

Electronic Transport in Correlated Single-Molecule Junctions

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Experimental techniques

Scanning tunnelling microscope break junction (STM-BJ)

Mechanically controlled break junction (MC-BJ)

STM (on thin insulating layer)



Electromigrated break junction (EM-BJ)

Correl19, Jülich 18.09.2019

P. Gehring et al., *Nature Reviews Physics* **1**, 381 (2019) I.Swart et al. *Chemical Communication* **47**, 9011 (2011)

Different approaches

Single controlled device





E.A.Osorio et al. Adv. Mater. **19**, 281 (2007)

Xu, B., and N. J. Tao, Science 301, 1221 (2003)



The role of the contacts





- Gating of 2 nm sized molecule
- Weak coupling realization with specific anchor groups

A. Danilov, S. Kubatkin, et al. Nanoletters 8, 1 (2008)

Correlation effects

Kondo effect



W. Liang et al., Nature 417, 725 (2002)

Orbital reversal





T. Miyamachi et al. Nature comm. 3, 993 (2012)



Spectroscopy & Topography





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

Single particle vs. Many-body



The two approaches only agree for uncorrelated systems close to equilibrium

Markow Non-equilibrium and correlation







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



Alteration of the molecular orbitals due electronic correlation

$$\phi(\mathbf{r}) = \sum_{\alpha,\beta} (C_{\alpha}^{N})^{*} C_{\beta}^{N+1} \sum_{i} \psi_{i}(\mathbf{r}) \langle \Phi_{\alpha}^{N} | \hat{d}_{i} | \Phi_{\beta}^{N+1} \rangle$$

STM experiments probe **quasiparticle wavefunctions** which differ from the single particle molecular orbitals



Visualization of many-body transitions in STM experiments

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

Liouville approach to transport



 $\hat{H} = \hat{H}_{\rm mol} + \hat{H}_{\rm leads} + \hat{H}_{\rm tun}$

The starting point is the Liouville-von Neumann equation

$$\dot{\hat{
ho}} = -rac{i}{\hbar} \left[\hat{H}, \hat{
ho}
ight] \equiv \mathcal{L}\hat{
ho}$$

For the density operator $\hat{\rho} = \sum_n P_n |\Psi_n\rangle \langle \Psi_n|$, with the total Hamiltonian \hat{H} for the nanojunction.

Reduced density operator

The full system dynamics is intractable. We aim to an equation of motion for the **reduced** density operator

$$\hat{\rho}_{\rm red} \equiv {\rm Tr}_{\rm leads} \hat{\rho}$$

which describes the evolution of the molecule **in presence** of the leads. For any molecule observable

$$\langle \hat{O} \rangle \equiv \text{Tr}\{\hat{O}\hat{\rho}\} = \text{Tr}_{\text{mol}}\{\hat{O}\text{Tr}_{\text{leads}}\{\hat{\rho}\}\} = \text{Tr}_{\text{mol}}\{\hat{O}\hat{\rho}_{\text{red}}\}$$

For simplicity we assume an initial condition with decoupled molecule and leads in thermal equilibrium

$$\hat{\rho}(0) = \hat{\rho}_{\mathrm{mol}}(0) \otimes \hat{\rho}_{\mathrm{leads}}$$

$$\hat{\rho}_{\text{leads}} = \frac{1}{Z_{G,L}} e^{-\beta(\hat{H}_L - \mu_L \hat{N}_L)} \otimes \frac{1}{Z_{G,R}} e^{-\beta(\hat{H}_R - \mu_R \hat{N}_R)}, \quad \mu_L - \mu_R = eV_{\text{bias}}$$

UR

Nakajima-Zwanzig equation

We follow Nakajima and separate the density operator into a relevant (factorized) and an irrelevant (entangled) contribution:

$$\hat{\rho} = \mathcal{P}\hat{\rho} + \mathcal{Q}\hat{\rho}$$

with

$$\mathcal{P}\hat{\rho}(t) = \hat{\rho}_{\mathrm{red}}(t) \otimes \hat{\rho}_{\mathrm{leads}} \qquad \mathcal{Q} = 1 - \mathcal{P}$$

