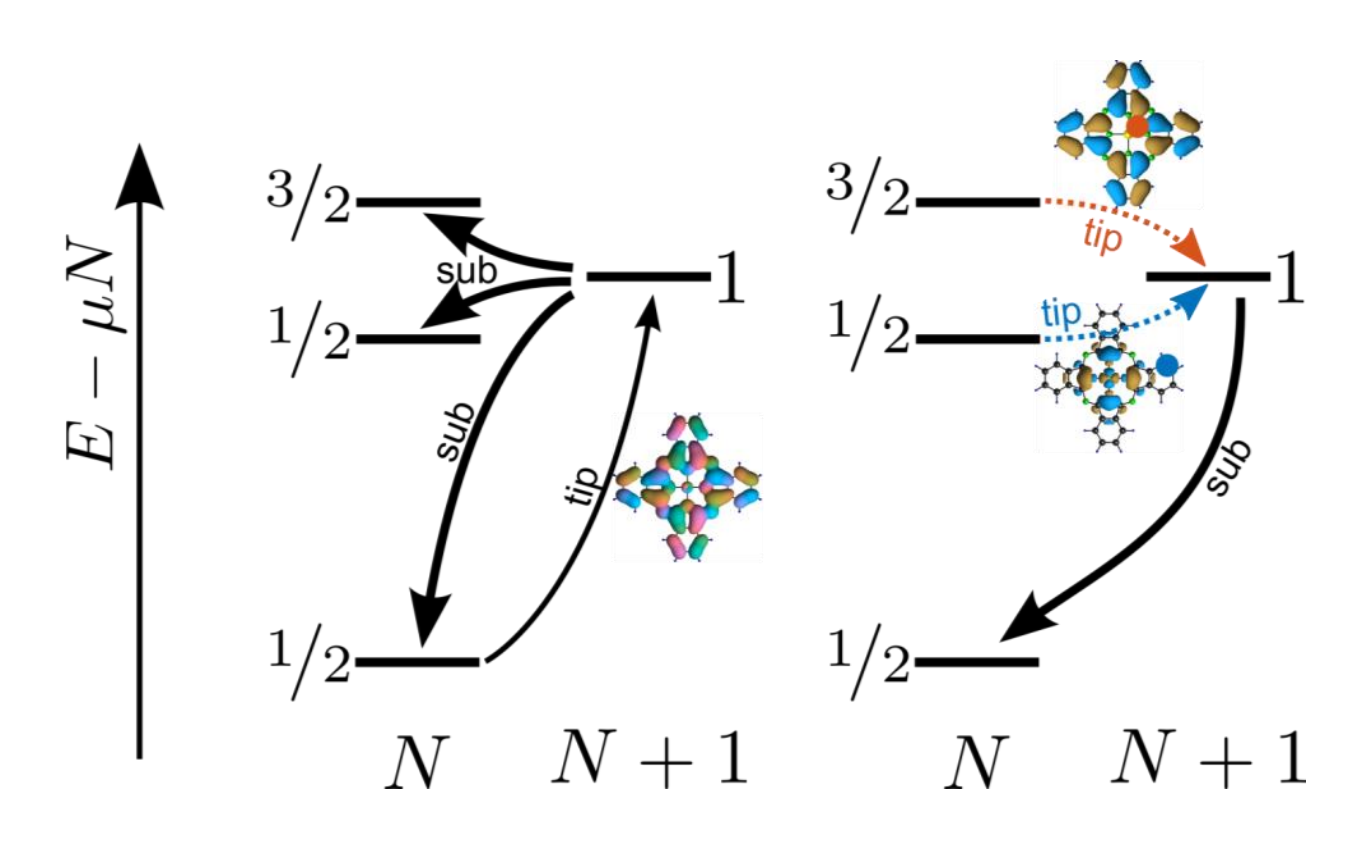
The average **spin** of the molecule varies with the tip position and does **not** correspond to the one of the **molecular ground state**





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

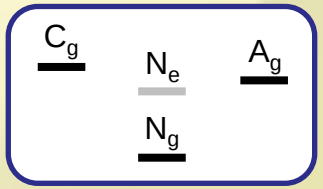
The anomalous current map



Is CuPc so special ?

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

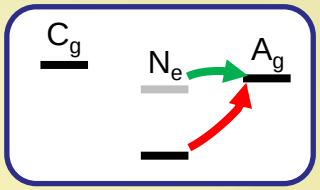
1 The energy of the excited neutral state should be lower than the ones of the cationic and anionic ground states



2 The spin of the gr te should be different

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

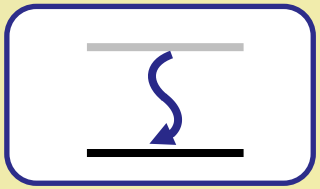
3 The (tip) transitio tate and the the neutral groun ve different molecular orbitals



