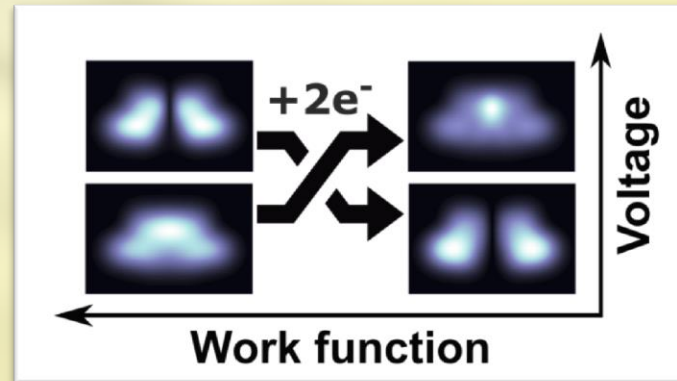
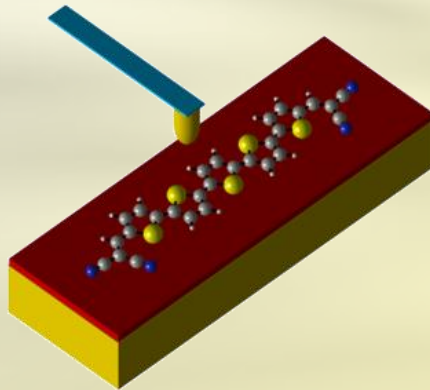


Apparent reversal of molecular orbitals reveals entanglement

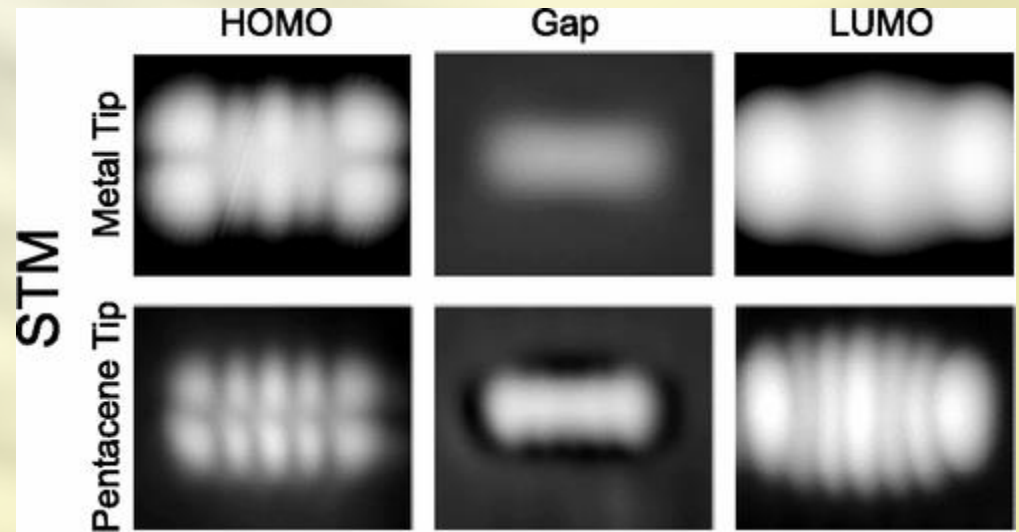
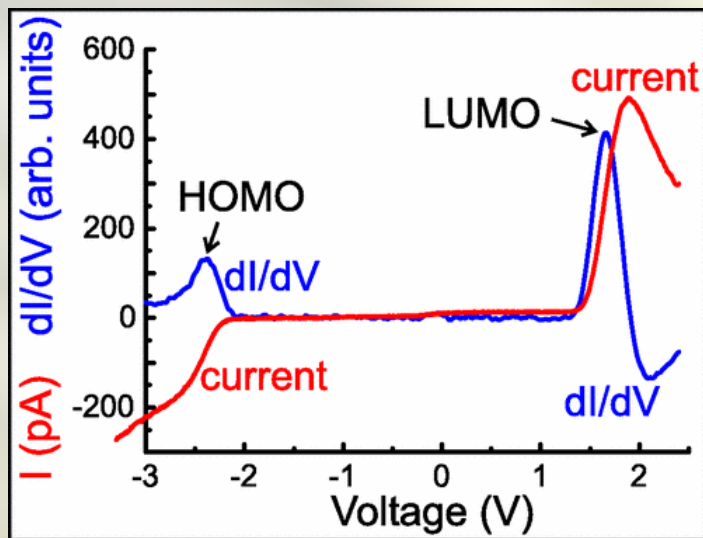
Andrea Donarini

P.Yu, N. Kocic, B.Siegert, J.Repp

University of Regensburg and Shanghai Tech University



Spectroscopy & Topography



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

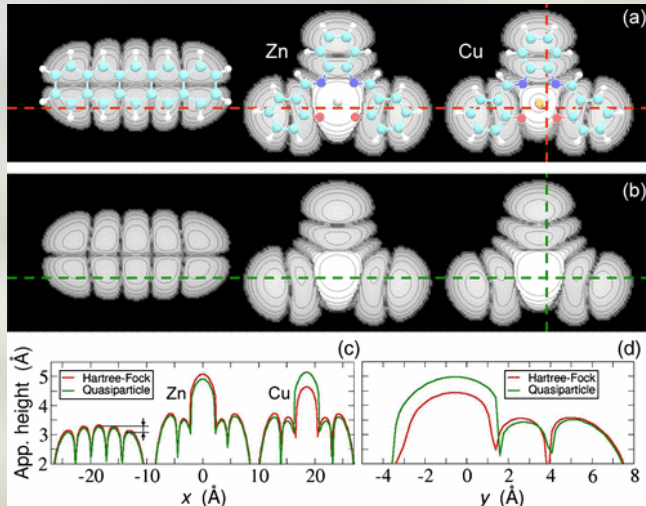
Motivation

Alteration of the molecular orbitals due to electronic correlation

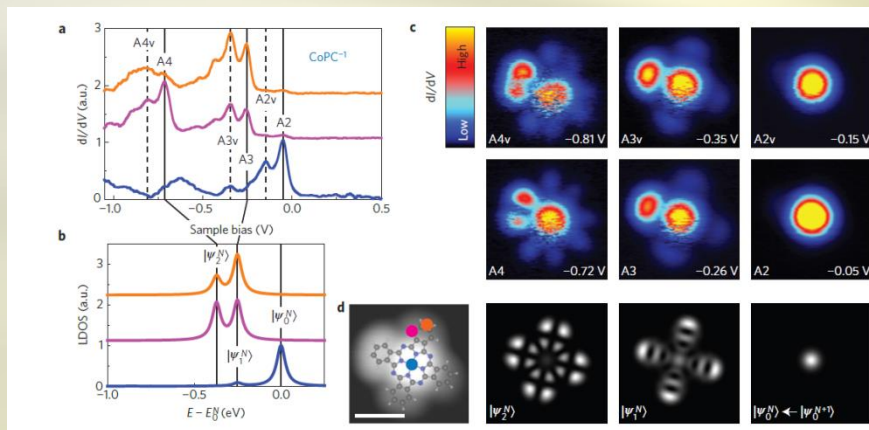
$$\varphi(\mathbf{r}) = \sum_{i,j} (C_j^{N-1})^* C_i^N \sum_{\alpha} \phi_{\alpha}(\mathbf{r}) \langle \Phi_j^{N-1} | \hat{c}_{\alpha} | \Phi_i^N \rangle.$$

STM experiments probe

quasiparticle wavefunctions \neq single particle molecular orbitals



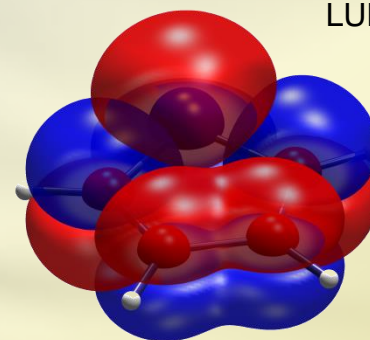
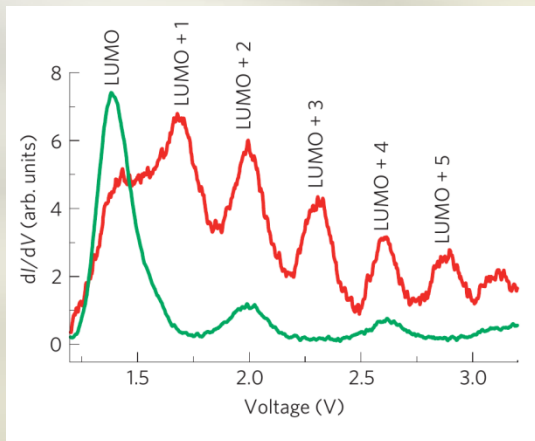
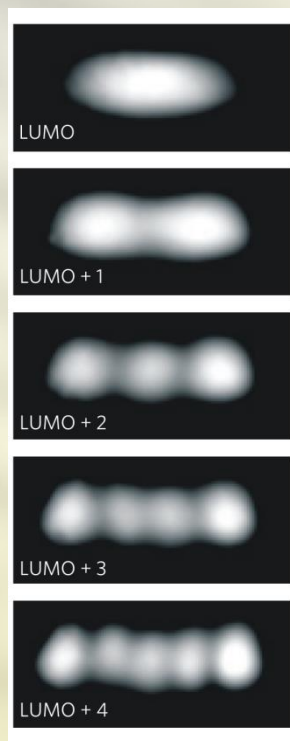
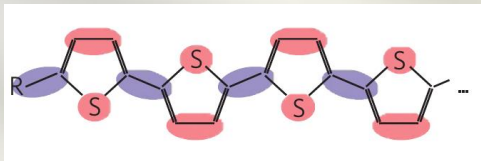
D. Toroz, et al. PRL **110**, 018305 (2013)



