Apparent Reversal of Molecular Orbitals Reveals Entanglement

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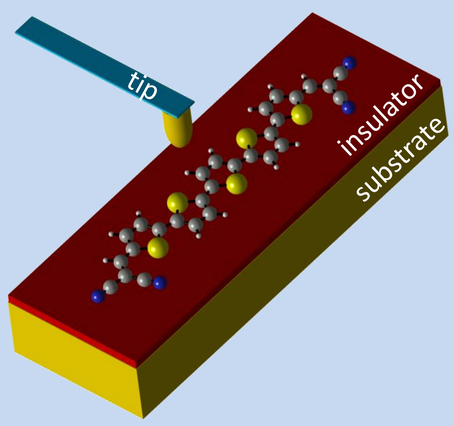
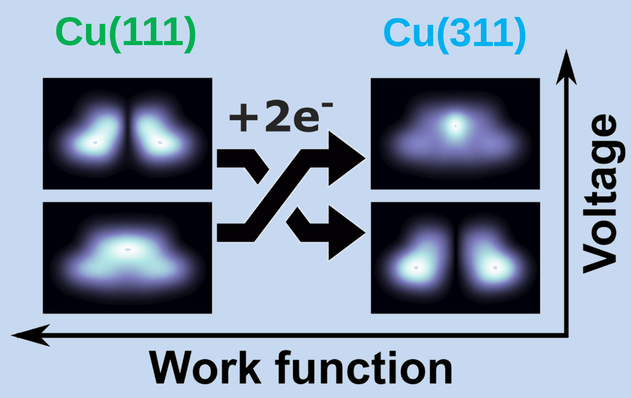
SFB 689



dicyanovinyl-substituted quinquethiophene (DCV5T)

ultrathin NaCl layer (100)

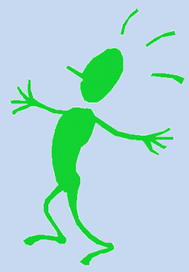
Cu(111) or Cu(311)



Open **contradiction with a single particle interpretation** (Sturm-Liouville theorem)

Explanation in **a many-body theory**

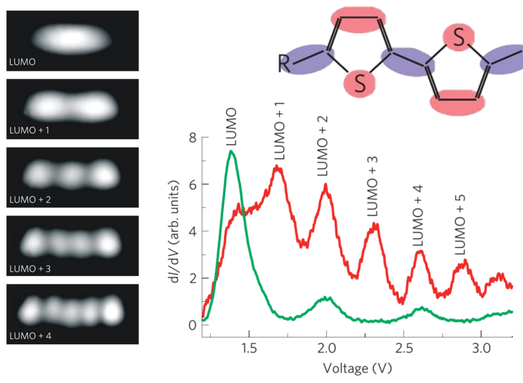
Strongly **entangled doubly charged ground state**

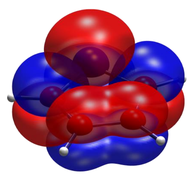


Phys. Rev. Lett. 119, 056801 (2017)

Electronic correlation

Particle-in-a-box-like states in oligothiophenes





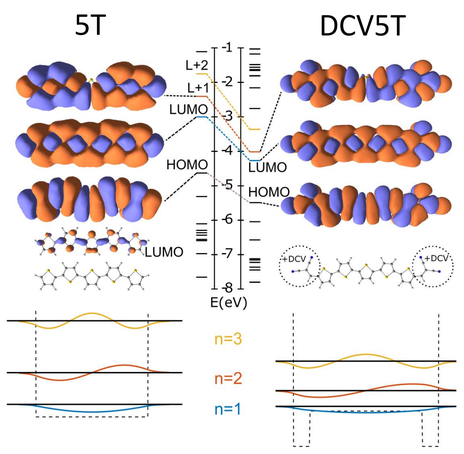
LUMO OF THIOPHENE

In agreement with the general statement of the Sturm-Liouville theory for differential equations:

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

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

Level spacing engineering: the role of the dicyanovinyl moieties



LUMO + 1 → antisymmetric state (AS)

LUMO → symmetric state (S)

$\Delta = \epsilon_{\rm AS} - \epsilon_{\rm S}$

The frontier orbitals are labeled according to their reflection symmetry

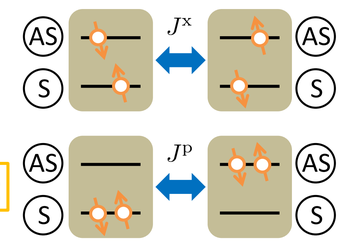
Due to their larger electron affinity, the dicyanovinyl moieties reduce the energy spacing between the symmatric and the antisymetric state.

