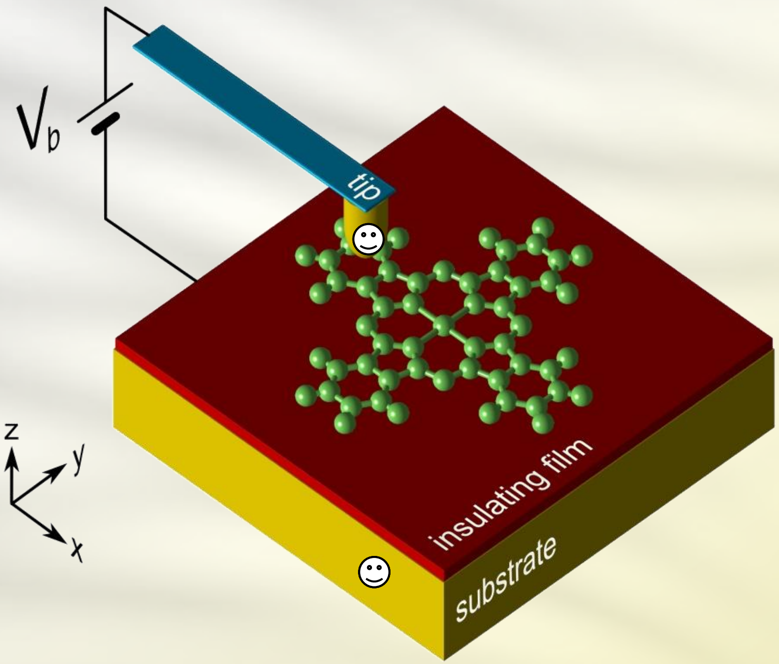
Theory of STM junctions for π-conjugated molecules on thin insulating films

Andrea Donarini

Sandra Sobczyk, Benjamin Siegert and Milena Grifoni

University of Regensburg, Germany

STM on thin insulating films

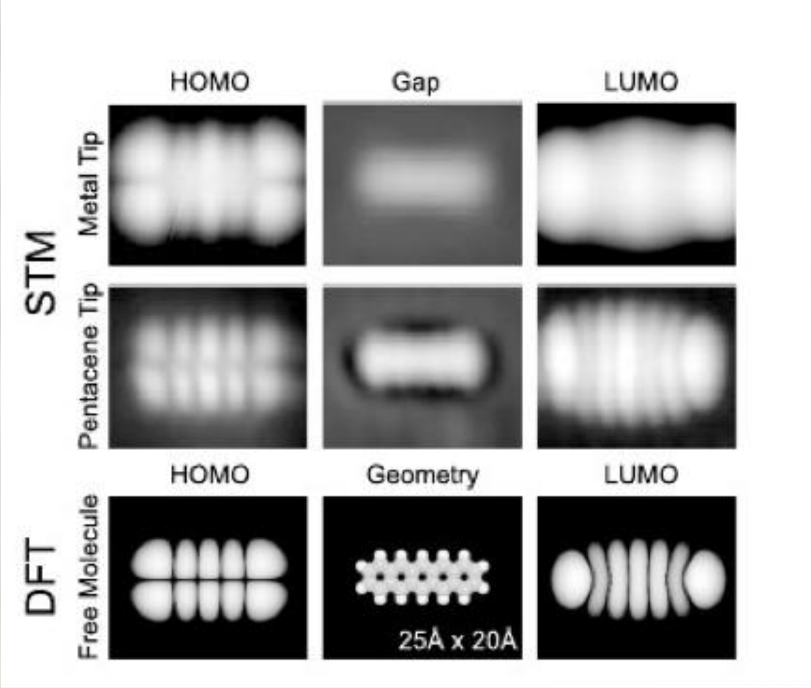


Weak tip-molecule **tunnelling coupling**
Low molecule-substrate **hybridization**

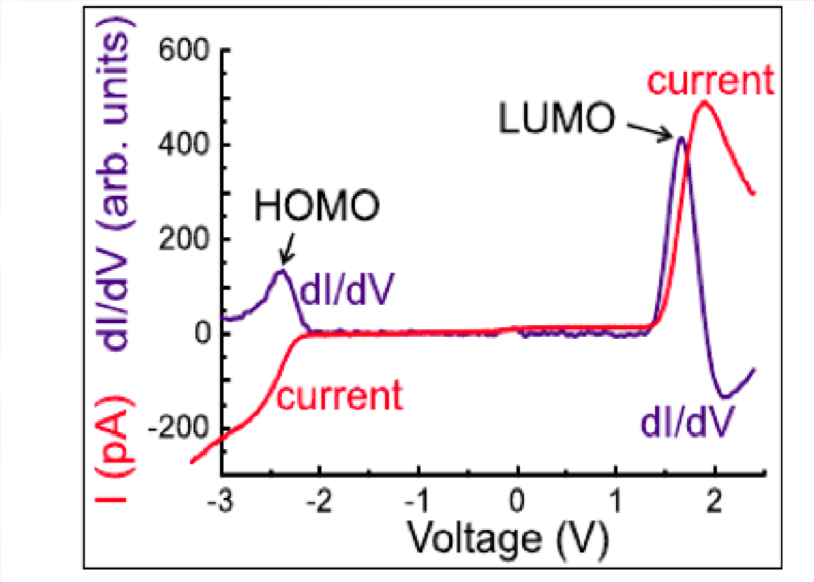
➡ **sequential tunnelling**

Visualization of molecular orbitals

Topography

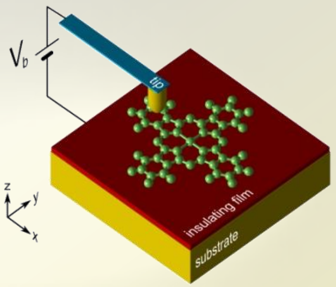


Spectroscopy



J. Repp and G. Meyer, Physical Review Letters **94**, 026803 (2005)

The total Hamiltonian



$$H = H_{\mathrm{m}} + H_{\mathrm{sub}} + H_{\mathrm{tip}} + H_{\mathrm{tun}}$$

$$H_{\mathrm{m}} = \underbrace{\sum_{\alpha\sigma} a_\alpha d^\dagger_{\alpha\sigma} d_{\alpha\sigma}}_{\text{on-site}} + \underbrace{\sum_{\alpha\neq\beta\sigma} b_{\alpha\beta} d^\dagger_{\alpha\sigma} d_{\beta\sigma}}_{\text{hopping}} + \underbrace{V_{\mathrm{e-e}}}_{\text{electron-electron interaction}} \left\{ \begin{array}{l} \text{Hubbard} \\ \text{Extended Hubbard} \\ \text{Constant interaction} \end{array} \right.$$

$$H_{\mathrm{sub}} = \sum_{\vec{k}\sigma} \varepsilon^S_{\vec{k}} c^\dagger_{S\vec{k}\sigma} c_{S\vec{k}\sigma} \qquad \varepsilon^S_{\vec{k}} = \varepsilon^S_0 + \frac{\hbar^2|\vec{k}|^2}{2m}$$

No confinement in the x-y directions

$$H_{\mathrm{tip}} = \sum_{k_z\sigma} \varepsilon^T_{k_z} c^\dagger_{Tk_z\sigma} c_{Tk_z\sigma} \qquad \varepsilon^T_{k_z} = \varepsilon^T_0 + \hbar\omega + \frac{\hbar^2 k_z^2}{2m}$$

Parabolic confinement in the x-y directions

$$H_{\mathrm{tun}} = \sum_{\chi k i\sigma} t^\chi_{ki} c^\dagger_{\chi k\sigma} d_{i\sigma} + h.c.$$

It is a **single particle** operator

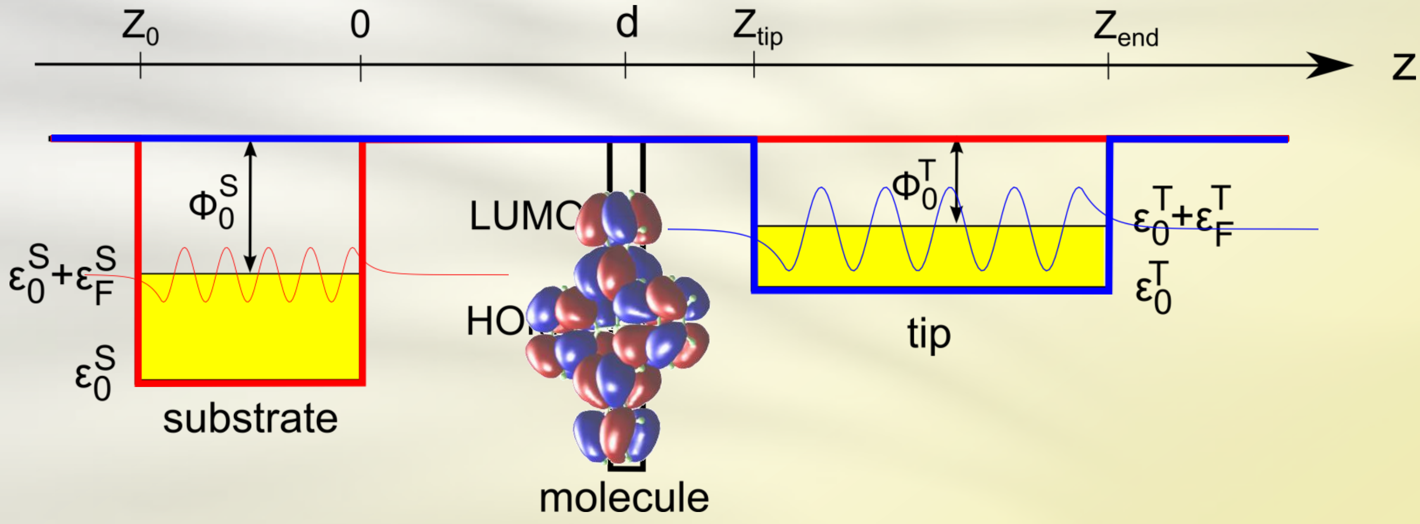
Molecular orbital

Bremen, 07.03.2013

Sobczyk, Donarini, Grifoni
Phys. Rev. B 85, 205408 (2012)

