Non-equilibrium Spin-crossover in Copper Phthalocyanine

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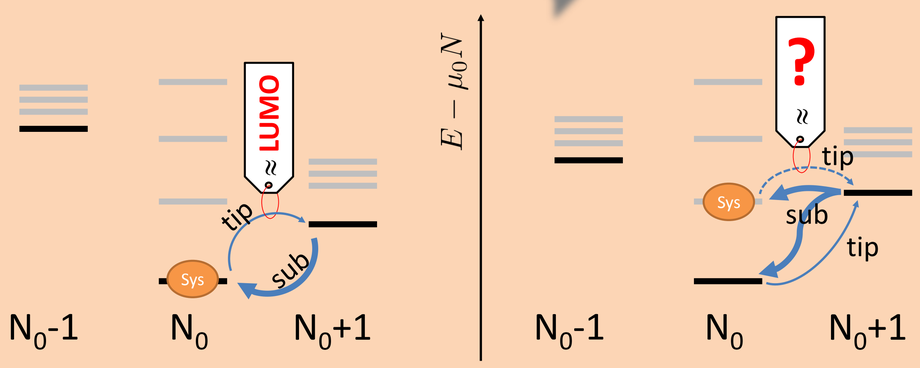
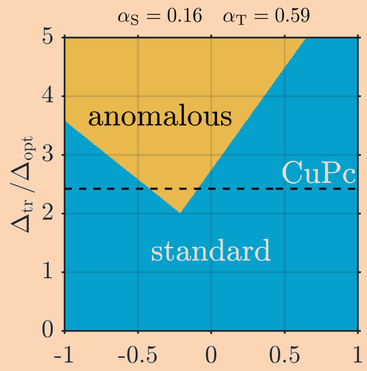
Standard → Anomalous

Work function modulation



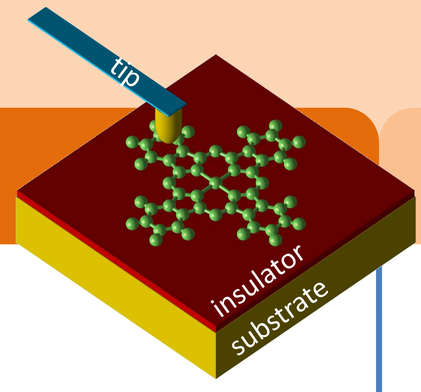
- Population inversion
- Topographical and spectroscopic anomalies
- Current induced control of the molecular spin

A wide class of anomalous junctions



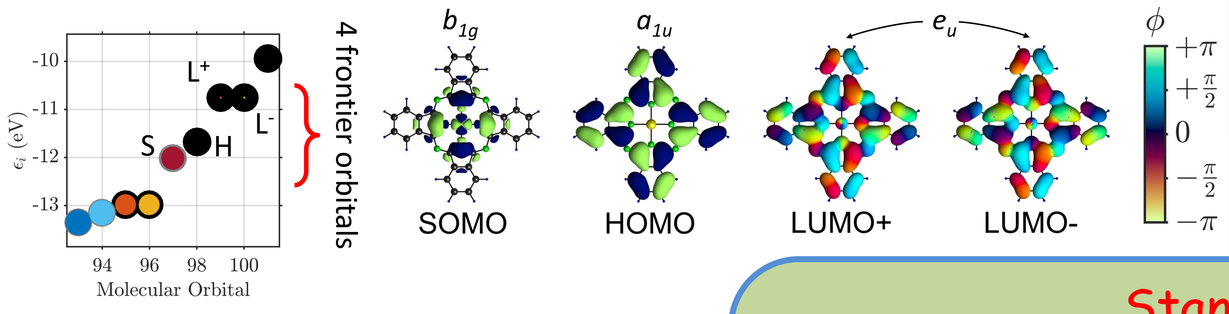
Transport gap	$\Delta_{tr} = IP - EA - 2\delta_{ic}$
Optical gap	$\Delta_{opt} = E_{N_0,1} - E_{N_0,0}$
Electroch. potentials	$\mu_{S/T} = -\phi_0 \pm \alpha_{S/T} e V_b$

- Transport gap > 2x Optical gap
- Work function close to $\phi_{sym} = (IP + EA)/2$
- Moderate internal relaxation rate
- Strong asymmetry between substrate and tip tunnelling rates



Many-body Hamiltonian

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



We restrict ourself 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

The many body Hamiltonian for the molecule reads:

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

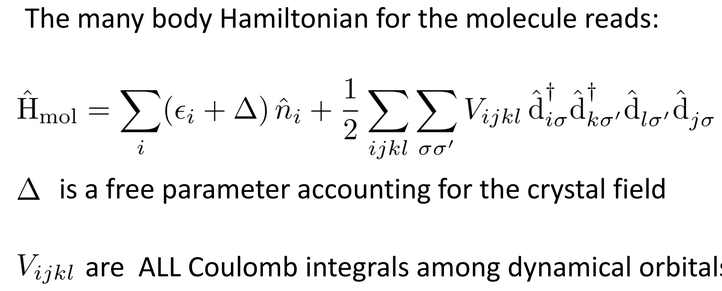
Δ is a free parameter accounting for the crystal field

V_{ijkl} are ALL Coulomb integrals among dynamical orbitals

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

The Coulomb integrals are calculated with the relative dielectric constant $\epsilon_{\mathrm{mol}} = 2.2$. The atomic orbitals are of Slater type with screening charges taken from [3].

