Many-body interference in STM single molecule junctions on thin insulating films

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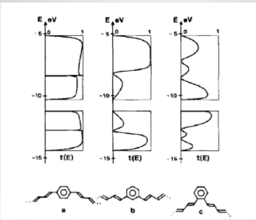
Interference in molecular electronics



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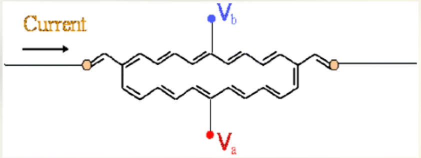
Chem. Phys. Lett. **153**, 511 (1988)



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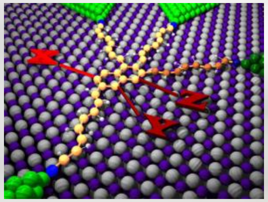
JACS, **124**, 4200 (2002)



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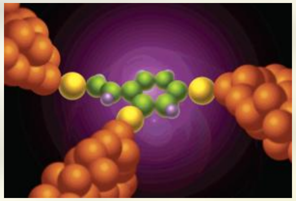
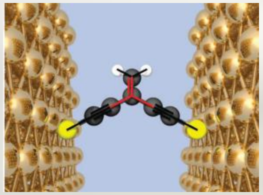
Nanotechnology, **14**, 138 (2003)



D. V. Cardamone, et al.
Nano Lett., **6**, 2422 (2006)



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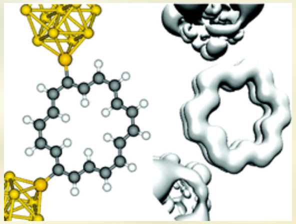
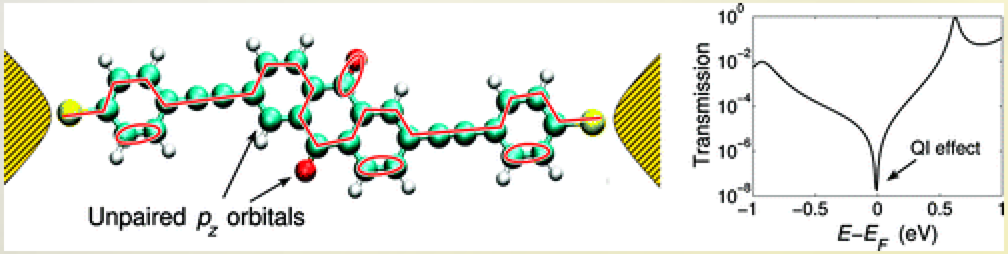
JACS **130**, 17307 (2008)



S.H. Ke, et al.
Nano Lett., **8**, 3257 (2008)



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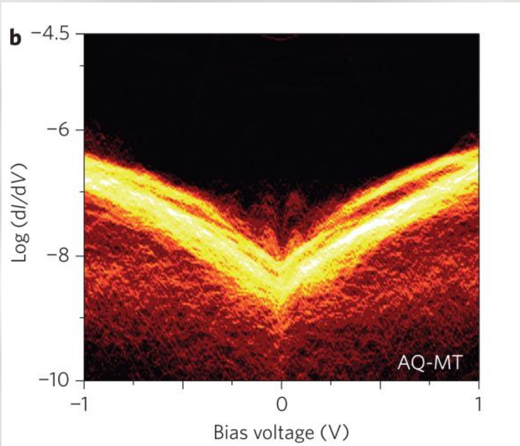
Nano Lett., **10**, 4260 (2010)

Experimental evidence



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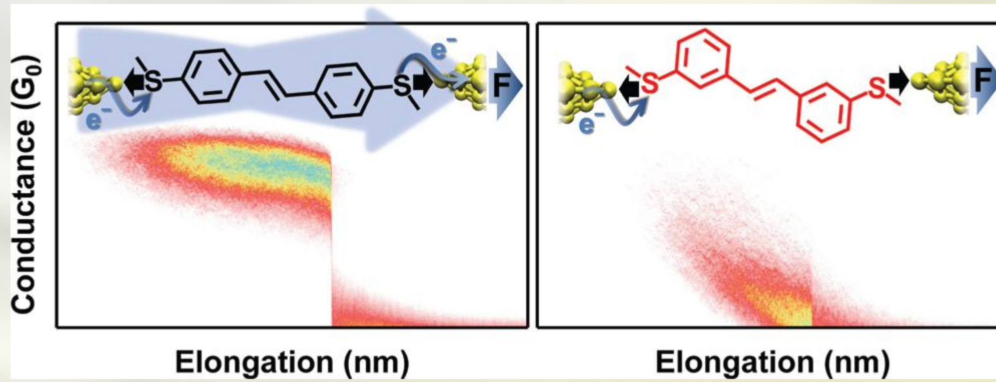

