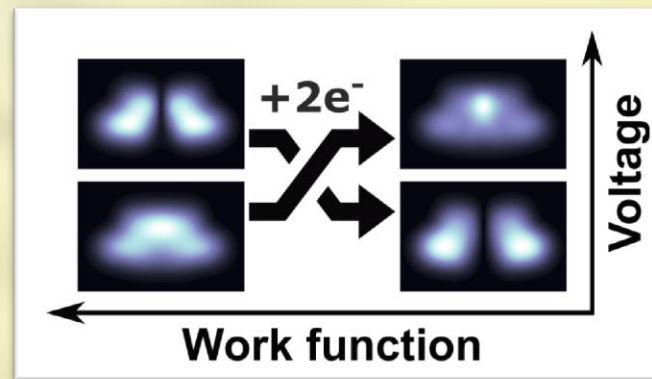
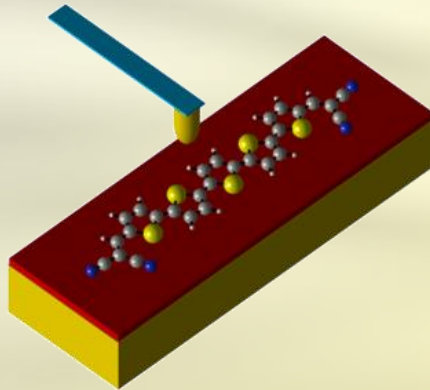


Apparent reversal of molecular orbitals reveals entanglement

Andrea Donarini

Institute of Theoretical Physics - University of Regensburg



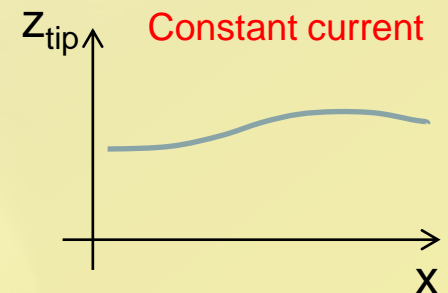
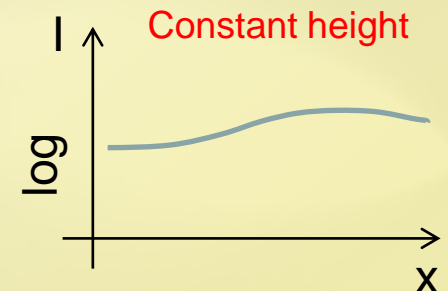
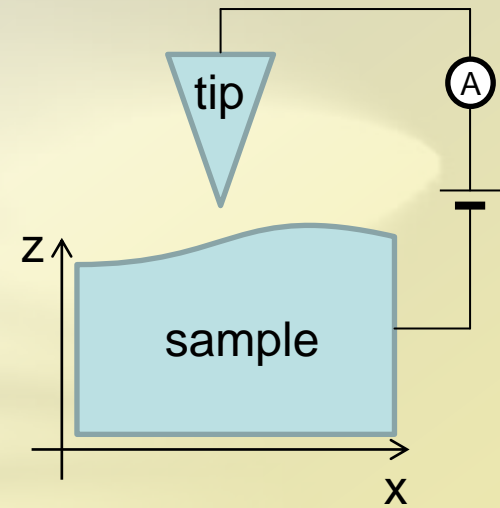


Basics on STM

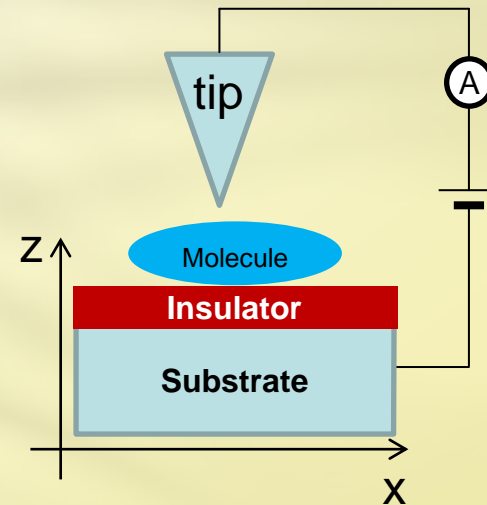
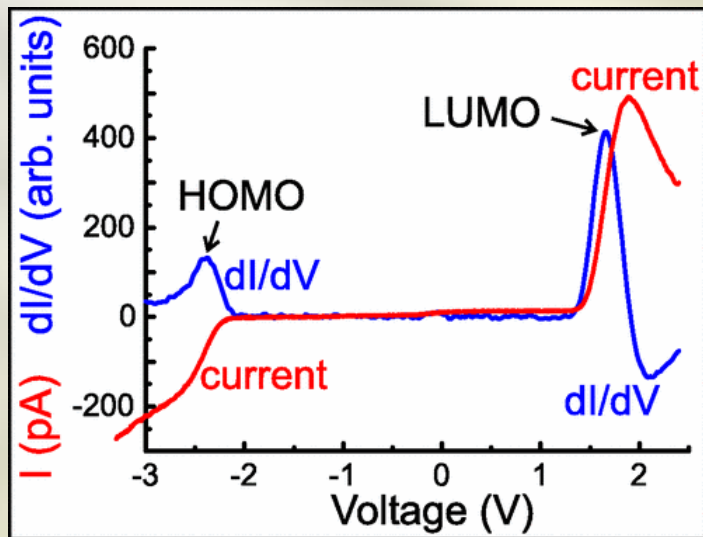
- The signal is the tunnelling current between a metallic tip and the conducting sample
- The tunnelling current depends exponentially on the tip-sample distance

$$I_t = I_0 e^{-2\kappa z} \quad \kappa = \sqrt{2m\phi_0}/\hbar$$

- The microscope can be used in **two** fundamental modes: constant **height** or constant **current**.
- One expects to record in both cases the **topography** of the sample

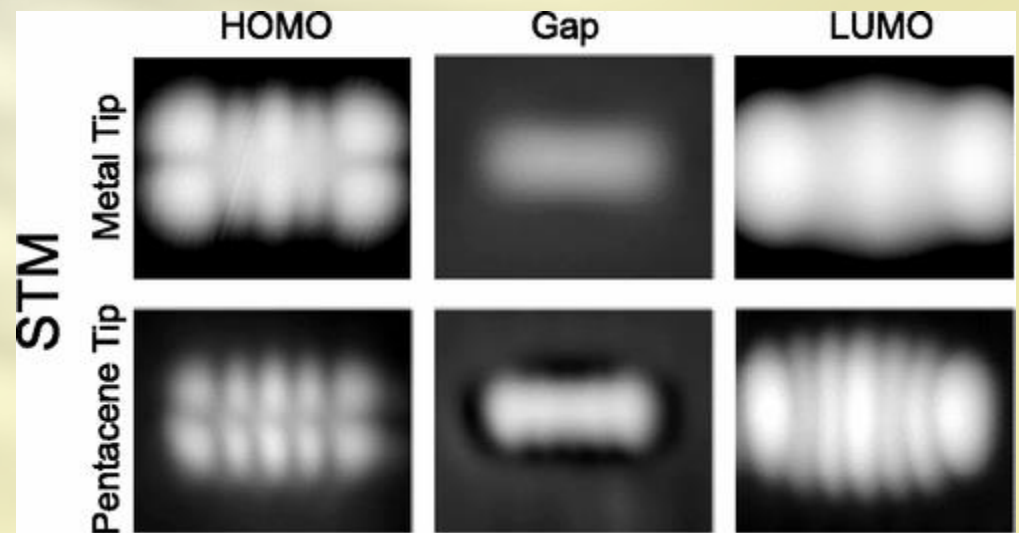
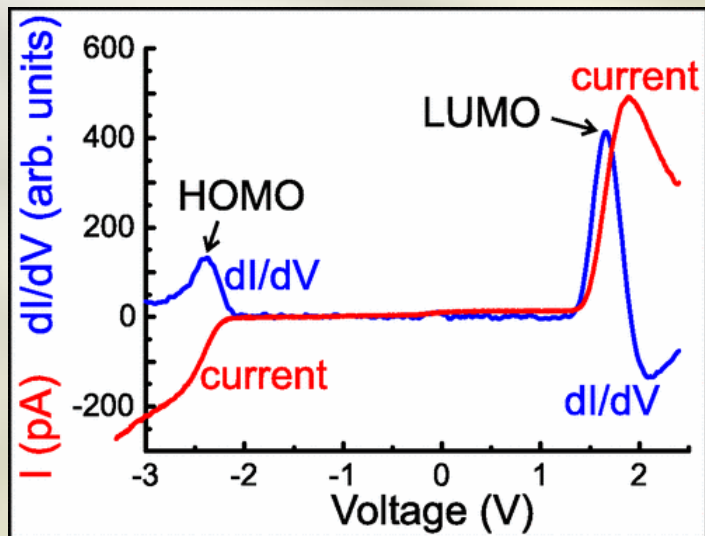


Spectroscopy & Topography



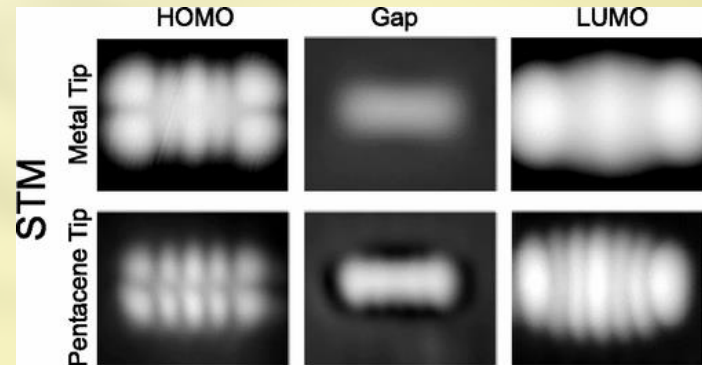
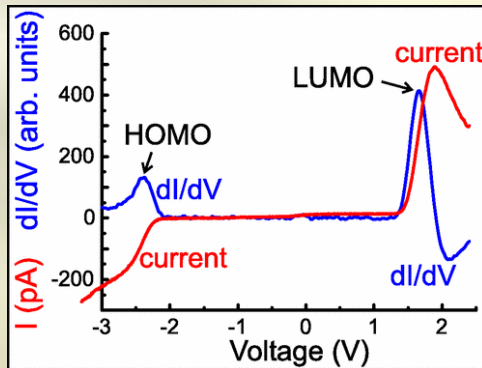
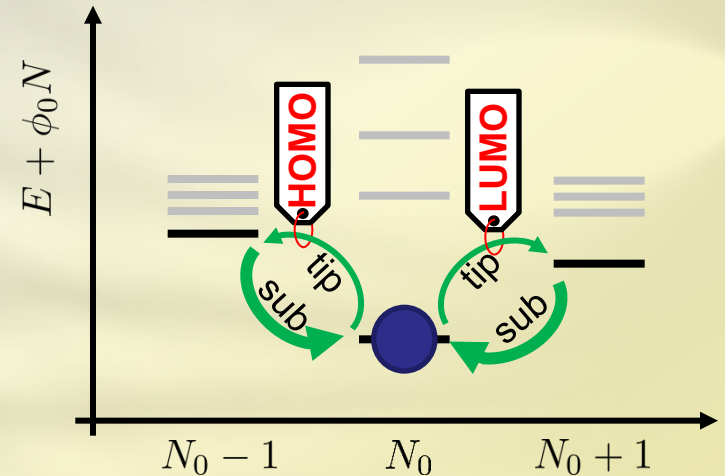
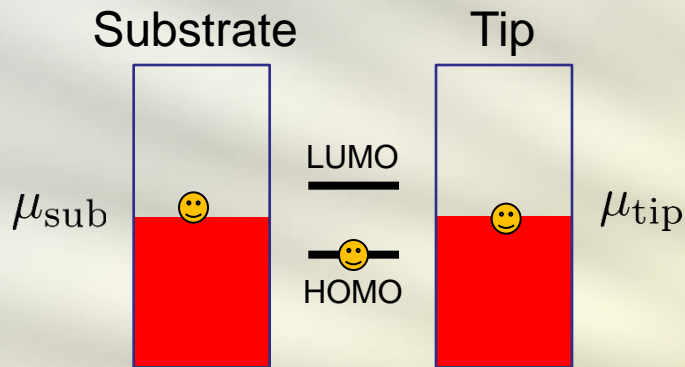
J.Repp et al. *PRL* **94**, 026803 (2005)