Tunnelling amplitudes

$$h = \frac{p^2}{2m} + v_{\mathrm{m}} + \boxed{v_{\mathrm{sub}}} + \boxed{v_{\mathrm{tip}}} \qquad t^{\chi}_{ki} := \langle \chi k \sigma | h | i \sigma \rangle$$



Sobczyk, Donarini, Grifoni
Phys. Rev. B 85, 205408 (2012)

Tunnelling amplitudes (ii)

$$t^{\chi}_{ki} = \langle \chi k \sigma | \frac{p^2}{2m} + v_{\mathrm{m}} | i\sigma \rangle + \cancel{\langle \chi k \sigma | v_{\mathrm{sub}} + v_{\mathrm{tip}} | i\sigma \rangle}$$

$$= \varepsilon_i \langle \chi k \sigma | i\sigma \rangle = \varepsilon_i \sum_{\alpha} \langle \chi k \sigma | \alpha\sigma \rangle \langle \alpha\sigma | i\sigma \rangle$$

Valence atomic orbitals larger in the leads than in the molecule

More perpendicular nodal planes in the molecule than in the leads

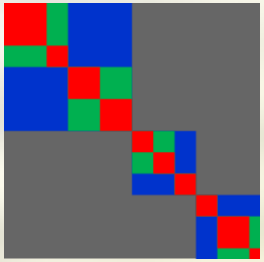
$$\psi_{\chi k}(\vec{r})\phi_i(\vec{r})$$

is **shifted towards the molecu**le

Generalized Master Equation

- We start with the **Liouville** equation: $\dot{\rho} = -\frac{\mathrm{i}}{\hbar}[H,\rho]$

- We define the reduced density matrix $\sigma = \mathrm{Tr}_{S+T}\{\rho\}$ which is block-diagonal in

$\sigma =$ 

particle number
spin
energy

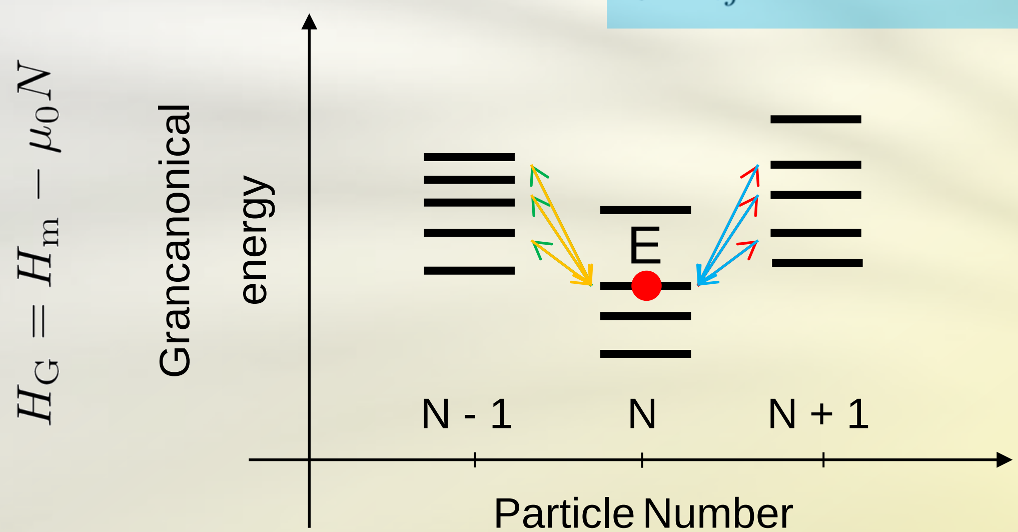
- We keep the coherences between orbitally degenerate states.

- The **Generalized Master Equation** is the equation of motion for σ :

$$\dot{\sigma} = \underbrace{-\frac{\mathrm{i}}{\hbar}[H_{\mathrm{m}},\sigma]}_{\substack{\textbf{Coherent}\\ \text{dynamics}}} \underbrace{-\frac{\mathrm{i}}{\hbar}[H_{\mathrm{eff}},\sigma]}_{\substack{\text{Effective}\\ \textbf{internal}\\ \text{dynamics}}} + \underbrace{\mathcal{L}_{\mathrm{tun}}\sigma}_{\substack{\textbf{Tunnelling}\\ \text{dynamics}}} \;:= \mathcal{L}\sigma$$

Tunnelling Liouvillean

$$
\begin{aligned}
\mathcal{L}_{\mathrm{tun}}\sigma^{NE} = -\frac{1}{2}\sum_{\chi\tau}\sum_{ij}\Big\{\mathcal{P}_{NE}\Big[&d^{\dagger}_{i\tau}\Gamma^{\chi}_{ij}(E-H_{\mathrm{m}})f^{-}_{\chi}(E-H_{\mathrm{m}})d_{j\tau} + \\
&+ d_{j\tau}\Gamma^{\chi}_{ij}(H_{\mathrm{m}}-E)f^{+}_{\chi}(H_{\mathrm{m}}-E)d^{\dagger}_{i\tau}\Big]\sigma^{NE} + h.c.\Big\} \\
+ \sum_{\chi\tau}\sum_{ijE'}\mathcal{P}_{NE}\Big[&d^{\dagger}_{i\tau}\Gamma^{\chi}_{ij}(E-E')\sigma^{N-1E'}f^{+}_{\chi}(E-E')d_{j\tau} + \\
&+ d_{j\tau}\Gamma^{\chi}_{ij}(E'-E)\sigma^{N+1E'}f^{-}_{\chi}(E'-E)d^{\dagger}_{i\tau}\Big]\mathcal{P}_{NE}
\end{aligned}
$$



$$
\mathcal{P}_{NE} = \sum_{\ell} |NE\ell\rangle\langle NE\ell|
$$

Projector on the subspace of N particles and energy E.

Single particle rate matrix

$$\boxed{\Gamma^{\chi}_{ij}(\Delta E) = \frac{2\pi}{\hbar} \sum_k (t^{\chi}_{ki})^* \, t^{\chi}_{kj} \, \delta(\varepsilon^{\chi}_k - \Delta E)}$$

$$H_{\text{eff}} = \frac{1}{2\pi} \sum_{NE} \sum_{\chi\sigma} \sum_{ij} \mathcal{P}_{NE} \Big[d^{\dagger}_{i\sigma} \Gamma^{\chi}_{ij}(E - H_{\text{m}}) p_{\chi}(E - H_{\text{m}}) d_{j\sigma} + d_{j\sigma} \Gamma^{\chi}_{ij}(H_{\text{m}} - E) p_{\chi}(H_{\text{m}} - E) d^{\dagger}_{i\sigma} \Big] \mathcal{P}_{NE}$$

Effective Hamiltonian

$$I_{\chi} = \sum_{NE\sigma ij} \mathcal{P}_{NE} \Big[d_{j\sigma} \Gamma^{\chi}_{ij}(H_{\text{m}} - E) f^{+}_{\chi}(H_{\text{m}} - E) d^{\dagger}_{i\sigma} - d^{\dagger}_{i\sigma} \Gamma^{\chi}_{ij}(E - H_{\text{m}}) f^{-}_{\chi}(E - H_{\text{m}}) d_{j\sigma} \Big] \mathcal{P}_{NE}$$

Current operator

Many-body rate matrix

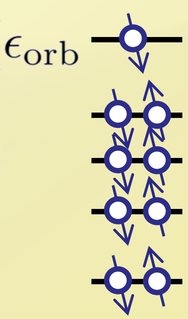
The **current** is proportional to the **transition rate** between **many-body states**

$$R^{\chi\tau}_{N\,E_0 \to N+1\,E_1} = \boxed{\sum_{ij}} \boxed{\langle N+1 E_1|} d^\dagger_{i\tau} | N E_0 \rangle \Gamma^{\chi}_{ij}(E_1 - E_0) \times \langle N E_0 | d_{j\tau} \boxed{|N+1 E_1\rangle} f^{+}(E_1 - E_0 - \mu_\chi)$$

where

$$\Gamma^{\chi}_{ij}(E_1 - E_0) = \frac{2\pi}{\hbar} \sum_k (t^{\chi}_{ki})^* t^{\chi}_{kj} \delta(\epsilon^{\chi}_k - E_1 + E_0)$$

