# Apparent reversal of molecular orbitals reveals entanglement

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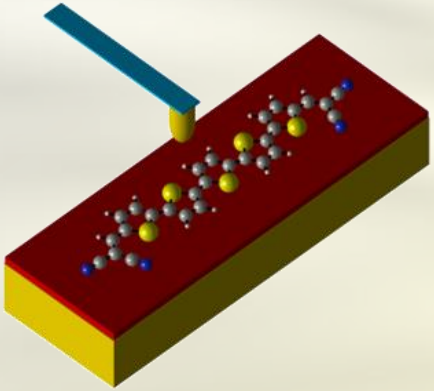
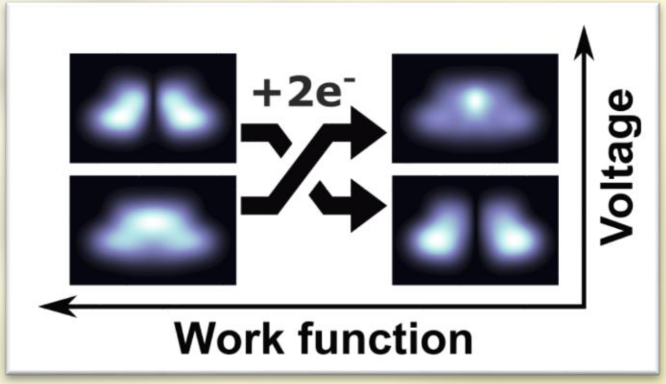
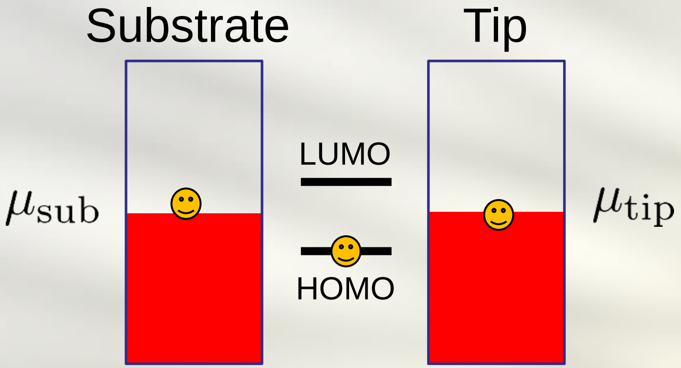
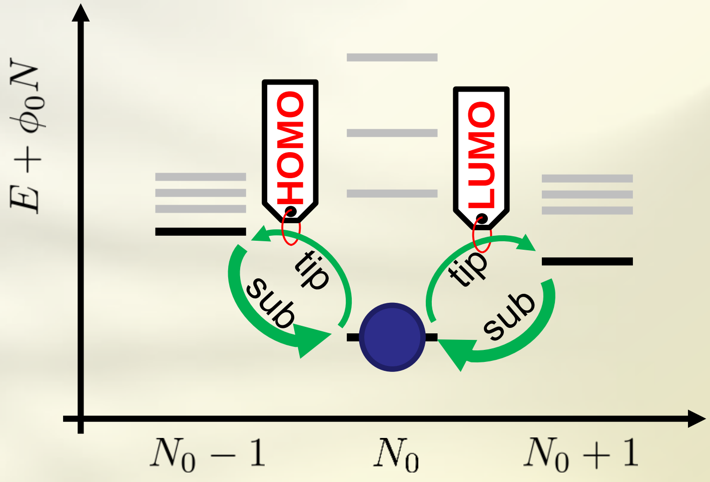