Spectroscopy & Topography



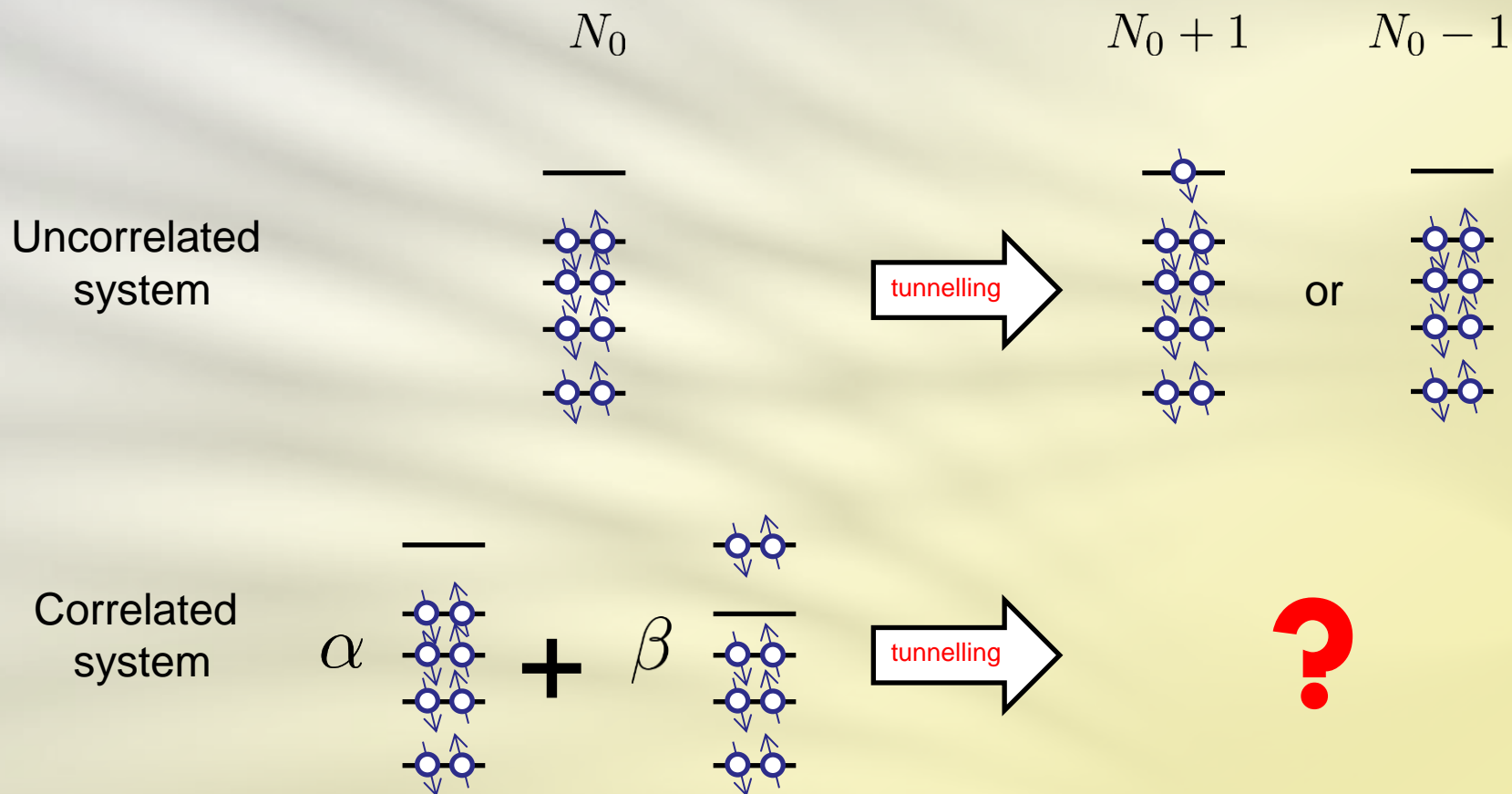
J.Repp et al. *PRL* **94**, 026803 (2005)

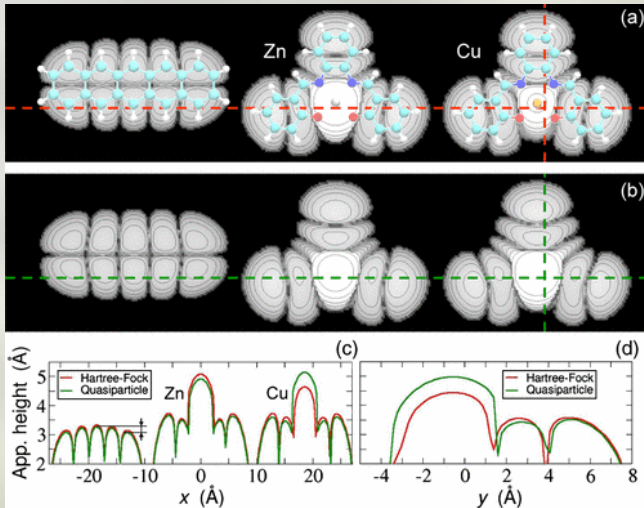
Single particle vs. Many-body



The two approaches coincide only for **uncorrelated** systems close to **equilibrium**

Tunnelling and correlation





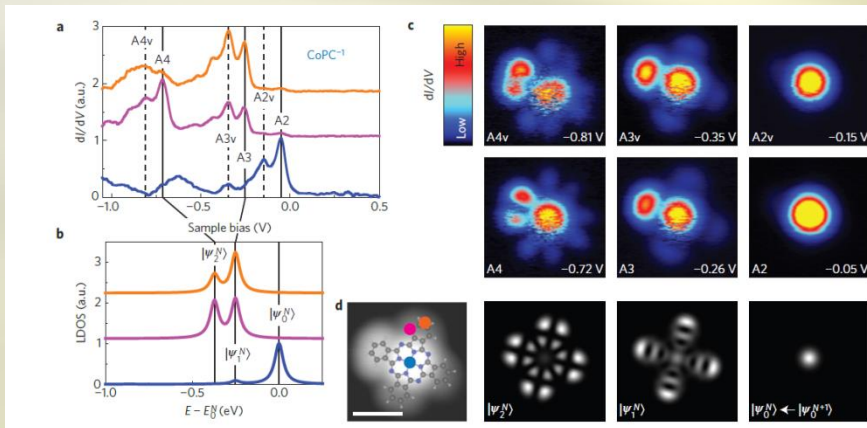
Alteration of the molecular orbitals due to electronic correlation.

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

STM experiments probe

quasiparticle wavefunctions \neq single particle molecular orbitals

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

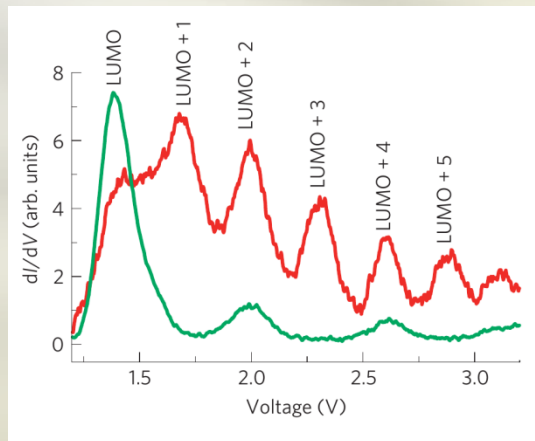
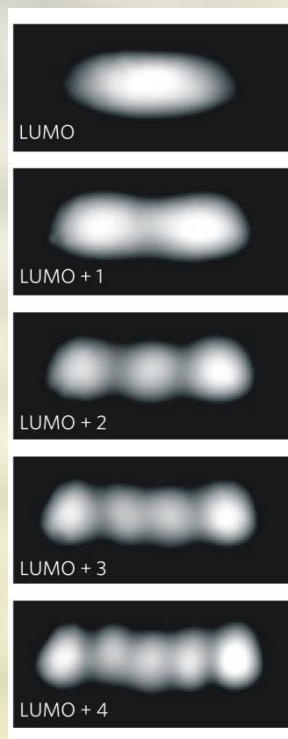
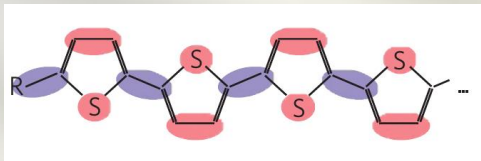


Visualization of intramolecular many-body correlation in STM experiments

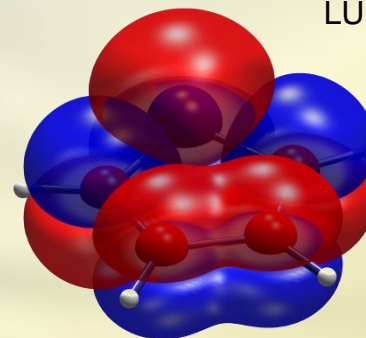
F. Schulz et al. *Nat. Physics* **11**, 229 (2015)