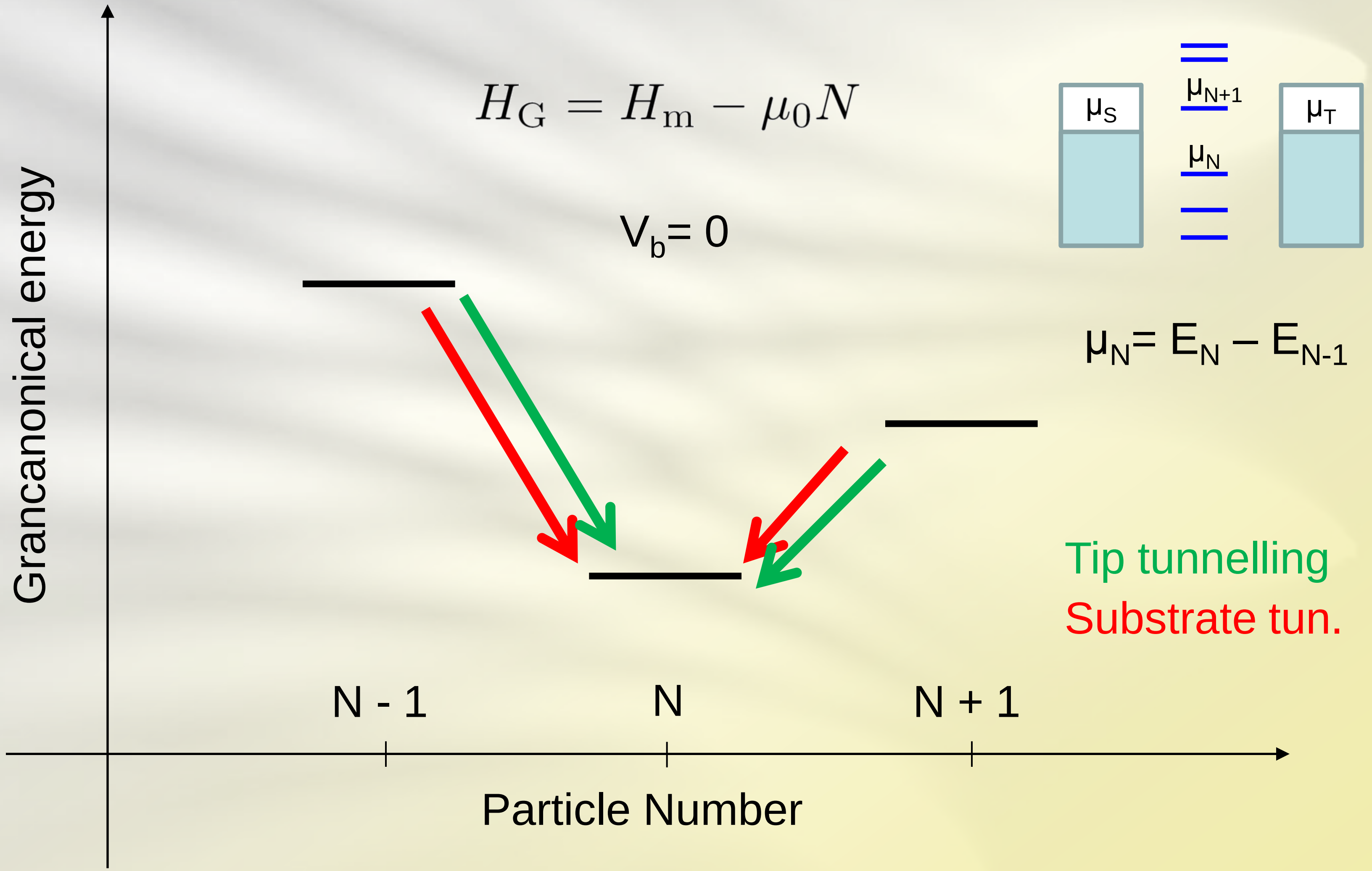
For **uncorrelated** and **non-degenerate systems** the many-body rate reduces to



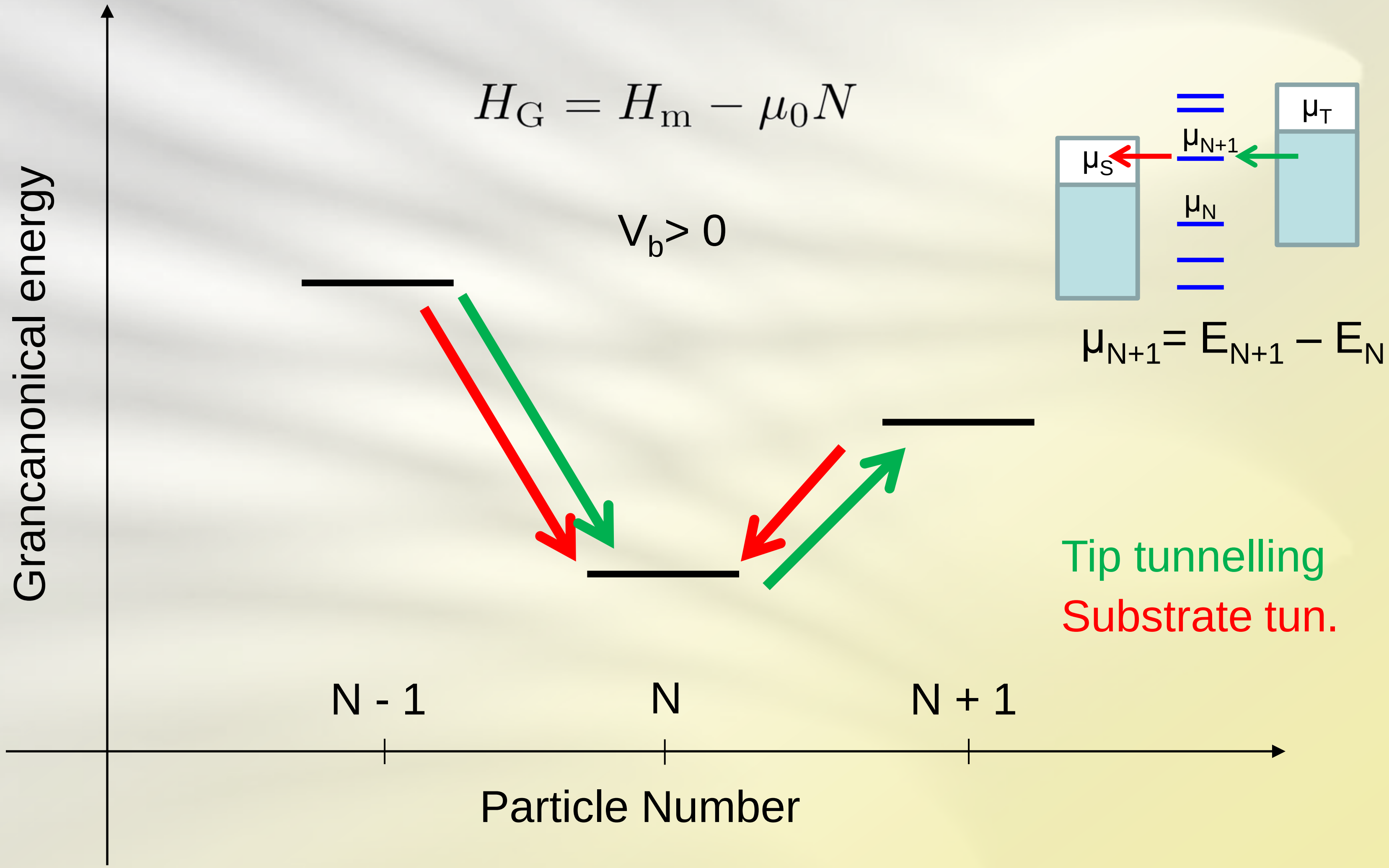
$$R^{\chi\tau}_{N\,E_0 \to N+1\,E_1} = \Gamma^{\chi}_{\mathrm{orb}}(\epsilon_{\mathrm{orb}}) f^{+}(\epsilon_{\mathrm{orb}} - \mu_\chi)$$

The **constant current map** is the **isosurface** of a **specific molecular orbital**.