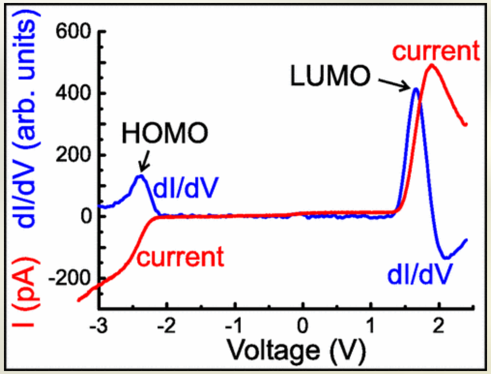


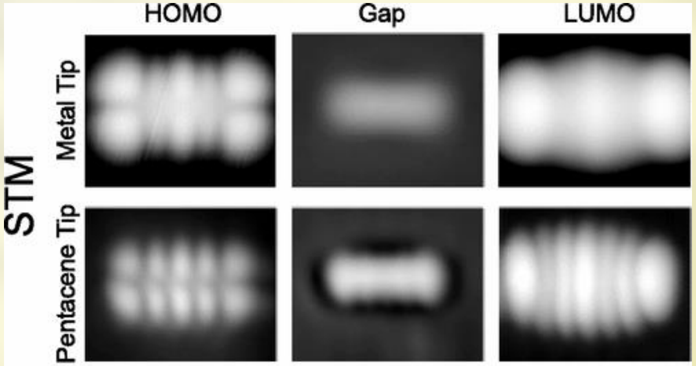
Frühjahrstagung Berlin 2018

# Single particle vs. Many-body



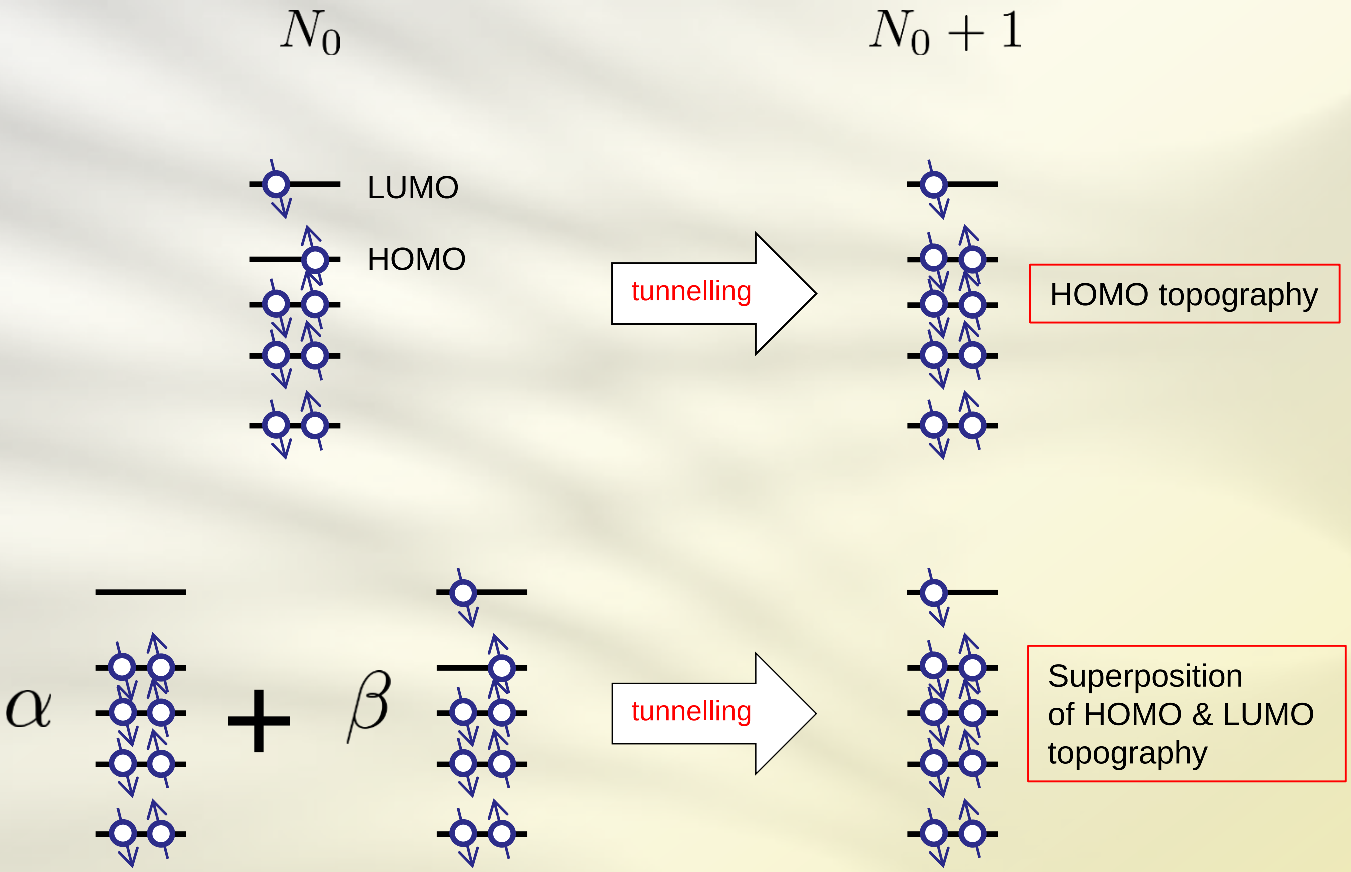






The two approaches agree only for **uncorrelated** systems close to **equilibrium**