In oligothiophenes



LUMO of thiophene



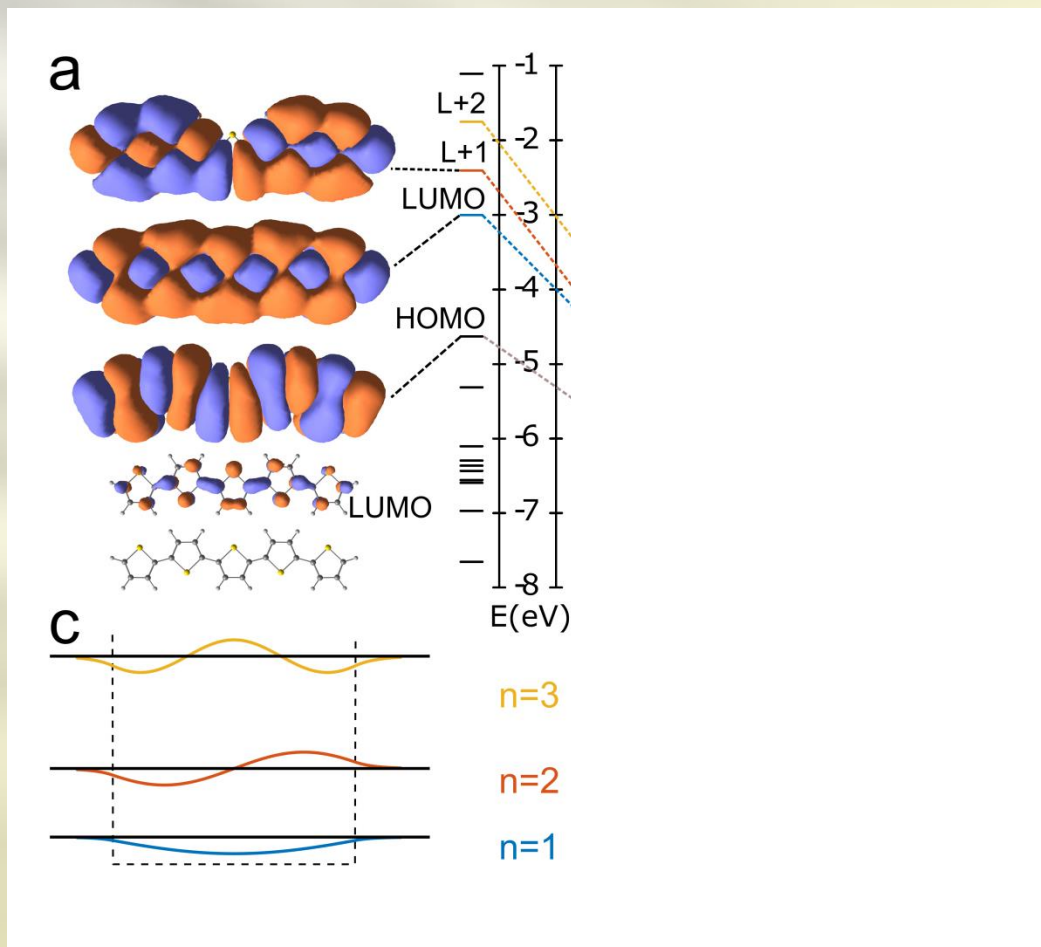
General statement of the **Sturm-Liouville theory** for differential equations:

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

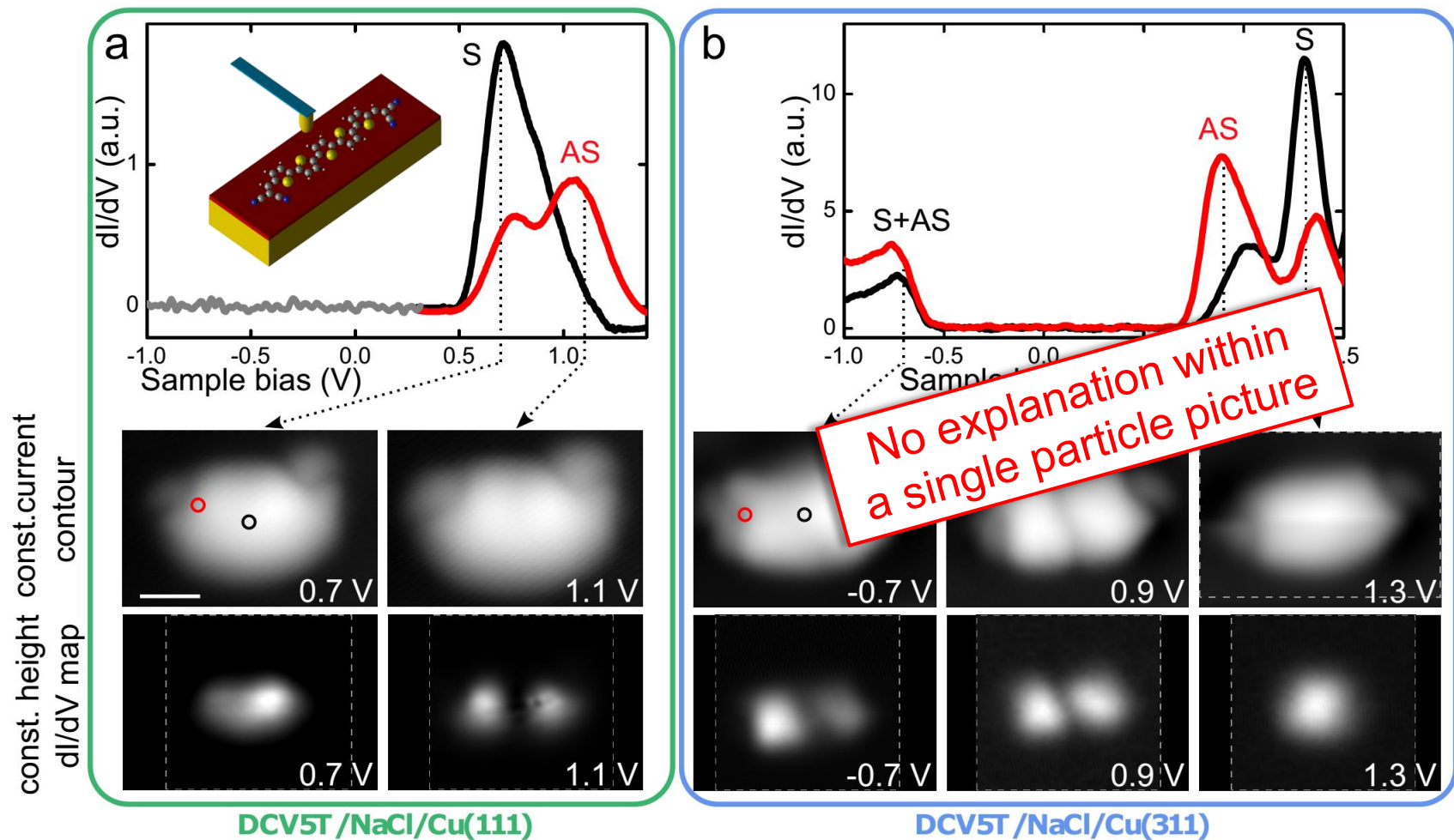
J. Repp *et al.*, *Nat. Phys.* **6**, 975 (2010)

Level-spacing engineering

Quinquethiophene
(5T)



Dicyanovinyl-
quinquethiophene
(DCV5T)



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

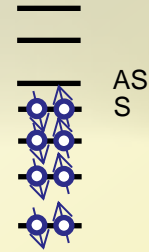


DFT and experiment:

- LUMO and LUMO+1 move together
- Large gap to the HOMO

Interacting model:

- Choose LUMO (S) and LUMO+1 (AS) as basis
- Freeze the other orbitals



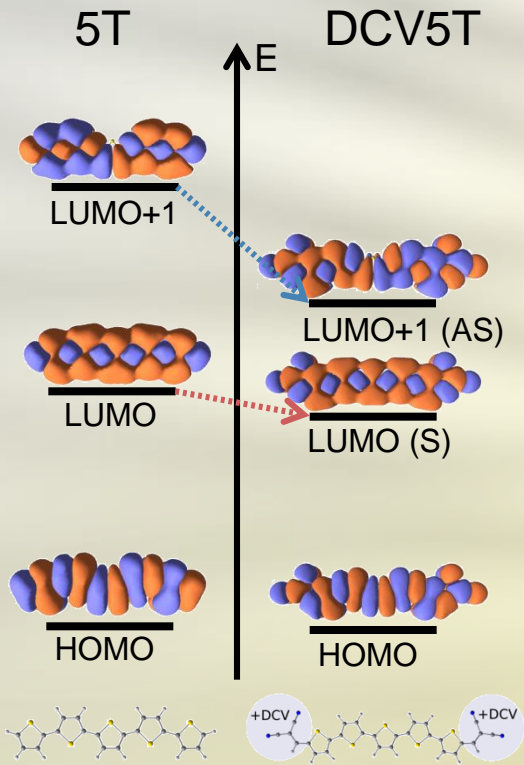
kinetic term

intra-orbital Coulomb

inter-orbital Coulomb

exchange

pair hopping



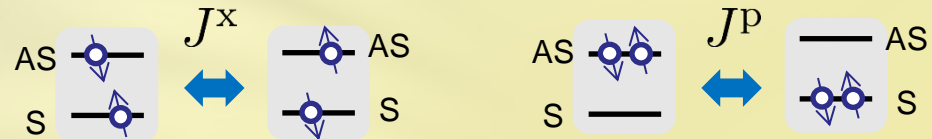
$$\hat{H}_{\text{mol}} = \epsilon_S \hat{n}_S + \epsilon_{AS} \hat{n}_{AS}$$

$$+ V_{S-S} \hat{n}_{S\uparrow} \hat{n}_{S\downarrow} + V_{AS-AS} \hat{n}_{AS\uparrow} \hat{n}_{AS\downarrow}$$

$$+ V_{S-AS} \hat{n}_S \hat{n}_{AS}$$

$$+ J_{S-AS}^x \sum_{\sigma\sigma'} \hat{d}_{S\sigma}^\dagger \hat{d}_{AS\sigma'}^\dagger \hat{d}_{S\sigma} \hat{d}_{AS\sigma}$$

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



Other interaction terms are forbidden by symmetry

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



- Coulomb integrals are calculated numerically from MOs:

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

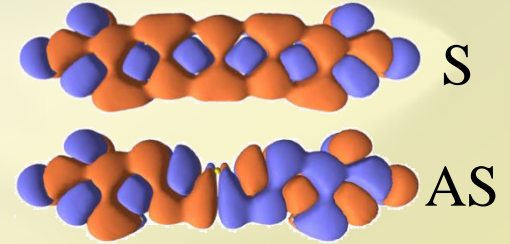
$$U_{AS-AS} = \iint d^3\mathbf{r}_1 d^3\mathbf{r}_2 |\psi_{AS}(\mathbf{r}_1)|^2 V(\mathbf{r}_1 - \mathbf{r}_2) |\psi_{AS}(\mathbf{r}_2)|^2$$

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

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

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

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



- 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

$$\hat{H}_{\text{mol}} = \epsilon_S \hat{n}_S + \epsilon_{AS} \hat{n}_{AS} + \frac{U}{2} \hat{N} (\hat{N} - 1) + J \sum_{\sigma\sigma'} \hat{d}_{S\sigma}^\dagger \hat{d}_{AS\sigma'}^\dagger \hat{d}_{S\sigma'} \hat{d}_{AS\sigma} + J \sum_{\sigma\sigma'} \left(\hat{d}_{S\sigma}^\dagger \hat{d}_{S\sigma'}^\dagger \hat{d}_{AS\sigma'} \hat{d}_{AS\sigma} + \text{h.c.} \right)$$