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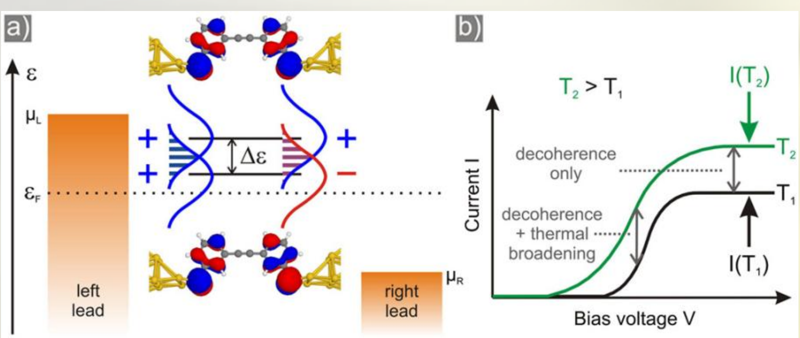

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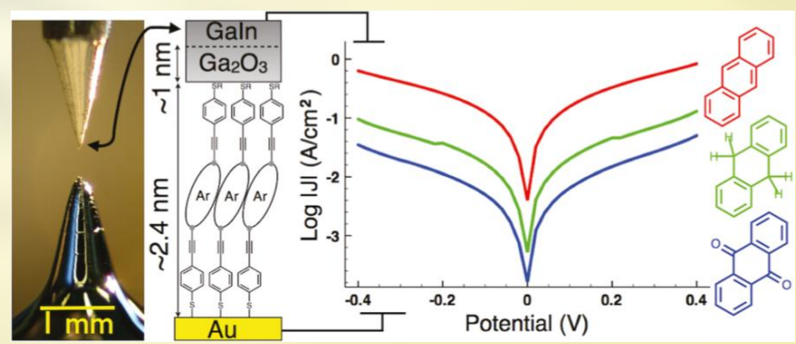
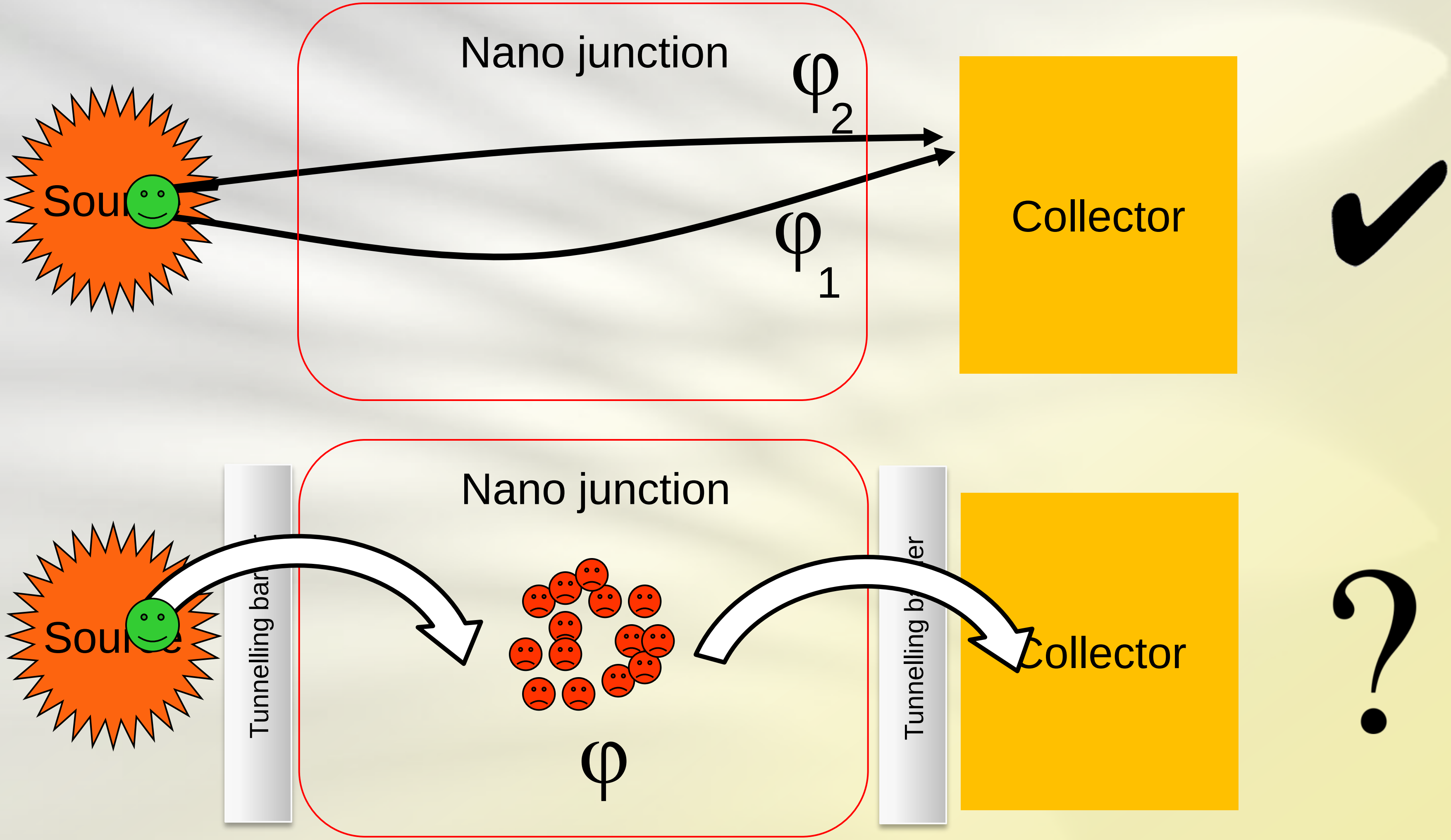
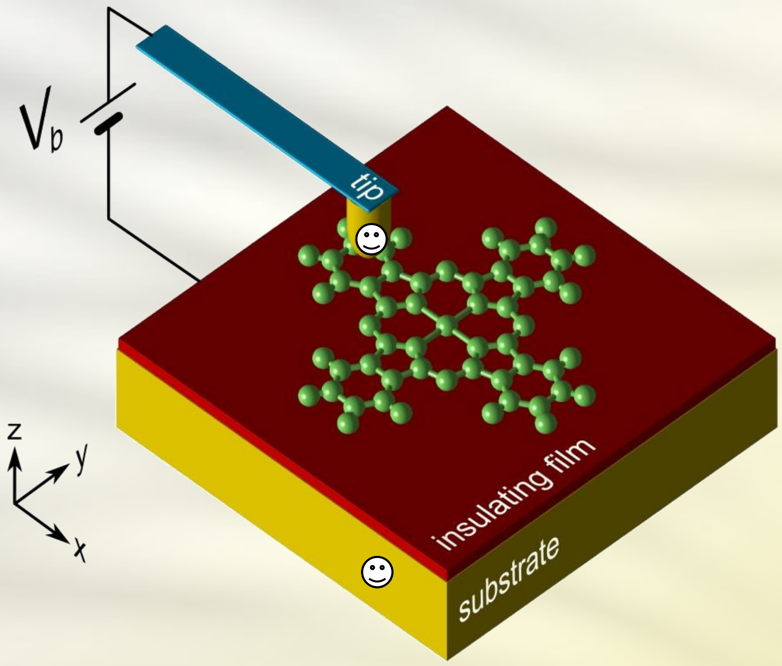