4 The tip and substrat ngly 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

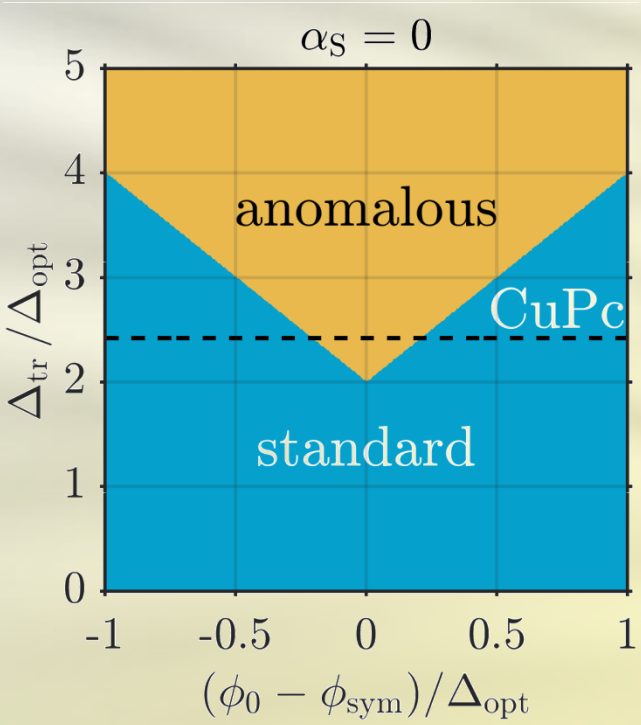
A class of single molecule junctions

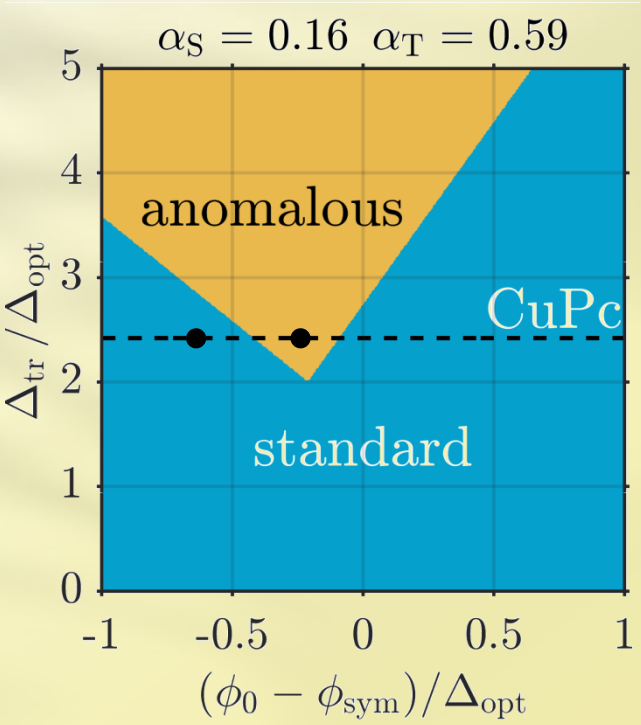
$$\Delta_{\mathrm{tr}} = \mathrm{IP} - \mathrm{EA} - 2\delta_{\mathrm{ic}}$$

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

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

$\phi_0 =$ Substrate workfunction





Conclusions

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

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

- For an experimentally accessible substrate workfunction of 5 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.

Outlook

- Incorporate a quantitative treatment of the electrostatic interactions within the junction
- Calculate the magnetotransport characteristics in presence of non-collinearly polarized ferromagnetic contacts
- Investigate the position resolved spin and/or orbital Kondo effect
- Study the time resolved evolution of electronic and spin excitations within an electronic or optoelectronic pump-probe scheme

Aknowledgments

Milena Grifoni

Benjamin Siegert

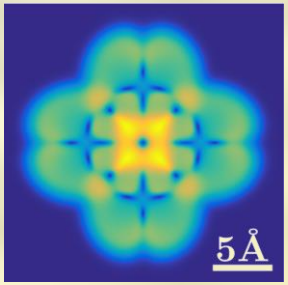
J. Repp

T. Niehaus

D. Ryndyk

R. Korytar

Thank you for your attention!



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Deutsche Forschungsgemeinschaft

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

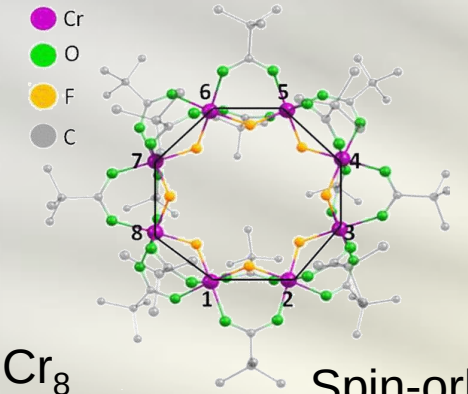
- Both for CuPc on NaCl(3ML)/Cu(100) and CuPc on NaCl(2ML)/Cu(111) -

Open Prediction

Non equilibrium spin-crossover for CuPc on a substrate with workfunction of 5 eV

Spin-orbit interaction (SOI) and Magnetic anisotropy

Motivation



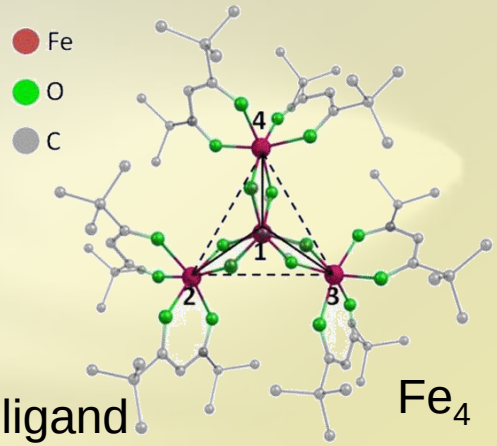
Cr_8

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

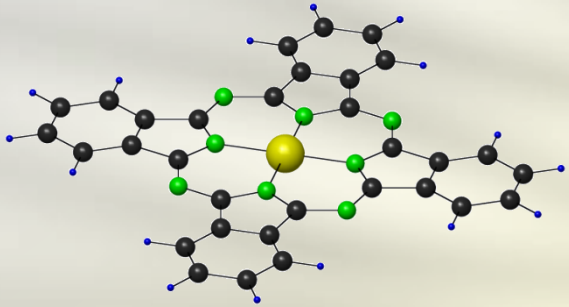
Metal-organic coordination networks

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)

SOI in the frontier orbitals basis

$$H_{\mathrm{mol}} = H_0 + V_{\mathrm{ee}} + \boxed{V_{\mathrm{SO}}}$$



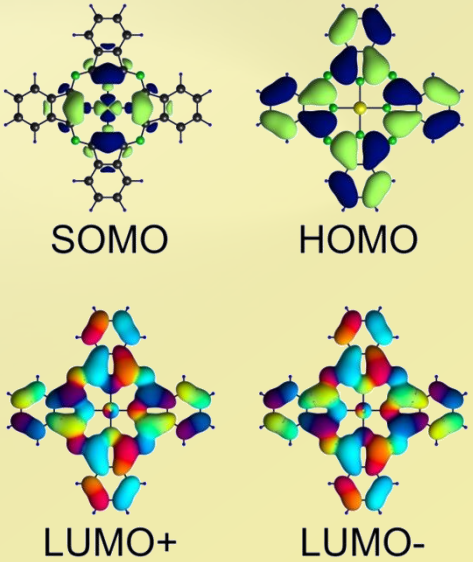
$$V_{\mathrm{SO}} = \sum_{\alpha,\ell_\alpha} \xi_{\ell_\alpha}\, \boldsymbol{\ell}_\alpha \cdot \mathbf{s}_\alpha$$