Many- body Hamiltonian for the molecule

We restrict ourself to the Fock space spanned by: $|\Psi\rangle \approx |\overbrace{11\dots11}^{2N_f}\ \overbrace{n_{S\uparrow}n_{S\downarrow}n_{AS\uparrow}n_{AS\downarrow}}^{2N_d}\ \overbrace{00\dots00}^{2N_e}\rangle$

Frozen | Dynamical | Empty

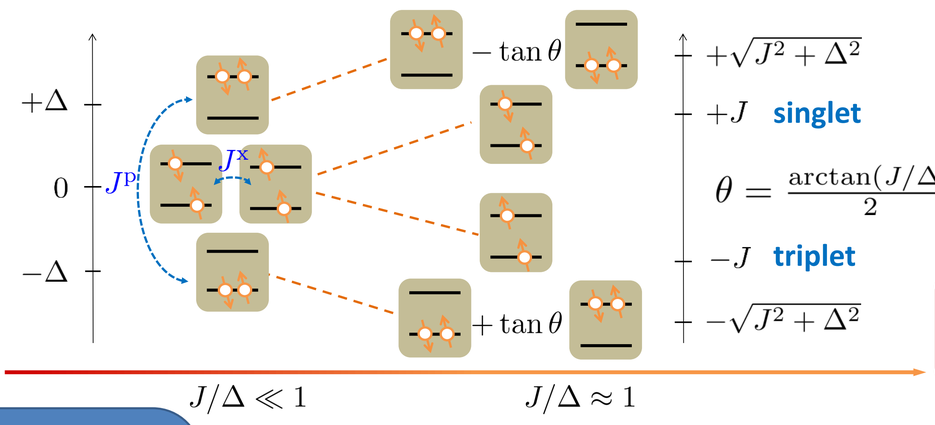
$$H_{\rm mol} = \epsilon_{\rm S}\hat{n}_{\rm S} + \epsilon_{\rm AS}\hat{n}_{\rm AS} + \frac{U}{2}\hat{N}(\hat{N}-1)$$
$$+ J\sum_{\sigma\sigma'} d^\dagger_{{\rm AS}\sigma} d^\dagger_{{\rm S}\sigma'} d_{{\rm AS}\sigma'} d_{{\rm S}\sigma} \quad \leftarrow \text{exchange}$$
$$+ J\left(d^\dagger_{{\rm AS}\uparrow} d^\dagger_{{\rm AS}\downarrow} d_{{\rm S}\downarrow} d_{{\rm S}\uparrow} + d^\dagger_{{\rm S}\uparrow} d^\dagger_{{\rm S}\downarrow} d_{{\rm AS}\downarrow} d_{{\rm AS}\uparrow}\right) \quad \leftarrow \text{pair hopping}$$



Other interaction terms are forbidden by symmetry

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

Two-particle spectrum and eigenstates



In DCV5T

$J/\Delta \approx 2.5$

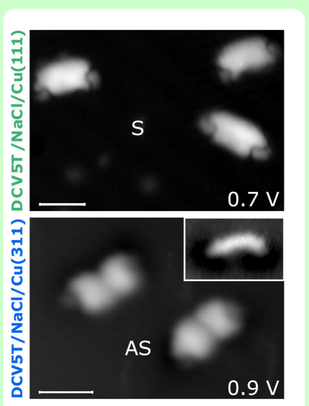
$\Delta_{\rm ST} \approx 58$ meV

$\tan\theta \approx 0.68$

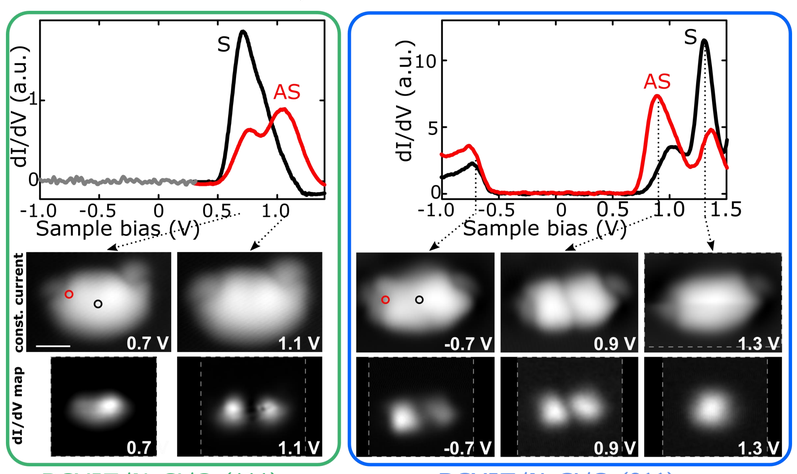
Strongly entangled ground state

Orbital reversal

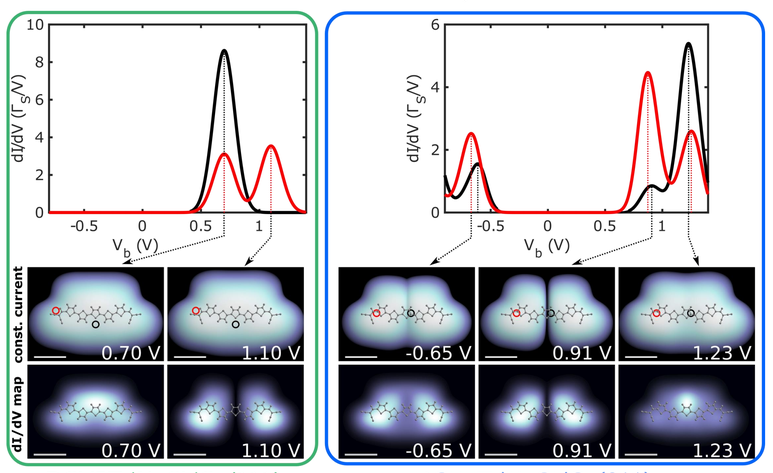
Topography of the lowest resonance



experiment



theory



Molecule-substrate interaction

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

grand canonical Hamiltonian | image charge, polaron shift | grand canonical potential