Fracasso et al. *JACS*, **133**, 9556 (2011)

Interference and dephasing



STM on thin insulating films

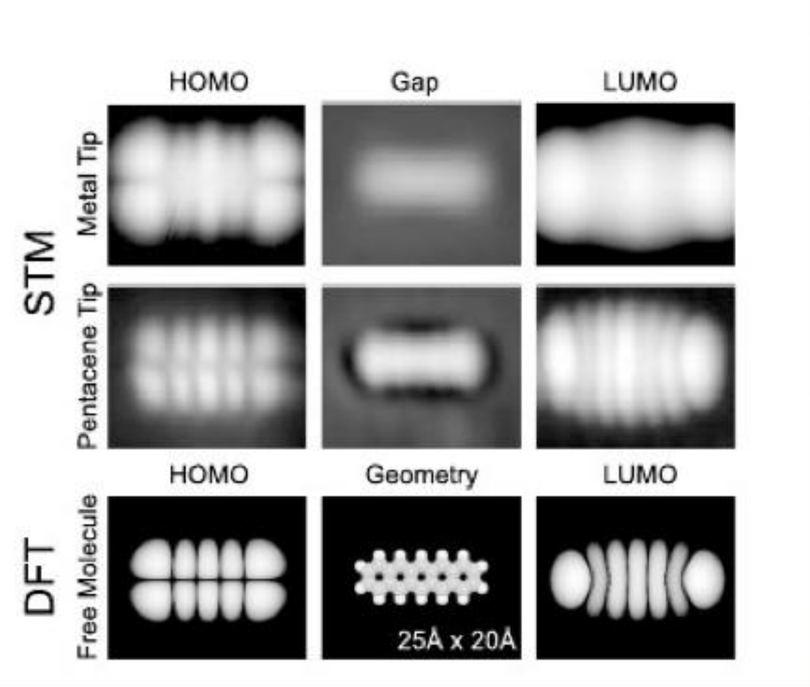


Weak tip-molecule **tunnelling coupling**
Low molecule-substrate **hybridization**