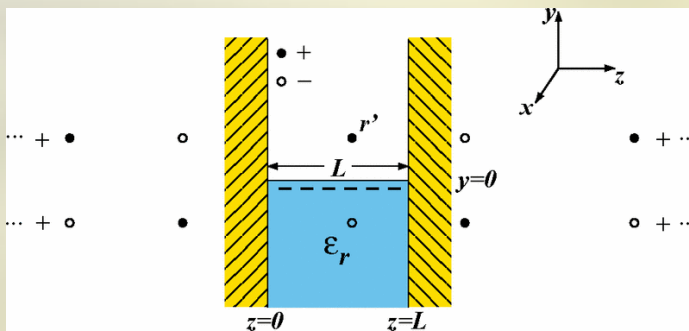
- the interaction between the molecule and the substrate is described by two additional terms:

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

↑
image charge/polaron shift

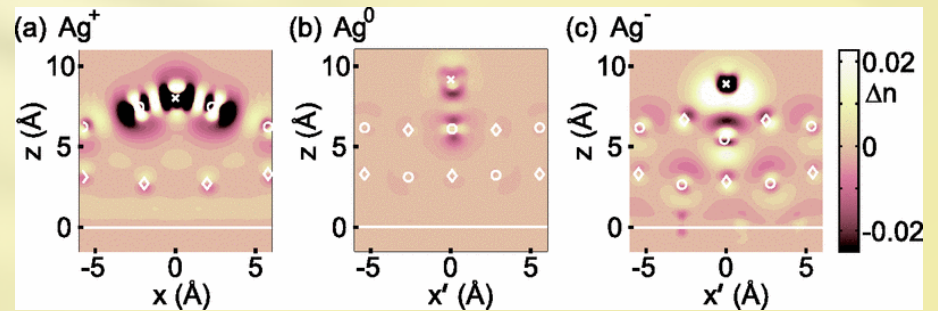
- δ incorporates two effects which stabilize the charge on the molecule:

image charge effect



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

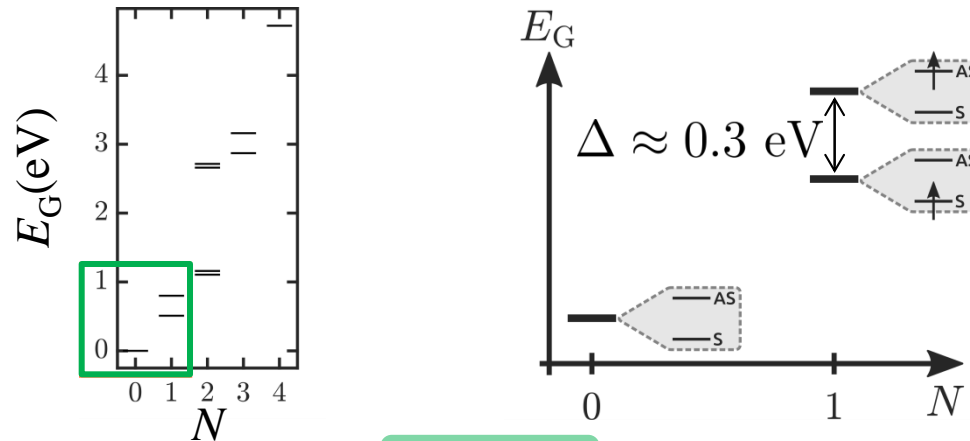
polaron formation



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

DCV5T on NaCl/Cu(111)

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

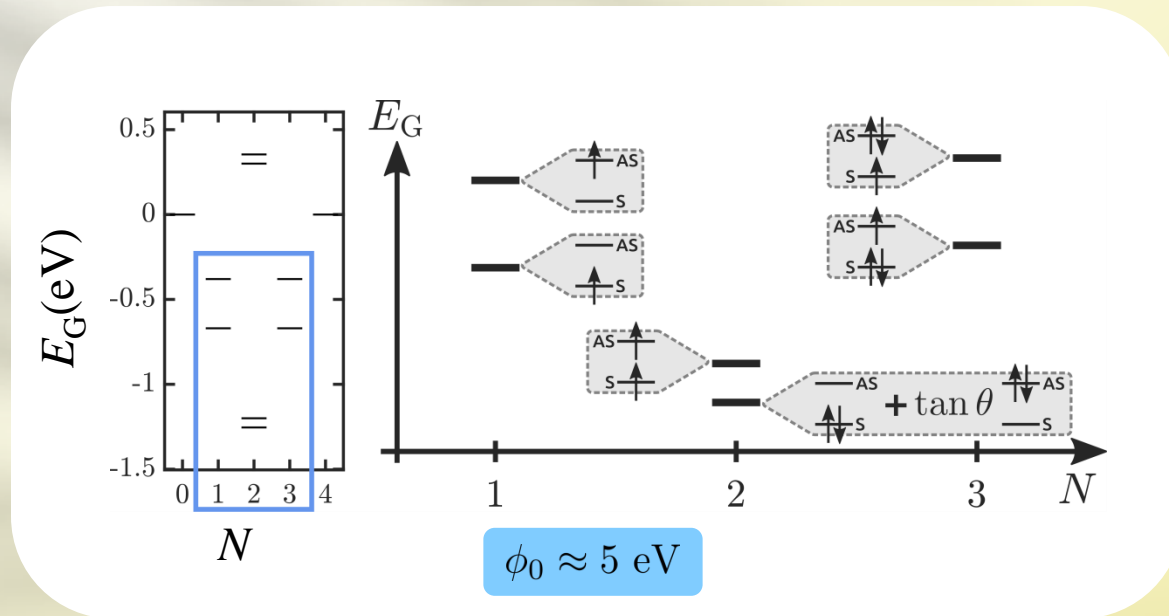


$$\phi_0 \approx 4 \text{ eV}$$

- The molecule is **neutral** on this substrate
- The **order** of the anionic states is in agreement with the single particle picture (and Sturm-Liouville theory)

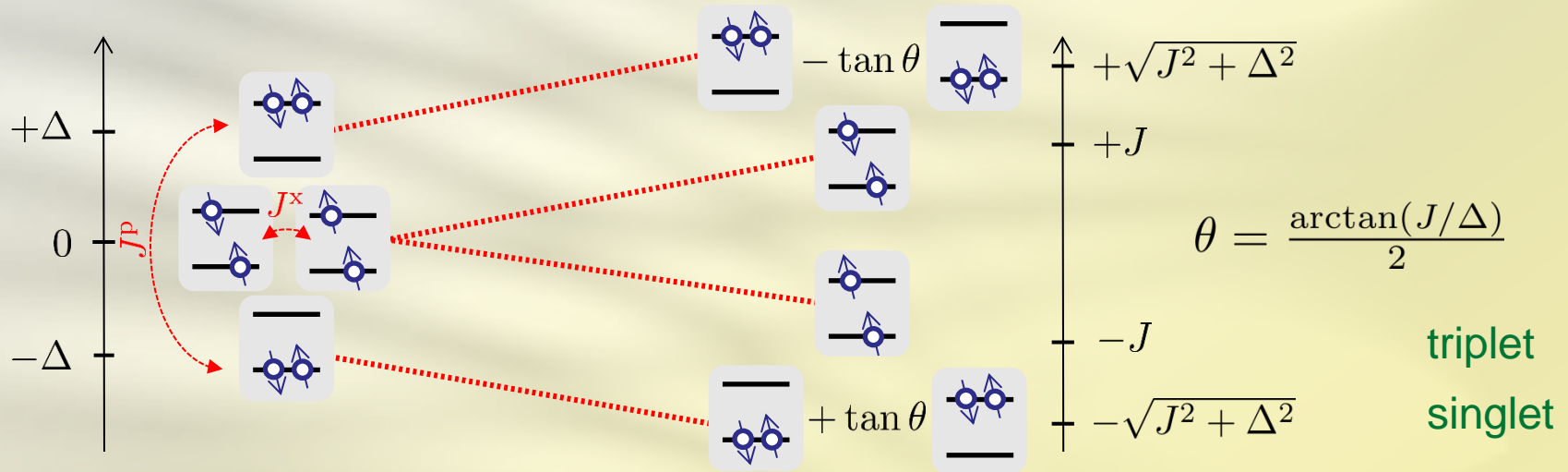
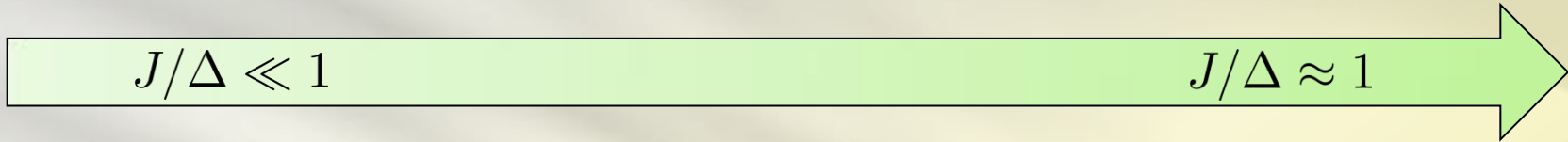
DCV5T on NaCl/Cu(311)