# Non-equilibrium and correlation



$N_0$

$N_0 + 1$

Non-equilibrium

LUMO

HOMO

tunnelling

HOMO topography

Correlated system

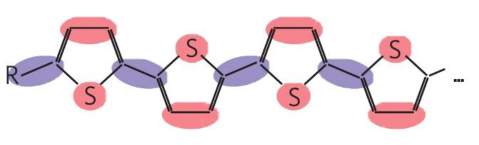
$\alpha$ $+$ $\beta$

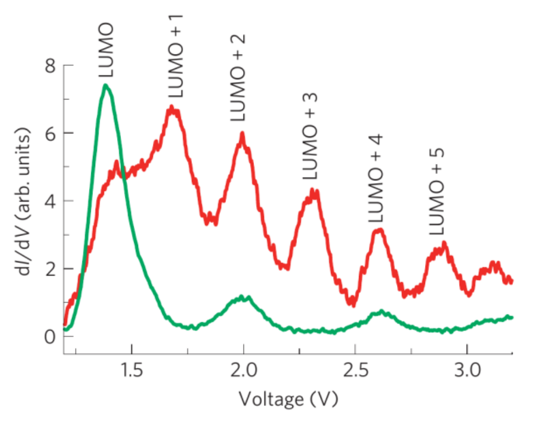
tunnelling

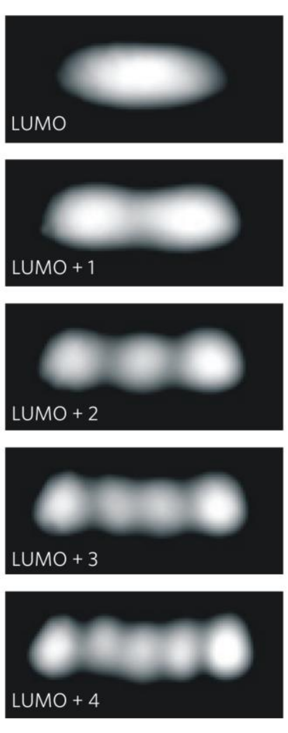
Superposition
of HOMO & LUMO
topography

# Particle-in-a-box like states

In oligothiophenes

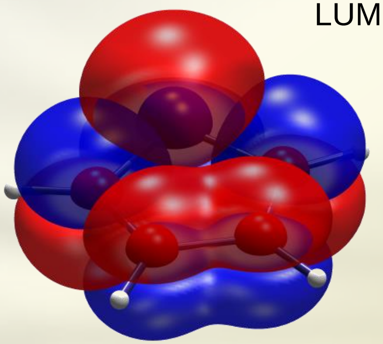






J. Repp *et al.*, *Nat. Phys.* **6**, 975 (2010)

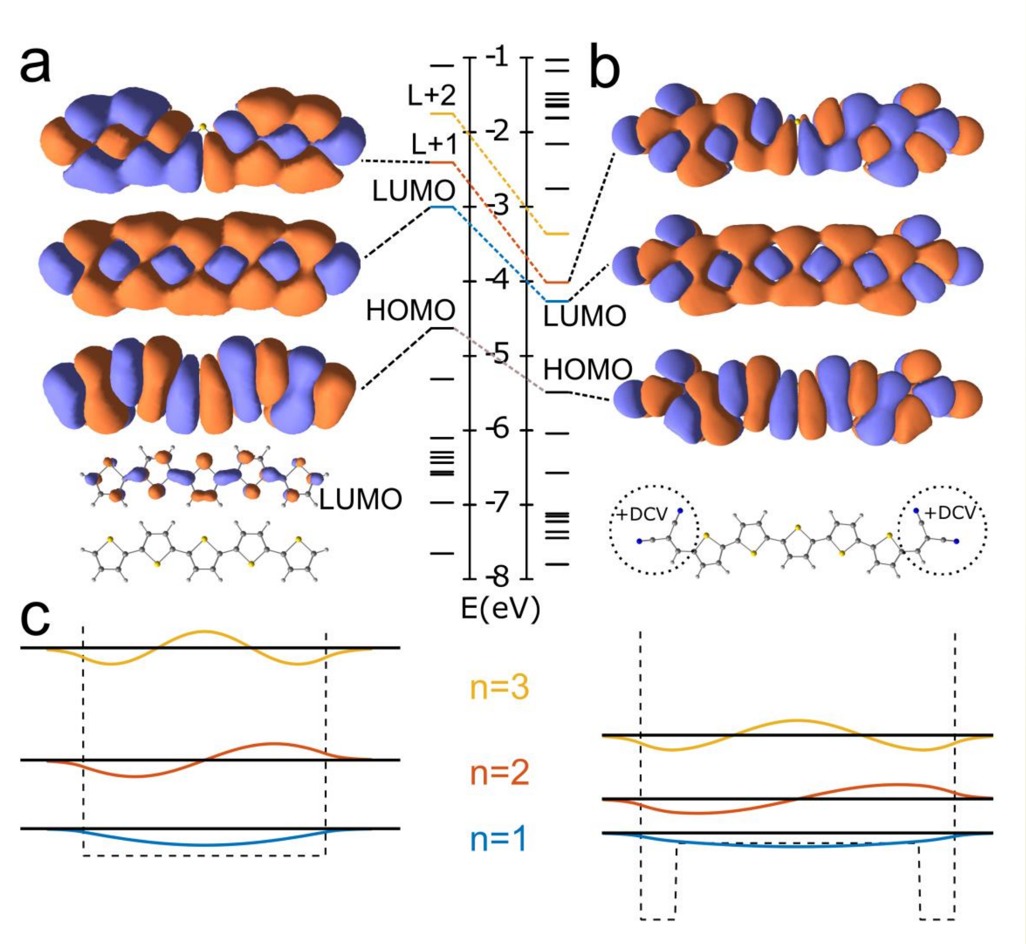
LUMO of thiophene



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.