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

Visualization of intramolecular many-body correlation in STM experiments

in oligothiophenes



LUMO of thiophene

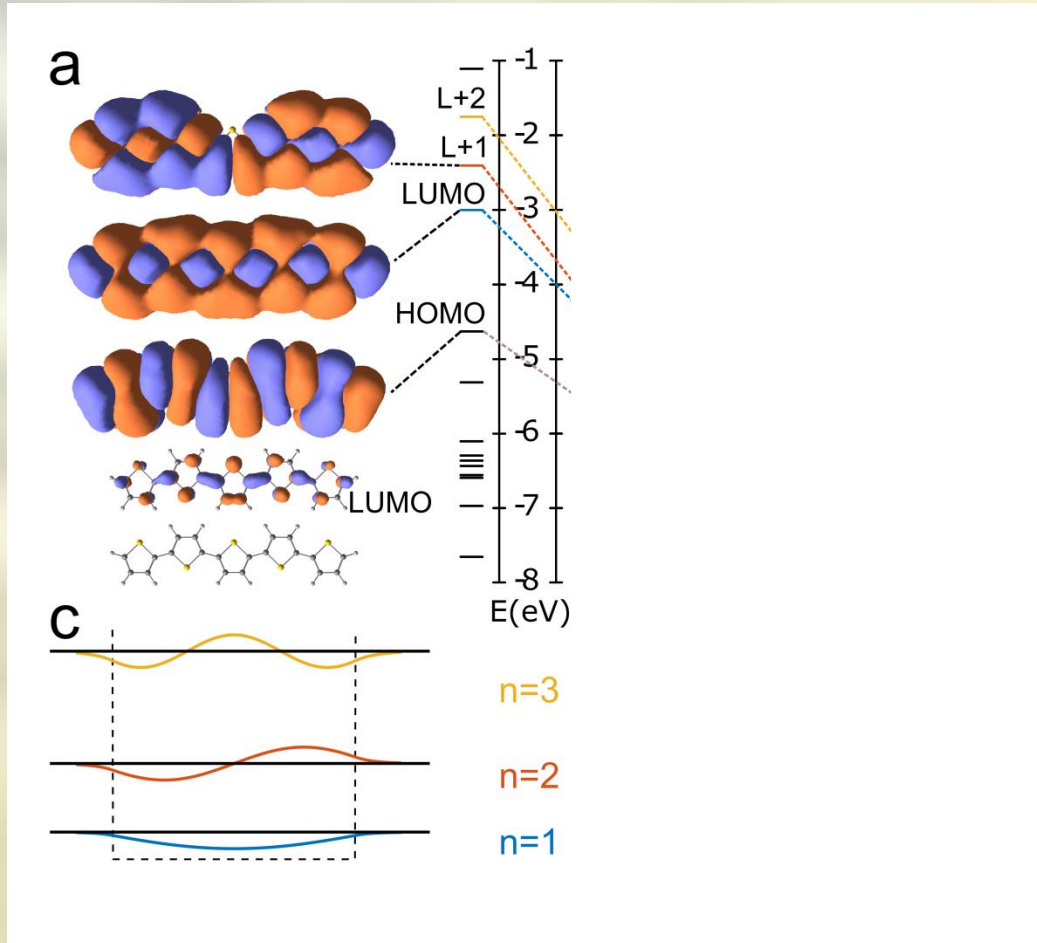
General statement of the Sturm-Liouville theory for differential equations:

In a one dimensional system the eigenfunction of the **n-th** excited state has **n-1** nodes.

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

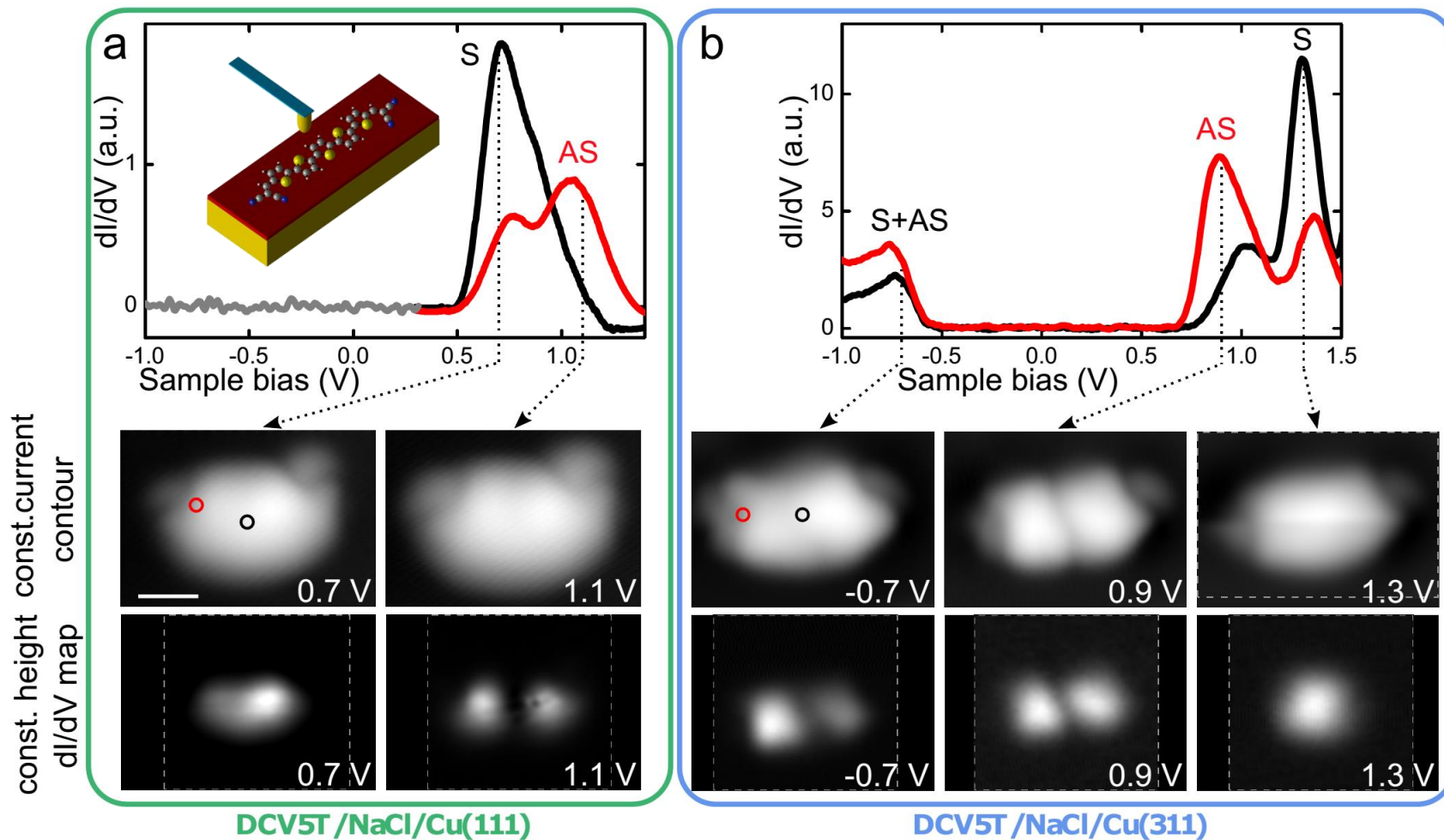
Orbital engineering

Quinquethiophene
(5T)



Dicyanovinyl-
quinquethiophene
(DCV5T)

Orbital inversion

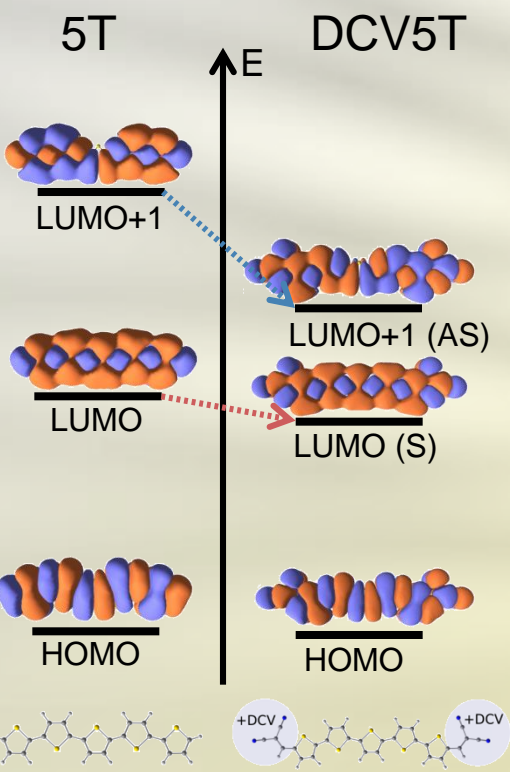


No explanation within single particle picture

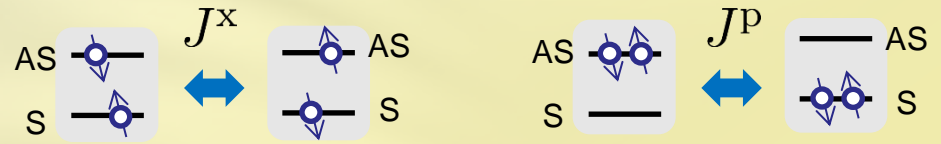


DFT and experiment:
LUMO and LUMO+1 move together + large gap to HOMO

- choose LUMO (S) and LUMO+1 (AS) as basis
- freeze other orbitals



$$\begin{aligned}
 \hat{H}_{\text{mol}} = & \epsilon_S \hat{n}_S + \epsilon_{AS} \hat{n}_{AS} && \text{kinetic term} \\
 & + V_{S-S} \hat{n}_{S\uparrow} \hat{n}_{S\downarrow} + V_{AS-AS} \hat{n}_{AS\uparrow} \hat{n}_{AS\downarrow} && \text{intra-orbital Coulomb} \\
 & + V_{S-AS} \hat{n}_S \hat{n}_{AS} && \text{inter-orbital Coulomb} \\
 & + J_{S-AS}^x \sum_{\sigma\sigma'} \hat{d}_{S\sigma}^\dagger \hat{d}_{AS\sigma'}^\dagger \hat{d}_{S\sigma} \hat{d}_{AS\sigma} && \text{exchange} \\
 & + J_{S-AS}^p \sum_{\sigma\sigma'} \left(\hat{d}_{S\sigma}^\dagger \hat{d}_{S\sigma'}^\dagger \hat{d}_{AS\sigma} \hat{d}_{AS\sigma'} + \text{h.c.} \right) && \text{pair hopping}
 \end{aligned}$$



Other interaction terms are forbidden by symmetry



- Coulomb integrals are calculated numerically from MOs:

$$U_{S-S} = \iint d^3\mathbf{r}_1 d^3\mathbf{r}_2 |\psi_S(\mathbf{r}_1)|^2 V(\mathbf{r}_1 - \mathbf{r}_2) |\psi_S(\mathbf{r}_2)|^2$$