Dynamics in energy space

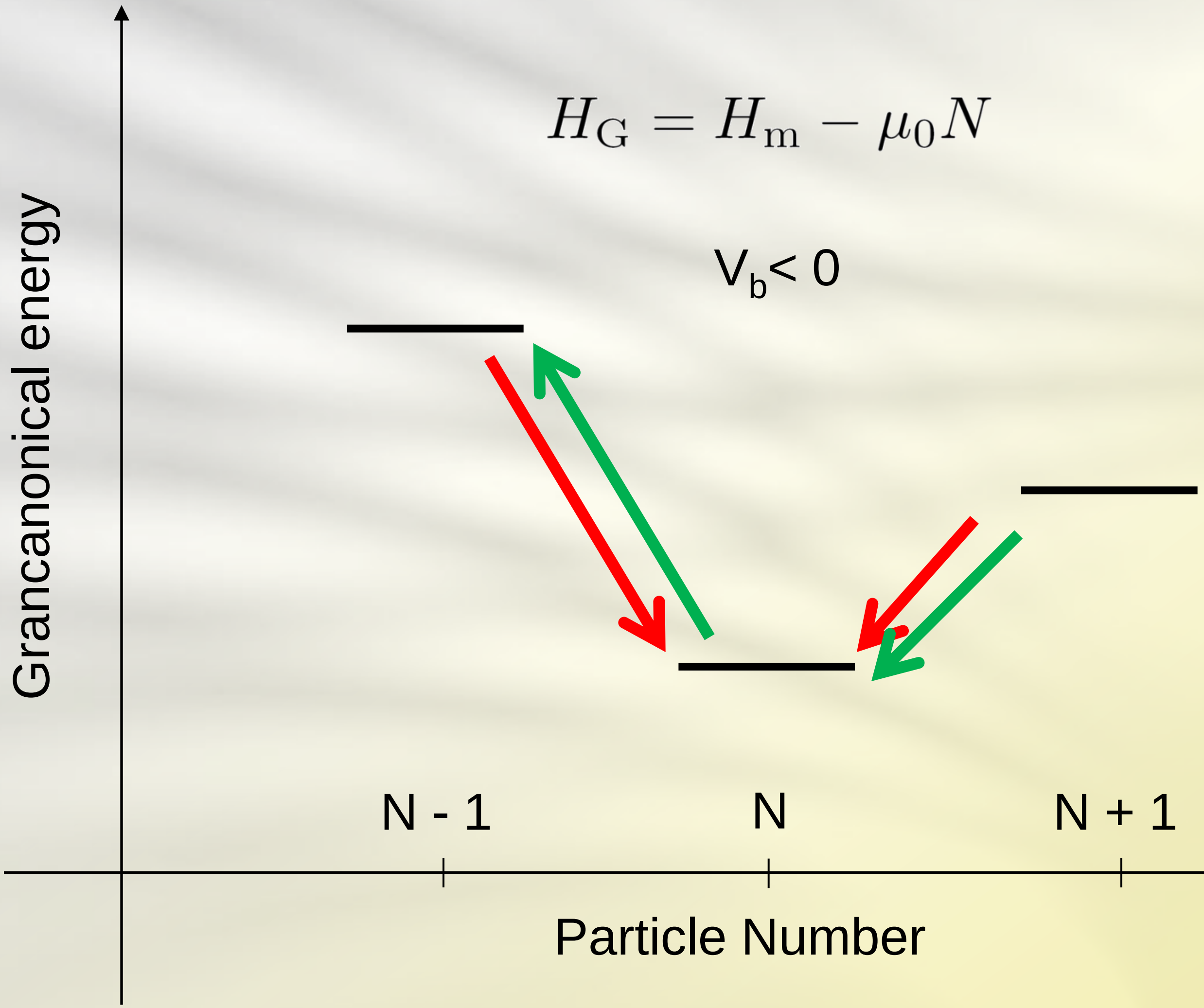


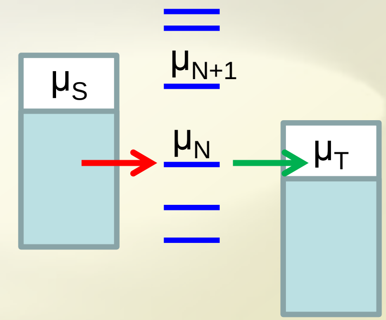
Dynamics in energy space



Dynamics in energy space

$$H_{\mathrm{G}} = H_{\mathrm{m}} - \mu_0 N$$





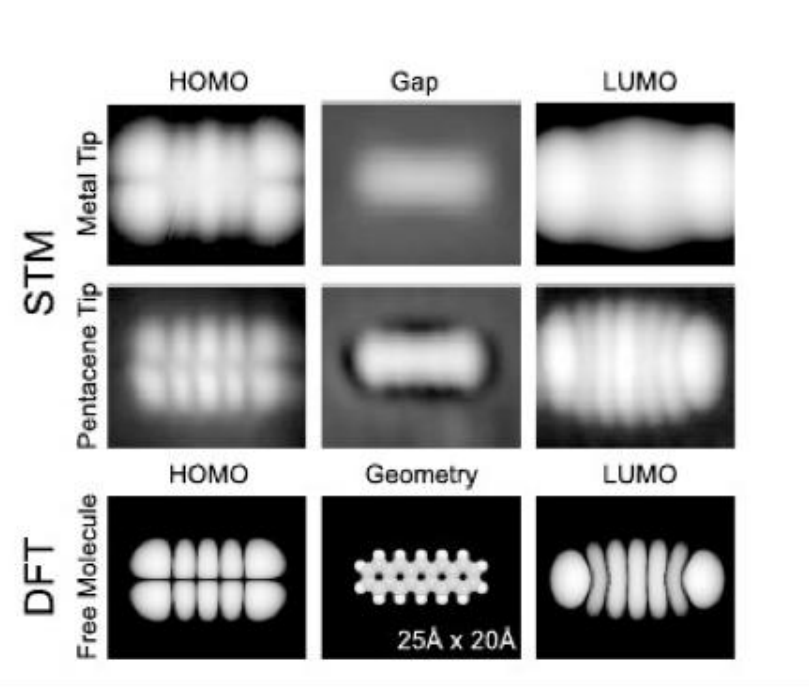
$\mu_N = E_N - E_{N-1}$

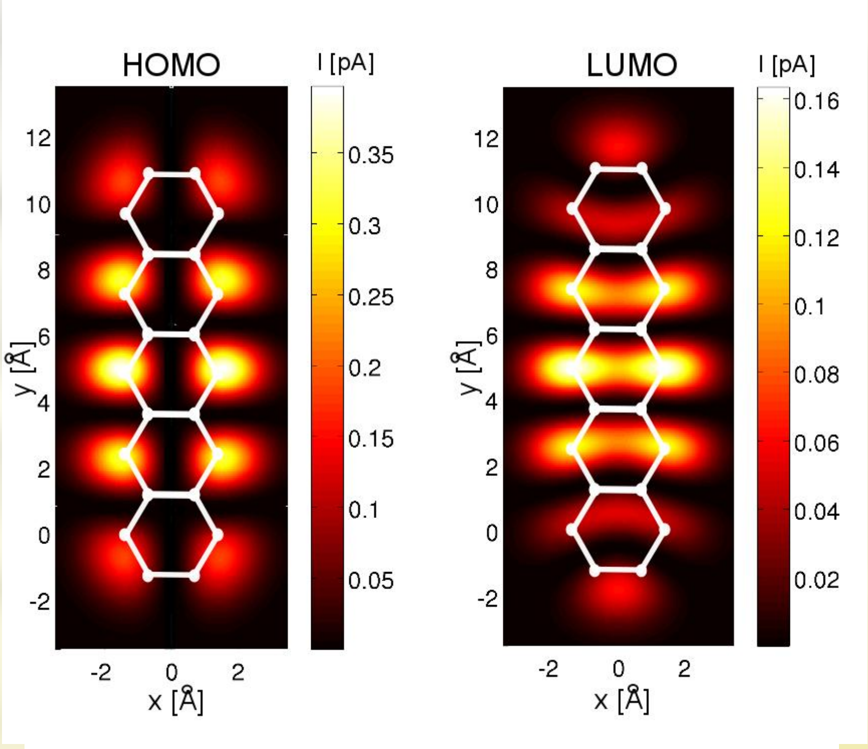
Tip tunnelling

Substrate tun.