# Level-spacing engineering



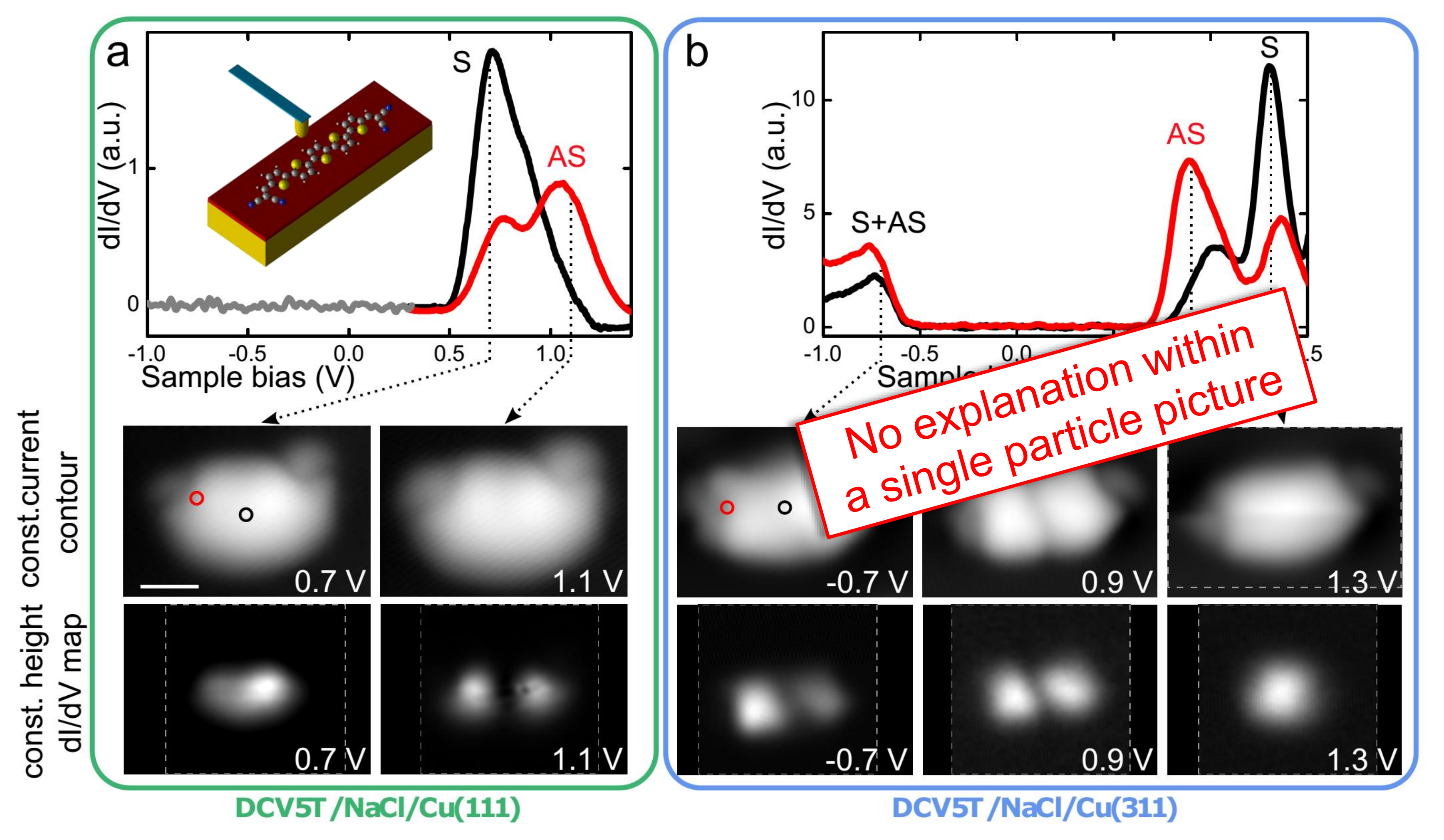
AS

S

Quinquethiophene
(5T)

Dicyanovinyl-
quinquethiophene
(DCV5T)

# Orbital inversion

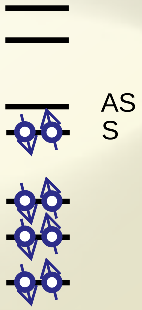


No explanation within a single particle picture

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

# The many-body Hamiltonian

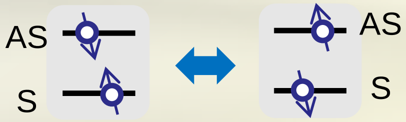
We concentrate on the dynamics of two orbitals only