Many-body spectrum



Symmetry considerations

The molecular orbitals are eigenstates of the C_4 rotation

$$R|j\rangle = \mathrm{e}^{-i\phi_j}|j\rangle \Rightarrow V_{ijkl} = \mathrm{e}^{-i(\phi_i-\phi_j+\phi_k-\phi_l)}V_{ijkl}$$

It follows that

$$V_{ijkl} \neq 0 \Leftrightarrow \phi_i - \phi_j + \phi_k - \phi_l = 0 \bmod 2\pi$$

where one should consider

$$\phi_S = \pi, \quad \phi_H = 0, \quad \phi_{L^\pm} = \pm\frac{\pi}{2}.$$

Low energy many-body states

	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

Spin-crossover and transport theory

The full system is characterized by the Hamiltonian $\hat{\mathrm{H}} = \hat{\mathrm{H}}_{\mathrm{mol}} + \hat{\mathrm{H}}_{\mathrm{mol-env}} + \hat{\mathrm{H}}_{\mathrm{S}} + \hat{\mathrm{H}}_{\mathrm{T}} + \hat{\mathrm{H}}_{\mathrm{tun}}$

- $\hat{\mathrm{H}}_{\mathrm{mol-env}} = -\delta_{\mathrm{ic}}(\hat{N} - N_0)^2$
- $\hat{\mathrm{H}}_{\mathrm{S/T}} = \sum_{\mathbf{k}\sigma}\epsilon^{S/T}_{\mathbf{k}}\,\hat{\mathrm{c}}^\dagger_{S/T\mathbf{k}\sigma}\hat{\mathrm{c}}_{S/T\mathbf{k}\sigma}$
- $\hat{\mathrm{H}}_{\mathrm{tun}} = \sum_{\eta\mathbf{k}i\sigma} t^\eta_{\mathbf{k}i}\,\hat{\mathrm{c}}^\dagger_{\eta\mathbf{k}\sigma}\hat{\mathrm{d}}_{i\sigma} + \mathrm{h.c.}$

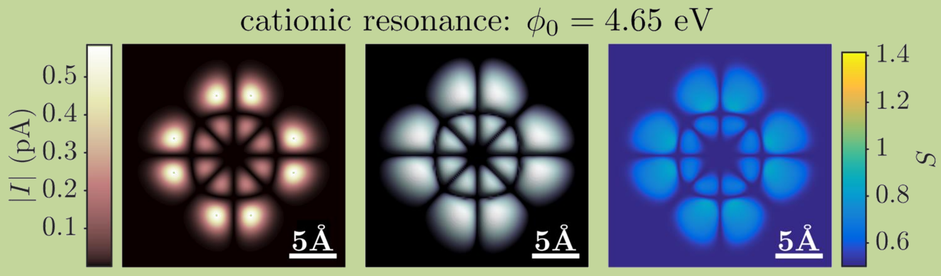
The system Hamiltonian is renormalized due to image charge effects.

The leads are reservoirs of non interacting particles.

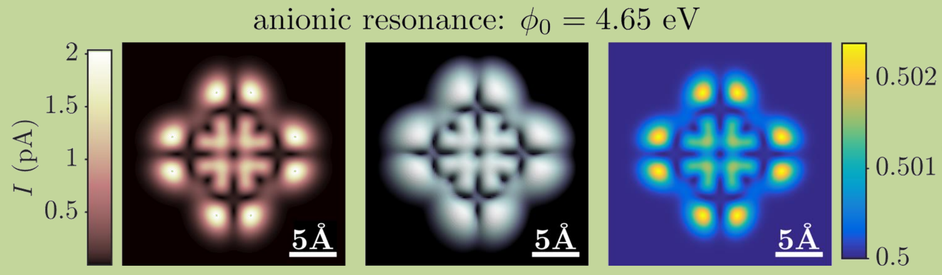
The tunnelling amplitudes $t^\eta_{\mathbf{k}i}$ encode for the geometry of the junction and are obtained analogously to [4].