Visualization of molecular orbitals

Topography



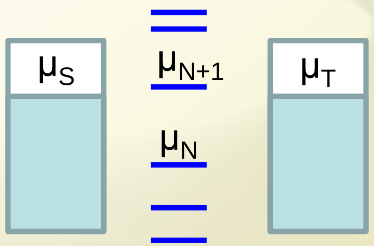


J. Repp and G. Meyer, Physical Review Letters **94**, 026803 (2005)

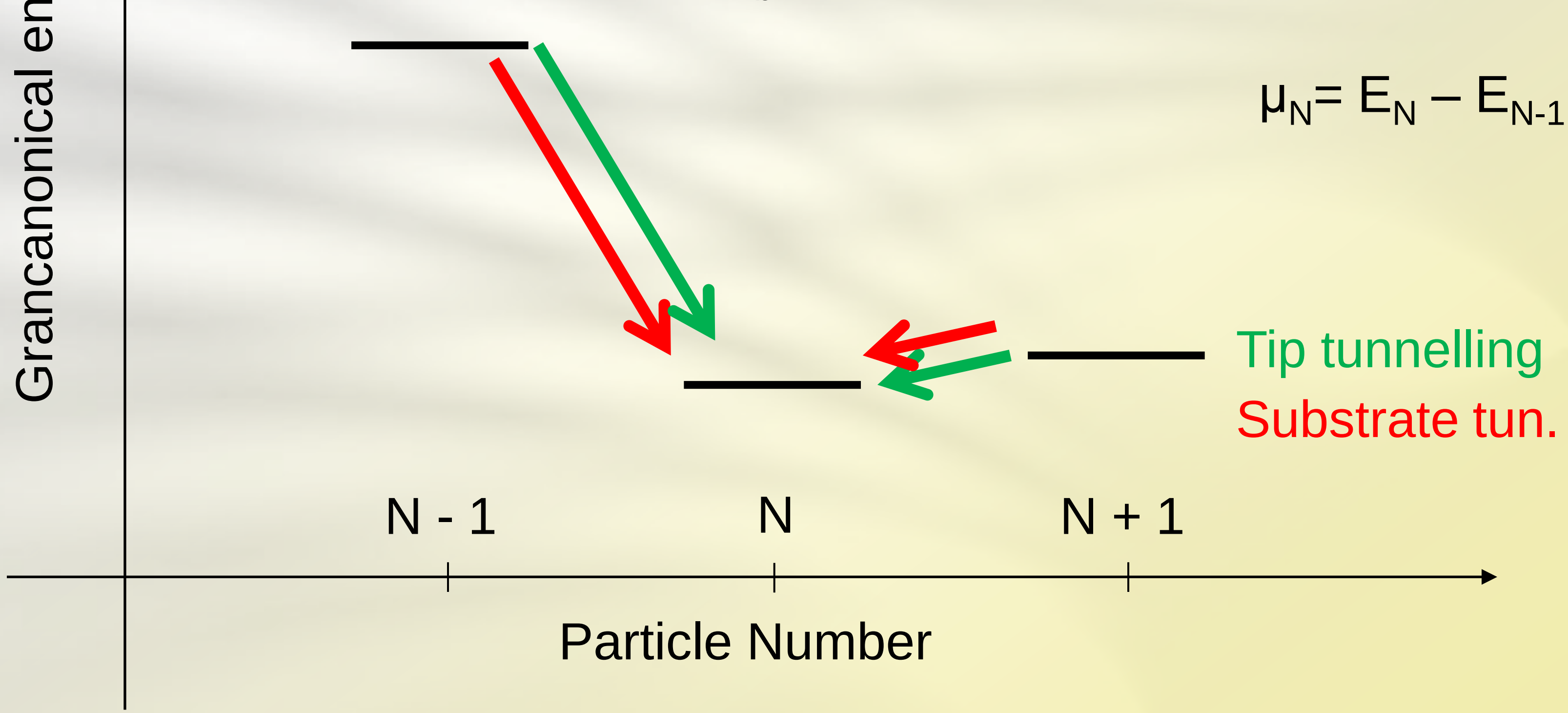
Dynamics in energy space

$$H_G = H_m - \mu_0 N$$

$V_b = 0$

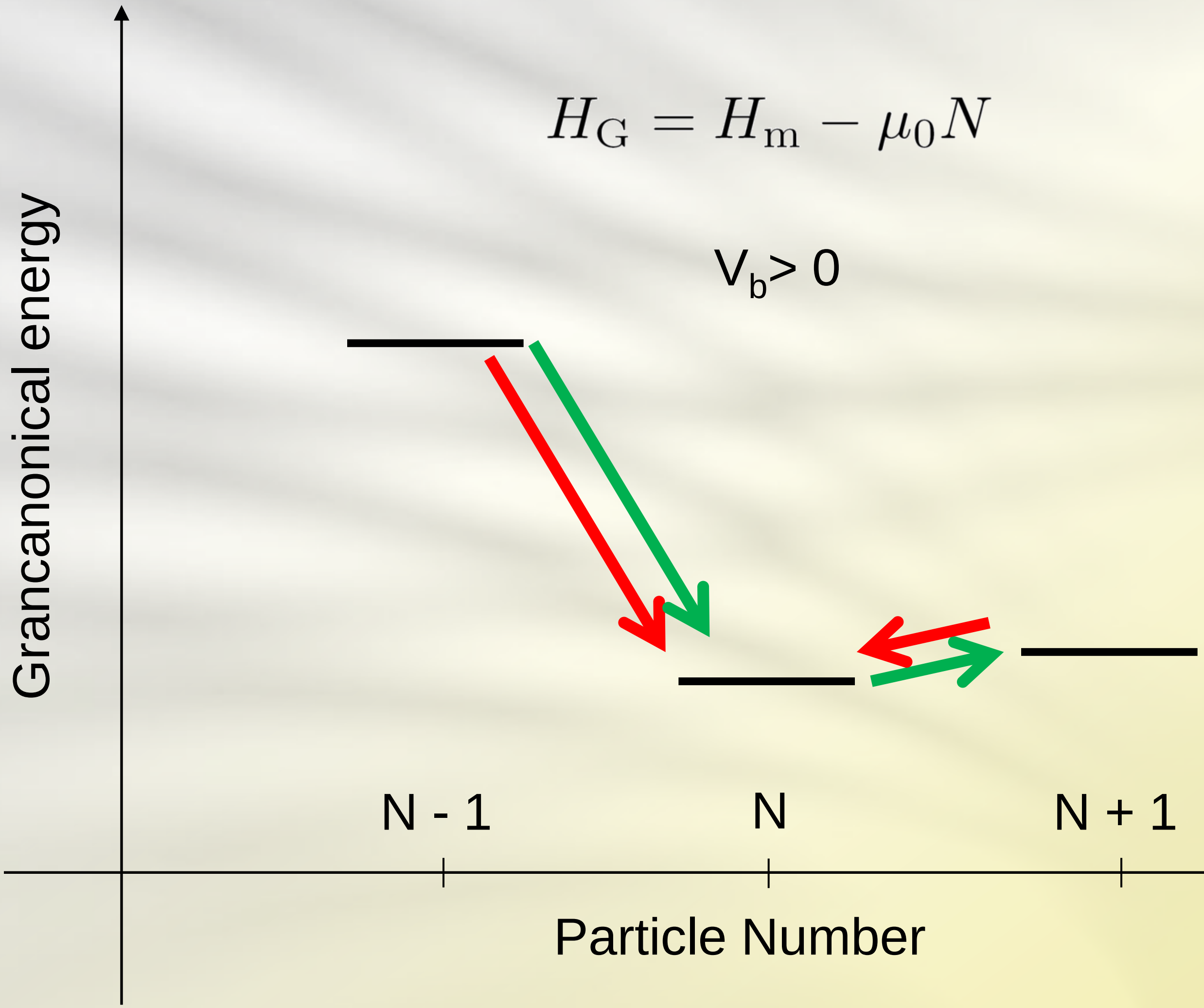


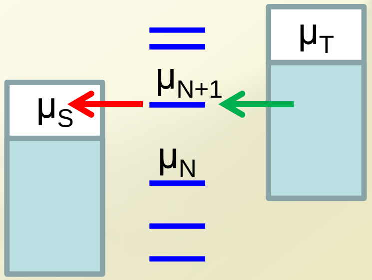
$\mu_N = E_N - E_{N-1}$



Dynamics in energy space

$$H_{\mathrm{G}} = H_{\mathrm{m}} - \mu_0 N$$



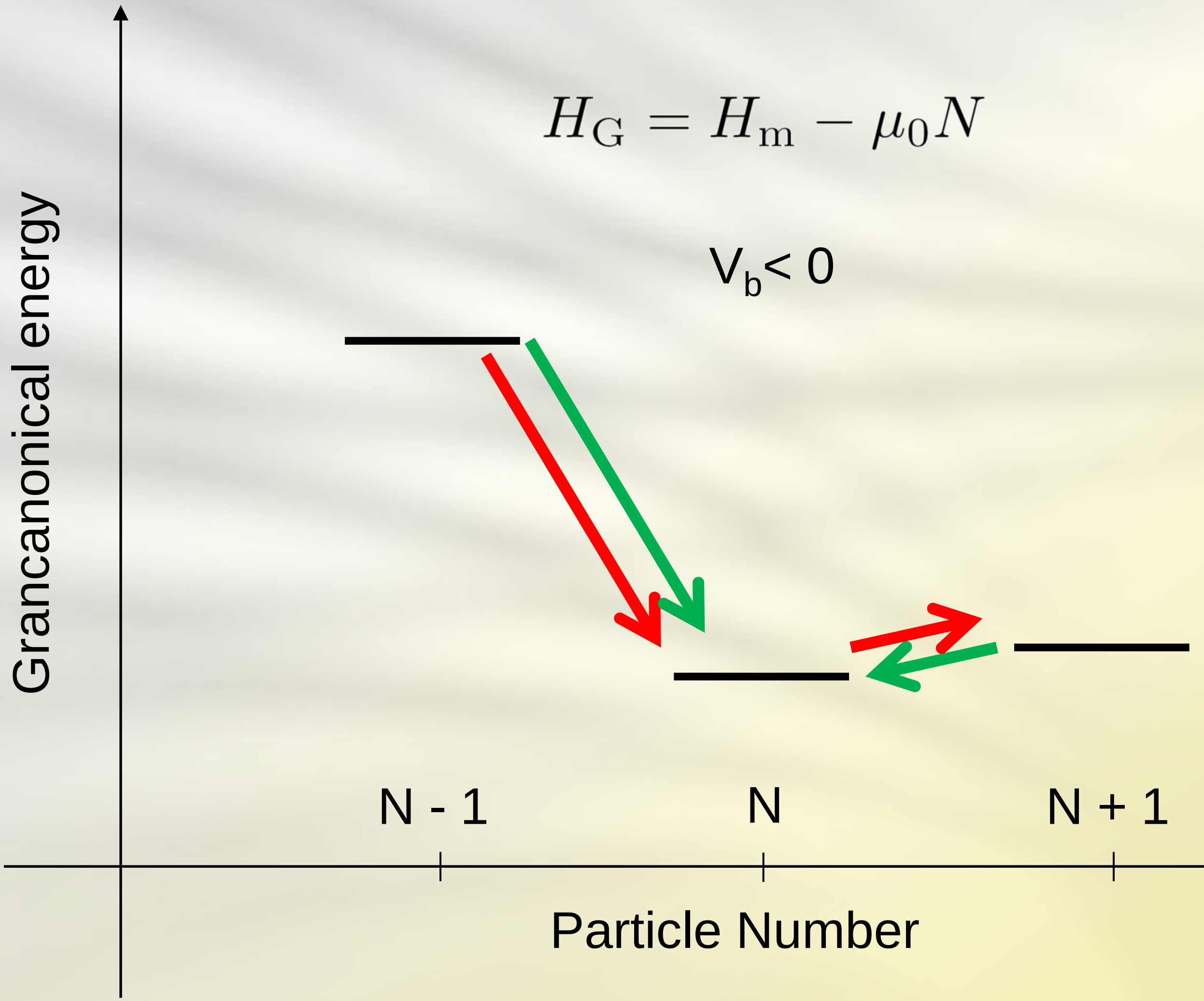