The dominat contribution is given by the third shell of Cu

Projection onto the frontier orbital basis yields

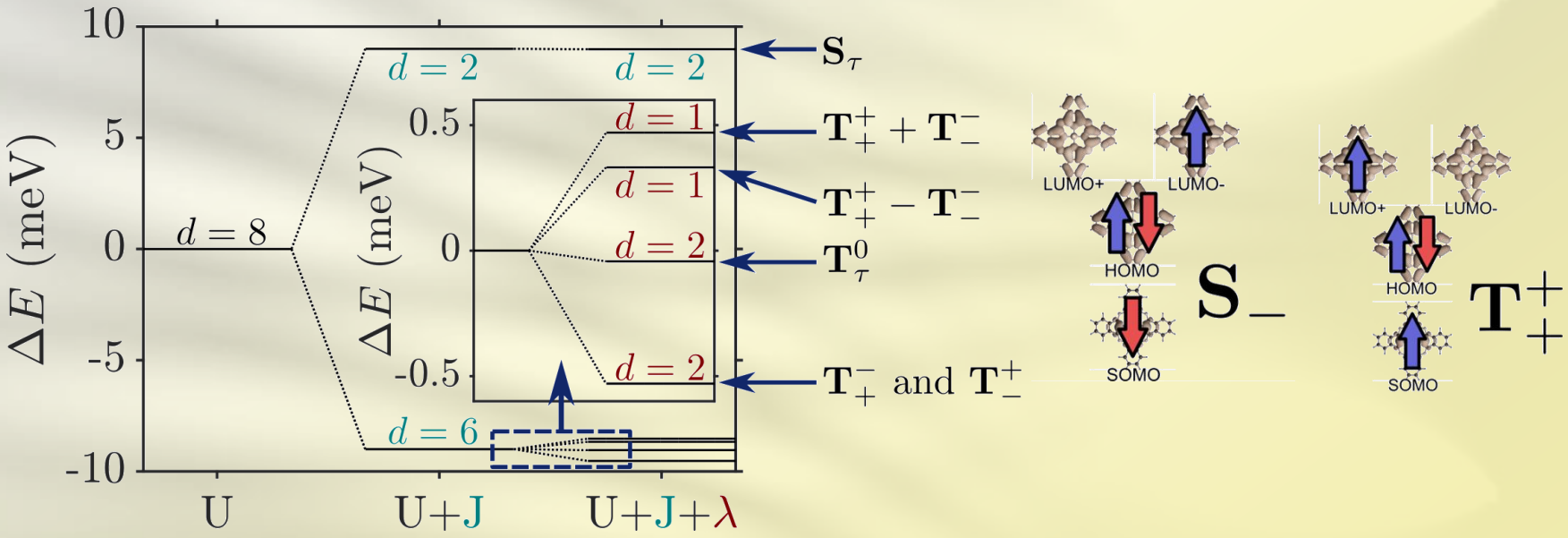
$$V_{\mathrm{SO}} = \lambda_1 \sum_{\tau=\pm} \tau \left(d^\dagger_{L\tau\uparrow} d_{L\tau\uparrow} - d^\dagger_{L\tau\downarrow} d_{L\tau\downarrow} \right) + \lambda_2 \left(d^\dagger_{S\uparrow} d_{L-\downarrow} + d^\dagger_{L+\uparrow} d_{S\downarrow} + \mathrm{h.c.} \right)$$

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



Low energy spectrum of CuPc

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



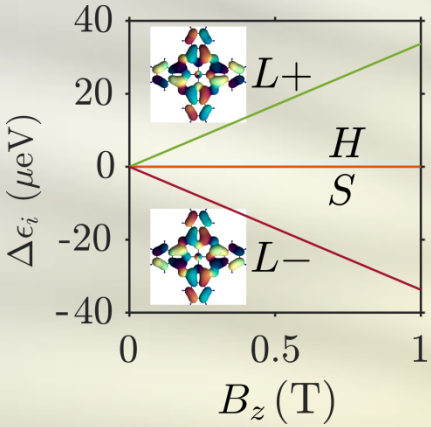
To first order in the spin orbit coupling

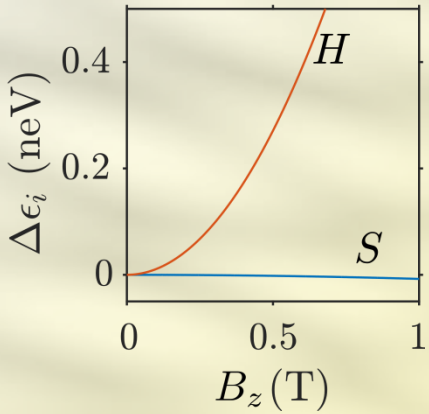
$$H_0^{N_0+1} = E^{\mathrm{g}}_{N_0+1} - J^{\mathrm{ex}}_{SL}\left(\hat{S}^2 - 1\right) + \lambda_1\, \hat{\tau}_z \hat{S}_z$$

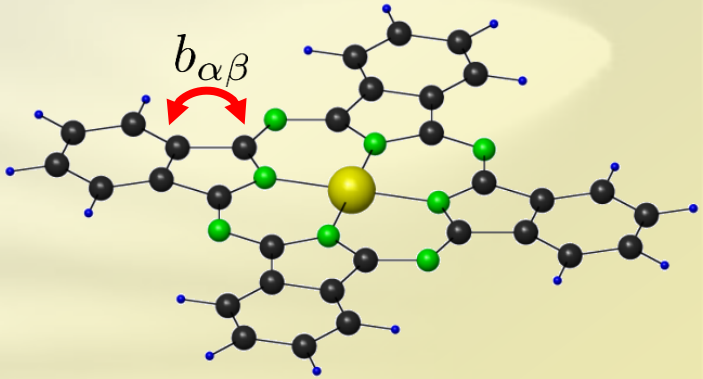
B. Siegert, A. Donarini and M. Grifoni, *Beilstein J. of Nanotech.* **6**, 2452 (2015)