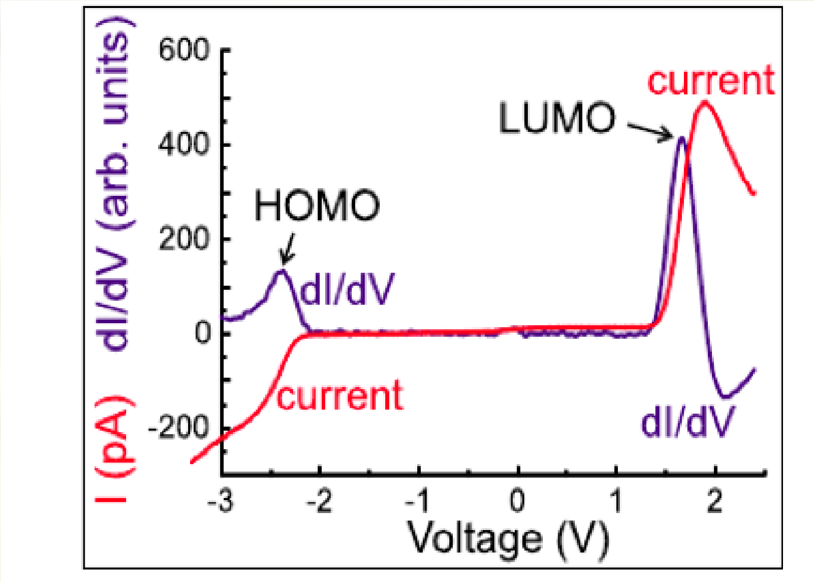
➡ **sequential tunnelling**

Visualization of molecular orbitals

Topography



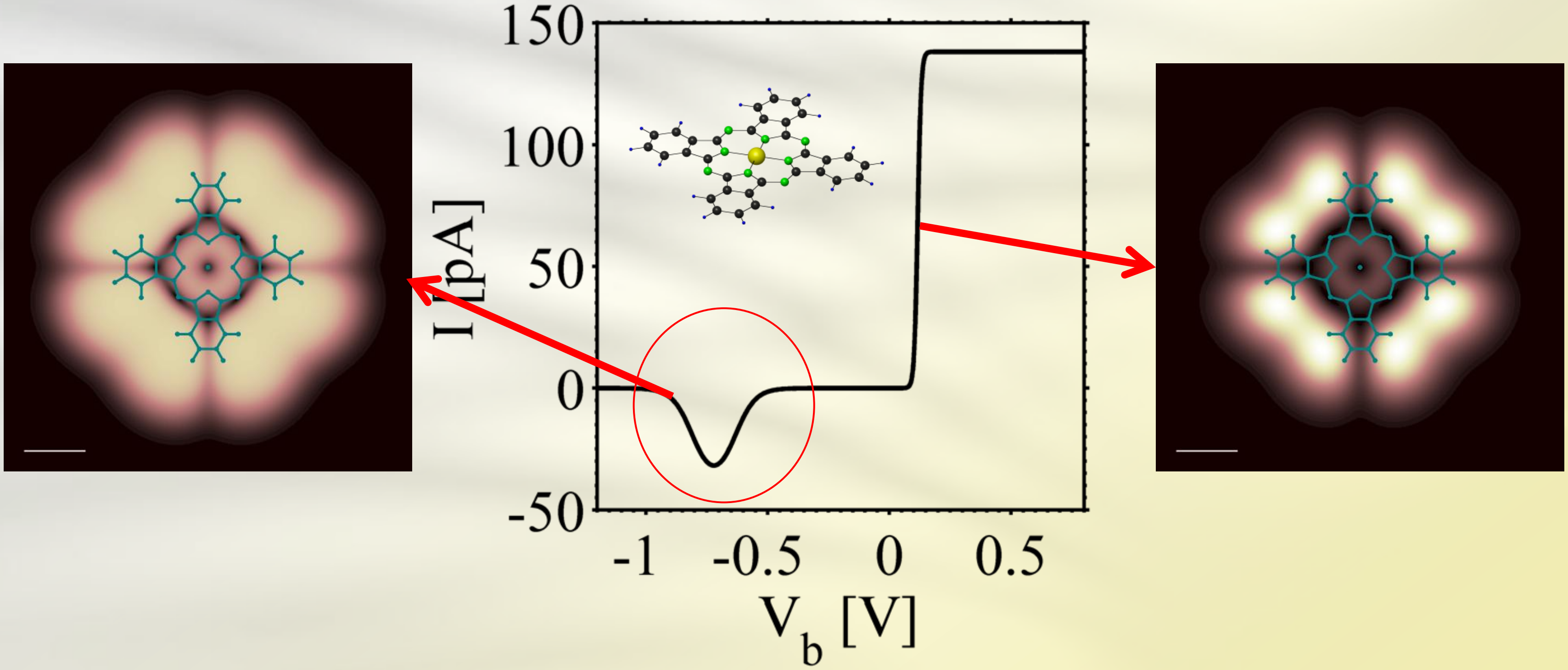
Spectroscopy



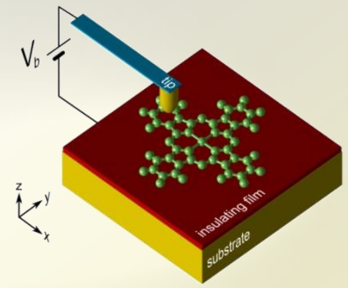
J. Repp and G. Meyer, Physical Review Letters **94**, 026803 (2005)

Interference fingerprints

Cu - Phthalocyanine



The total Hamiltonian



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

$$H_{\rm m} = \underbrace{\sum_{\alpha\sigma} a_\alpha d^\dagger_{\alpha\sigma} d_{\alpha\sigma}}_{\text{on-site}} + \underbrace{\sum_{\alpha\neq\beta\sigma} b_{\alpha\beta} d^\dagger_{\alpha\sigma} d_{\beta\sigma}}_{\text{hopping}} + \underbrace{V_{\rm e-e}}_{\text{electron-electron interaction}}$$