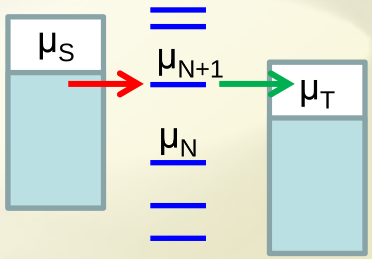
$\mu_{N+1} = E_{N+1} - E_N$

Dynamics in energy space

$$H_G = H_m - \mu_0 N$$

$V_b < 0$



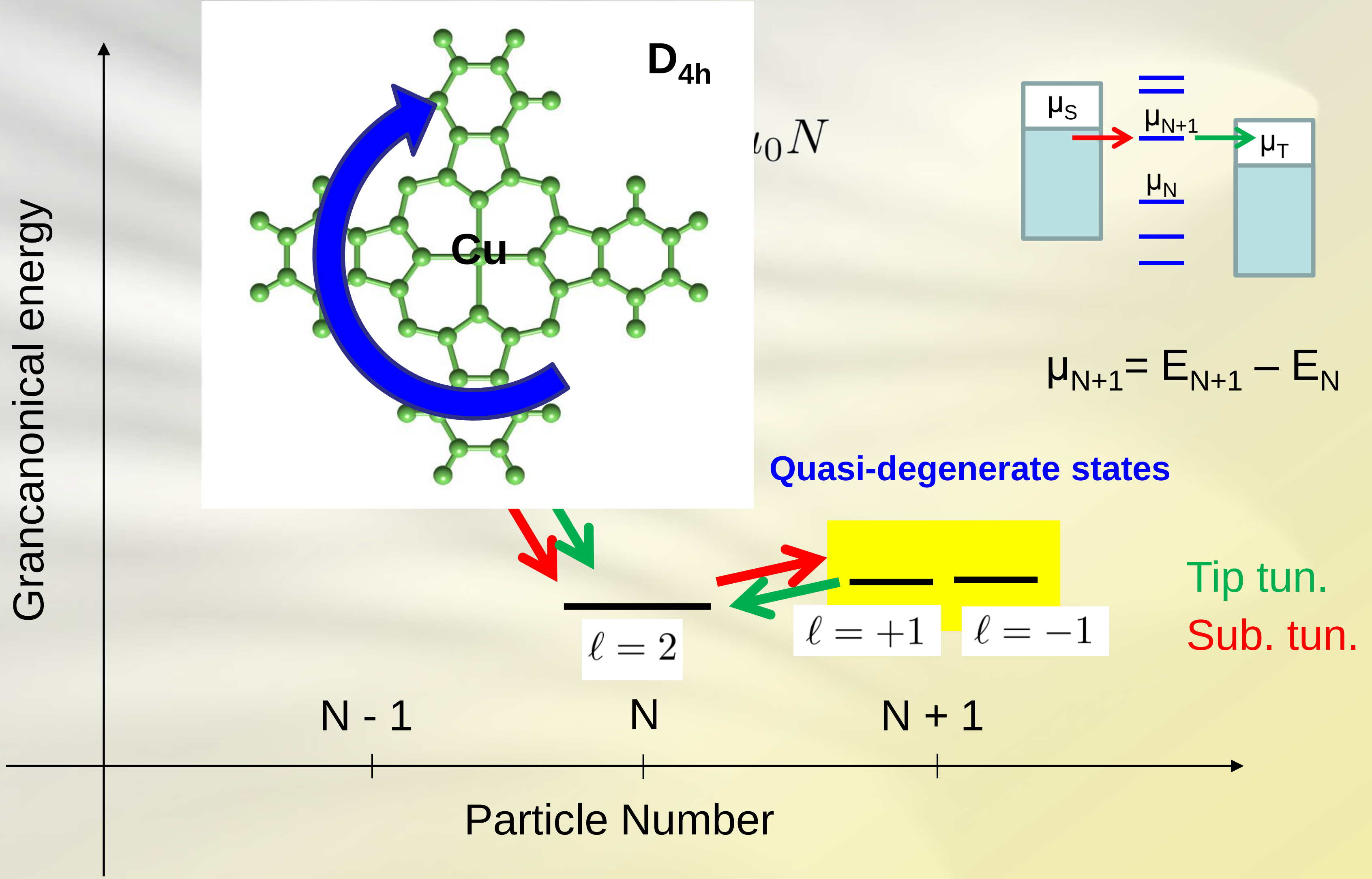


$\mu_{N+1} = E_{N+1} - E_N$

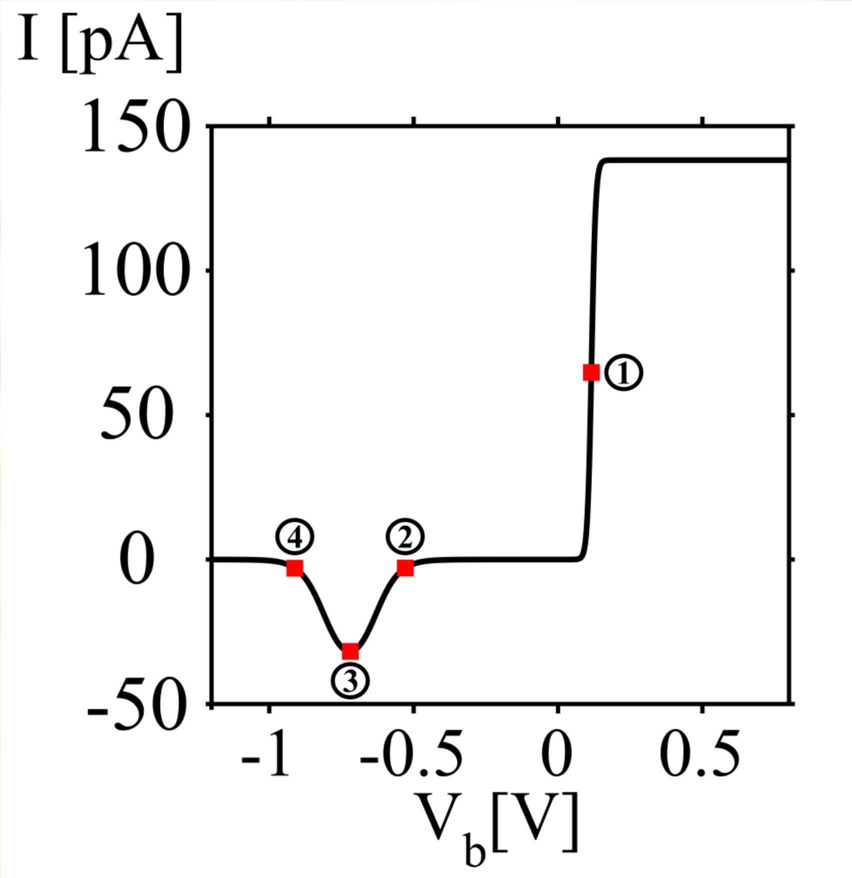
Tip tun.

Sub. tun.

Dynamics in energy space

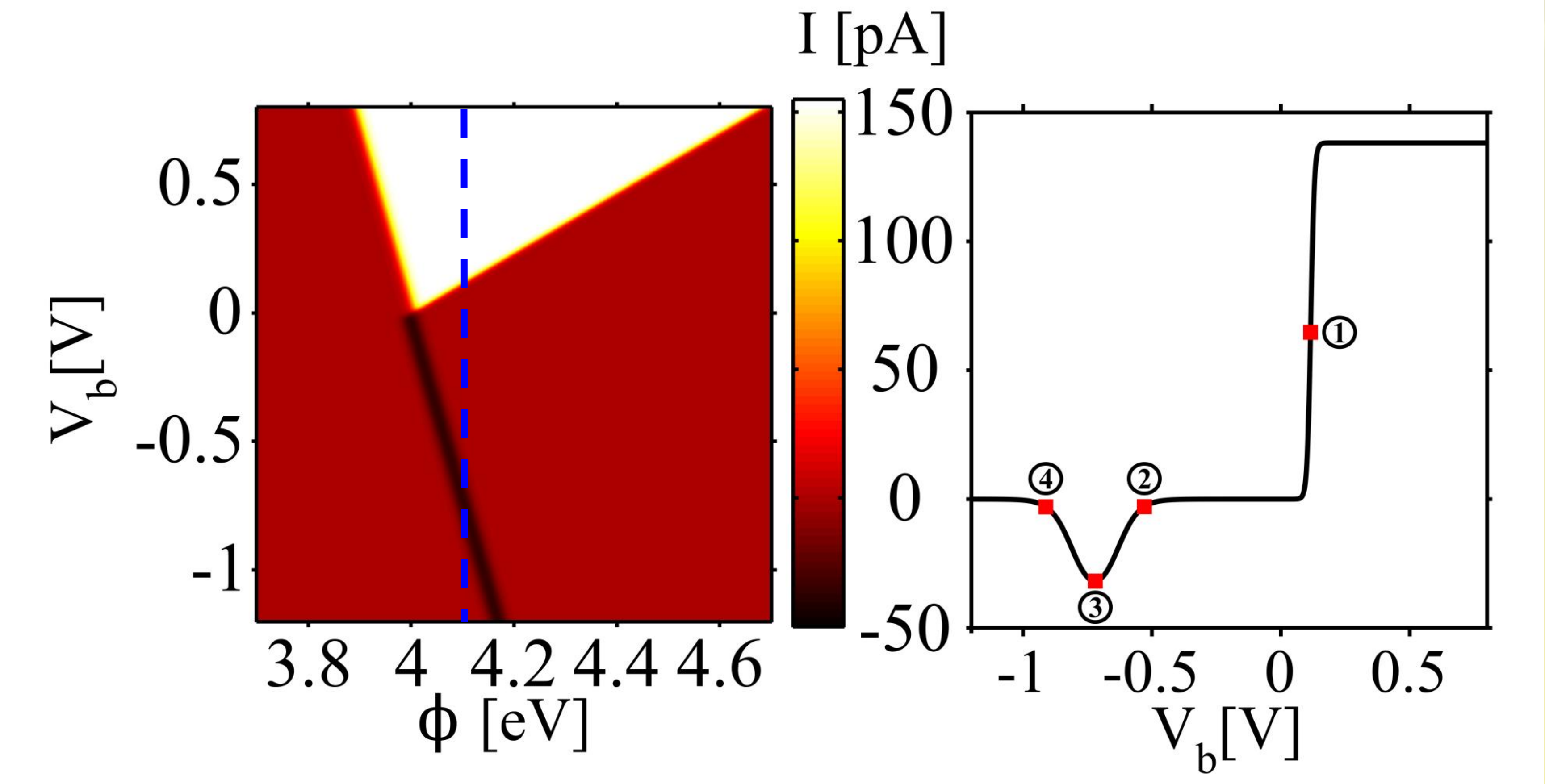


Interference blocking



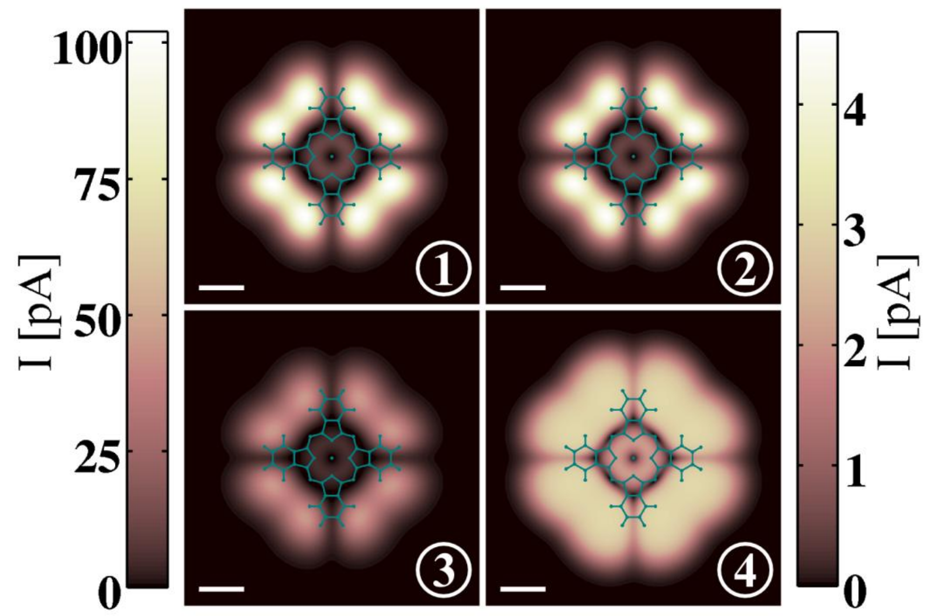
Donarini, Siegert, Sobczyk and Grifoni **Phys. Rev. B 86, 155451 (2012)**