The equation of motion for the separable component of the density operator reads

$$\mathcal{P}\dot{\hat{\rho}}(t) = \mathcal{L}_{\mathrm{mol}}\mathcal{P}\hat{\rho}(t) + \int_{0}^{t} \mathcal{K}(t-s)\mathcal{P}\hat{\rho}(s) \,\mathrm{d}s$$

with

$$\mathcal{K}(t-s) = \mathcal{P}\mathcal{L}_{\mathrm{tun}} e^{(\mathcal{L}_{\mathrm{mol}} + \mathcal{L}_{\mathrm{leads}} + \mathcal{Q}\mathcal{L}_{\mathrm{tun}}\mathcal{Q})(t-s)} \mathcal{L}_{\mathrm{tun}} \mathcal{P}$$

 $\mathcal{L}_{i} = -\frac{i}{\hbar}[\hat{H}_{i}, \bullet]$





We project the Liouville-von Neumann equation

$$\begin{cases} \mathcal{P}\dot{\hat{\rho}} = \mathcal{P}\mathcal{L}\mathcal{P}\hat{\rho} + \mathcal{P}\mathcal{L}\mathcal{Q}\hat{\rho} \\ \mathcal{Q}\dot{\hat{\rho}} = \mathcal{Q}\mathcal{L}\mathcal{P}\hat{\rho} + \mathcal{Q}\mathcal{L}\mathcal{Q}\hat{\rho} \end{cases}$$

We formally solve the second equation with the help of the propagator

$$\mathcal{G}_{\mathcal{Q}}(t,s,) = e^{\mathcal{QL}(t-s)}$$

$$\mathcal{G}_{\mathcal{Q}}(0,t) \,\mathcal{Q}\dot{\hat{\rho}} - \mathcal{G}_{\mathcal{Q}}(0,t) \,\mathcal{QLQ}\hat{\rho} = \frac{\mathrm{d}}{\mathrm{d}t} \left[\mathcal{G}_{\mathcal{Q}}(0,t) \mathcal{Q}\hat{\rho} \right] = \mathcal{G}_{\mathcal{Q}}(0,t) \mathcal{QLP}\hat{\rho}$$

Which, by integration, implies

$$\mathcal{G}_{\mathcal{Q}}(0,t) \,\mathcal{Q}\dot{\hat{\rho}} - \mathcal{Q}\hat{\rho}(0) = \int_{0}^{t} \mathcal{G}_{\mathcal{Q}}(0,s) \mathcal{QLP}\hat{\rho}(s) \,\mathrm{d}s$$

And, finally

$$Q\hat{\rho}(t) = \mathcal{G}_{\mathcal{Q}}(t,0)\mathcal{Q}\hat{\rho}(0) + \int_{0}^{t} \mathcal{G}_{\mathcal{Q}}(t,s)\mathcal{QLP}\hat{\rho}(s) \,\mathrm{d}s.$$



Proof...

From the definition of the projector \mathcal{P} and the fact that \hat{H}_{tun} does not conserve particles in the leads:

$$\mathcal{PL}_{tun}\mathcal{P} = 0, \quad [\mathcal{P}, \mathcal{L}_{mol}] = [\mathcal{P}, \mathcal{L}_{leads}] = \mathcal{PL}_{leads} = 0$$

We can write the closed integro-differential equation for $\mathcal{P}\hat{
ho}$

$$\mathcal{P}\dot{\hat{\rho}}(t) = \mathcal{L}_{\mathrm{mol}}\mathcal{P}\hat{\rho}(t) + \int_{0}^{t} \mathcal{P}\mathcal{L}\mathcal{G}_{\mathcal{Q}}(t,s)\mathcal{Q}\mathcal{L}\mathcal{P}\hat{\rho}(s)\,\mathrm{d}s$$

and identify a kernel of the form

$$\mathcal{K}(t-s) = \mathcal{PL}e^{\mathcal{QL}(t-s)}\mathcal{QLP}$$

We finally manipulate further the kernel to better emphasize the perturbation expansion in $\mathcal{L}_{\rm tun}$





We Taylor expand the exponential

$$\mathcal{PL}e^{\mathcal{QL}t}\mathcal{QLP} = \sum_{n=0}^{\infty} \frac{1}{n!} \mathcal{PLQ} \left(\mathcal{QLQ}\right)^n \mathcal{QLP} t^n$$