$V_{\rm e-e}$:
- Hubbard
- Extended Hubbard
- Constant interaction

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

No confinement in the x-y directions

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

Parabolic confinement in the x-y directions

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

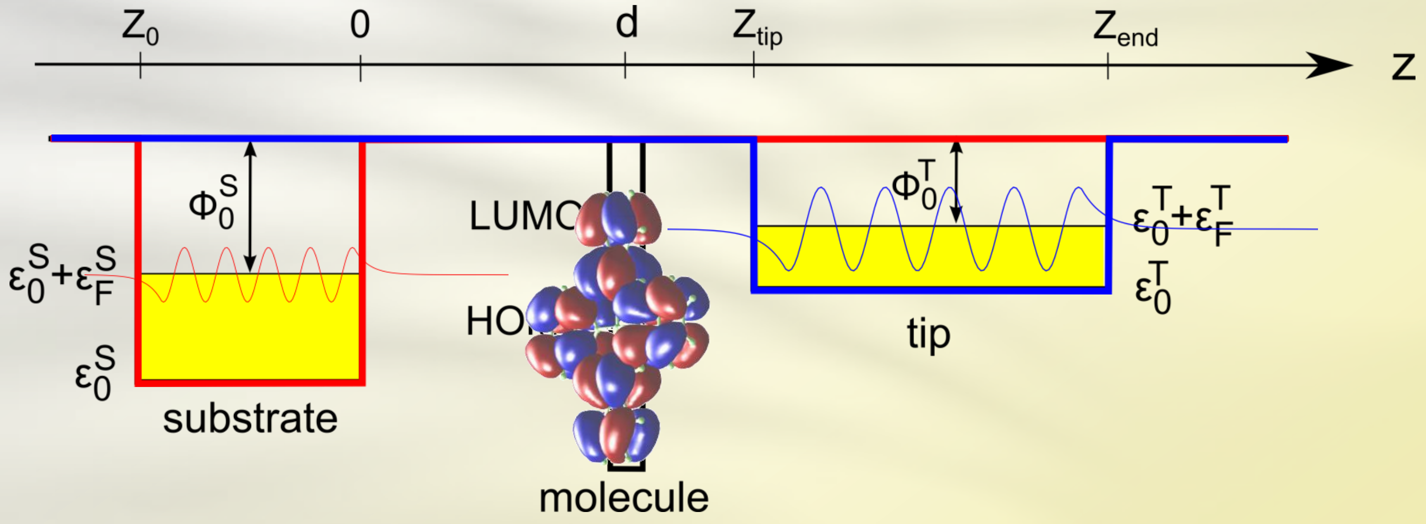
It is a **single particle** operator

$d_{i\sigma}$ ← Molecular orbital

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

Tunnelling amplitudes

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



Regensburg, 10.04.2013

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

UR

Tunnelling amplitudes (ii)

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

$$= \varepsilon_i \langle \chi k \sigma | i \sigma \rangle$$

Valence atomic orbitals
larger in the leads than
in the molecule

More perpendicular nodal planes
in the molecule than in the leads

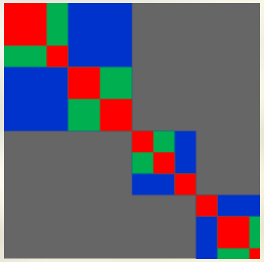
$$\psi_{\chi k}(\vec{r})\phi_i(\vec{r})$$

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 :

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

Coherent dynamics

Effective **internal** dynamics

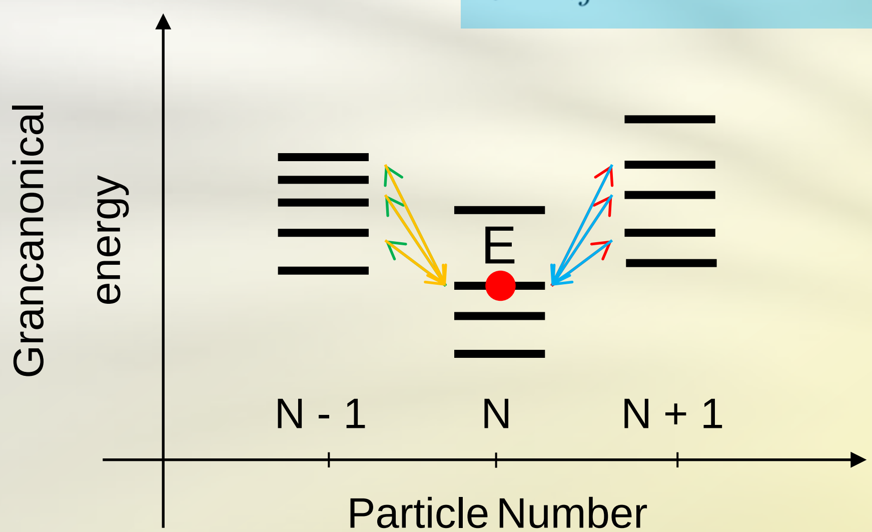
Tunnelling dynamics

Tunnelling Liouvillean

$$\mathcal{L}_{\rm tun}\sigma^{NE} = -\frac{1}{2}\sum_{\chi\tau}\sum_{ij}\Big\{\mathcal{P}_{NE}\Big[d^\dagger_{i\tau}\Gamma^\chi_{ij}(E-H_{\rm m})f^-_\chi(E-H_{\rm m})d_{j\tau} + d_{j\tau}\Gamma^\chi_{ij}(H_{\rm m}-E)f^+_\chi(H_{\rm m}-E)d^\dagger_{i\tau}\Big]\sigma^{NE} + h.c.\Big\}$$

$$+\sum_{\chi\tau}\sum_{ijE'}\mathcal{P}_{NE}\Big[d^\dagger_{i\tau}\Gamma^\chi_{ij}(E-E')\sigma^{N-1E'}f^+_\chi(E-E')d_{j\tau} + d_{j\tau}\Gamma^\chi_{ij}(E'-E)\sigma^{N+1E'}f^-_\chi(E'-E)d^\dagger_{i\tau}\Big]\mathcal{P}_{NE}$$

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



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

Projector on the subspace of N particles and energy E.