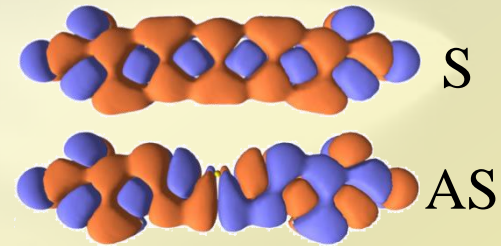
$$U_{AS-AS} = \iint d^3\mathbf{r}_1 d^3\mathbf{r}_2 |\psi_{AS}(\mathbf{r}_1)|^2 V(\mathbf{r}_1 - \mathbf{r}_2) |\psi_{AS}(\mathbf{r}_2)|^2$$

$$U_{S-AS} = \iint d^3\mathbf{r}_1 d^3\mathbf{r}_2 |\psi_S(\mathbf{r}_1)|^2 V(\mathbf{r}_1 - \mathbf{r}_2) |\psi_{AS}(\mathbf{r}_2)|^2$$

$$J_{S-AS}^x = \iint d^3\mathbf{r}_1 d^3\mathbf{r}_2 \psi_S^*(\mathbf{r}_1) \psi_{AS}(\mathbf{r}_1) V(\mathbf{r}_1 - \mathbf{r}_2) \psi_{AS}^*(\mathbf{r}_2) \psi_S(\mathbf{r}_2)$$

$$J_{S-AS}^p = \iint d^3\mathbf{r}_1 d^3\mathbf{r}_2 \psi_S^*(\mathbf{r}_1) \psi_{AS}(\mathbf{r}_1) V(\mathbf{r}_1 - \mathbf{r}_2) \psi_S^*(\mathbf{r}_2) \psi_{AS}(\mathbf{r}_2)$$

$$V(\mathbf{r}) = \frac{e^2}{4\pi\epsilon_0\epsilon_r|\mathbf{r}|}$$



- Some simplifications

$$U_{S-S} \approx U_{AS-AS} \approx U_{S-AS} =: U = 1.4 \text{ eV}$$

$$J_{S-S}^x \equiv J_{S-AS}^p =: J = 0.75 \text{ eV}$$

← similar spatial distribution

← real MOs

← comparatively large

fit to the experiment

$$\hat{H}_{\text{mol}} = \epsilon_S \hat{n}_S + \epsilon_{AS} \hat{n}_{AS} + \frac{U}{2} \hat{N} (\hat{N} - 1)$$

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



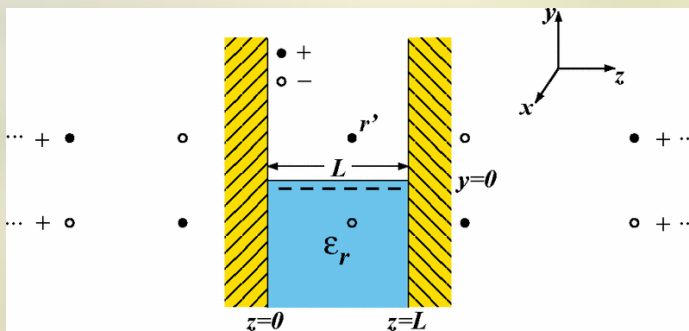
- the interaction between the molecule and the substrate is described by two additional terms:

$$\hat{H}_{\text{sys}}^{\text{G}} = \hat{H}_{\text{mol}} - \delta \hat{N}^2 + \phi_0 \hat{N} \quad \leftarrow \text{grand canonical potential}$$

↑
image charge/polaron shift

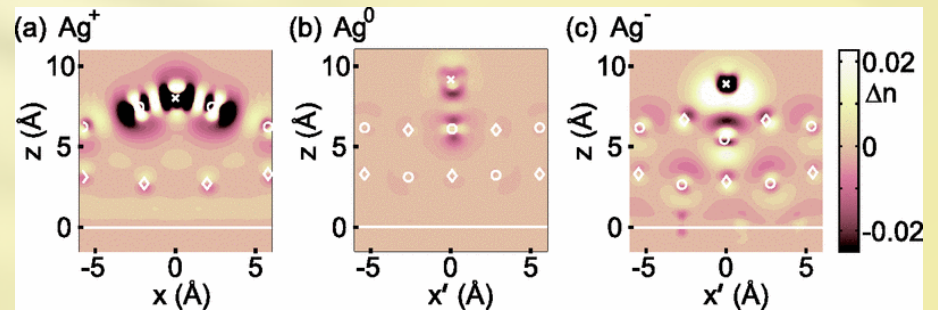
- δ incorporates two effects which stabilize the charge on the molecule:

image charge effect



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

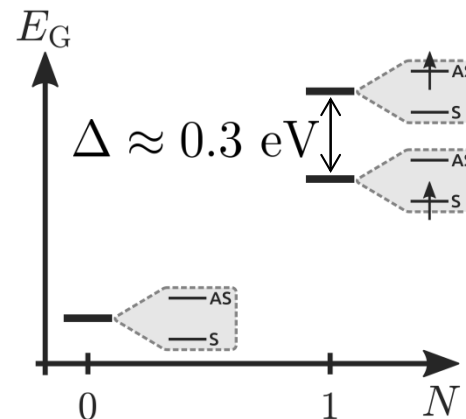
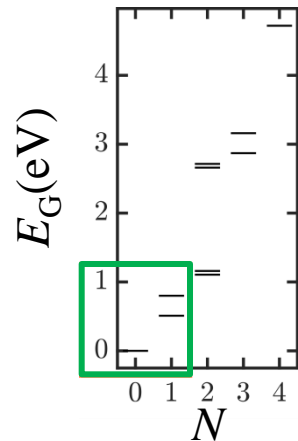
polaron formation



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

DCV5T on NaCl/Cu(111)

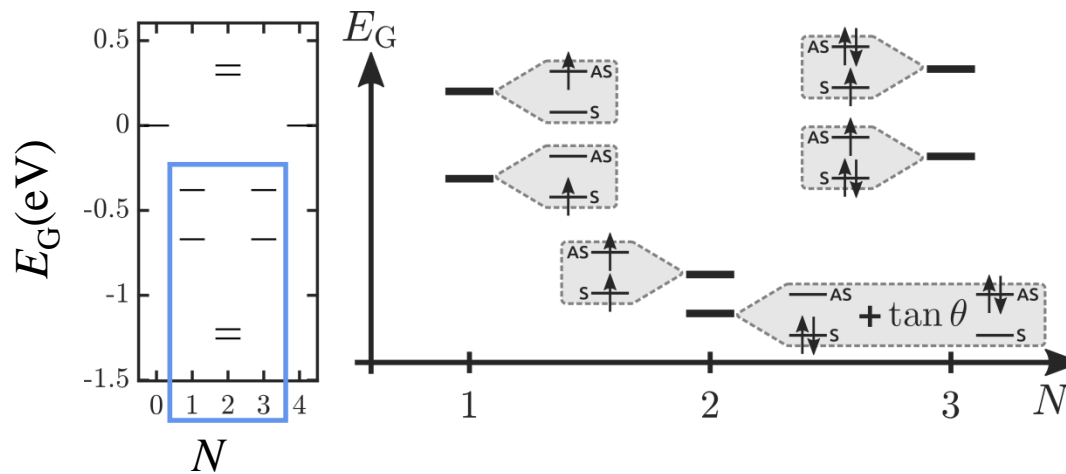
$$\hat{H}_{\text{sys}}^{\text{G}} = \hat{H}_{\text{mol}} - \delta \hat{N}^2 + \phi_0 \hat{N}$$



- The molecule is neutral on this substrate
- The order of the anionic states is in agreement with the single particle picture

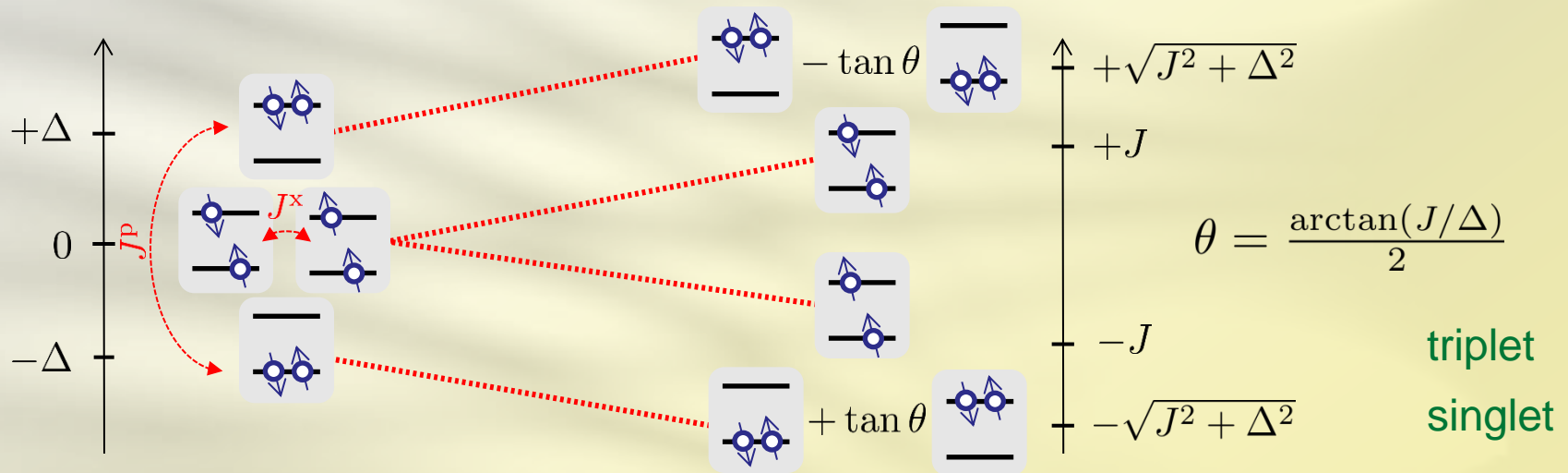
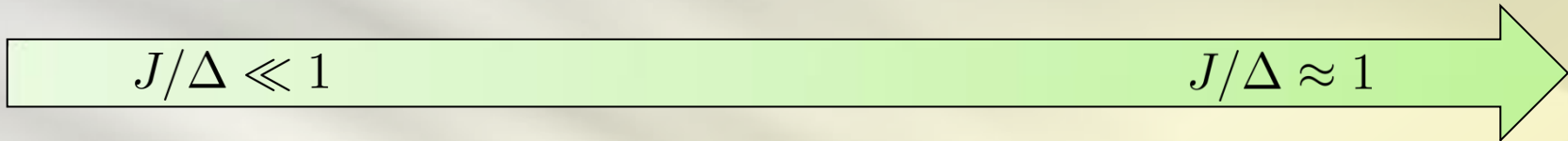
DCV5T on NaCl/Cu(311)

$$\hat{H}_{\text{sys}}^{\text{G}} = \hat{H}_{\text{mol}} - \delta \hat{N}^2 + \phi_0 \hat{N}$$