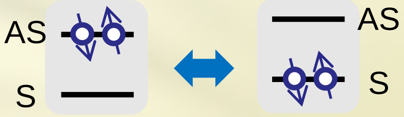
and freeze the occupation of the other single particle states

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

exchange



pair-hopping



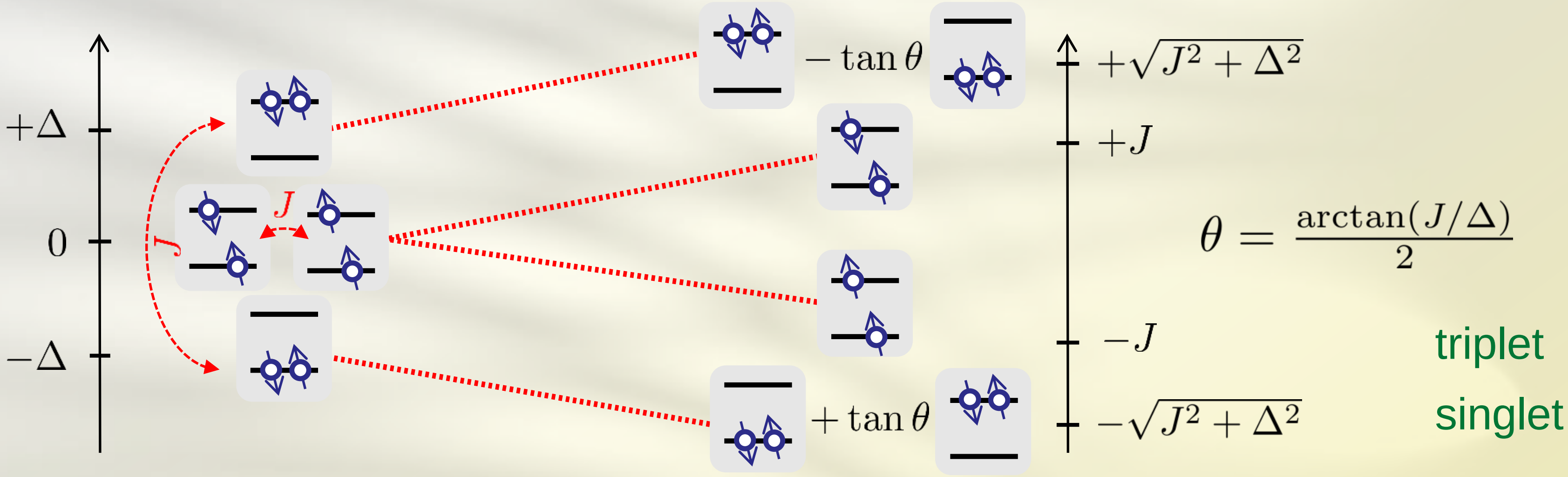
$\Delta = \epsilon_{\mathrm{AS}} - \epsilon_{\mathrm{S}} = 0.3\ \mathrm{eV}$ $U = 1.4\ \mathrm{eV}$ $J = 0.75\ \mathrm{eV}$