Single particle rate matrix

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

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

Effective Hamiltonian

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

Current operator

Many-body rate matrix

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

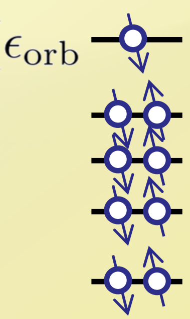
$$R^{\chi\tau}_{N\,E_0 \to N+1\,E_1} = \sum_{ij} \langle N+1 E_1 | d^\dagger_{i\tau} | N E_0 \rangle \Gamma^\chi_{ij}(E_1 - E_0) \times \langle N E_0 | d_{j\tau} | N+1 E_1 \rangle f^+(E_1 - E_0 - \mu_\chi)$$

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

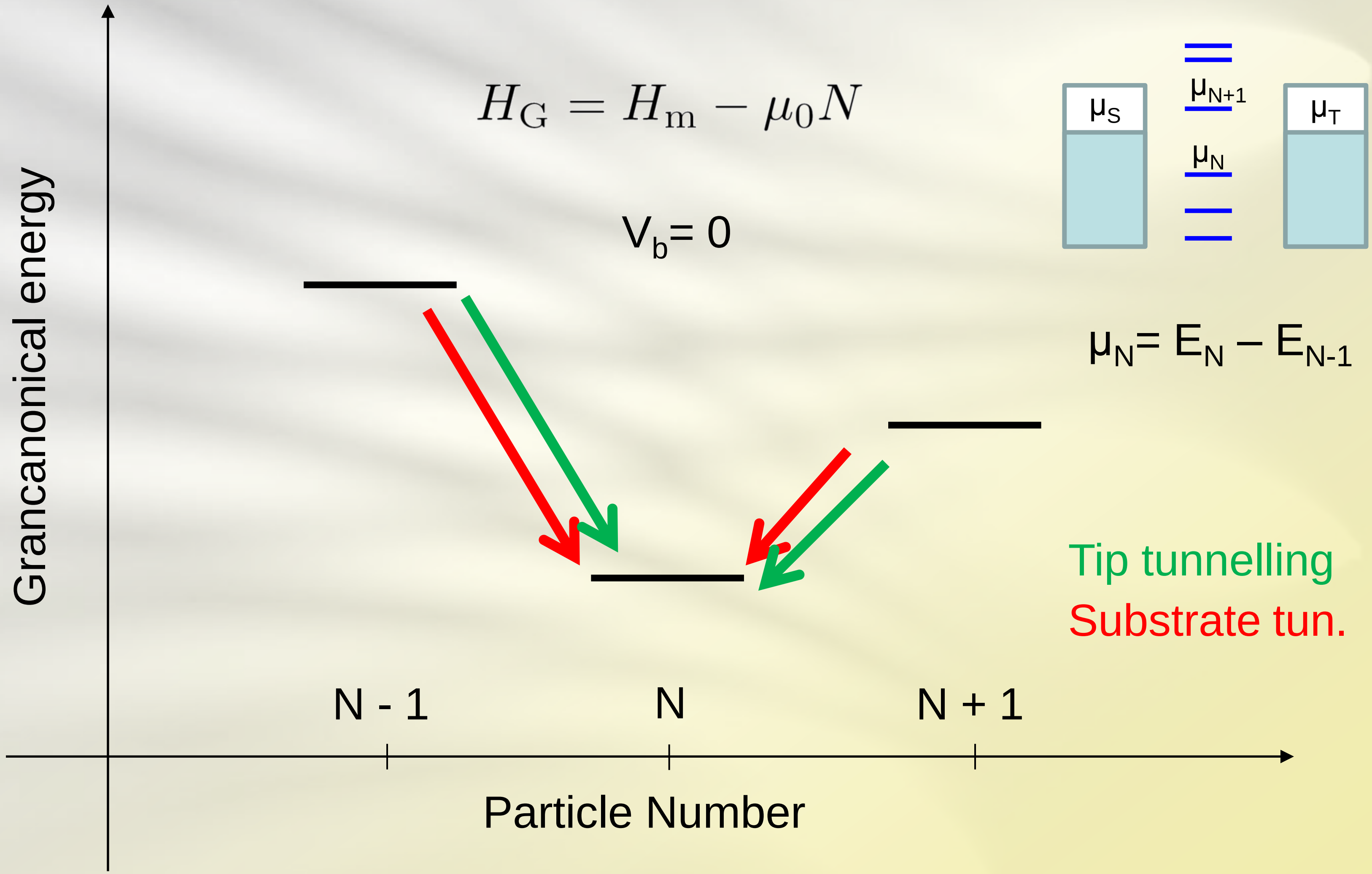
$$R^{\chi\tau}_{N\,E_0 \to N+1\,E_1} = \Gamma^\chi_{\rm orb}(\epsilon_{\rm orb}) f^+(\epsilon_{\rm orb} - \mu_\chi)$$