- The molecule is doubly charged on this substrate
- The two particle states are correlated

The two-particle spectrum



In DCV5T
 $J/\Delta \approx 3$

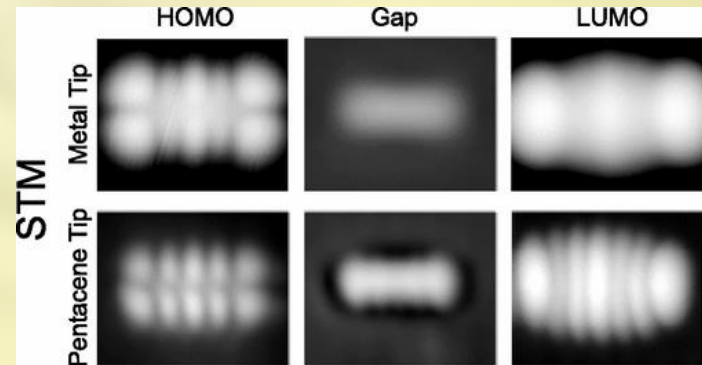
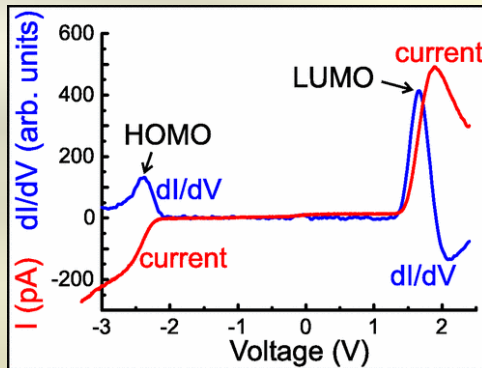
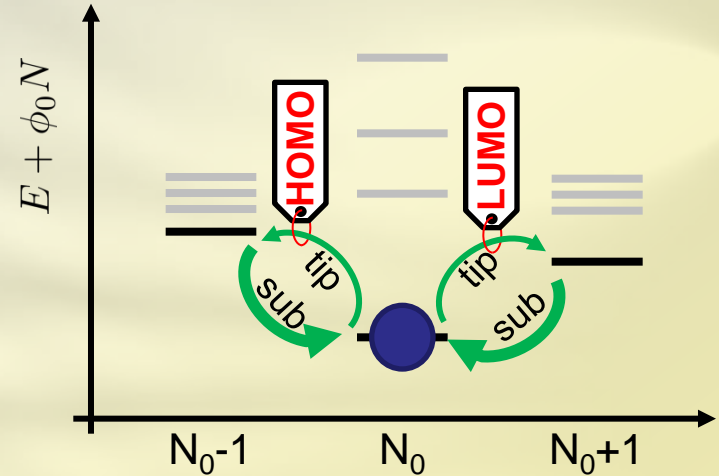
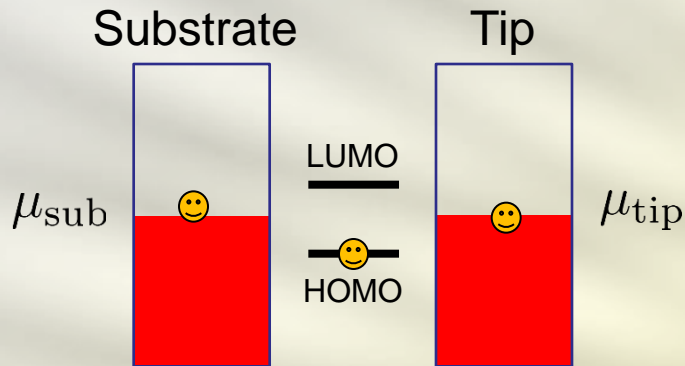


$\tan \theta \approx 0.86$
 $\Delta_{ST} \approx 54 \text{ meV}$

Strongly entangled
ground state

Orbital reversal:
qualitative explanation

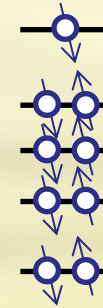
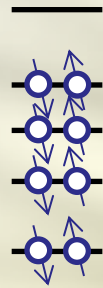
Single particle vs. Many-body



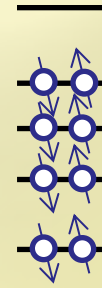
The two approaches coincide only for uncorrelated systems close to equilibrium