Using the relations between the projector and the Liouvillean one easily obtains

$$\mathcal{PLQ} = \mathcal{PL}_{tun}, \quad \mathcal{QLP} = \mathcal{L}_{tun}\mathcal{P}, \quad \mathcal{QLQ} = \mathcal{Q}(\mathcal{L}_{mol} + \mathcal{L}_{leads} + \mathcal{QL}_{tun}\mathcal{Q})$$

and thus

$$\mathcal{K}(t) = \sum_{n=0}^{\infty} \frac{1}{n!} \mathcal{P}\mathcal{L}_{tun} \mathcal{Q}(\mathcal{L}_{mol} + \mathcal{L}_{leads} + \mathcal{Q}\mathcal{L}_{tun}\mathcal{Q})^n t^n \mathcal{L}_{tun}\mathcal{P}$$

$$\mathcal{K}(t-s) = \mathcal{P}\mathcal{L}_{tun}e^{(\mathcal{L}_{mol} + \mathcal{L}_{leads} + \mathcal{Q}\mathcal{L}_{tun}\mathcal{Q})(t-s)}\mathcal{L}_{tun}\mathcal{P}$$



Current kernel

The goal of a transport theory is to calculate the **current** through the junction.

We start from the definition of average current

$$I_{\eta}(t) = \frac{\mathrm{d}\langle \hat{N}_{\eta} \rangle}{\mathrm{d}t} = \mathrm{Tr}\{\hat{N}_{\eta}\dot{\hat{\rho}}\} = \mathrm{Tr}\{\hat{I}_{\eta}\mathcal{Q}\hat{\rho}\}$$

which can be expressed as (exercise!):

$$I_{\eta}(t) = \operatorname{Tr}\left[\int_{0}^{t} \mathcal{K}_{I_{\eta}}(t-s)\mathcal{P}\hat{\rho}(s) \,\mathrm{d}s\right]$$

with the current kernel given by

$$\mathcal{K}_{I_{\eta}}(t-s) = \mathcal{P}\hat{I}_{\eta}e^{(\mathcal{L}_{\mathrm{mol}} + \mathcal{L}_{\mathrm{leads}} + \mathcal{Q}\mathcal{L}_{\mathrm{tun}}\mathcal{Q})(t-s)}\mathcal{L}_{\mathrm{tun}}\mathcal{P}$$

$$\mathcal{K}(t-s) = \mathcal{P}\mathcal{L}_{\mathrm{tun}}e^{(\mathcal{L}_{\mathrm{mol}} + \mathcal{L}_{\mathrm{leads}} + \mathcal{Q}\mathcal{L}_{\mathrm{tun}}\mathcal{Q})(t-s)}\mathcal{L}_{\mathrm{tun}}\mathcal{P}$$



$$\hat{I}_{\eta} \equiv \frac{i}{\hbar} [\hat{H}_{,} \hat{N}_{\eta}]$$





Stationary limit

Due to the convolutive form of the propagator and the current kernels, it is useful to go to the **Laplace** space. Thanks to the final value theorem

$$\left[\mathcal{L}_{\rm mol} + \tilde{\mathcal{K}}(0)\right] \mathcal{P}\hat{\rho}(t \to \infty) = 0$$

where

$$\tilde{\mathcal{K}}(0) = \lim_{\lambda \to 0^+} \int_0^\infty e^{-\lambda t} \mathcal{K}(t) \mathrm{d}t$$

The stationary density matrix is the nullspace of a superoperator.

The stationary current reads

$$I_{\eta}(t \to \infty) = \operatorname{Tr}\left[\tilde{\mathcal{K}}_{I_{\eta}}(0)\mathcal{P}\hat{\rho}(t \to \infty)\right]$$



Perturbative expansion

The Laplace form of the propagating kernel:

$$\begin{split} \tilde{\mathcal{K}}(\lambda) &= \mathcal{P}\mathcal{L}_{\mathrm{tun}}[\lambda - \mathcal{L}_{\mathrm{mol}} - \mathcal{L}_{\mathrm{leads}} - \mathcal{Q}\mathcal{L}_{\mathrm{tun}}\mathcal{Q}]^{-1}\mathcal{L}_{\mathrm{tun}}\mathcal{P} \\ &= \mathcal{P}\mathcal{L}_{\mathrm{tun}}[1 - \tilde{\mathcal{G}}_{0}(\lambda)\mathcal{Q}\mathcal{L}_{\mathrm{tun}}\mathcal{Q}]^{-1}\tilde{\mathcal{G}}_{0}(\lambda)\mathcal{L}_{\mathrm{tun}}\mathcal{P} \end{split}$$

with the bare propagator

$$\tilde{\mathcal{G}}_0(\lambda) \equiv [\lambda - \mathcal{L}_{mol} - \mathcal{L}_{leads}]^{-1}$$