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



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

The two-particle spectrum



In DCV5T
 $J/\Delta \approx 3$

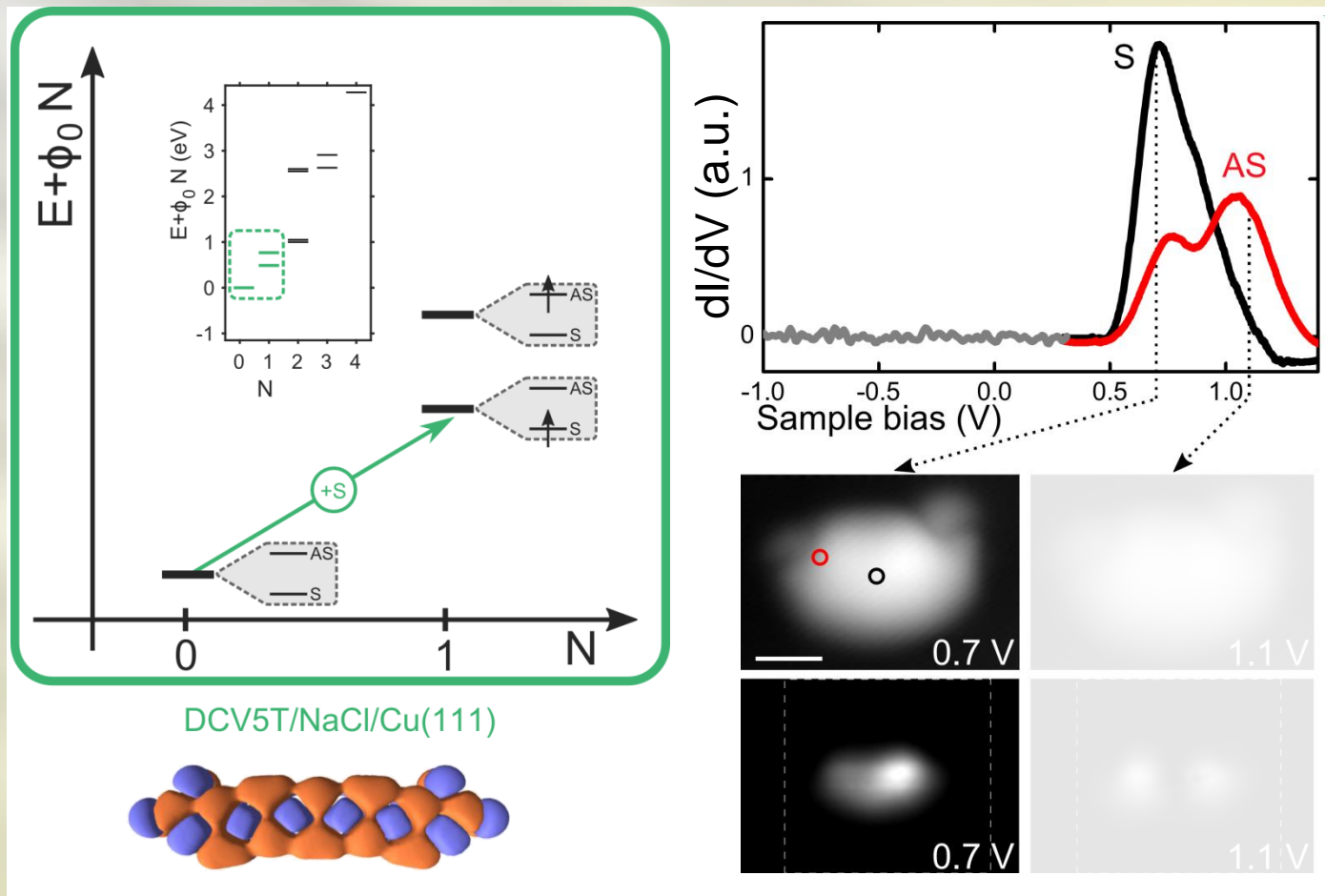


$\tan \theta \approx 0.86$
 $\Delta_{\text{ST}} \approx 58 \text{ meV}$

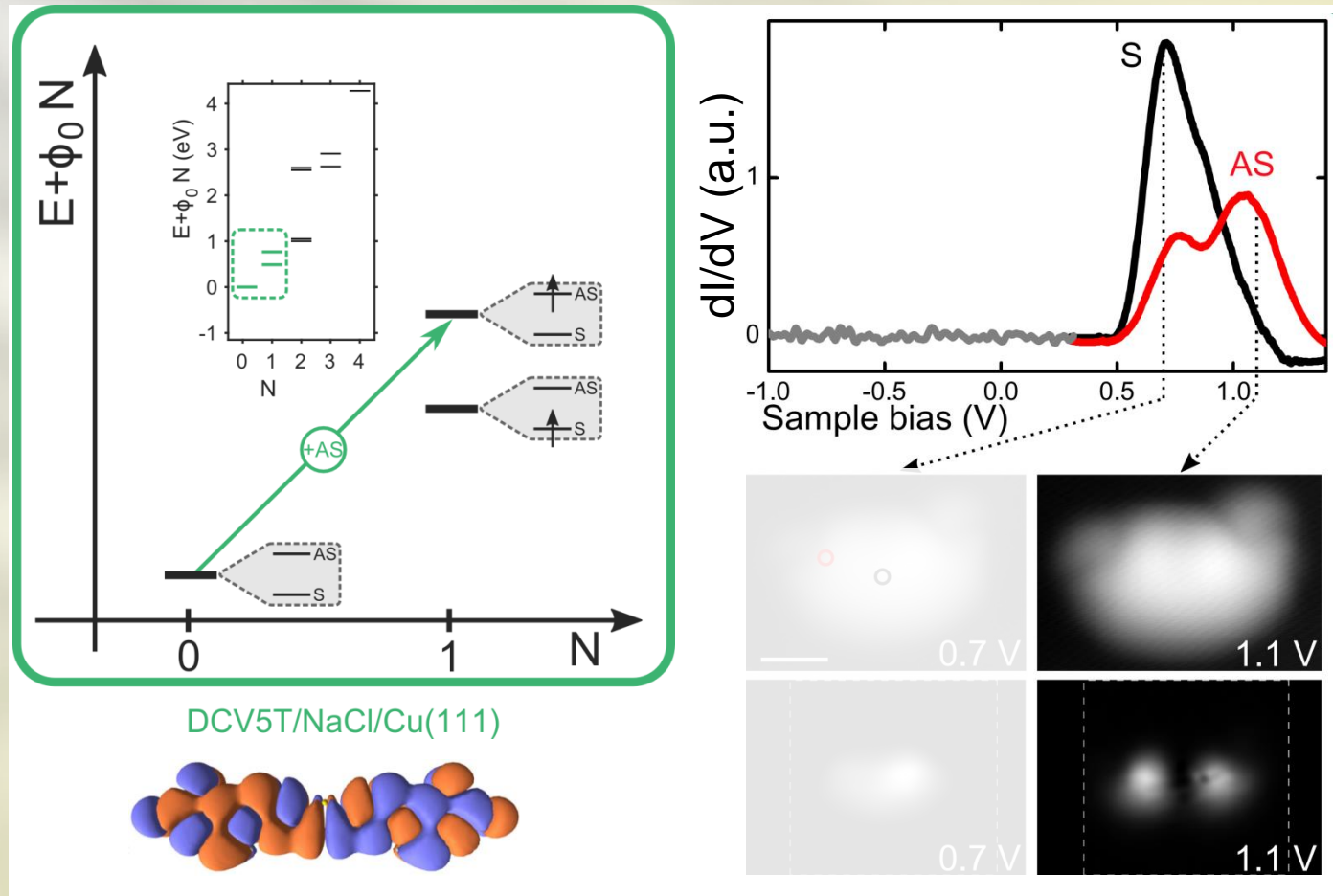
Strongly entangled
ground state

Orbital reversal:
qualitative explanation

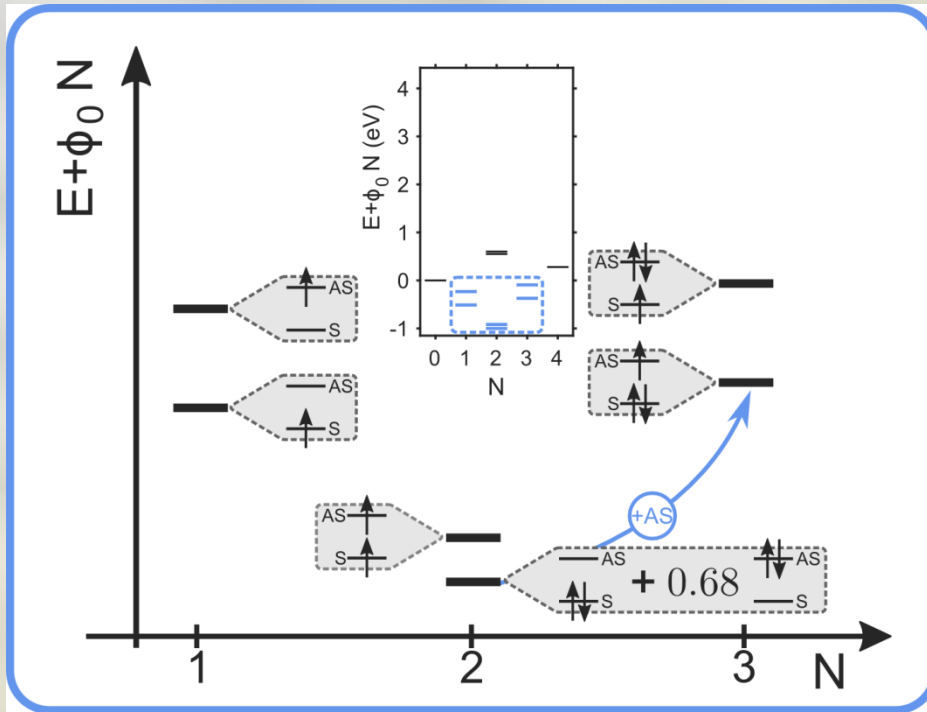
Mechanism of orbital reversal



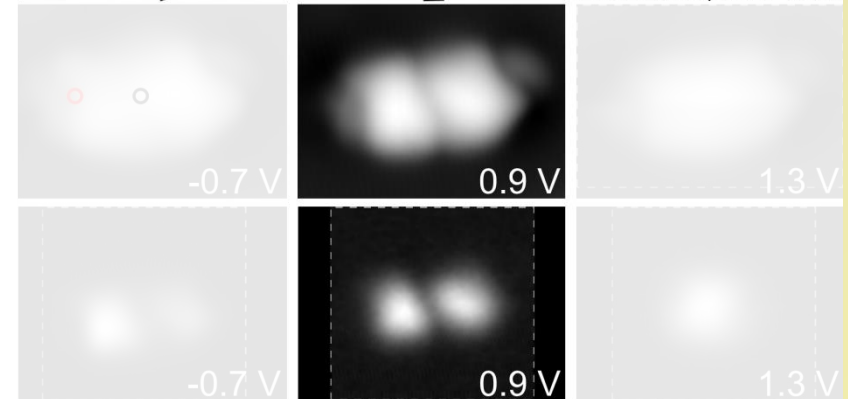
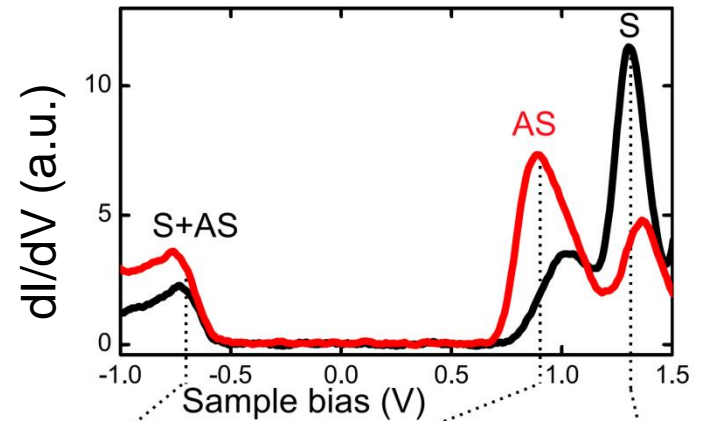
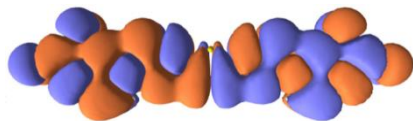
Mechanism of orbital reversal