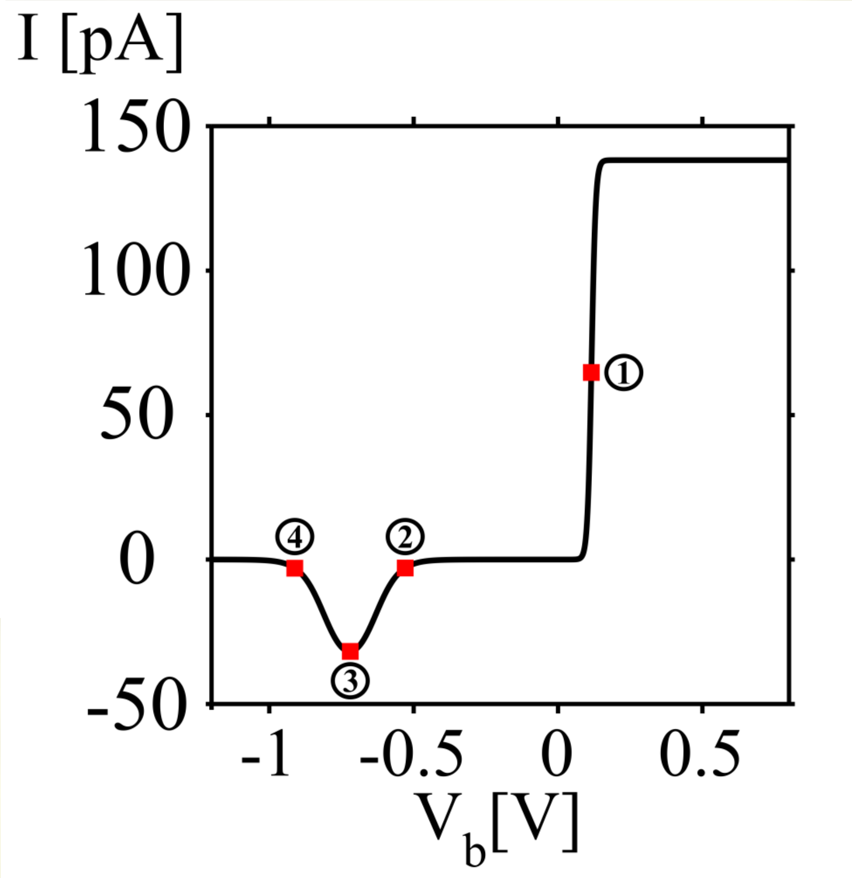
Interference blocking

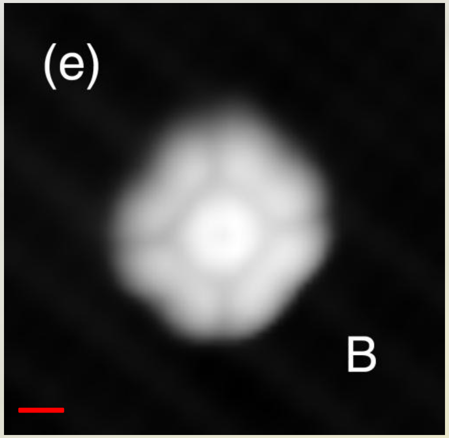


Donarini, Siegert, Sobczyk and Grifoni **Phys. Rev. B 86, 155451 (2012)**

Topographical fingerprint







Experiment:
Cu-Pc on
two-atomic-layer NaBr

W. Ho et al.
PRL 100, 126807 (2008)

Donarini, Siegert, Sobczyk and Grifoni
Phys. Rev. B 86, 155451 (2012)

Interference blocking

Necessary conditions:

1. **Quasi-degeneracy** of the anionic ground state (e.g. Due to rotational symmetry);

2. **Electron affinity** approximately **equals** the (effective) substrate **work function**.

Fingerprints:

1. Strong **negative differential conductance** at **negative sample biases**;

2. **Flattening** of the **constant height current images** in the vicinity of the interference blockade regime.

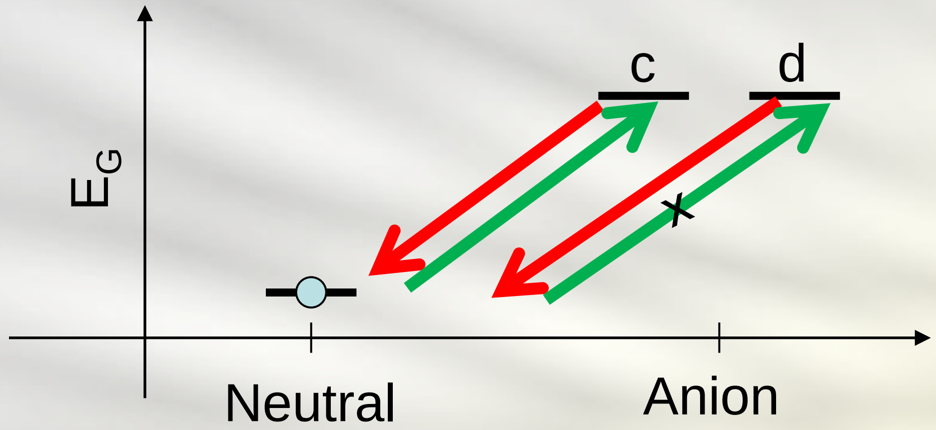
Interference: decoupling basis

Degenerate anionic ground state ⇒ **Matrix form** for the **many-body tunnelling rate** between the neutral and anionic ground states.

	Angular momentum basis	Decoupling basis
Tip	$$\mathbf{R}^T = R_0^T \begin{array}{c} \begin{array}{cc} \boxed{\ell=+1} & \boxed{\ell=-1} \end{array} \\ \begin{pmatrix} 1 & e^{-2i\phi} \\ e^{+2i\phi} & 1 \end{pmatrix} \end{array}$$ **Mixes** angular momentum	$$\tilde{\mathbf{R}}^T = R_0^T \begin{pmatrix} 2 & 0 \\ 0 & 0 \end{pmatrix}$$ One of the anionic state is **decoupled from the tip**
Substrate	$$\mathbf{R}^S = R_0^S \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$ **Conserves** angular momentum	$$\tilde{\mathbf{R}}^S = R_0^S \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

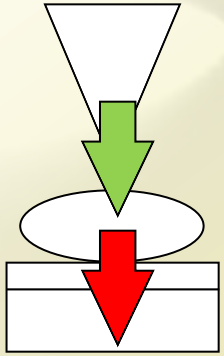
Notice that the decoupling basis **depends** on the **tip position**.