Tunnelling and correlation

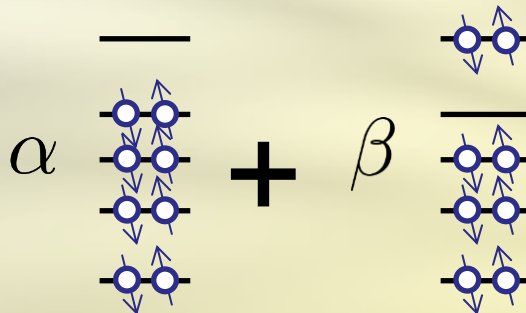
Uncorrelated
system



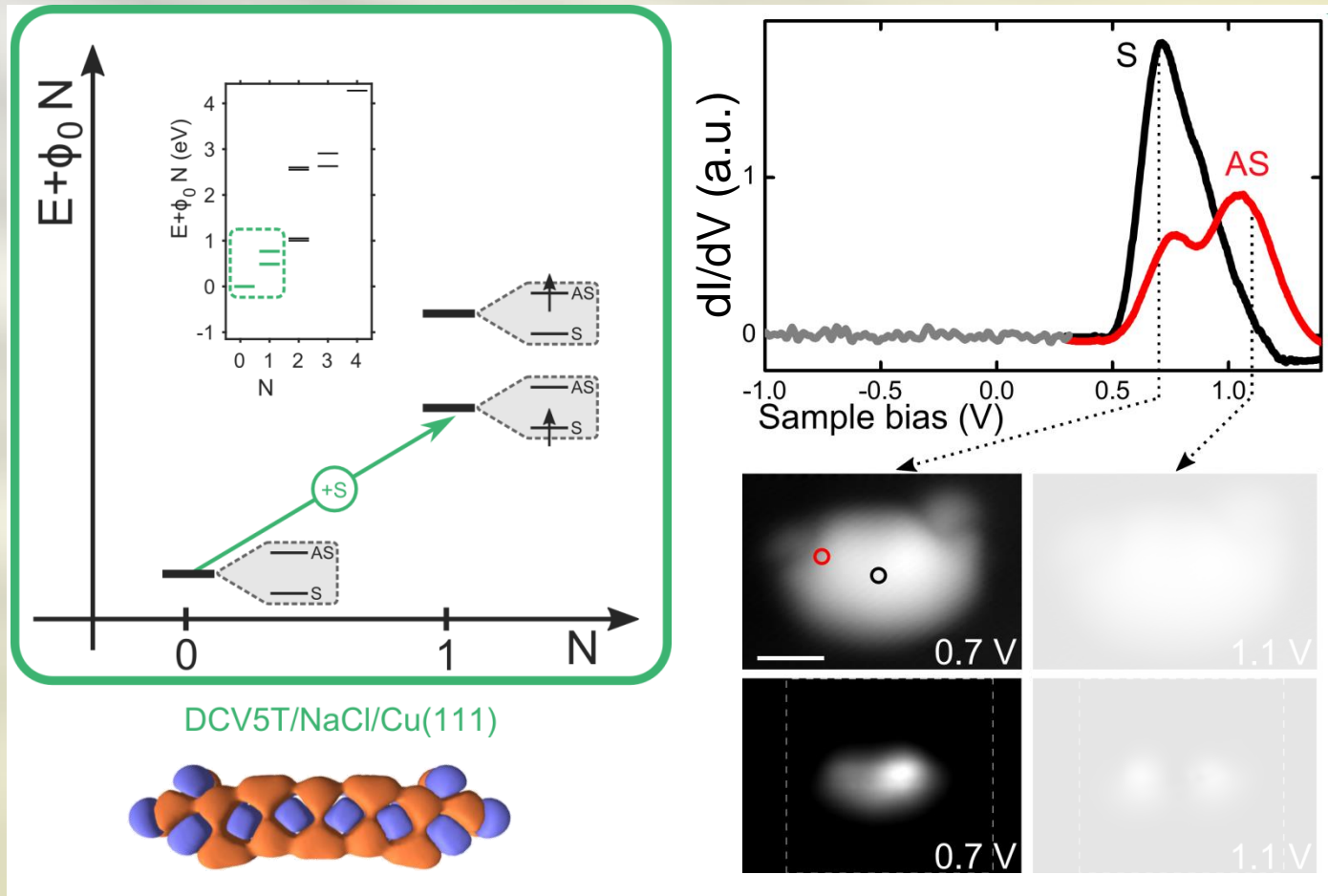
or



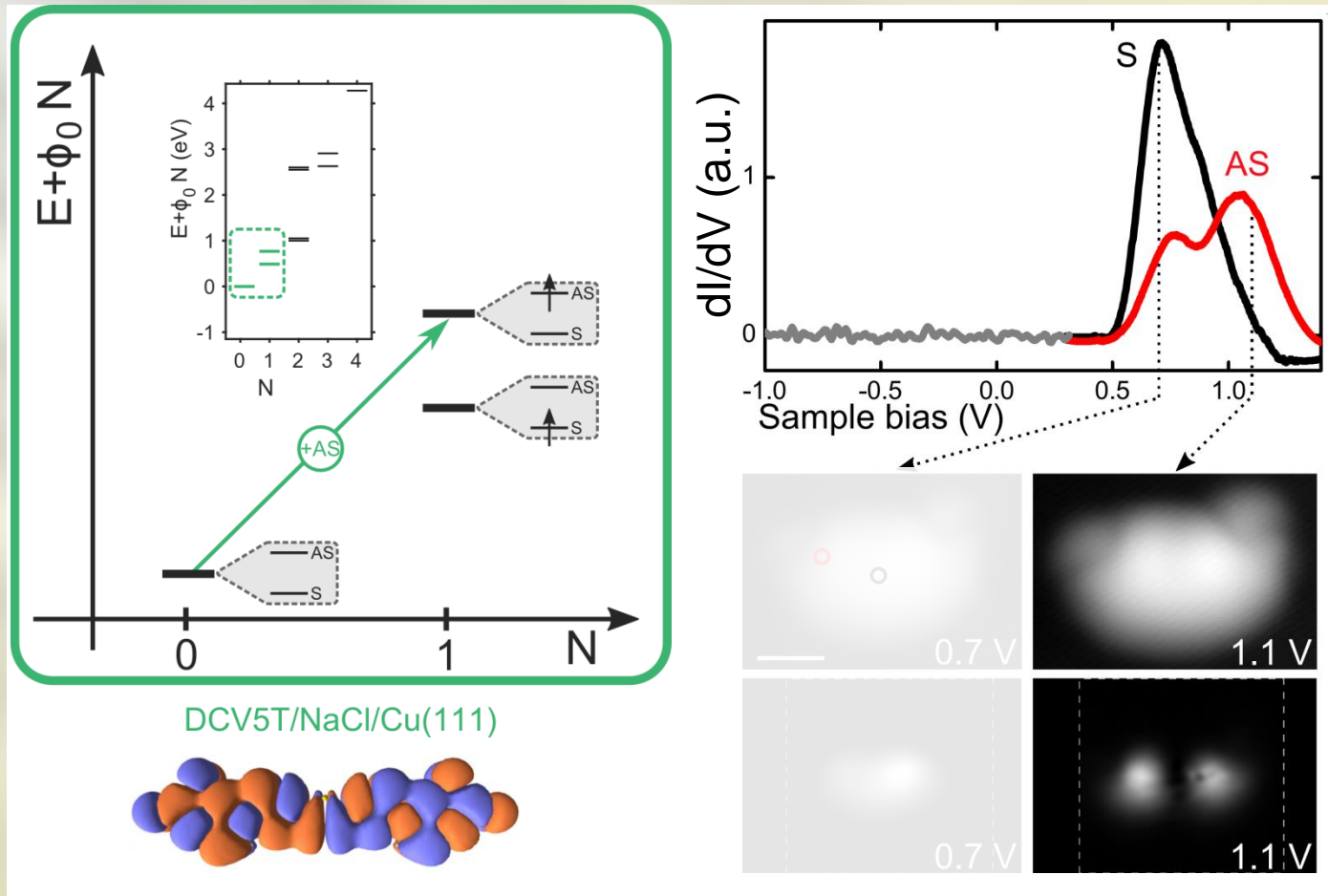
Correlated
system



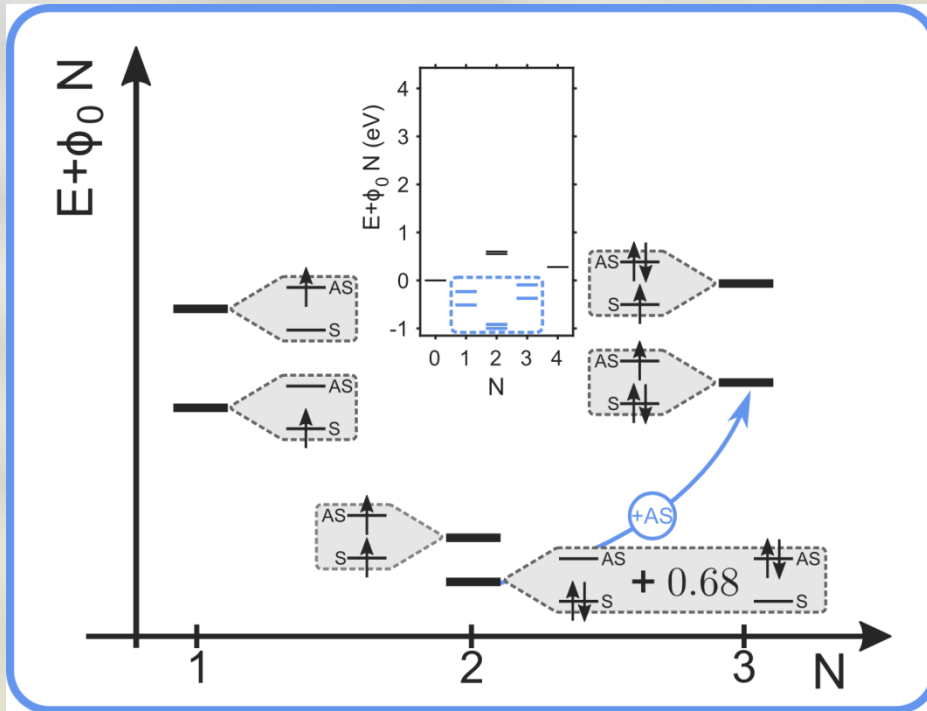
Mechanism of orbital reversal



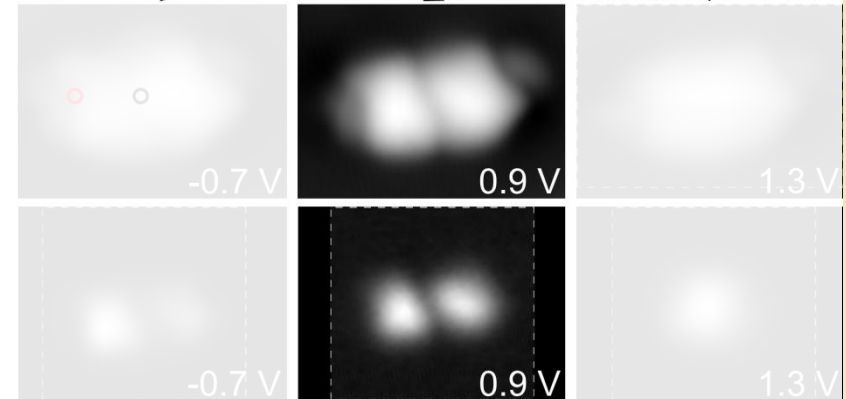
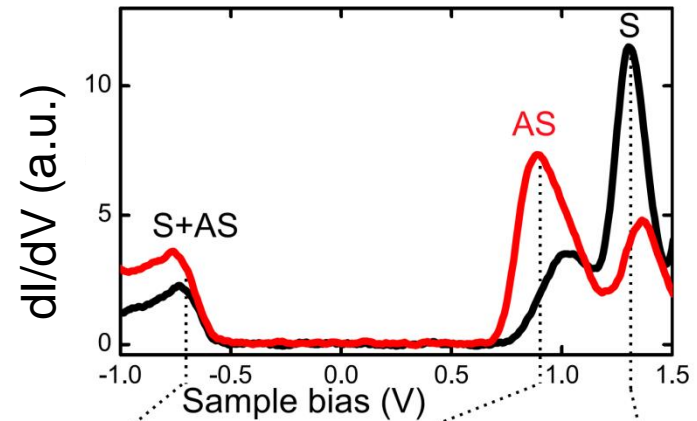
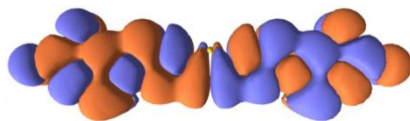
Mechanism of orbital reversal



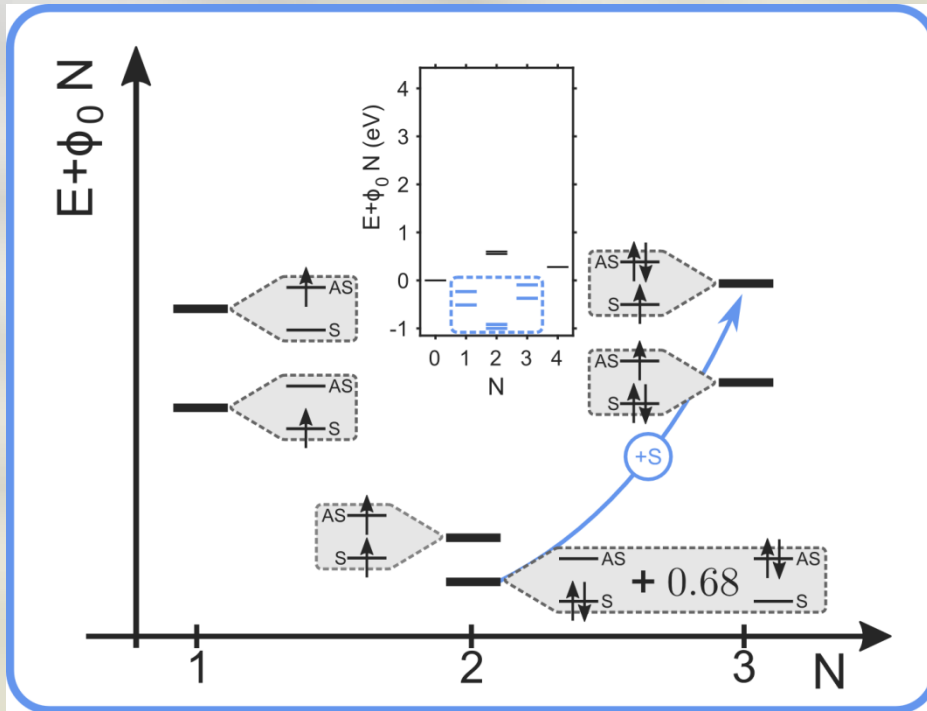
Mechanism of orbital reversal



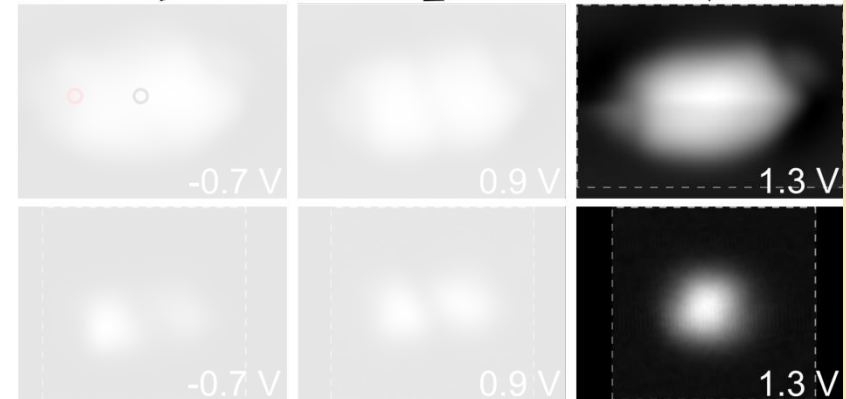
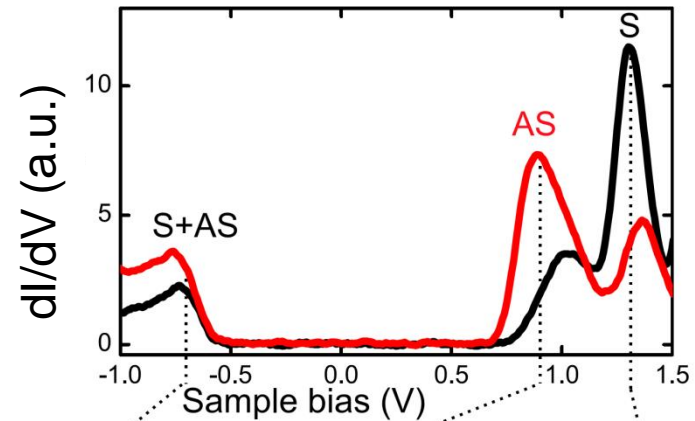
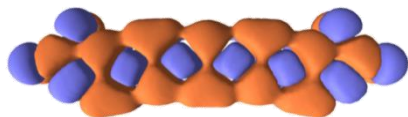
DCV5T/NaCl/Cu(311)