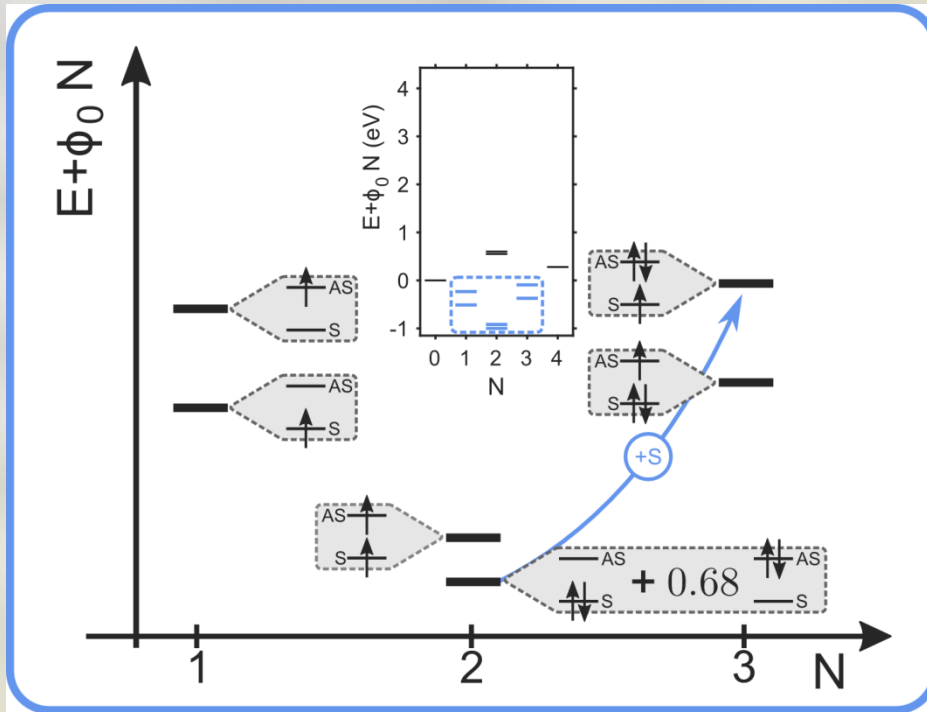
Mechanism of orbital reversal



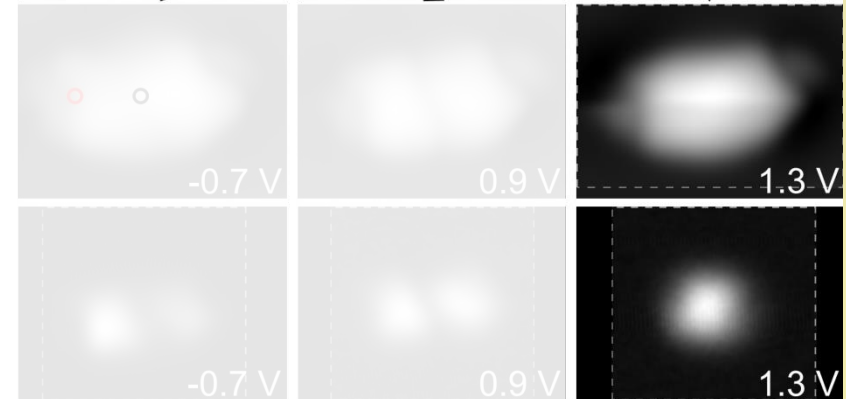
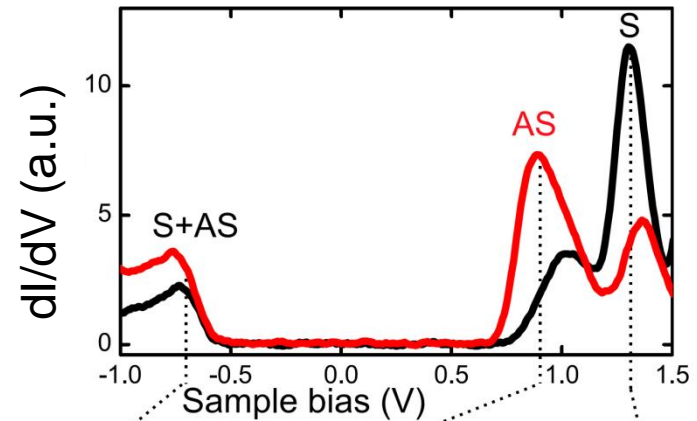
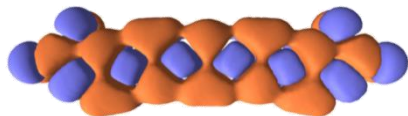
DCV5T/NaCl/Cu(311)



Mechanism of orbital reversal

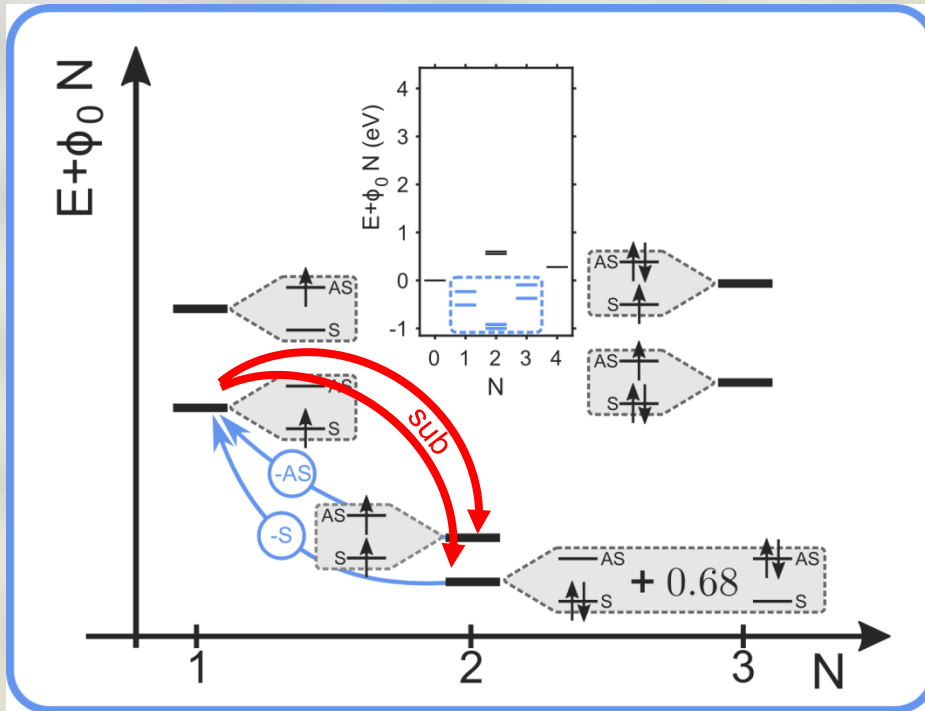


DCV5T/NaCl/Cu(311)

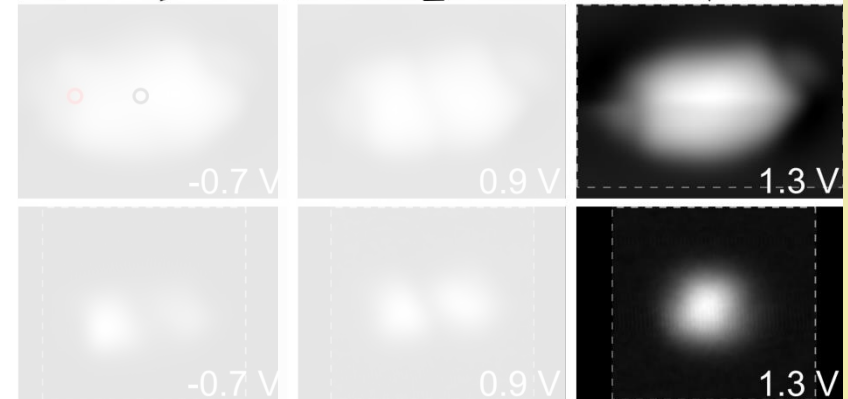
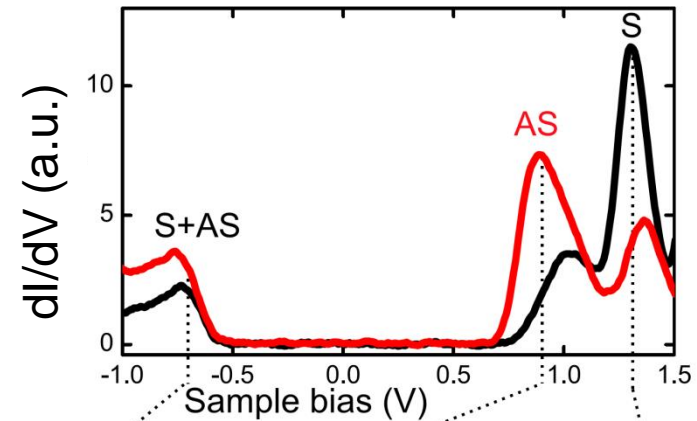
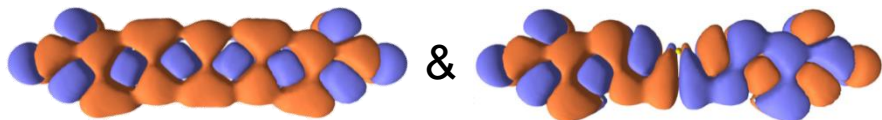


This transition would be forbidden if $J/\Delta = 0$

Mechanism of orbital reversal



DCV5T/NaCl/Cu(311)

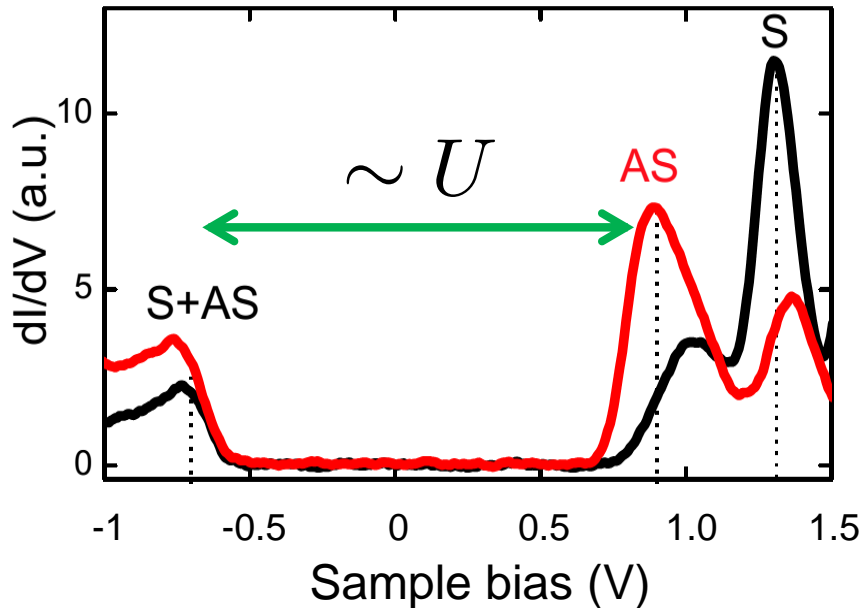


The antisymmetric component is a strictly **non-equilibrium** effect

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)

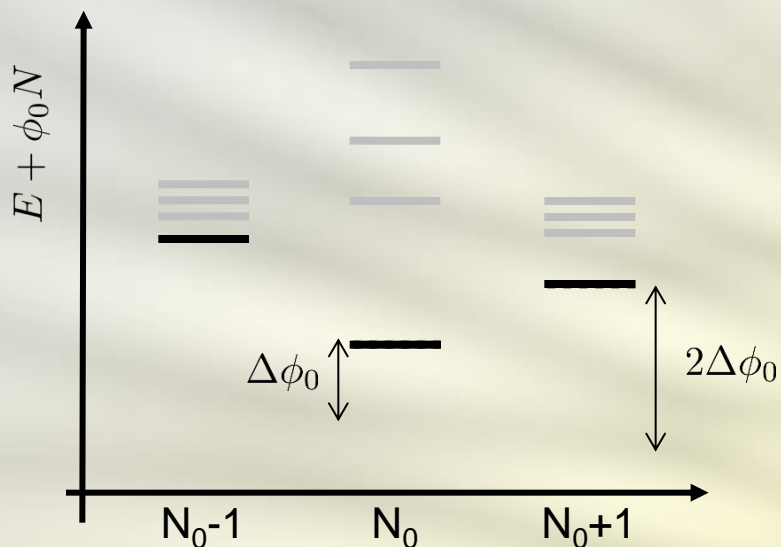
Charging energy of DCV5T $U \approx 1.5 \text{ eV}$

- 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.