fit to the experiment

calculated from the molecular orbitals

# The two-particle spectrum

$J/\Delta \ll 1$ → $J/\Delta \approx 1$



$$\theta = \frac{\arctan(J/\Delta)}{2}$$

In DCV5T

$J/\Delta \approx 3$

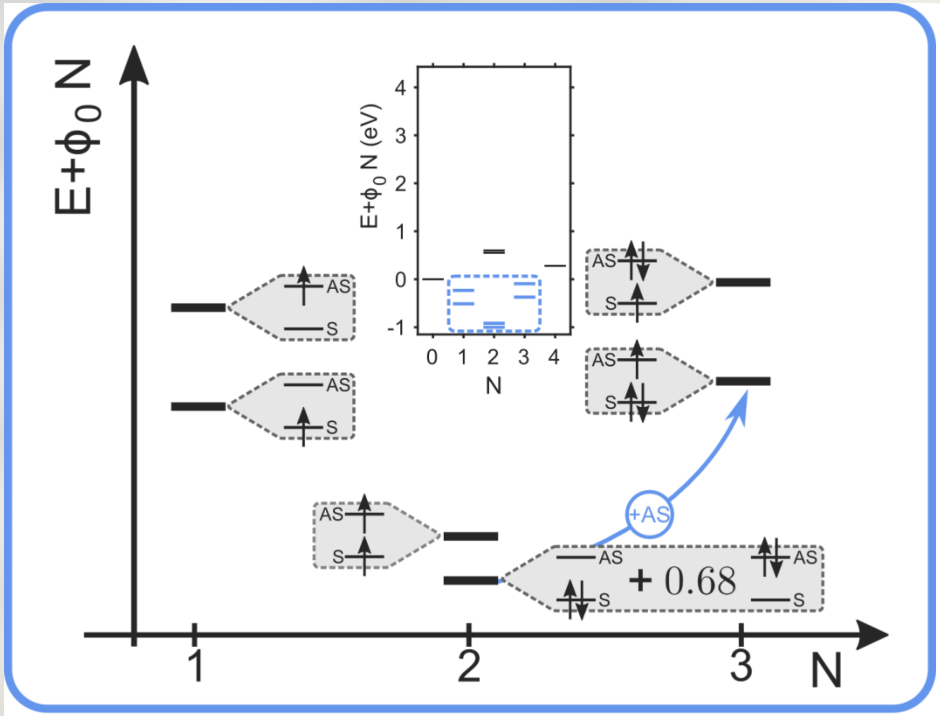
⇒

$\tan\theta \approx 0.68$

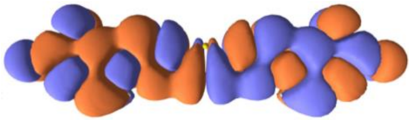
$\Delta_{\mathrm{ST}} \approx 58\ \mathrm{meV}$