Mechanism of orbital reversal

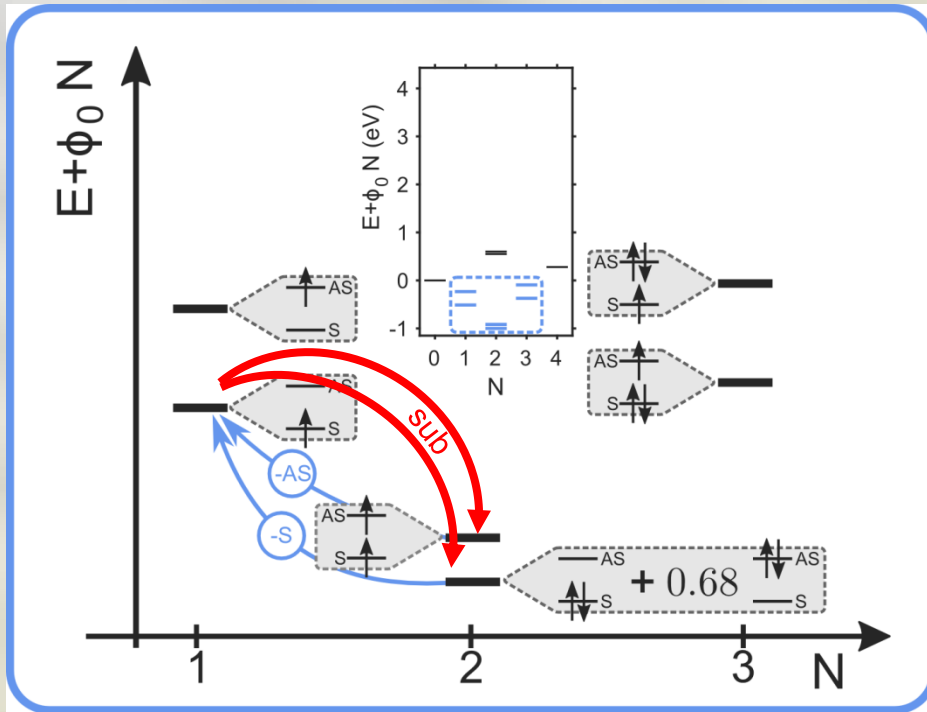


DCV5T/NaCl/Cu(311)

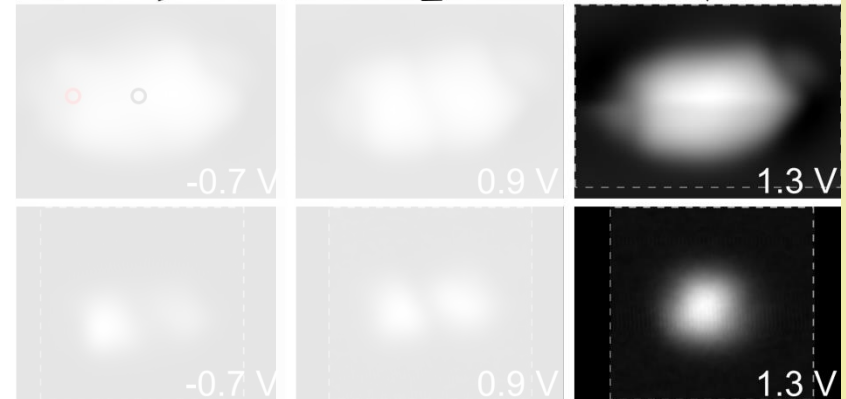
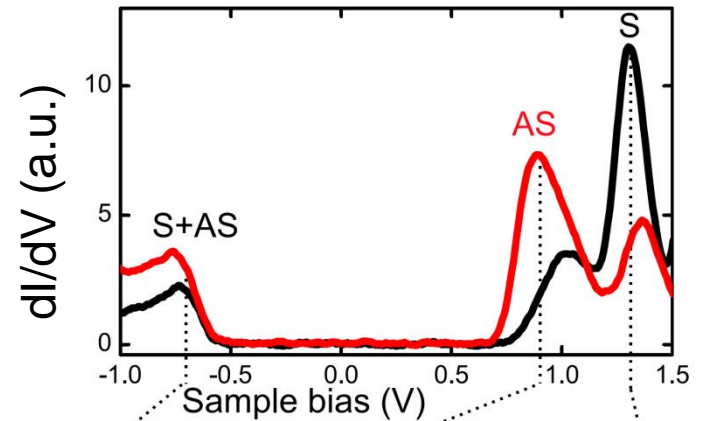
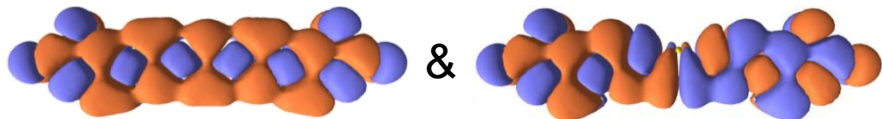


This transition is forbidden if $J/\Delta = 0$

Mechanism of orbital reversal



DCV5T/NaCl/Cu(311)

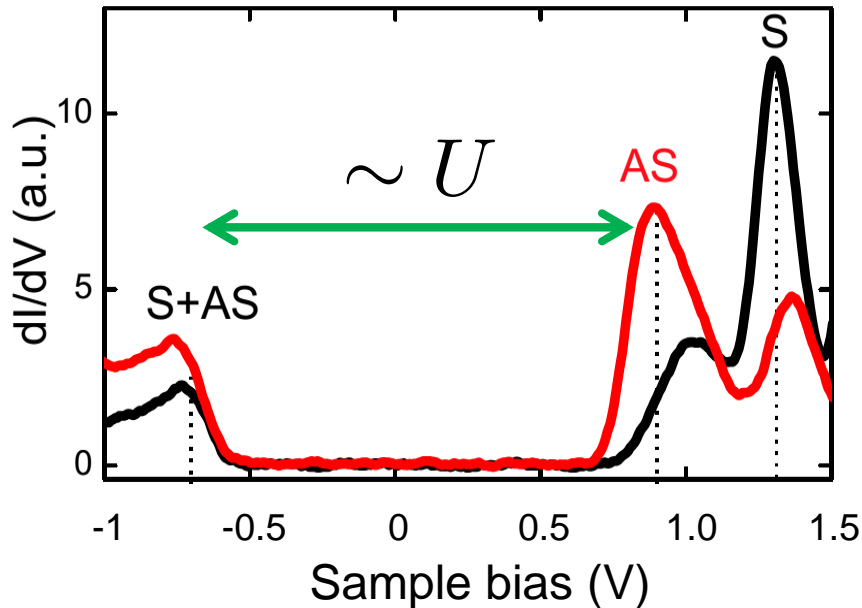


The antisymmetric component would not be detected in presence of strong relaxation

Double charging

Charging energy

For the **addition** of an electron into a quantum dot, at least its **charging energy** is required.



- From transport characteristics on NaCl/Cu(311)

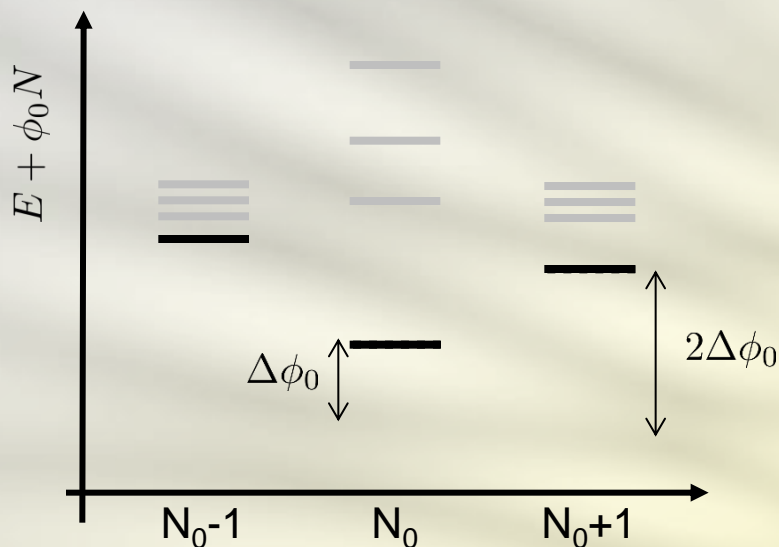
Charging energy of DCV5T $U \approx 1.5 \text{ eV}$

- Change of crystallographic orientation of the substrate from NaCl/Cu(111) to NaCl/Cu(311)

Work function change $\Delta\phi_0 \approx -1 \text{ eV}$

How can the molecule be possibly **neutral** on NaCl/Cu(111) and **doubly charged** on NaCl/Cu(311) ?

Addition energies



A variation of the substrate work function can change the charge state of the molecule.