External magnetic field

Orbital component described by the Peierls phase







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

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

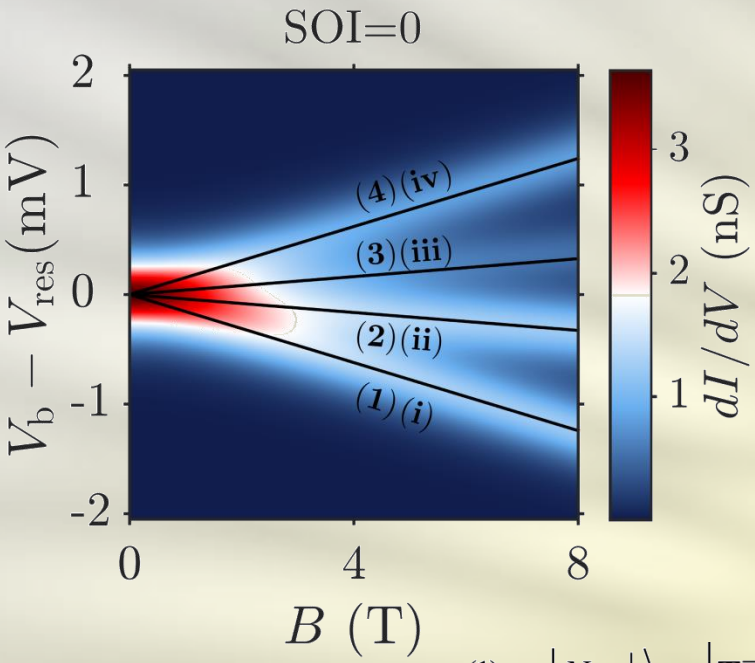
By adding also the Zeeman term we obtain the effective Hamiltonian

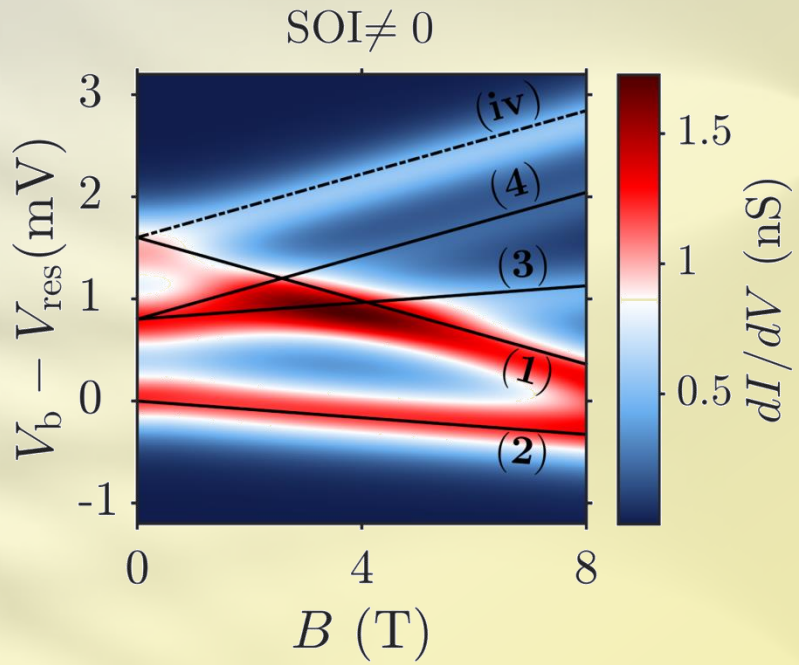
$$H^N_{\mathrm{eff}} = H^N_0 + \mu_{\mathrm{orb}}\,\hat{\tau}_z B_z + g_S \mu_{\mathrm{B}}\,\hat{\mathbf{S}}\cdot\mathbf{B}$$