Standard

cationic resonance: $\phi_0 = 4.65$ eV

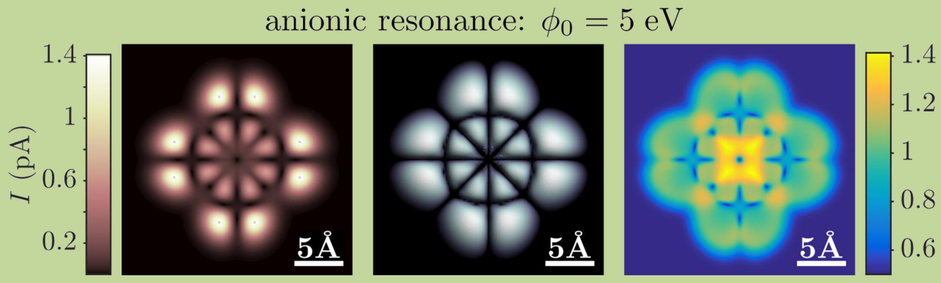


anionic resonance: $\phi_0 = 4.65$ eV



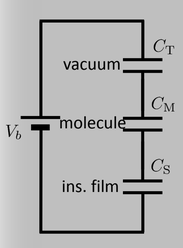
Anomalous

anionic resonance: $\phi_0 = 5$ eV



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

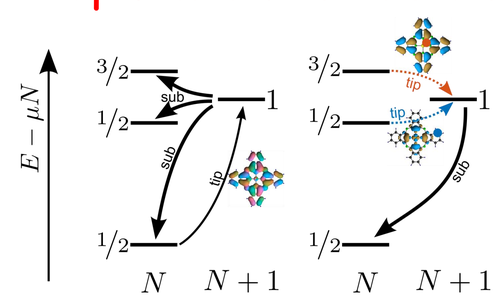
Fitting parameters

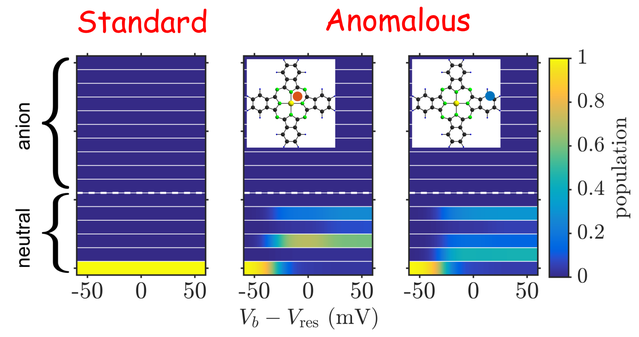


	NaCl(3ML) Cu(100)	NaCl(2ML) Cu(111)
ϕ_0 (eV)	4.65	5.00
d (Å)	8.1	6.0
Δ (eV)	1.83	1.74
δ_{ic} (eV)	0.32	0.44
α_S	0.16	0.12
α_T	0.59	0.62
V^{exp}_{an} (V)	0.81	0.95
V^{th}_{an} (V)	0.81	1.01
V^{exp}_{cat} (V)	-2.62	-2.15
V^{th}_{cat} (V)	-2.72	-2.00

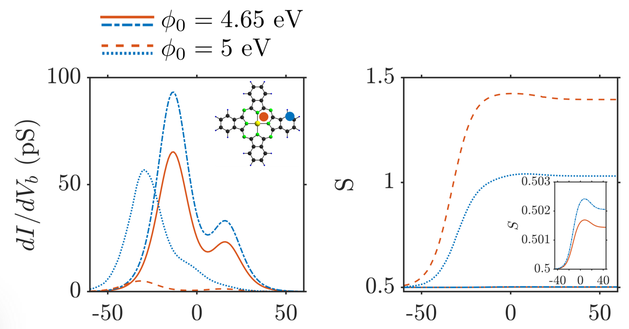
$\mu_{S/T} = -\phi_0 \pm \alpha_{S/T}\,eV_b$

Population inversion





Spectroscopic fingerprints



The dynamics is calculated via a generalized master equation for the reduced density matrix $\rho_{\mathrm{red}} = \mathrm{Tr}_{\mathrm{S,T}}(\rho)$

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

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

$\mathcal{L}[\rho^\infty_{\mathrm{red}}] \equiv 0$ defines the stationary reduced density matrix.

The stationary **current** and the **molecular spin** depend on the **bias** and the **tip position**

$$I_\eta(\mathbf{r}_T, V_b) = \mathrm{Tr}_{\mathrm{mol}}\left(\hat{N}\mathcal{L}_\eta[\rho^\infty_{\mathrm{red}}(\mathbf{r}_T, V_b)]\right) \qquad S(\mathbf{r}_T, V_b) = \sqrt{\langle\hat{S}^2\rangle(\mathbf{r}_T, V_b) + \tfrac{1}{4}} - \tfrac{1}{2}$$

with $\langle\hat{S}^2\rangle(\mathbf{r}_T, V_b) = \mathrm{Tr}_{\mathrm{mol}}\left(\hat{S}^2\rho^\infty_{\mathrm{red}}(\mathbf{r}_T, V_b)\right)$

[1] S. Froyen and W.A. Harrison, Phys. Rev. B **20,** 2420 (1979)
[2] J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954)
[3] E. Clementi and D. L. Raimondi, J. Chem Phys. **38**, 2686 (1963)
[4] S. Sobczyk, A. Donarini, and M. Grifoni Phys. Rev. B **85**, 205408 (2012)

For the role of Spin-orbit coupling in CuPc junctions *Beilstein J. Nanotechnol.*, ***6,*** 2452 (2015)