The stability of a given charge is given by its addition energy

$$E_N^{\text{add}} = E_{N+1}^0 - 2E_N^0 + E_{N-1}^0$$

Addition energies for the two orbital model of DCV5T:

$$E_1^{\text{add}} = U - 2\delta + \Delta - \sqrt{\Delta^2 + J^2}$$

$$E_2^{\text{add}} = U - 2\delta - \Delta - J + 2\sqrt{\Delta^2 + J^2}$$

$$J/\Delta \ll 1$$

$$E_1^{\text{add}} \rightarrow U - 2\delta$$

$$E_2^{\text{add}} \rightarrow U - 2\delta + \Delta$$

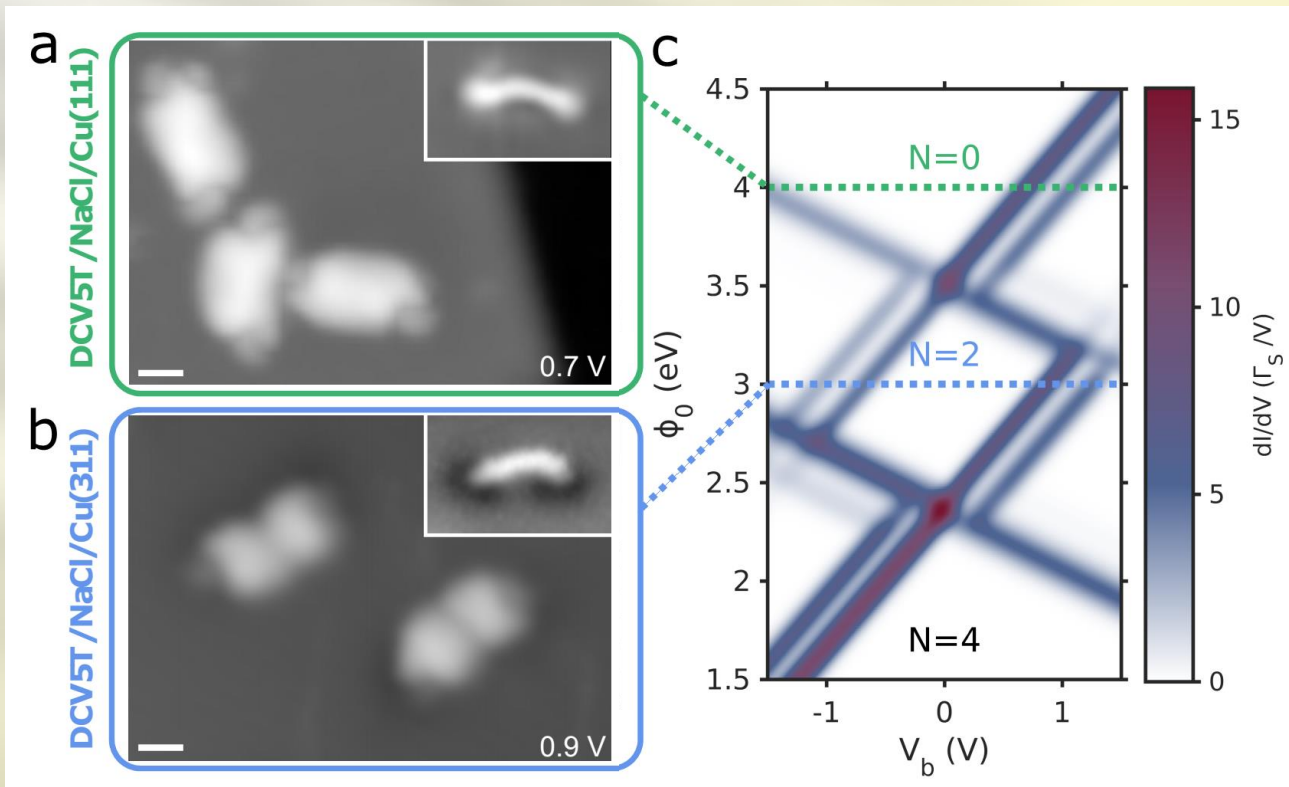
**The singly charged DCV5T
is extremely unstable**

$$J/\Delta \gg 1$$

$$E_1^{\text{add}} \rightarrow U - 2\delta - J$$

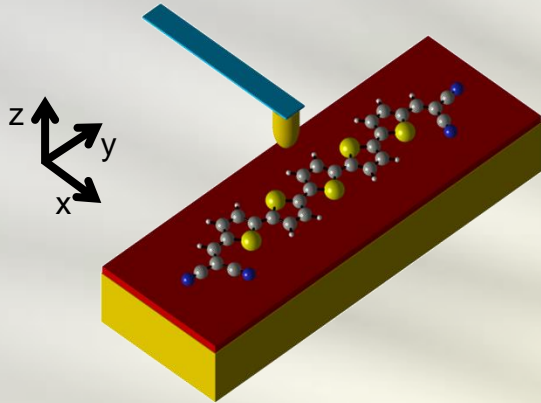
$$E_2^{\text{add}} \rightarrow U - 2\delta + J$$

Stability diagram



Quantitative description of transport

Leads and tunnelling



$$\hat{H} = \hat{H}_{\text{sys}} + \hat{H}_S + \hat{H}_T + \hat{H}_{\text{tun}}$$

The tip and substrate are modeled as **reservoirs of non interacting fermions**

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

Sub: no xy-confinement
Tip: parabolic xy-confinement

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

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

The 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

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

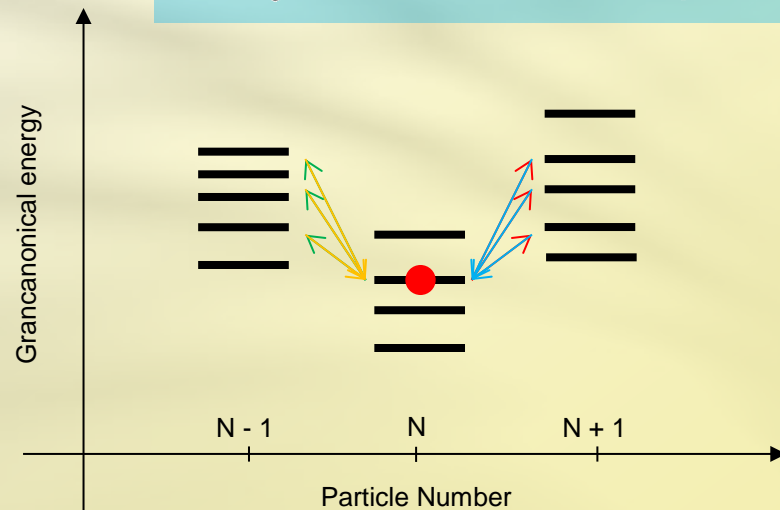
$$\begin{aligned} \dot{\sigma} = & \underbrace{-\frac{i}{\hbar}[\hat{H}_{\text{sys}}, \sigma]}_{\text{Coherent dynamics}} - \underbrace{\frac{i}{\hbar}[\hat{H}_{\text{eff}}, \sigma]}_{\text{Effective internal dynamics}} \\ & + \underbrace{\mathcal{L}_{\text{tun}}[\sigma]}_{\text{Tunnelling dynamics}} + \underbrace{\mathcal{L}_{\text{rel}}[\sigma]}_{\text{Phenom. relaxation}} := \mathcal{L}[\sigma] \end{aligned}$$

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

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

Tunnelling Liouvillean

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



$$\mathcal{P}_{NE} := \sum_l |NEl\rangle \langle NEl|$$

Tunnelling rate matrix

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

Effective
Hamiltonian

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

Current
operator

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

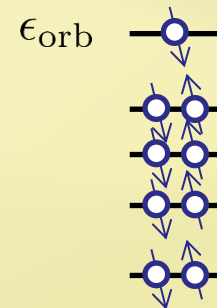
Many-body rate matrix

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

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

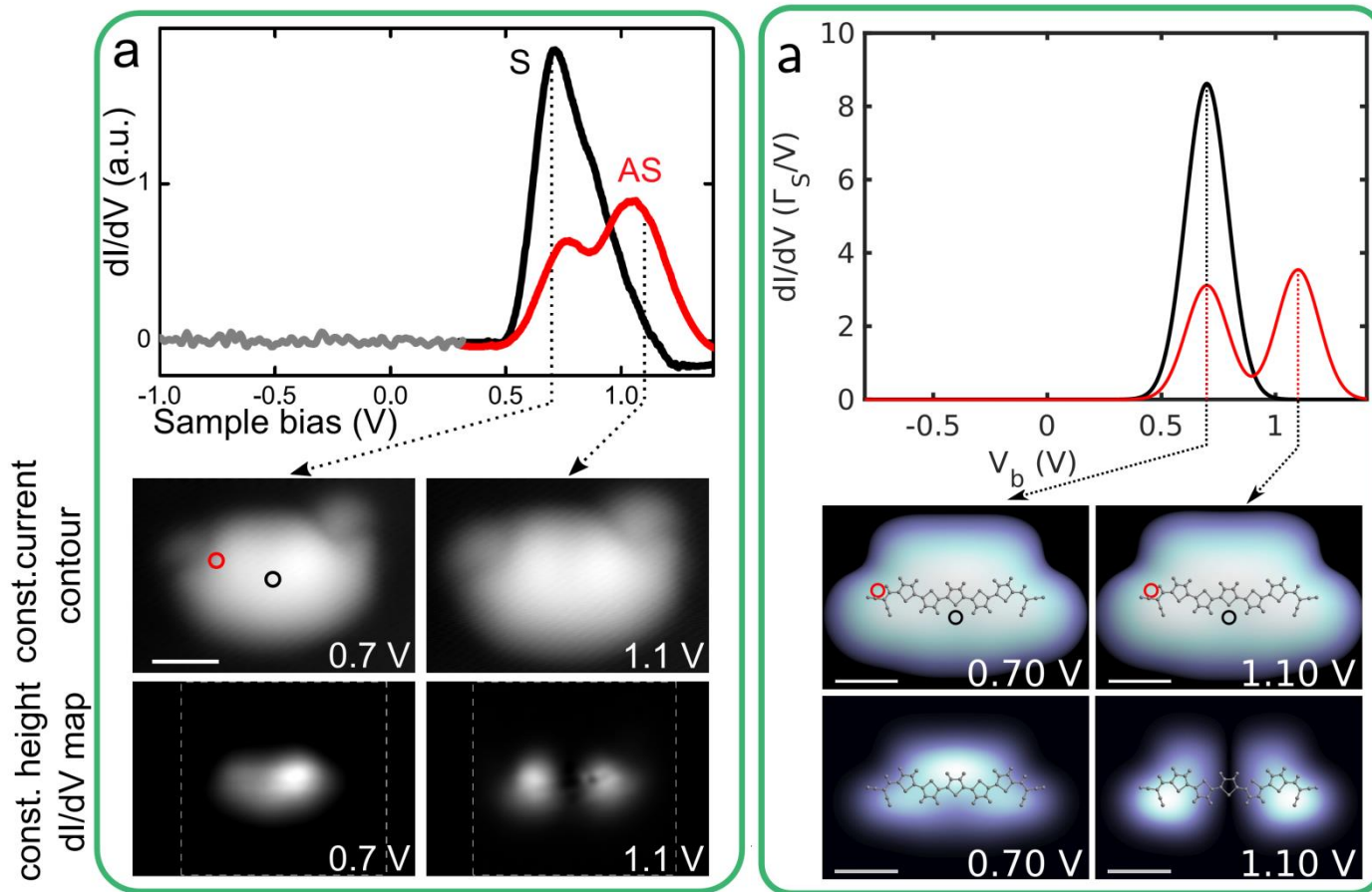
For **uncorrelated** and **non-degenerate systems** the many-body rate reduces to