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

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

Magnetotransport





$(1): \ |N_0,\downarrow\rangle \rightarrow |\mathbf{T}_-^-\rangle$

$(2): \ |N_0,\downarrow\rangle \rightarrow |\mathbf{T}_+^-\rangle$

$(3): \ |N_0,\downarrow\rangle \rightarrow |\mathbf{T}_-^0\rangle$

$(4): \ |N_0,\downarrow\rangle \rightarrow |\mathbf{T}_+^0\rangle$

$(i): \ |N_0,\uparrow\rangle \rightarrow |\mathbf{T}_-^0\rangle$

$(ii): \ |N_0,\uparrow\rangle \rightarrow |\mathbf{T}_+^0\rangle$

$(iii): \ |N_0,\uparrow\rangle \rightarrow |\mathbf{T}_-^+\rangle$

$(iv): \ |N_0,\uparrow\rangle \rightarrow |\mathbf{T}_+^+\rangle$

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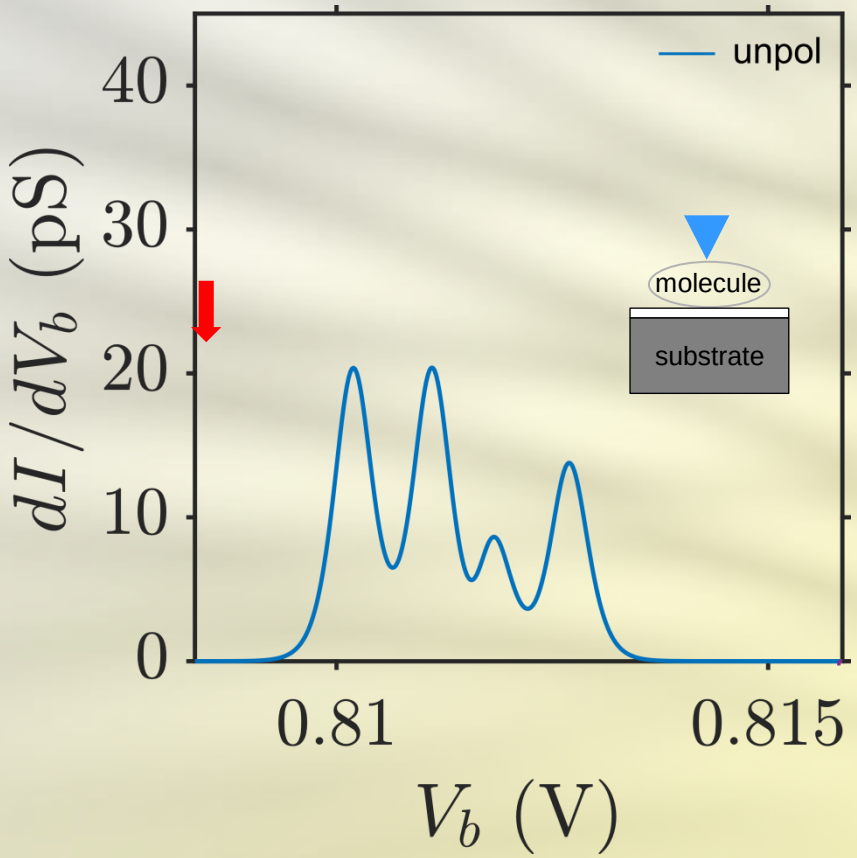
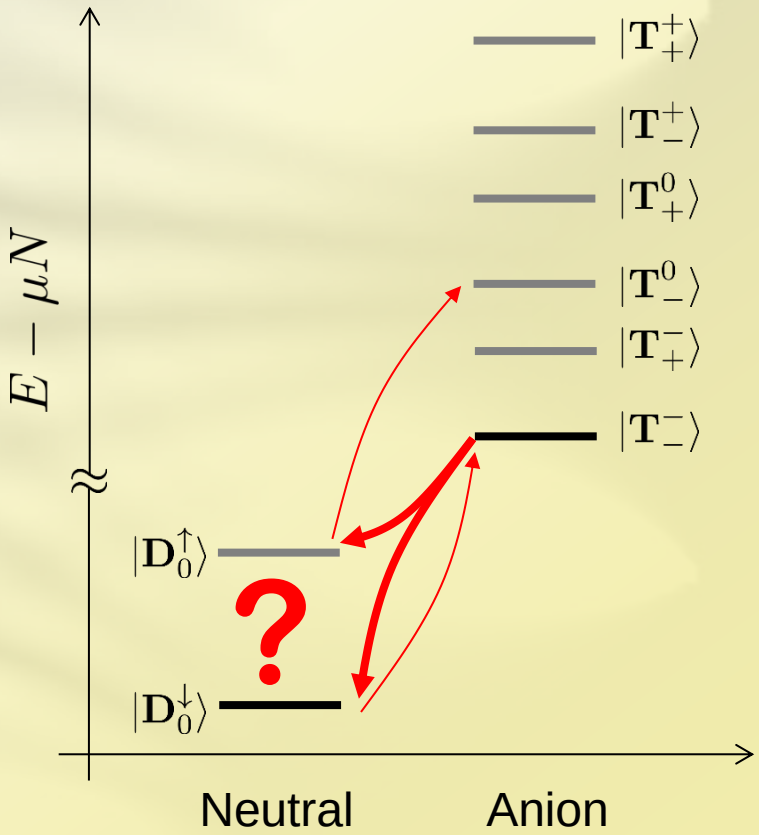
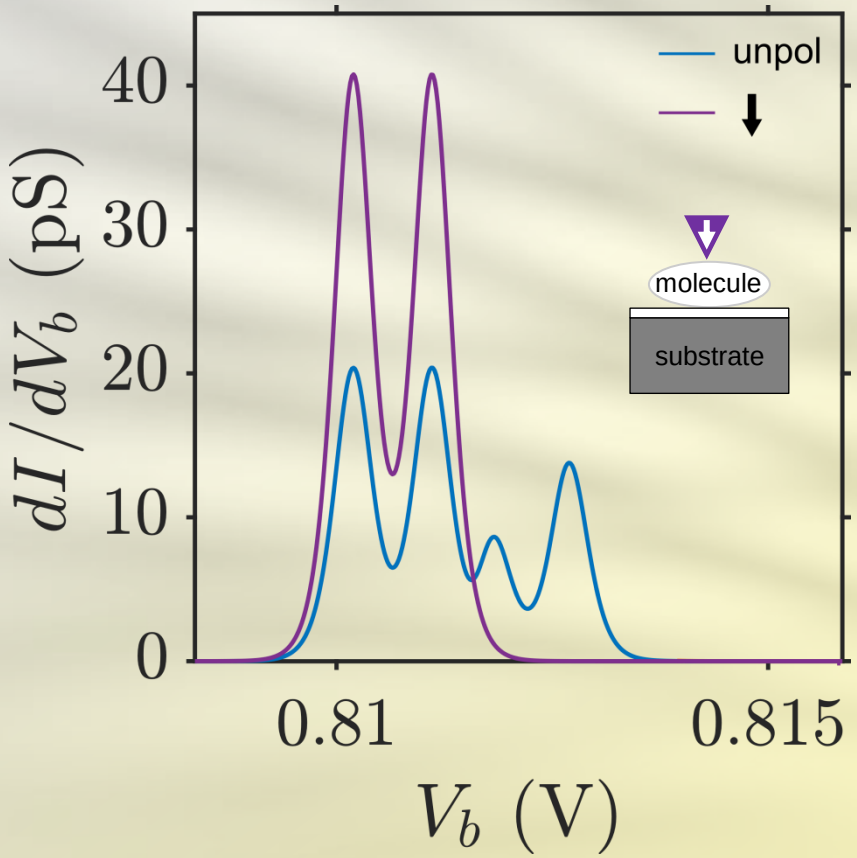
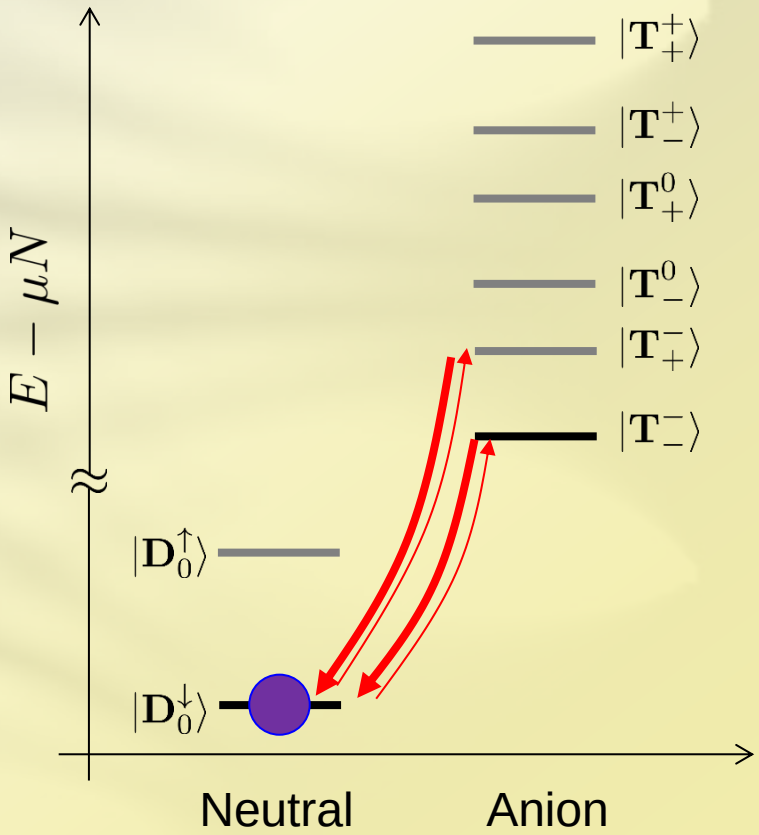
Asymmetric conductance peaks