K. Kaasbjerg and K. Flensberg, PRB **84**, 115457 (2011)
F. E. Olsson *et al.*, PRL **98**, 176803 (2007)

$\delta = 0.43$ eV

$$\phi_0 = \begin{cases} 3\,\text{eV} & \text{Cu(311)} \\ 4\,\text{eV} & \text{Cu(111)} \end{cases}$$

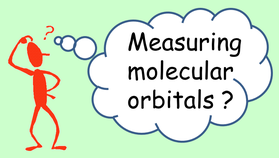
Many-body tunnelling rates

$$\hat{H}_{\rm tun} = \sum_{\eta{\bf k}i\sigma} t^\eta_{{\bf k}i}\,\hat{c}^\dagger_{\eta{\bf k}\sigma}\hat{d}_{i\sigma} + \text{h.c.}$$

Tunnelling Hamiltonian

$$\Gamma^\eta_{ij}(E) = \tfrac{2\pi}{\hbar}\textstyle\sum_{\bf k} t^\eta_{i{\bf k}}\left(t^\eta_{j{\bf k}}\right)^*\delta(\epsilon_{\eta{\bf k}} - E)$$

Single particle rate matrices

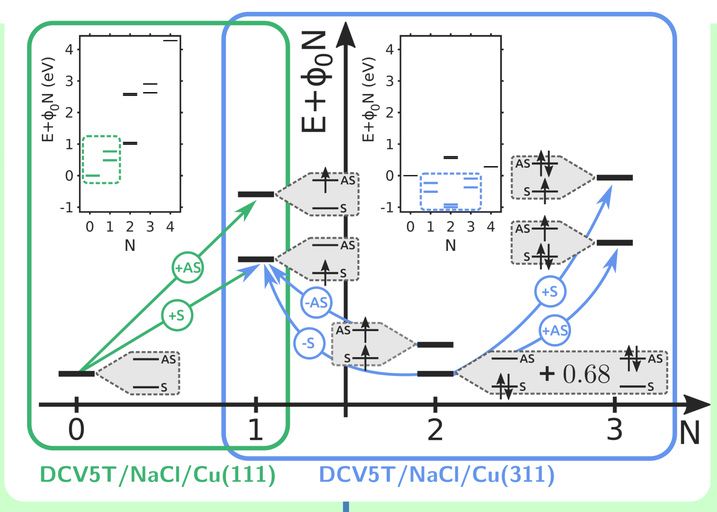


The transition rates connecting many-body energy eigenstates:

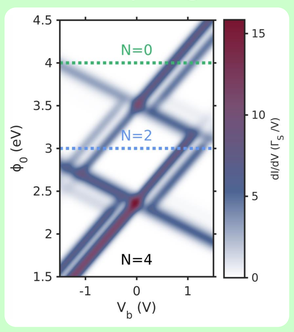
$$R^{N,n\to N+1,m}_{\sigma\eta} = \sum_{ij}\Gamma^\eta_{ji}(E^G_{N+1,m} - E^G_{N,n})$$
$$\langle N+1,m|\hat{d}^\dagger_{i\sigma}|N,n\rangle\langle N,n|\hat{d}_{j\sigma}|N+1,m\rangle f^+(E^G_{N+1,m} - E^G_{N,n} - \alpha_\eta eV_{\rm bias}, T)$$
$$R^{N,n\to N-1,m}_{\sigma\eta} = \sum_{ij}\Gamma^\eta_{ij}(E^G_{N-1,m} - E^G_{N,n})$$
$$\langle N-1,m|\hat{d}_{i\sigma}|N,n\rangle\langle N,n|\hat{d}^\dagger_{j\sigma}|N-1,m\rangle f^-(E^G_{N,n} - E^G_{N-1,m} - \alpha_\eta eV_{\rm bias}, T)$$

For **uncorrelated systems** this theory reduces to the Tersoff Hamann theory of STM.

S. Sobczyk, A. Donarini, and M. Grifoni Phys. Rev. B **85**, 205408 (2012)



Stability diagram



Non-equilibrium dynamics

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

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

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

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

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

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

$$I_\eta({\bf r}_{\rm T}, V_b) = {\rm Tr}_{\rm mol}\left(\hat{N}\mathcal{L}_\eta[\rho^\infty_{\rm red}({\bf r}_{\rm T}, V_b)]\right)$$

The one-particle ground state is extremely unstable in DCV5T.

$$E^{\rm add}_1 = U - 2\delta + \Delta - \sqrt{\Delta^2 + J^2}$$
$$E^{\rm add}_2 = U - 2\delta - \Delta - J + 2\sqrt{\Delta^2 + J^2}$$