Thus, we obtain the perturbative expansion

$$\tilde{\mathcal{K}}(\lambda) = \mathcal{P}\mathcal{L}_{\mathrm{tun}} \sum_{n=0}^{\infty} [\tilde{\mathcal{G}}_0(\lambda)\mathcal{Q}\mathcal{L}_{\mathrm{tun}}\mathcal{Q}]^{2n} \tilde{\mathcal{G}}_0(\lambda)\mathcal{L}_{\mathrm{tun}}\mathcal{P}$$



Perturbative expansion

$$\tilde{\mathcal{K}}(\lambda) = \mathcal{P}\mathcal{L}_{\mathrm{tun}} \sum_{n=0}^{\infty} [\tilde{\mathcal{G}}_0(\lambda)\mathcal{Q}\mathcal{L}_{\mathrm{tun}}\mathcal{Q}]^{2n} \tilde{\mathcal{G}}_0(\lambda)\mathcal{L}_{\mathrm{tun}}\mathcal{P}$$

The perturbative expansion allows for a diagrammatic representation

$$\tilde{\mathcal{K}}^{(4)} = \mathcal{P}\mathcal{L}_{tun}\tilde{\mathcal{G}}_{0}\mathcal{L}_{tun}\tilde{\mathcal{G}}_{0}\mathcal{L}_{tun}\tilde{\mathcal{G}}_{0}\mathcal{L}_{tun}\mathcal{P} - \mathcal{P}\mathcal{L}_{tun}\tilde{\mathcal{G}}_{0}\mathcal{L}_{tun}\mathcal{P}\tilde{\mathcal{G}}_{0}\mathcal{P}\mathcal{L}_{tun}\tilde{\mathcal{G}}_{0}\mathcal{L}_{tun}\mathcal{P}$$



The propagating kernel is the self-energy of the full propagator of ${\cal P}\hat{
ho}$:

$$ilde{\mathcal{G}}_{\mathcal{P}} = ilde{\mathcal{G}}_0 + ilde{\mathcal{G}}_0 \, ilde{\mathcal{K}} \, ilde{\mathcal{G}}_{\mathcal{P}}$$

S. Koller, et al. *PRB* **82**, 235307 (2010) R. Saptsov and M. R. Wegewijs, Phys. Rev. B **86**, 235432 (2012)

To fix the ideas, let us consider the leads and tunnelling Hamiltonians

$$\hat{H}_{\text{leads}} = \sum_{\eta \mathbf{k}\sigma} \epsilon_{\eta \mathbf{k}\sigma} \hat{c}^{\dagger}_{\eta \mathbf{k}\sigma} \hat{c}_{\eta \mathbf{k}\sigma},$$
$$\hat{H}_{\text{tun}} = \sum_{\eta \mathbf{k}\sigma np} p t^{p}_{\eta \mathbf{k}\sigma n} \hat{d}^{p}_{n\sigma} \hat{c}^{\bar{p}}_{\eta \mathbf{k}\sigma} \qquad p = \pm 1 \qquad \hat{c}^{+} \equiv \hat{c}^{\dagger}, \quad \hat{c}^{-} \equiv \hat{c}$$
$$\hat{d}^{+} \equiv \hat{d}^{\dagger}, \quad \hat{d}^{-} \equiv \hat{d}$$

The second order kernel reads, explicitly

$$\tilde{\mathcal{K}}^{(2)}(0) = -\frac{i}{2\pi} \sum_{\alpha_1 \alpha_2} \sum_{p\eta\sigma} \sum_{nm} \int \alpha_1 \alpha_2 \Gamma^p_{nm}(\epsilon, \eta\sigma) \mathcal{D}^{\bar{p}}_{n\sigma\alpha_2} \frac{f^{(p\alpha_1)}_{\eta}(\epsilon)}{p\epsilon - i\hbar \mathcal{L}_{\text{mol}} + i0^+} \mathcal{D}^p_{m\sigma\alpha_1} \mathrm{d}\epsilon.$$

where we introduced the super-operators $\mathcal{D}^p_{n\sigma+}\hat{\rho} \equiv \hat{d}^p_{n\sigma}\hat{\rho}, \quad \mathcal{D}^p_{n\sigma-}\hat{\rho} \equiv \hat{\rho}\,\hat{d}^p_{n\sigma}$

and the tunnelling rate matrix

$$\Gamma^{p}_{nm}(\epsilon,\eta\sigma) = \frac{2\pi}{\hbar} \sum_{\mathbf{k}} t^{\bar{p}}_{\eta\mathbf{k}\sigma n} t^{p}_{\eta\mathbf{k}\sigma m} \delta(\epsilon - \epsilon_{\eta\mathbf{k}\sigma})$$