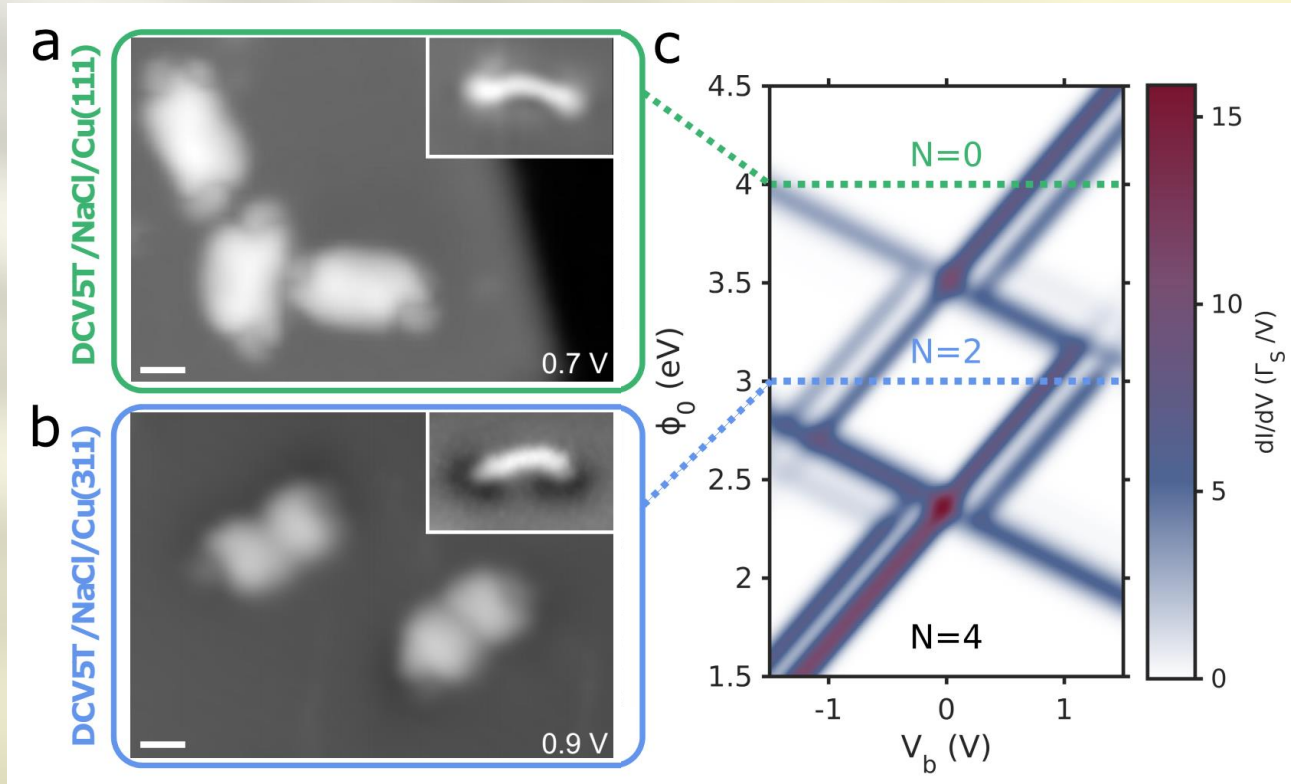
The **stability** of a given charge is given by its **addition energy**

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

Addition energies for the two orbital model of DCV5T:

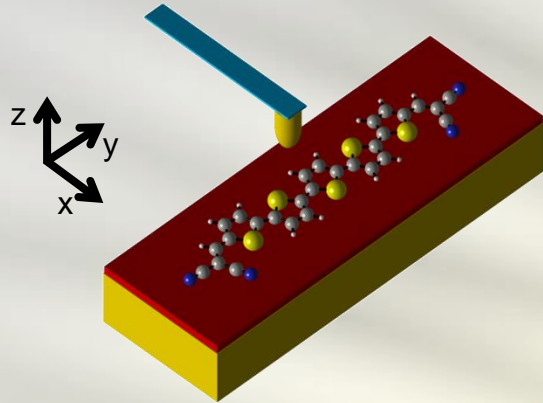
$J/\Delta \ll 1$ 	$E_1^{\text{add}} \rightarrow U - 2\delta + \Delta - \sqrt{\Delta^2 + J^2}$ $E_2^{\text{add}} \rightarrow U - 2\delta - \Delta - J + 2\sqrt{\Delta^2 + J^2}$	$J/\Delta \gg 1$
$E_1^{\text{add}} \rightarrow U - 2\delta$ $E_2^{\text{add}} \rightarrow U - 2\delta + \Delta$	<p style="color: red; font-weight: bold;">The singly charged DCV5T is extremely unstable</p>	$E_1^{\text{add}} \rightarrow U - 2\delta - J$ $E_2^{\text{add}} \rightarrow U - 2\delta + J$

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

Transport calculations

The dynamics is calculated via a generalized master equation for the reduced density matrix

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

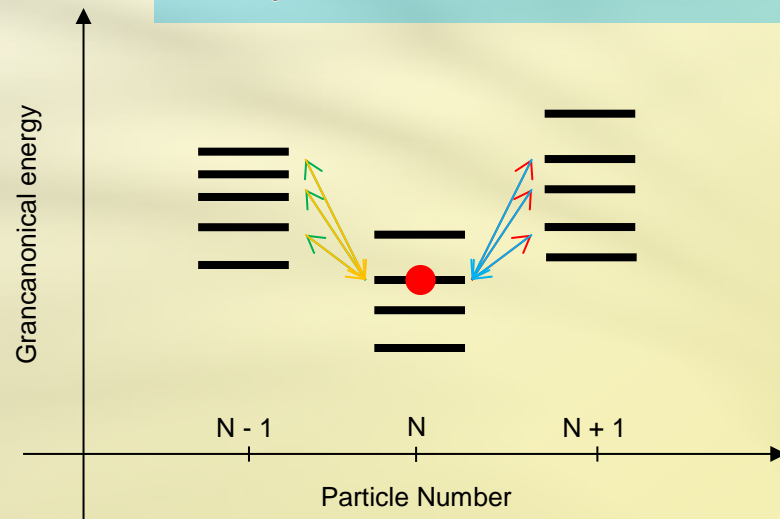
$$\begin{aligned} \dot{\sigma} = & \underbrace{-\frac{i}{\hbar}[\hat{H}_{\text{sys}}, \sigma]}_{\text{Coherent dynamics}} - \underbrace{\frac{i}{\hbar}[\hat{H}_{\text{eff}}, \sigma]}_{\text{Effective internal dynamics}} \\ & + \underbrace{\mathcal{L}_{\text{tun}}[\sigma]}_{\text{Tunnelling dynamics}}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

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

$\mathcal{L}[\sigma^\infty] \equiv 0$ 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

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

Single particle tunnelling rate matrix

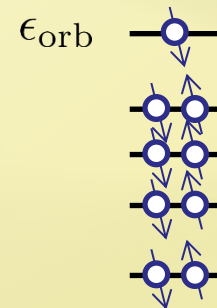
Many-body rate matrix

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

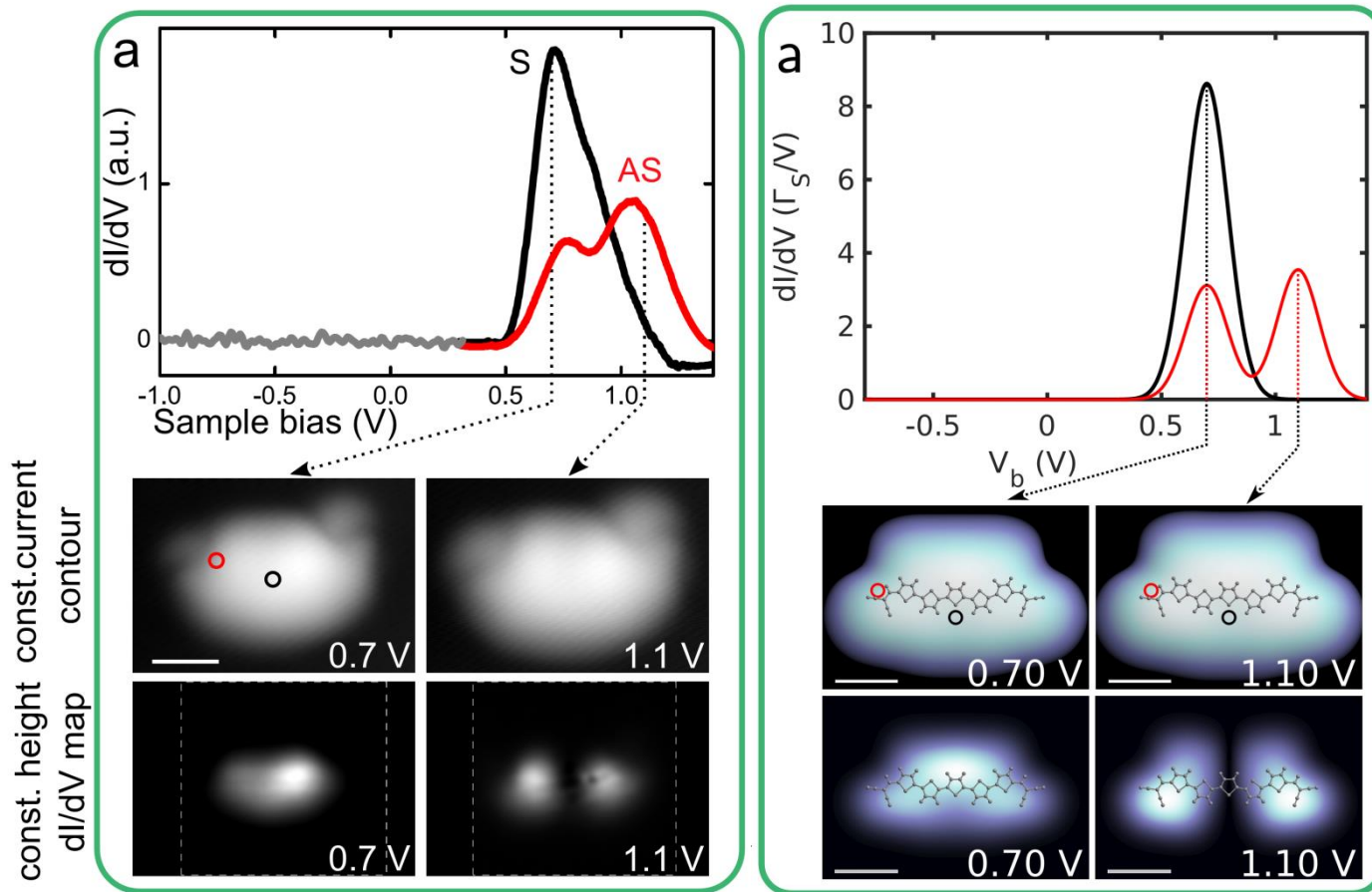
$$R_{N E_0 \rightarrow N+1 E_1}^{\chi\tau} = \Gamma_{\text{orb}}^\chi(\epsilon_{\text{orb}}) f^+(\epsilon_{\text{orb}} - \mu_\chi)$$