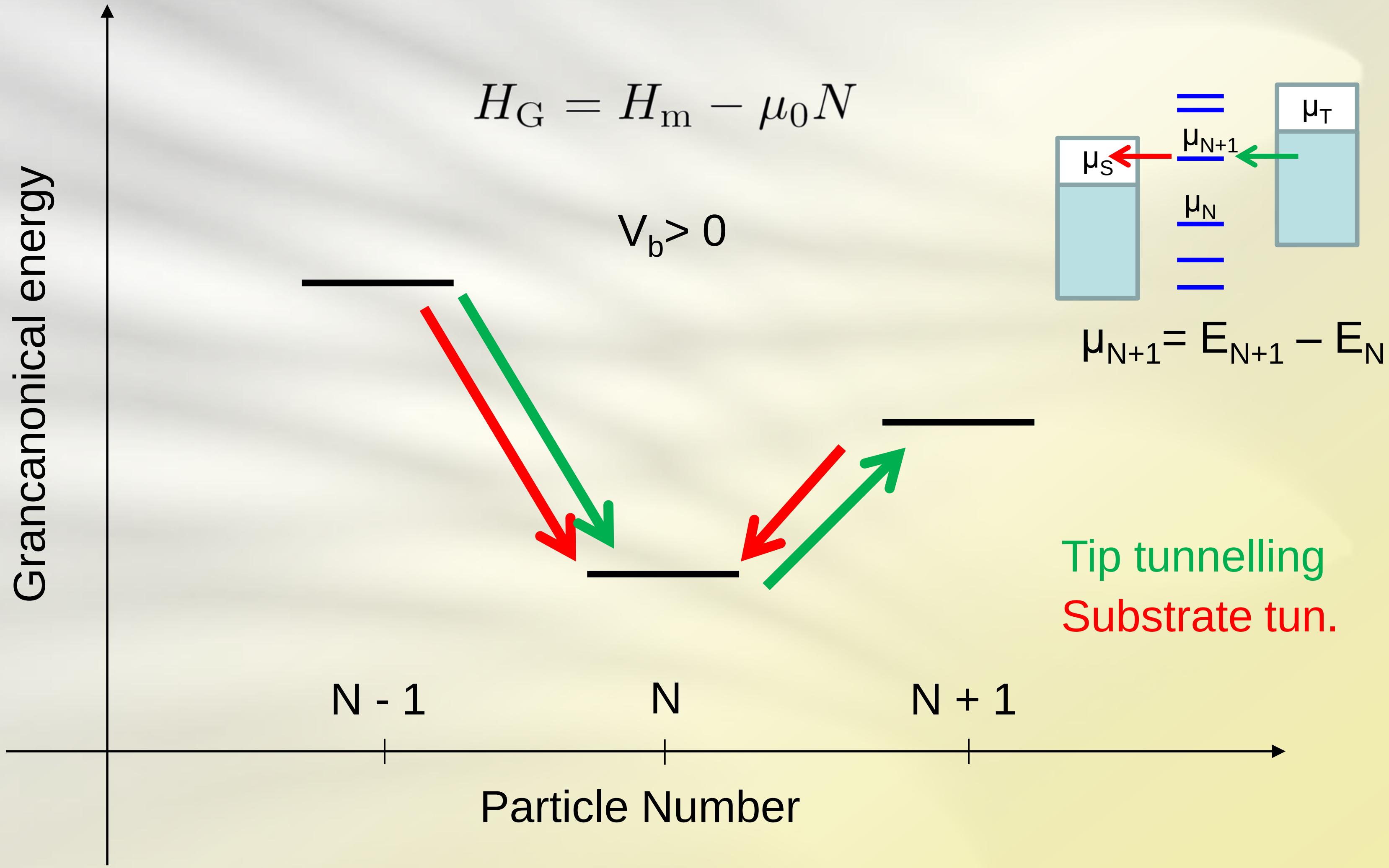
The **constant current map** is the **isosurface** of a **specific molecular orbital**.