The STM single molecule junction is described by the Hamiltonian

$$\hat{H} = \hat{H}_{\rm mol} + \hat{H}_{\rm mol-env} + \hat{H}_{\rm S} + \hat{H}_{\rm T} + \hat{H}_{\rm tun}$$



The molecule: interacting Hamiltonian for a small set of frontier orbitals

$$\hat{H}_{\rm mol} = \sum_{i} \epsilon_i \, \hat{n}_i + \frac{1}{2} \sum_{ijkl} \sum_{\sigma\sigma'} V_{ijkl} \, \hat{d}^{\dagger}_{i\sigma} \hat{d}^{\dagger}_{k\sigma'} \hat{d}_{l\sigma'} \hat{d}_{j\sigma}$$





Image charge effects

$$\hat{H}_{\rm mol-env} = -\delta_{\rm ic}(\hat{N} - N_0)^2$$

This term incorporates the two main effects which stabilize the excess 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)



Leads and tunnelling

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

$$\hat{H}_{\eta} = \sum_{\eta \mathbf{k}\sigma} \epsilon_{\eta \mathbf{k}} \hat{c}^{\dagger}_{\eta \mathbf{k}\sigma} \hat{c}_{\eta \mathbf{k}\sigma} \quad \eta = \mathrm{S}, \mathrm{T}$$

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

$$\hat{H}_{\rm tun} = \sum_{\eta \mathbf{k} \sigma n} t_{\eta \mathbf{k} \sigma n} \, \hat{c}^{\dagger}_{\eta \mathbf{k} \sigma} \hat{d}_{n\sigma} + \text{h.c.}$$

Tip tunnelling amplitudes follow the Chen's derivative rule.

Substrate tunnelling amplitudes are proportional to the **overlap** of the molecular orbital and the delocalized substrate wavefunction (plane wave).

$$\begin{split} \Gamma_{ij}^{T}(\mathbf{r}_{tip}) \propto \psi_{i}^{*}(\mathbf{r}_{tip}) \psi_{j}(\mathbf{r}_{tip}) & \Gamma_{ij}^{S} \propto \Gamma_{i} \delta_{ij} \\ \end{split} \\ \begin{array}{l} \textbf{Localized tunnelling} & \textbf{Delocalized tunnelling} \end{split}$$

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



Transport calculations

The system dynamics is obtained by solving a generalized master equation for the reduced density matrix $\hat{\rho}_{red} = Tr_{S\&T} (\hat{\rho})$



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

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



Tunnelling Liouvillean

$$\mathcal{L}_{tun}\hat{\rho}_{red}^{NE} = -\frac{1}{2}\sum_{\eta\sigma}\sum_{ij}\left\{\mathcal{P}_{NE}\left[\hat{d}_{i\sigma}^{\dagger}\Gamma_{ij}^{-}(E-\hat{H}_{mol},\eta\sigma)f_{\eta}^{-}(E-\hat{H}_{mol})\hat{d}_{j\sigma} + \\ +\hat{d}_{j\sigma}\Gamma_{ij}^{+}(\hat{H}_{mol}-E,\eta\sigma)f_{\eta}^{+}(\hat{H}_{mol}-E)\hat{d}_{i\sigma}^{\dagger}\right]\hat{\rho}_{red}^{NE} + H.c.\right\}$$

$$+\sum_{\eta\sigma}\sum_{ijE'}\mathcal{P}_{NE}\left[\hat{d}_{i\sigma}^{\dagger}\Gamma_{ij}^{-}(E-E',\eta\sigma)\hat{\rho}_{red}^{N-1E'}f_{\eta}^{+}(E-E')\hat{d}_{j\sigma} + \\ +\hat{d}_{j\sigma}\Gamma_{ij}^{+}(E'-E,\eta\sigma)\hat{\rho}_{red}^{N+1E'}f_{\eta}^{-}(E'-E)\hat{d}_{i\sigma}^{\dagger}\right]\mathcal{P}_{NE}$$

$$=\int_{\ell}|NE\ell\rangle\langle NE\ell|$$
S. Sobczyk, A. Donarini, and M. Grifoni, *PRB* 85, 205408 (2012) Correl19, Jülich 18.09.2019