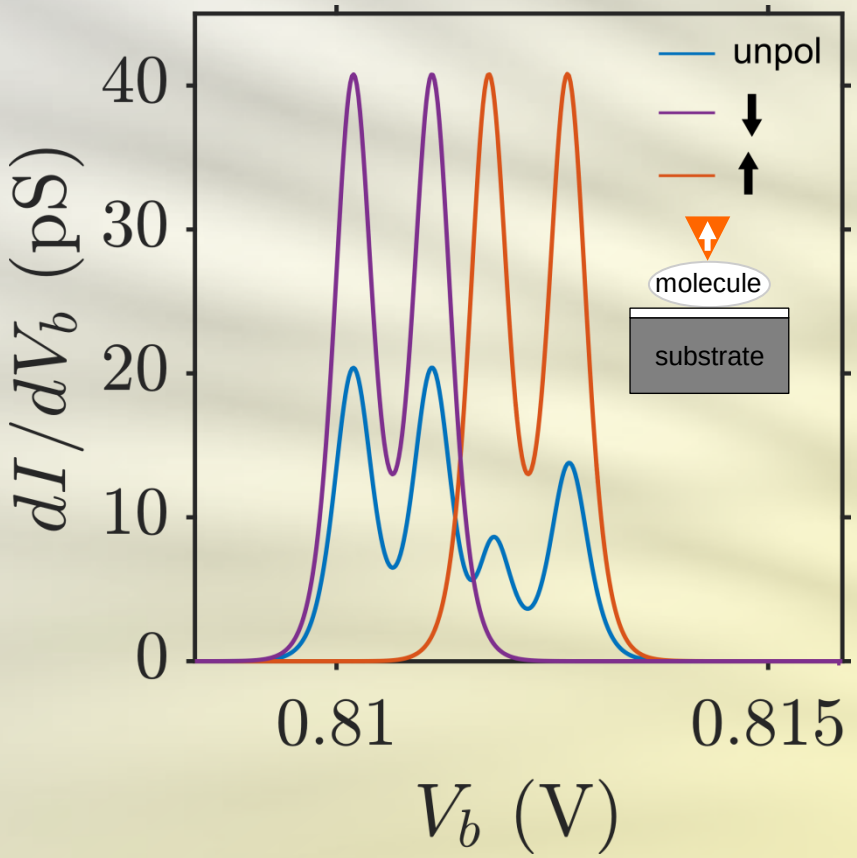


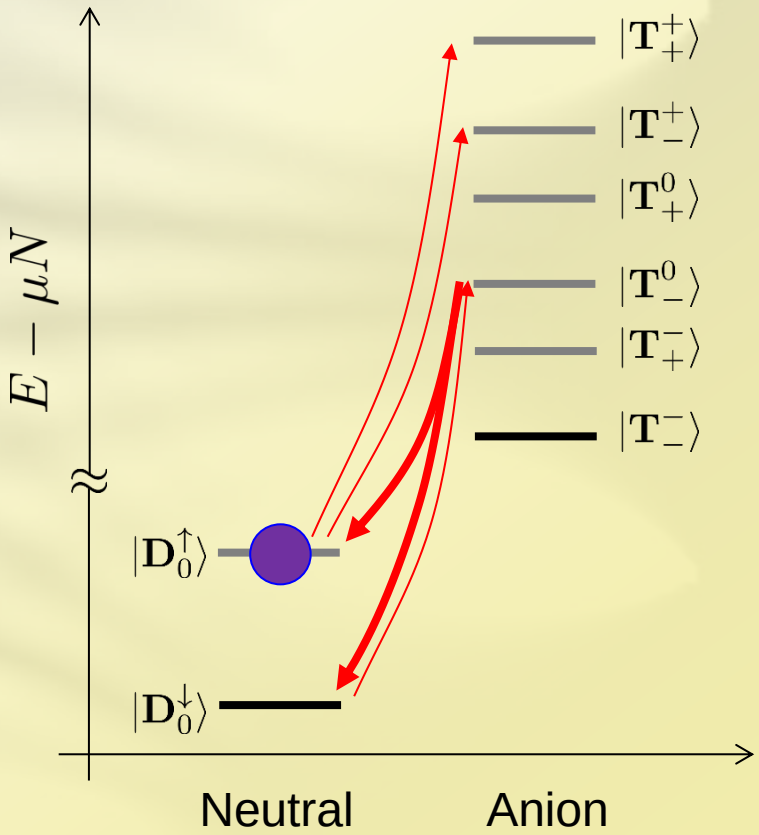
Asymmetric conductance peaks



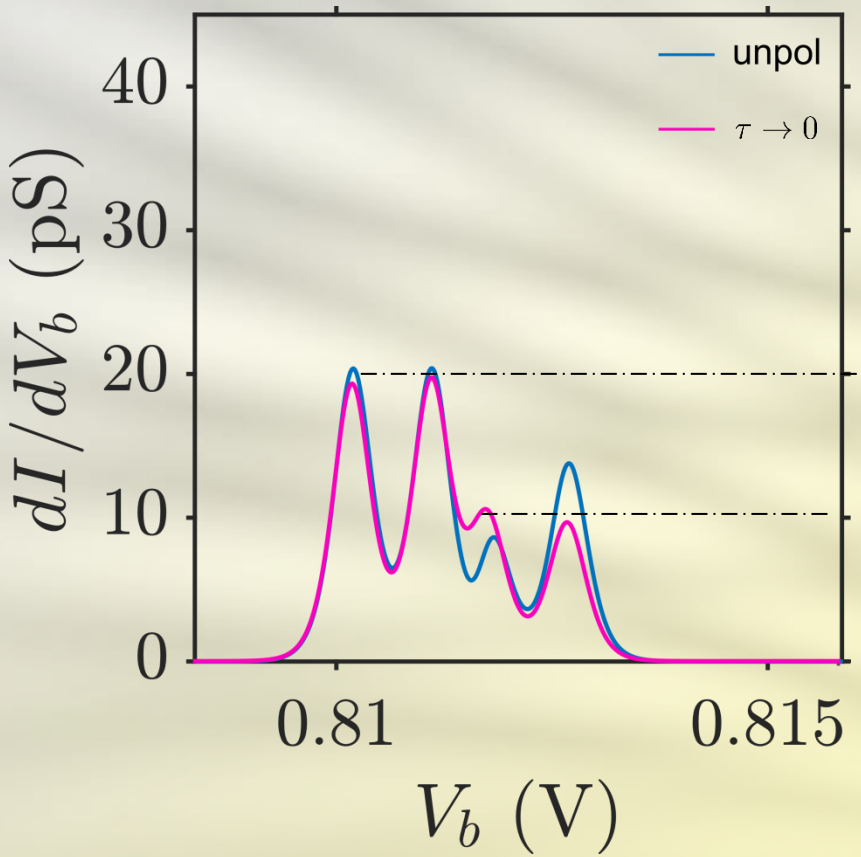


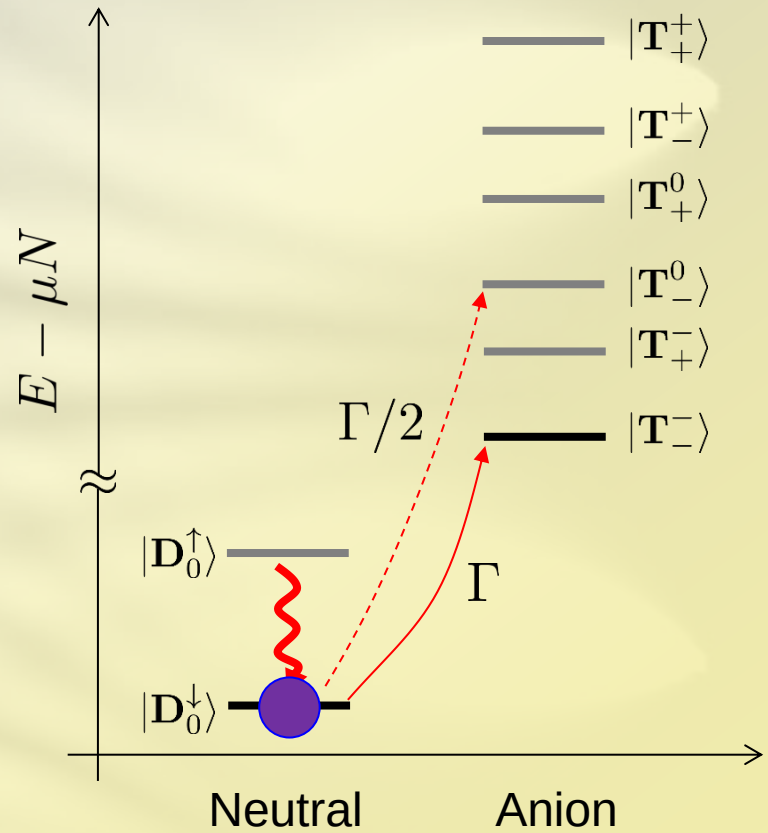