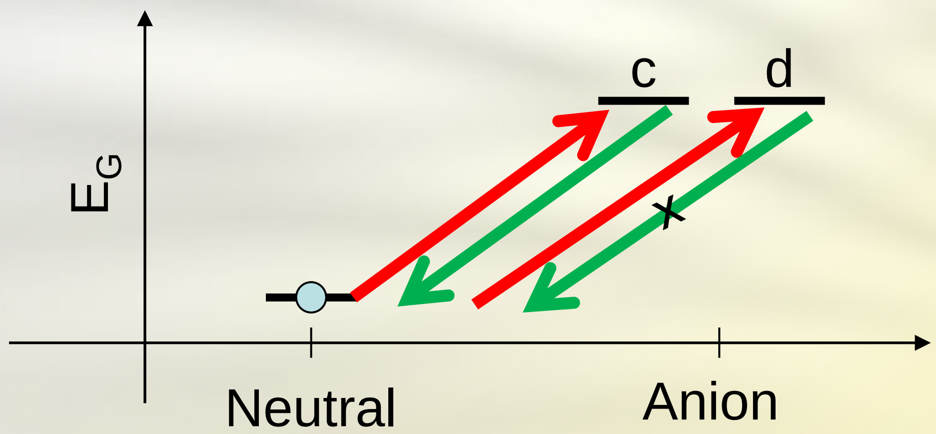
Interference: current blocking



$V_b > -\Delta E_G/ec$

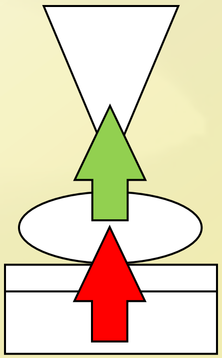
Current





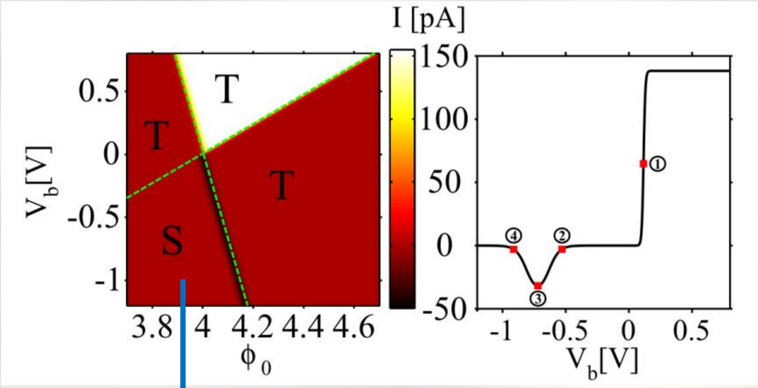
$V_b < \Delta E_G/e(1-c)$

No current

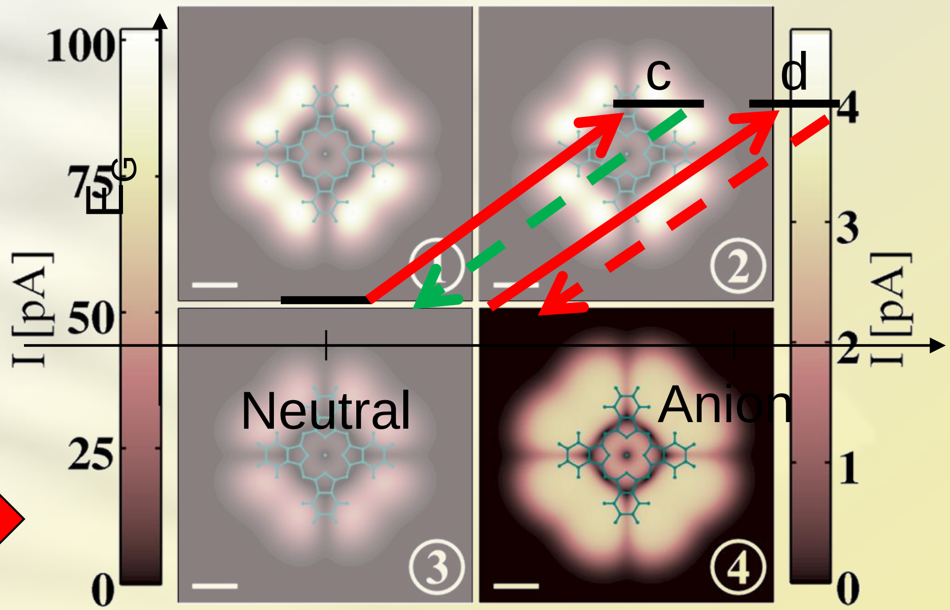


$$\mu_T = \mu_0 - c\,eV_b \qquad \mu_S = \mu_0 + (1-c)eV_b \qquad c \approx 0.9$$

A new bottle-neck process



$$I_{\mathrm{IB}} = e\frac{R_0^S f_S^- R_0^T f_T^-}{R_0^S f_S^- + R_0^T f_T^-}$$



The **depopulation** of the blocking state via a **substrate transition** dominates the transport.

Conclusions

- We developed a **semi-quantitative model** for the description of "weakly coupled" STM junctions with pi-conjugated molecules.
- The dynamics is described in terms of **many-body** transitions.
- Transport through **degenerate states** is associated to **electron interference** blockade at negative sample biases.
- In the vicinity of the interference blocking regime, **flat constant height current maps** indicate that the substrate tunnelling event becomes the new bottle-neck process.

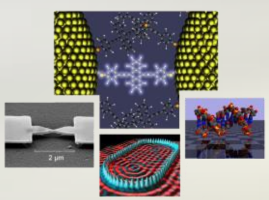
Thanks

Milena Grifoni

Benjamin Siegert

Sandra Sobczyk

DFG Deutsche Forschungsgemeinschaft



SPP 1243 Quantum Transport at the molecular scale

SFB 689 Spinphenomena in reduced dimensions

SFB 689

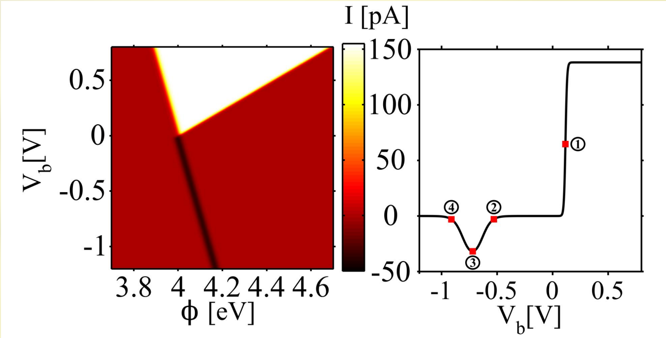
Thank you for your attention…

Bremen, 07.03.2013

Dynamics in a reduced space

$$\begin{pmatrix} \dot\sigma^N \\ \dot\sigma_{\mathrm{c}}^{N+1\tau} \\ \dot\sigma_{\mathrm{d}}^{N+1\tau} \end{pmatrix} = \left[2R^T \begin{pmatrix} -2f_T^+ & 2f_T^- & 0 \\ f_T^+ & -f_T^- & 0 \\ 0 & 0 & 0 \end{pmatrix} + R^S \begin{pmatrix} -4f_S^+ & 2f_S^- & 2f_S^- \\ f_S^+ & -f_S^- & 0 \\ f_S^+ & 0 & -f_S^- \end{pmatrix} \right] \begin{pmatrix} \sigma^N \\ \sigma_{\mathrm{c}}^{N+1\tau} \\ \sigma_{\mathrm{d}}^{N+1\tau} \end{pmatrix}$$

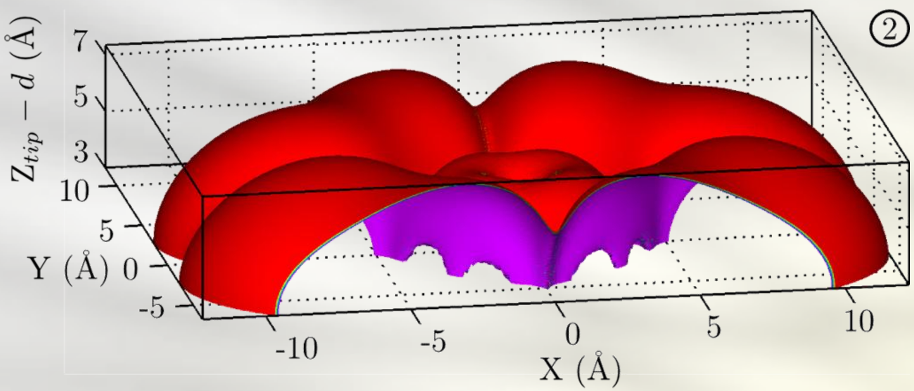
$$I(\vec{R}_{\mathrm{tip}}, V_{\mathrm{b}}) = 2eR^S f_S^+ \sigma^N \left(1 - \frac{\sigma_{\mathrm{c}}^{N+1\tau}}{\sigma_{\mathrm{d}}^{N+1\tau}} \right)$$

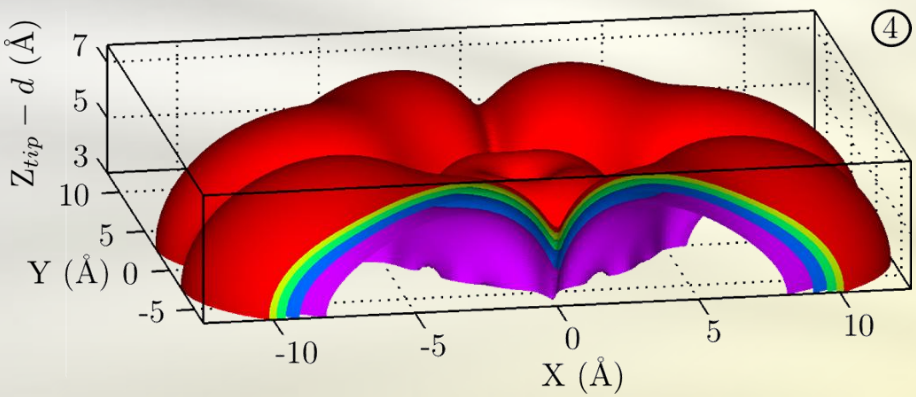


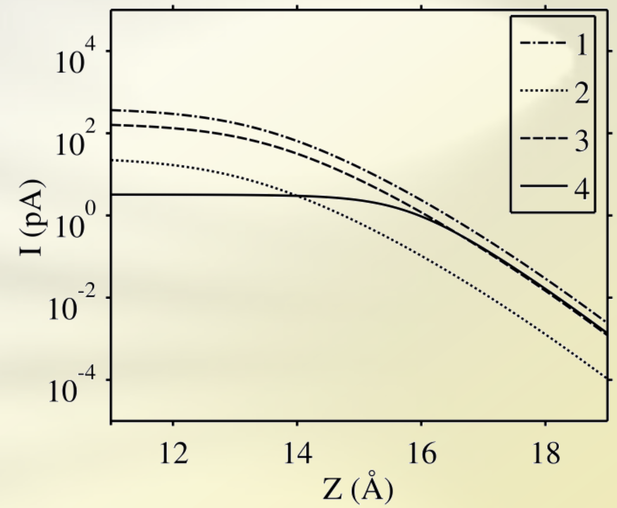
$$\sigma^N = \left(1 + 2\frac{R^S f_S^+ + 2R^T f_T^+}{R^S f_S^- + 2R^T f_T^-} + 2\frac{f_S^+}{f_S^-} \right)^{-1}$$

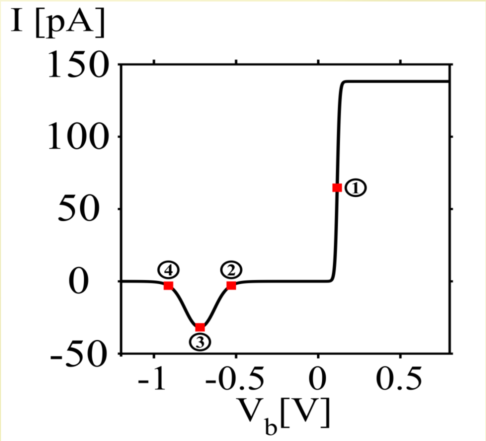
$$\frac{\sigma_{\mathrm{c}}^{N+1\tau}}{\sigma_{\mathrm{d}}^{N+1\tau}} = \frac{R^S f_S^+ + 2R^T f_T^+}{R^S f_S^- + 2R^T f_T^-} \cdot \frac{f_S^-}{f_S^+}.$$

Constant current maps









Constant current maps calculated
at working currents: I = 3.15, 3.075, 3.0, 2.925, and 2.85 pA