Tunnelling rate matrix

$$\hat{H}_{\text{eff}} = \frac{1}{2\pi} \sum_{NE} \sum_{\eta\sigma} \sum_{ij} \mathcal{P}_{NE} \left[\hat{d}_{i\sigma}^{\dagger} \Gamma_{ij}^{-} (E - \hat{H}_{\text{mol}}, \eta\sigma) p_{\eta} (E - \hat{H}_{\text{mol}}) \hat{d}_{j\sigma} + \hat{d}_{j\sigma} \Gamma_{ij}^{+} (\hat{H}_{\text{mol}} - E, \eta\sigma) p_{\eta} (\hat{H}_{\text{mol}} - E) \hat{d}_{i\sigma}^{\dagger} \right] \mathcal{P}_{NE}$$
Effective Hamiltonian

$$I_{\eta} = \sum_{NE} \sum_{\sigma} \sum_{ij} \mathcal{P}_{NE} \left[\hat{d}_{j\sigma} \Gamma_{ij}^{+} (\hat{H}_{mol} - E, \eta\sigma) f_{\eta}^{+} (\hat{H}_{mol} - E) \hat{d}_{i\sigma}^{\dagger} - \hat{d}_{i\sigma}^{\dagger} \Gamma_{ij}^{-} (E - \hat{H}_{mol}, \eta\sigma) f_{\eta}^{-} (E - \hat{H}_{mol}) \hat{d}_{j\sigma} \right] \mathcal{P}_{NE}$$
Current operator

$$\Gamma^{p}_{ij}(\Delta E, \eta\sigma) = \frac{2\pi}{\hbar} \sum_{\mathbf{k}} t^{\bar{p}}_{\eta\mathbf{k}i} t^{p}_{\eta\mathbf{k}j} \delta(\epsilon^{\eta}_{\mathbf{k}} - \Delta E)$$

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

Many-body rate matrix

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

$$R_{NE_0 \to N+1E_1}^{\eta\tau} = \sum_{ij} \langle N+1E_1 \hat{d}_{i\tau}^{\dagger} | NE_0 \rangle \Gamma_{ij}^{+} (E_1 - E_0, \eta\sigma) \times \langle NE_0 | \hat{d}_{j\tau} N + 1E_1 \rangle f_{\eta}^{+} (E_1 - E_0)$$

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

$$R_{NE_0 \to N+1E_1}^{\eta} = \Gamma_{\text{orb}} f^+ (\epsilon_{\text{orb}} - \mu_{\eta})$$

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

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

Copper-Phthalocyanine



Non-equilibrium spin crossover



Spin crossover



Change in the occupation of the metal *d*-orbitals:

Interplay of:

- (Octahedral) ligand field splitting
- Exchange interaction



V. Meded, et al.PRB 83, 245415 (2011)

Non equilibrium spin-crossover



B. Siegert, A. Donarini, and M. Grifoni, PRB 93, 121406(R) (2016)



V_b = 1.38 V Correl19, Jülich 18.09.2019



Anomalous current maps







In the **anomalous** configuration the **current map** depends on the nature of the excited state

The **population inversion** relies on the strong asymmetry between substrate and tip tunneling rates and on the weak internal relaxation rate

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



Minimal basis set

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



C.Uhlmann et al., Nano Lett. 13, 777 (2013)

[1] S. Froyen and W.A. Harrison, *PRB* **20**, 2420 (1979)
[2] J. C. Slater and G. F. Koster, *Phys. Rev.* **94**, 1498 (1954)



Many-body Hamiltonian

The many-body Hamiltonian for the molecule reads

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

 Δ is a free parameter accounting for the crystal field of the core ions and the frozen electrons

 V_{ijkl} are ALL Coulomb integrals among the dynamical orbitals

The Coulomb integrals are calculated with the relative dielectric constant $\epsilon_{mol} = 2.2$. The atomic orbitals are of Slater type.