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

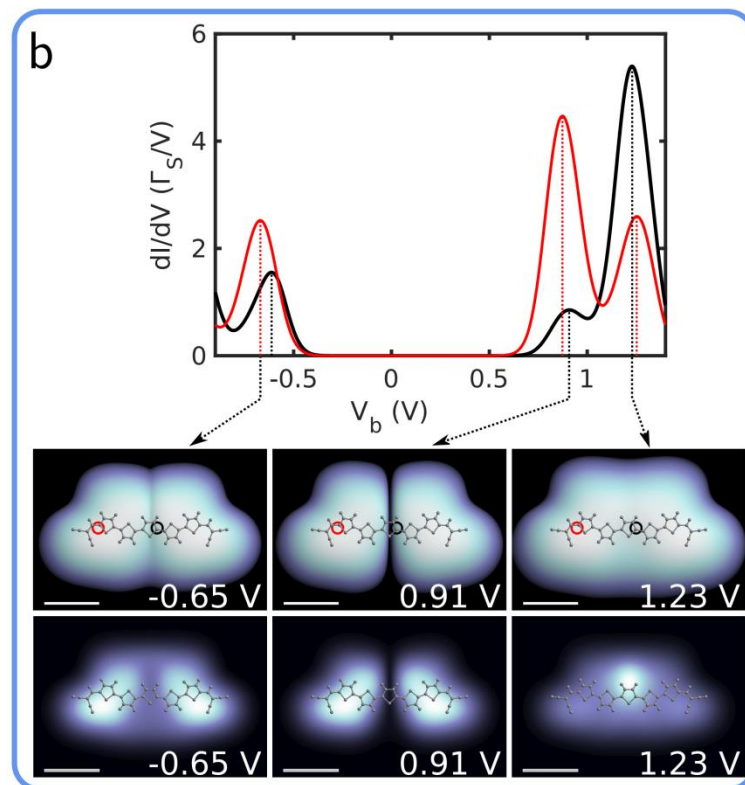
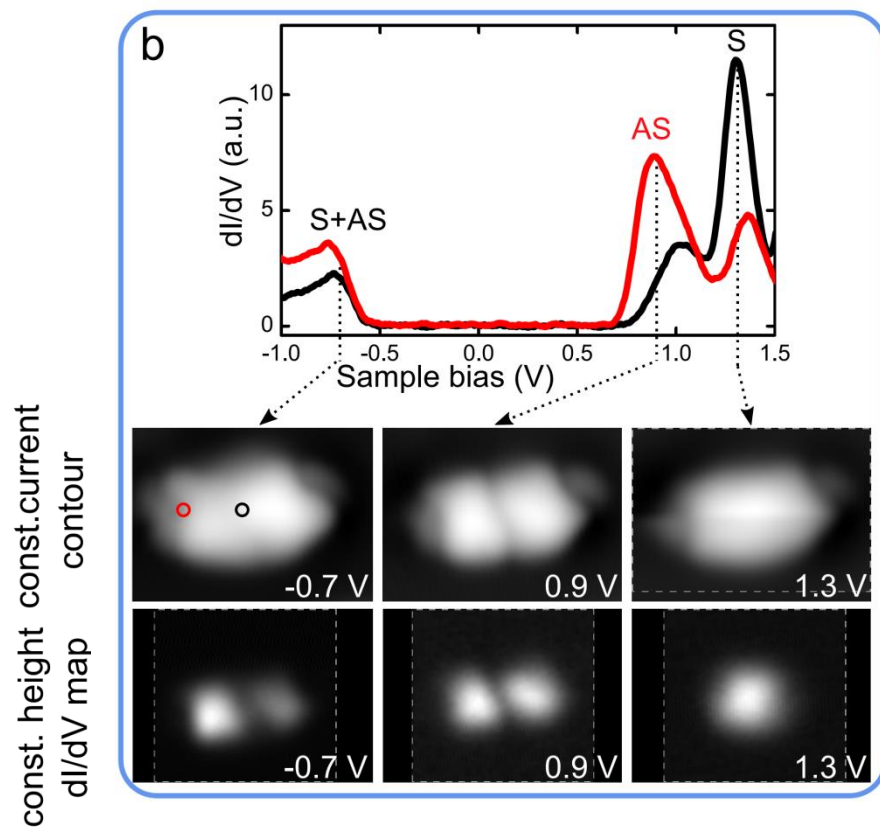


DCV5T/NaCl/Cu(111)





DCV5T/NaCl/Cu(311)

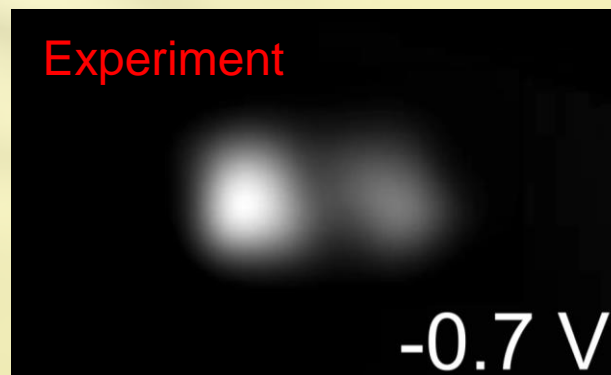
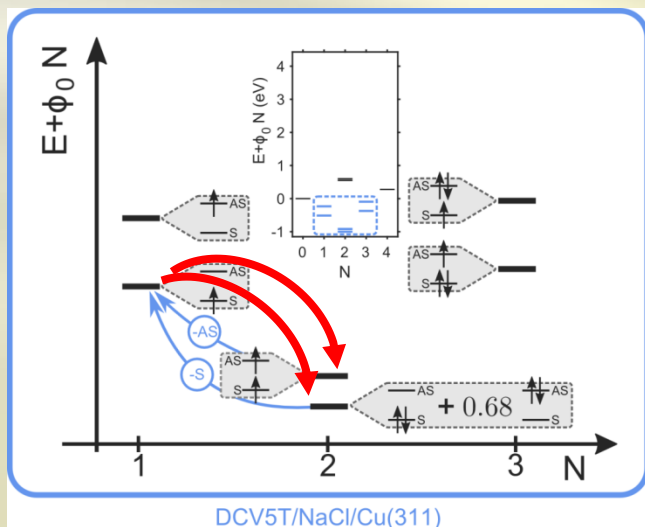
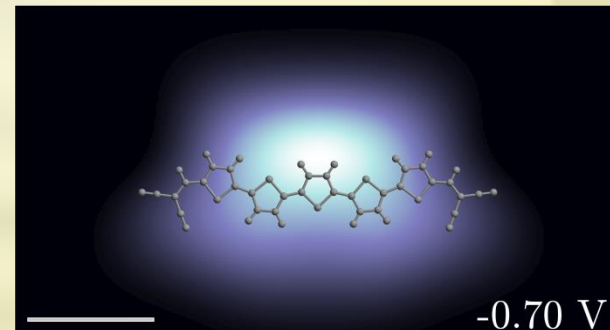
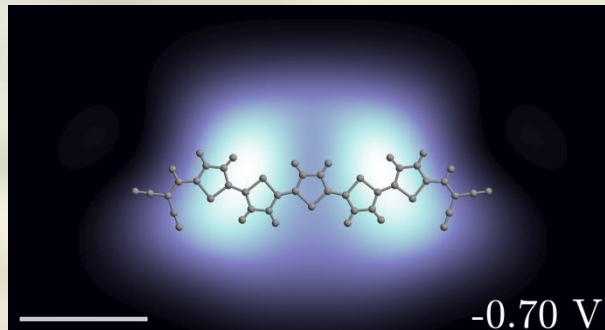
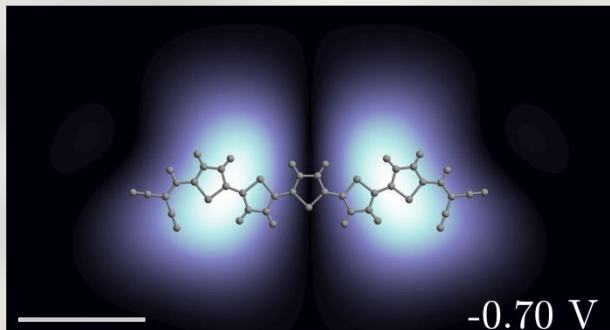


Intramolecular relaxation

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

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

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

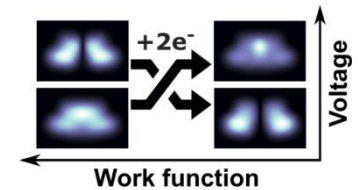




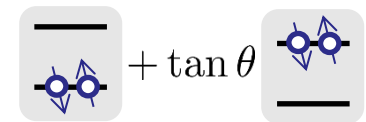
By **chemical engineering** of the single-particle level spacing between two frontier orbitals we **control** the degree of **electronic-correlation** in single molecule junctions



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



The orbital reversal is the signature of an **entangled ground state** which we understand in terms of a minimal interacting model



Criteria for such entanglement are clearly formulated in terms of the parameters in the **minimal model** and allow us to **predict** and **control** its occurrence for other molecules.

$$J/\Delta \approx 1$$

↓

Correlation

Aknowledgments

Theory



Benjamin Siegert

Experiment



Nemanja Kocić



Ping Yu



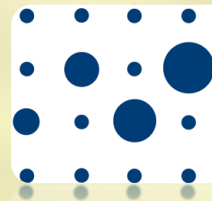
Jascha Repp



GRK 1570



SFB 689



VolkswagenStiftung

Lichtenberg Programm

Thank you for your attention