Asymmetric conductance peaks





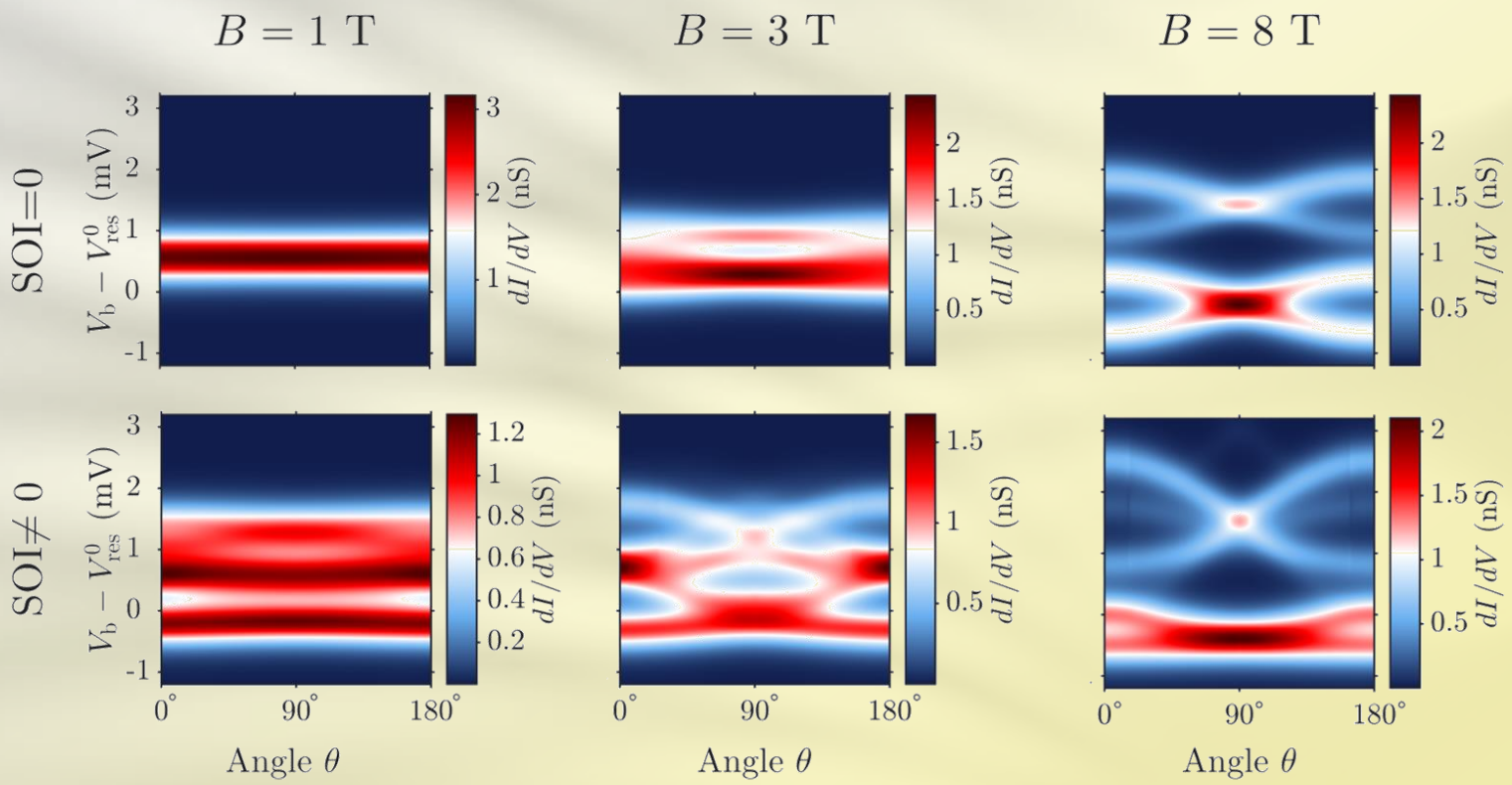
Asymmetric conductance peaks





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

Magnetic anisotropy



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