U_S	11.352 eV J_{HL}^{ex}	$=-\tilde{J}_{H+-}^{\mathrm{p}}$ 548 meV
U_H	$1.752 \text{ eV} \ J_{+-}^{\text{ex}}$	258 meV
$U_L = U_{+-}$	$1.808 \text{ eV} J_{+-}^{\text{p}}$	$168 { m meV}$
U_{SH}	$1.777 \text{ eV } J_{SL}^{ex}$ =	$= -\tilde{J}_{S+-}^{\mathrm{p}}$ 9 meV
U_{SL}	$1.993 \text{ eV} \ J_{SH}^{\text{ex}}$:	$= J_{SH}^{\mathrm{p}}$ 2 meV
U_{HL}	$1.758~{\rm eV}$	



Many-body spectrum



B. Siegert, A. Donarini, and M. Grifoni, PRB 93, 121406(R) (2016)

Low energy eigenstates



Topography of CuPc



$$I_{\chi}(\mathbf{r}_{\mathrm{T}}, V_b) = \mathrm{Tr}_{\mathrm{mol}}\left(\hat{N}\mathcal{L}_{\chi}[\sigma^{\infty}(\mathbf{r}_{\mathrm{T}}, V_b)]
ight)$$

B. Siegert, A. Donarini, and M. Grifoni, PRB 93, 121406(R) (2016)



Current and spin maps



$$S(\mathbf{r}_{\mathrm{T}}, V_b) = \sqrt{\langle \hat{S}^2 \rangle(\mathbf{r}_{\mathrm{T}}, V_b) + \frac{1}{4}} - \frac{1}{2} \quad \text{with} \quad \langle \hat{S}^2 \rangle(\mathbf{r}_{\mathrm{T}}, V_b) = \mathrm{Tr}_{\mathrm{mol}}\left(\hat{S}^2 \hat{\rho}_{\mathrm{red}}^{\infty}(\mathbf{r}_{\mathrm{T}}, V_b)\right)$$

B. Siegert, A. Donarini, and M. Grifoni, PRB 93, 121406(R) (2016)



Standard vs. anomalous



B. Siegert, A. Donarini, and M. Grifoni, *PRB* **93**, 121406(R) (2016)



Population inversion

Current and topographic maps of an anionic transition resembles the HOMO

The average **spin** of the molecule varies with the tip position and does **not** correspond to the one of the **molecular ground state**





The molecular state undergoes a **population inversion** which depends on the tip position





B. Siegert, A. Donarini, and M. Grifoni, *PRB* **93**, 121406(R) (2016)



Is CuPc so special?

Necessary and sufficient conditions for the appearance of non equilibrium spin-crossover:



B. Siegert, A. Donarini, and M. Grifoni, PRB 93, 121406(R) (2016)

CARA class of single molecule junctions



B. Siegert, A. Donarini, and M. Grifoni, *PRB* **93**, 121406(R) (2016)



We developed a **minimal model** for the Cu-Phthalocyanine in terms of **four**

 For an experimentally accessible substrate workfunction of 5 eV, we predict the appearance, close to the anionic resonance of non equilibrium spincrossover.

• **Dramatic changes in the current and topographical maps** with respect to standard LUMO resonances are found as fingerprints of the spin-crossover

• A class of single molecule junctions candidates for the observation of non equilibrium spin-crossover is defined in terms of relations between transport gap, optical gap and substrate workfunction.











Dicyanovinyl-quinquethiophene



Entanglement in the two particles groundstate



In oligothiophenes





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



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



Quinquethiophene (5T)

Correl19, Jülich 18.09.2019

(DCV5T)



Orbital reversal



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

AS S

The two-particle spectrum





Mechanism of orbital reversal



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



Mechanism of orbital reversal



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

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



Theory vs. Experiment



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

P. Yu, N. Kocić, J. Repp, B. Siegert, and A. Donarini, *PRL* **119**, 056801 (2017) Correl19, Jülich 18.09.2019

Criteria for such entanglement are clearly formulated in terms of the parameters in the minimal model and allow us to predict and

which we understand in terms of a minimal interacting model

control its occurrence for other molecules.

The orbital reversal is the signature of an **entangled ground state**

We observe the **apparent reversal** in the orbital sequence of a dicyanovinyl-quinquethiophene (DCV5T) in STM upon changing the crystallographic orientation of the insulator-coated copper substrate

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

Conclusions II













Aknowledgments

Theory

Experiment



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Jascha Repp





Thank you for your attention