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

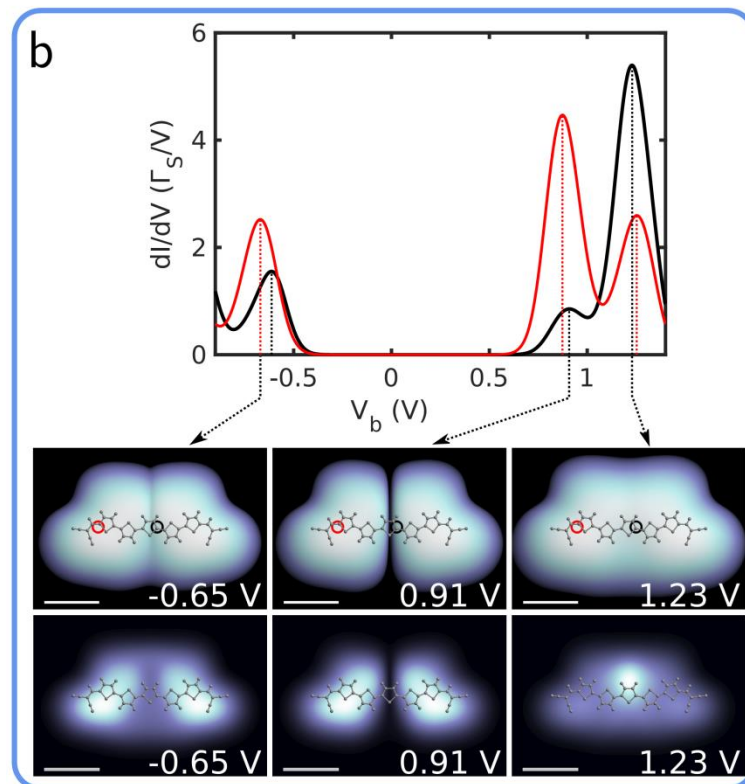
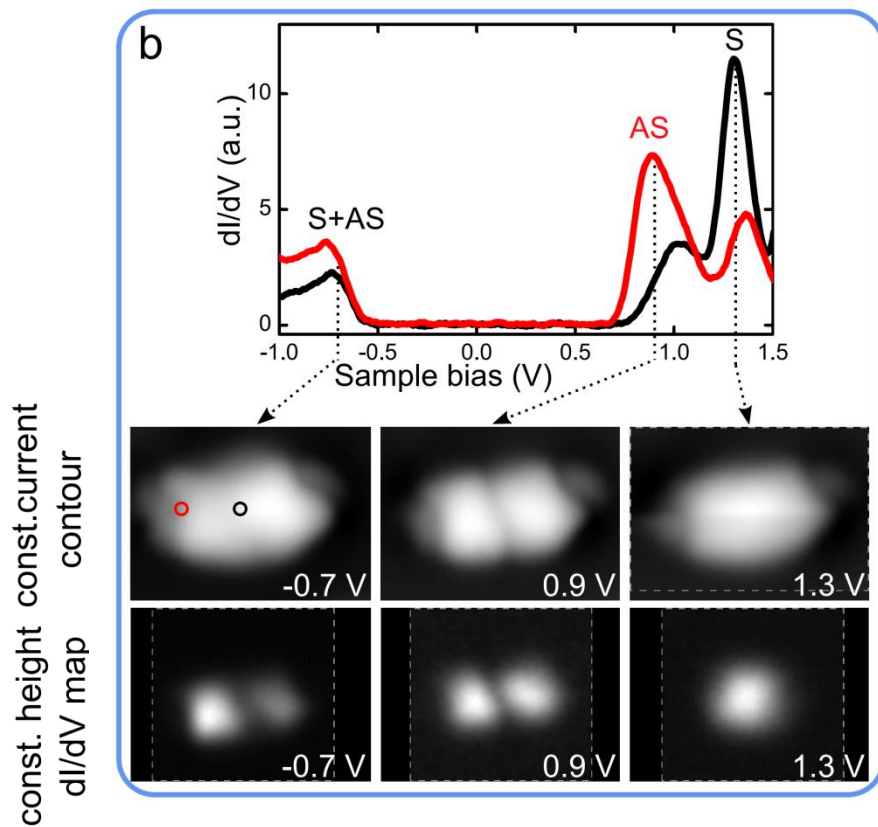


Close to equilibrium, the **constant current map** is the **isosurface** of a **specific molecular orbital** (Tersoff-Hamann theory of STM)

DCV5T/NaCl/Cu(111)



DCV5T/NaCl/Cu(311)

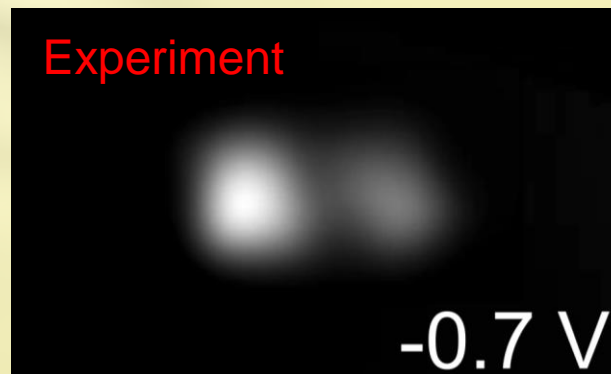
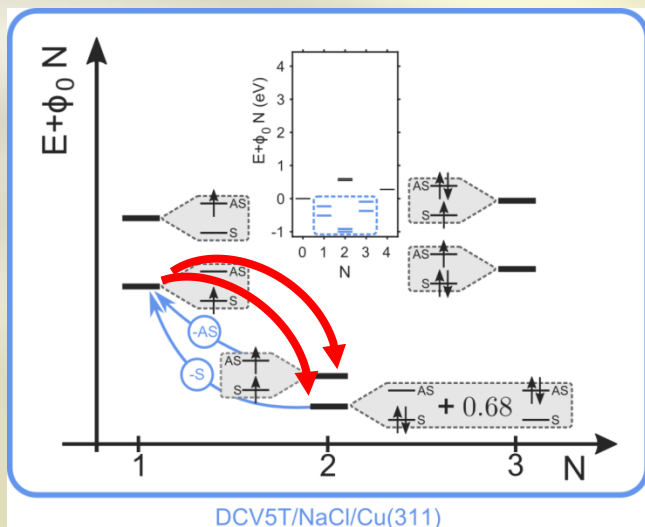
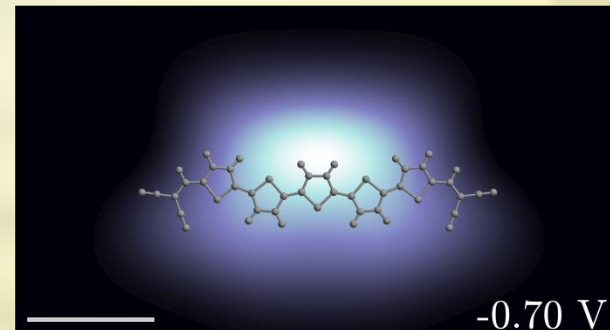
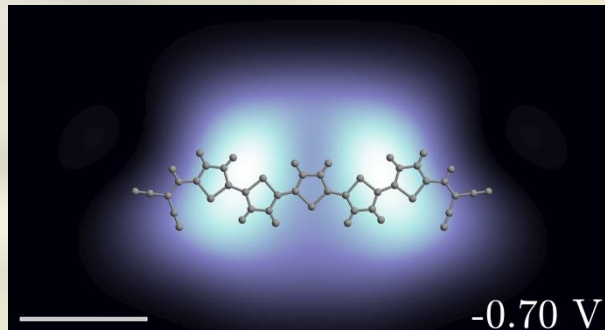
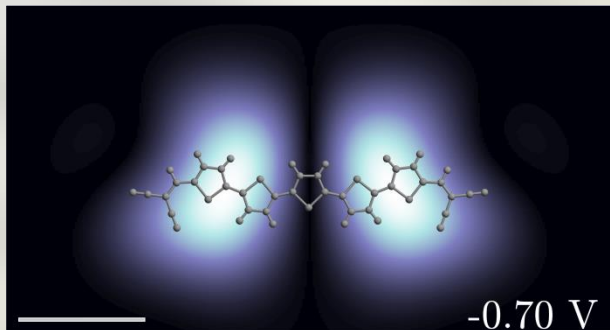


Intramolecular relaxation

$$\Gamma_{\text{rel}}/\Gamma^{\text{S}} \ll 1$$

$$\Gamma_{\text{rel}}/\Gamma^{\text{S}} \approx 1$$

$$\Gamma_{\text{rel}}/\Gamma^{\text{S}} \gg 1$$

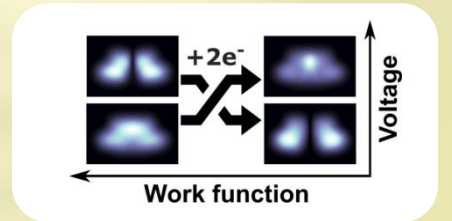




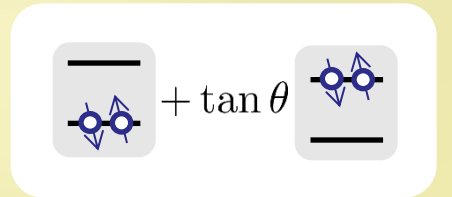
The chemical engineering of the single-particle level spacing between two frontier orbitals can control electronic-correlation in single molecule junctions



With the help of a STM, the apparent reversal in the orbital sequence of a dicyanovinyl-quinquethiophene (DCV5T) has been observed, upon changing the crystallographic orientation of the insulator-coated copper substrate



The orbital reversal is the signature of the formation 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

Thank you for your attention