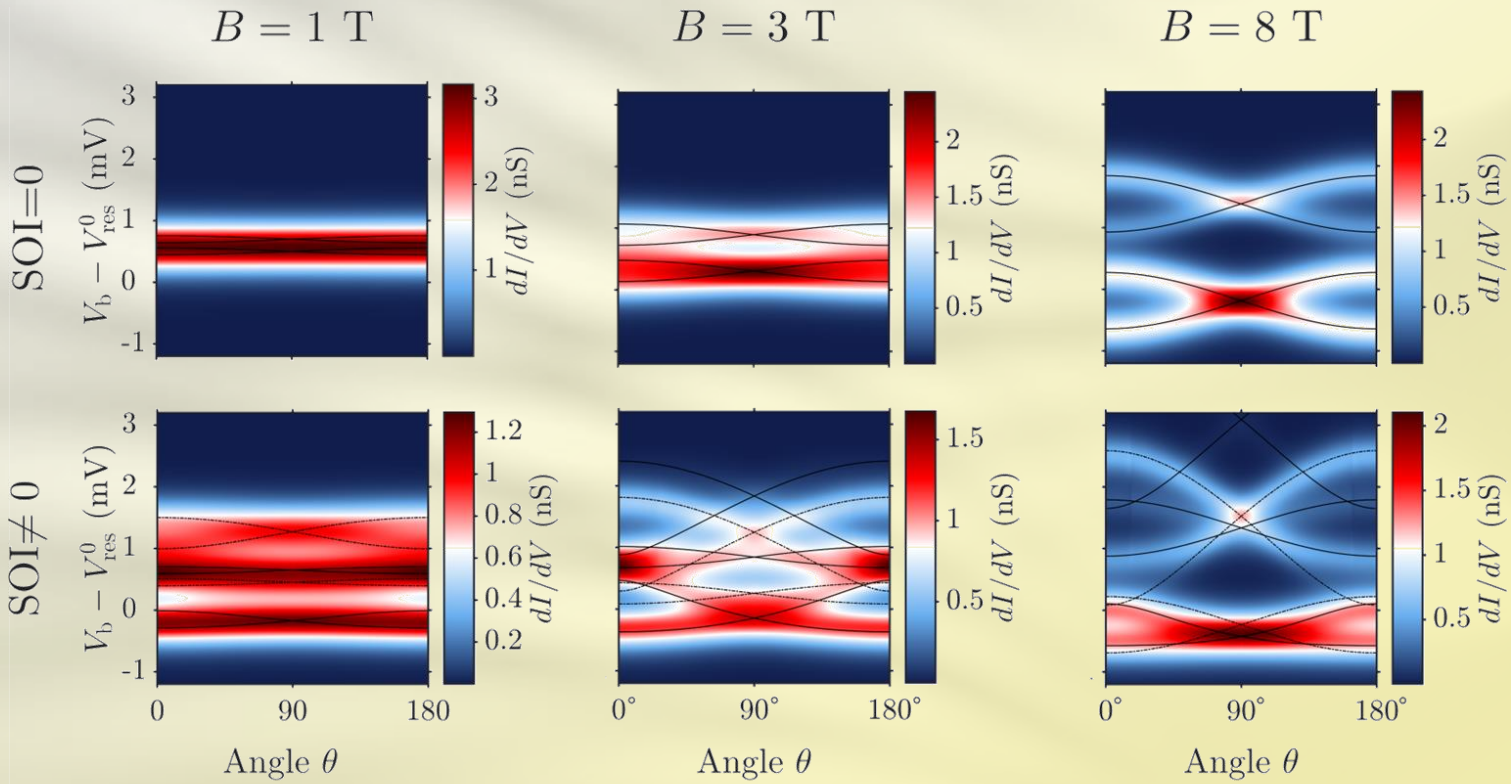
Magnetic anisotropy



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Conclusions II

- 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**