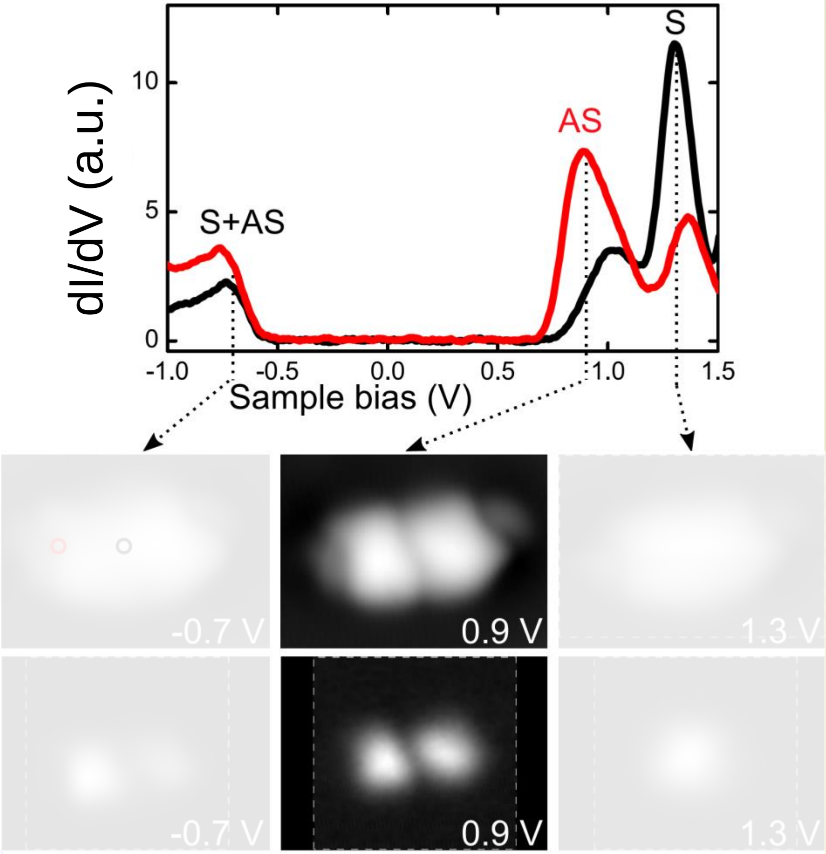
**Strongly entangled ground state**

# Mechanism of orbital reversal

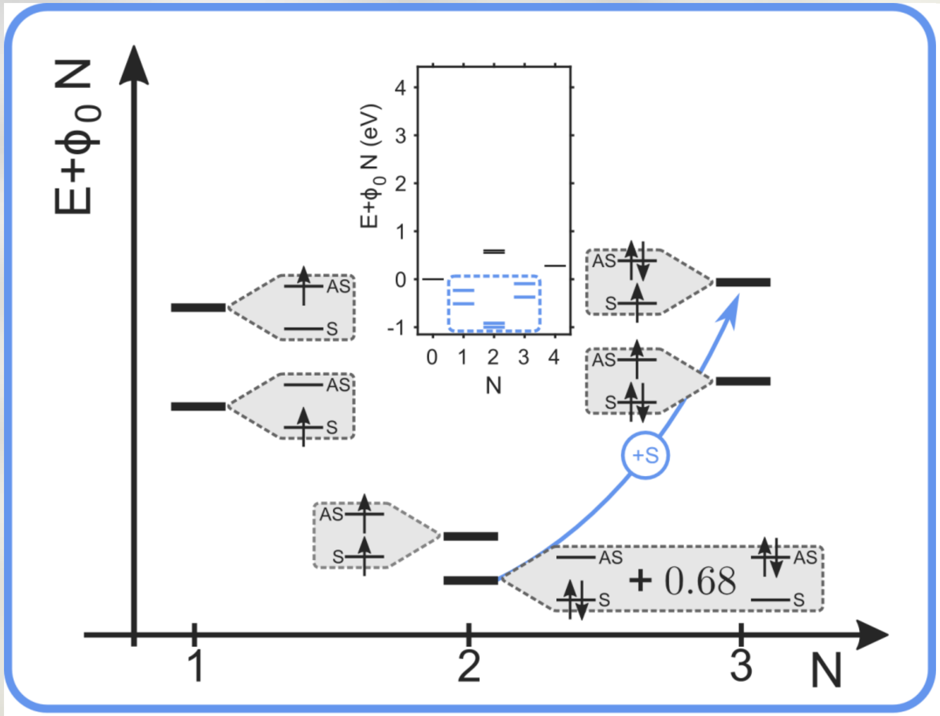


DCV5T/NaCl/Cu(311)

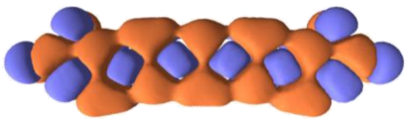


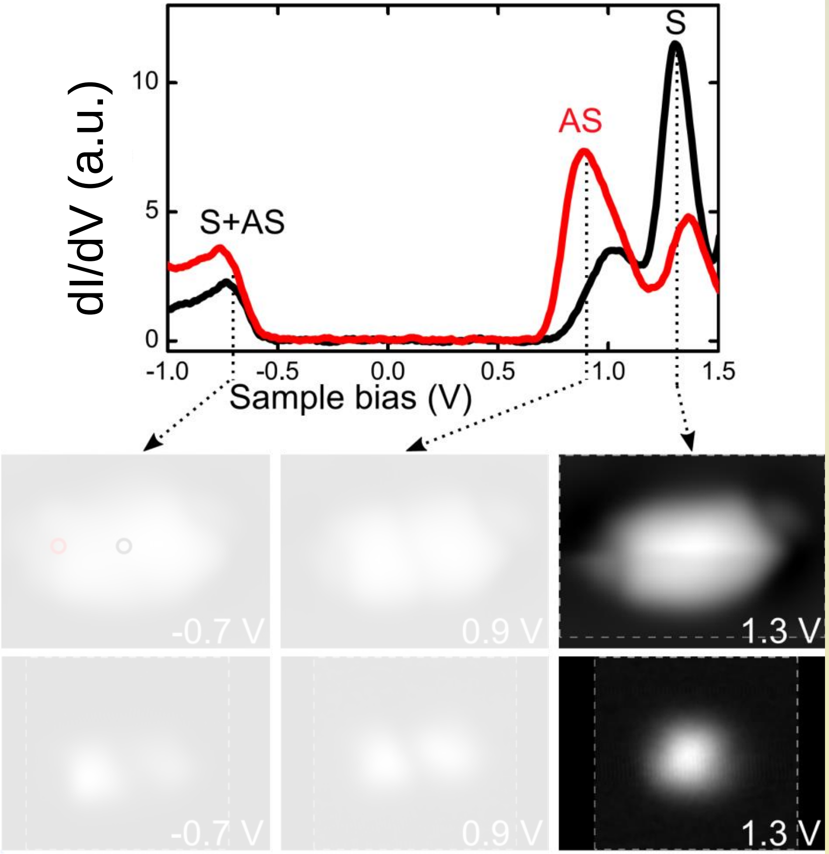


# Mechanism of orbital reversal



DCV5T/NaCl/Cu(311)





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

# Dynamics

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

$$\dot{\rho}_{\mathrm{red}} = \underbrace{\mathcal{L}_{\mathrm{tun}}\left[\rho_{\mathrm{red}}\right]}_{\substack{\textbf{Tunnelling}\\ \text{Dynamics}}} + \underbrace{\mathcal{L}_{\mathrm{rel}}[\rho_{\mathrm{red}}]}_{\substack{\textbf{Phenomenological}\\ \text{relaxation}}} := \mathcal{L}[\rho_{\mathrm{red}}]$$

The tunnelling dynamics is written in terms of tunnelling rates between many-body states. The relaxation dynamics is phenomenological:

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

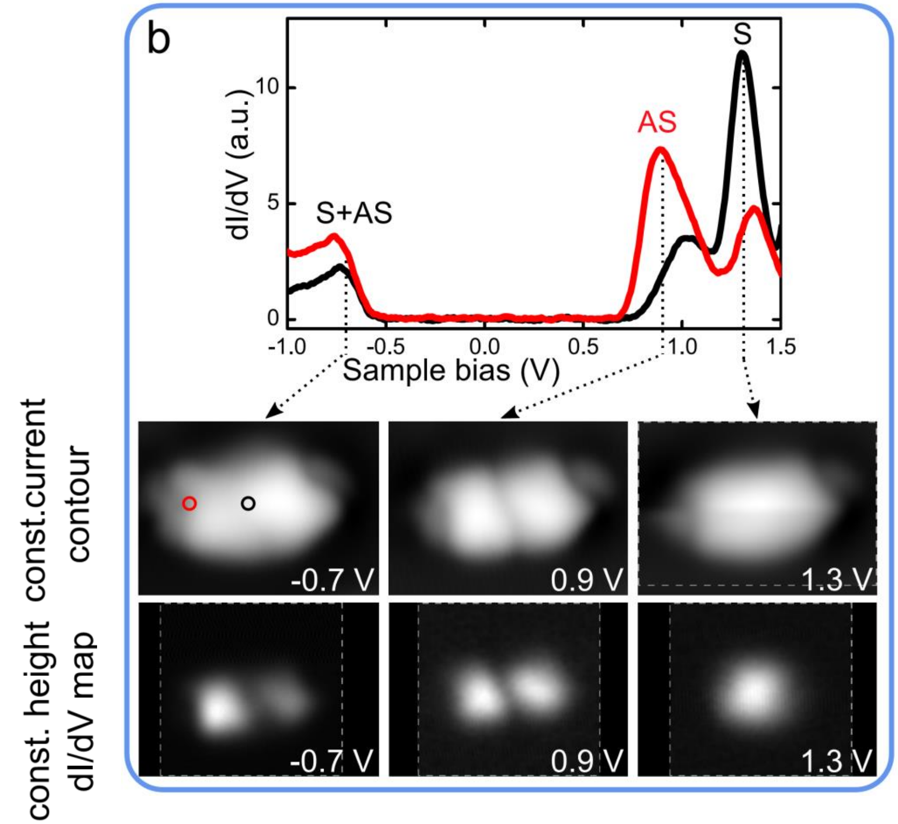
$\mathcal{L}[\rho_{\mathrm{red}}^{\infty}] \equiv 0$ defines the stationary reduced density matrix.

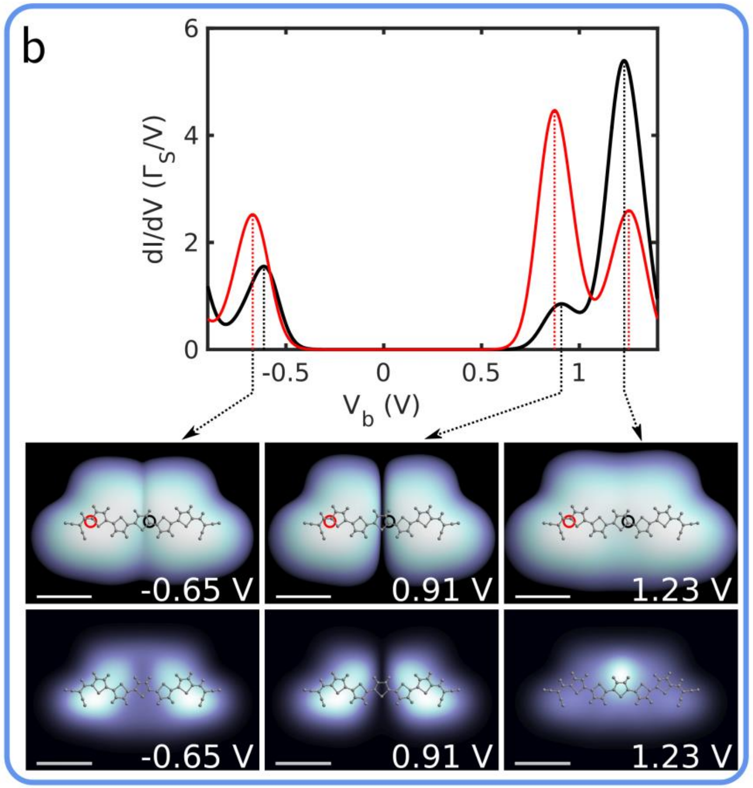
The stationary **current** depends on the **bias** and the **tip position**.

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

# Theory vs. Experiment

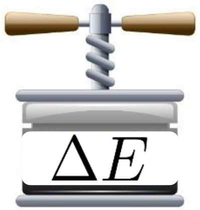
DCV5T/NaCl/Cu(311)



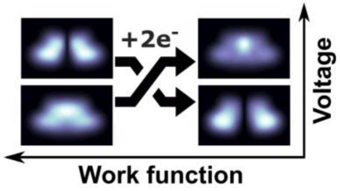


# Conclusions

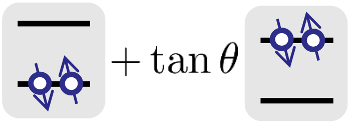
By **chemical engineering** of the single-particle level spacing between two frontier orbitals we **control** the degree of **electronic-correlation** in single molecule junctions



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

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

# Aknowledgments

## *Theory*

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## *Experiment*

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Lichtenberg Programm

# Thank you for your attention