Dynamics in energy space

$$H_G = H_m - \mu_0 N$$

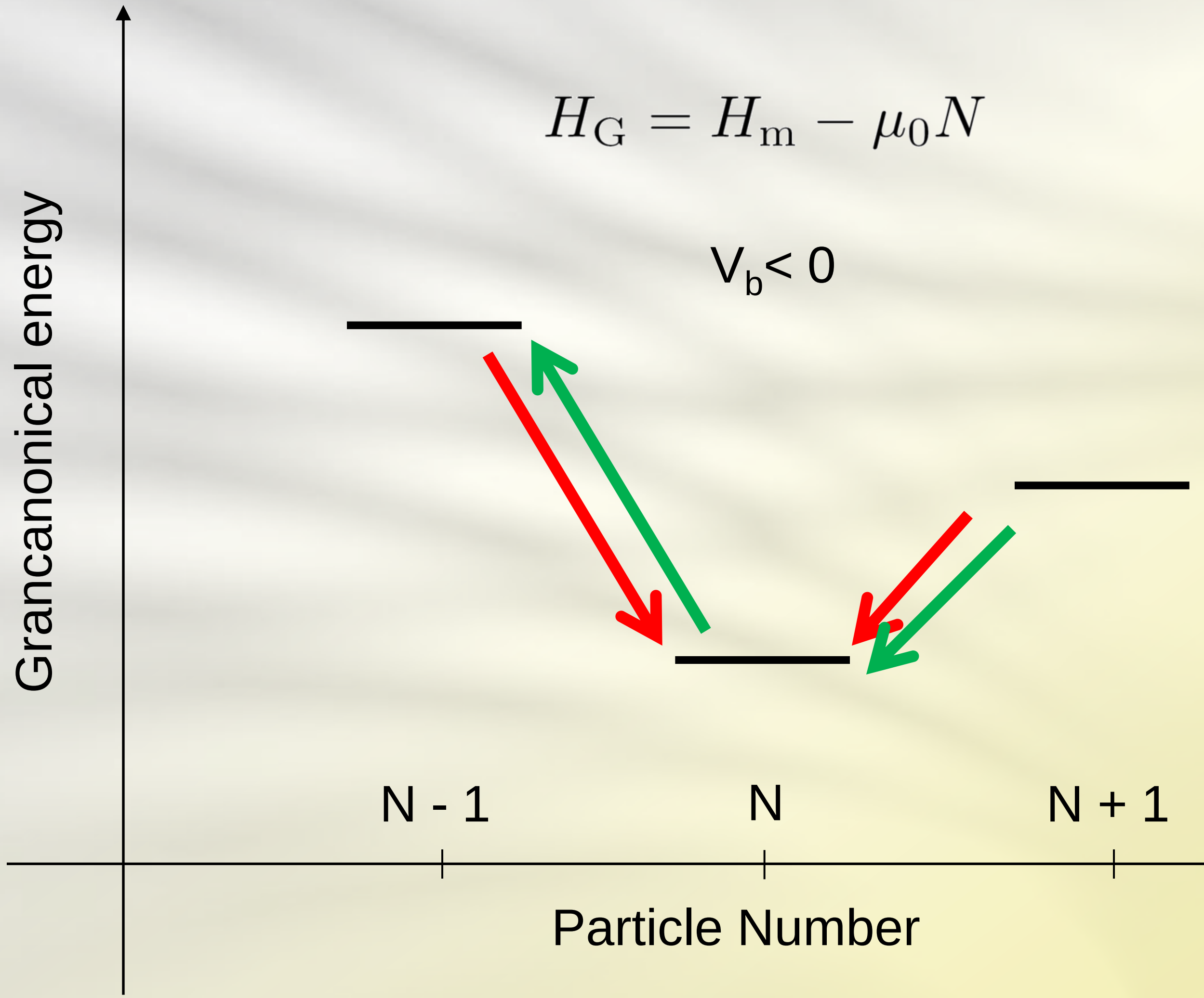


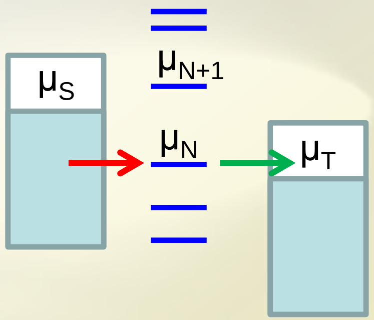
Dynamics in energy space



Dynamics in energy space

$$H_G = H_m - \mu_0 N$$





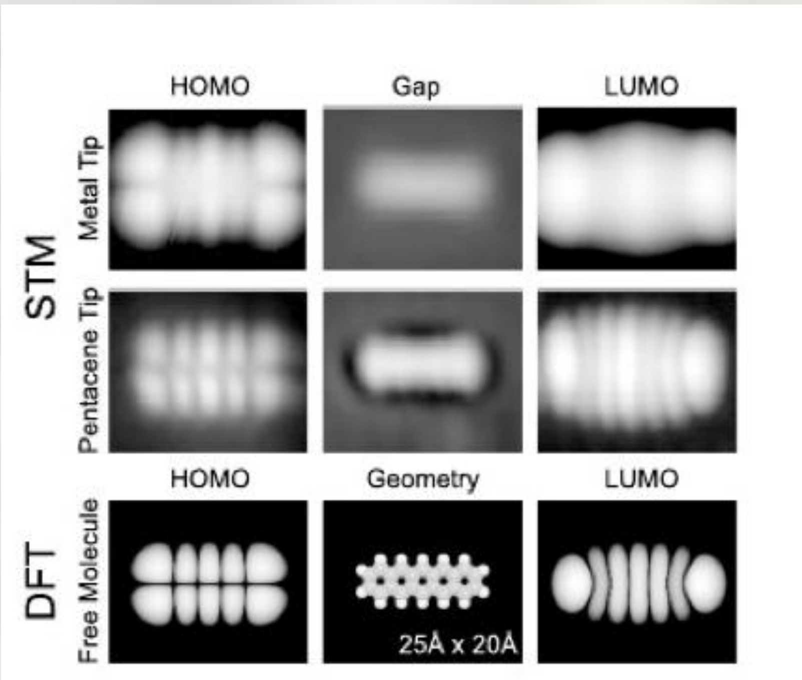
$\mu_N = E_N - E_{N-1}$

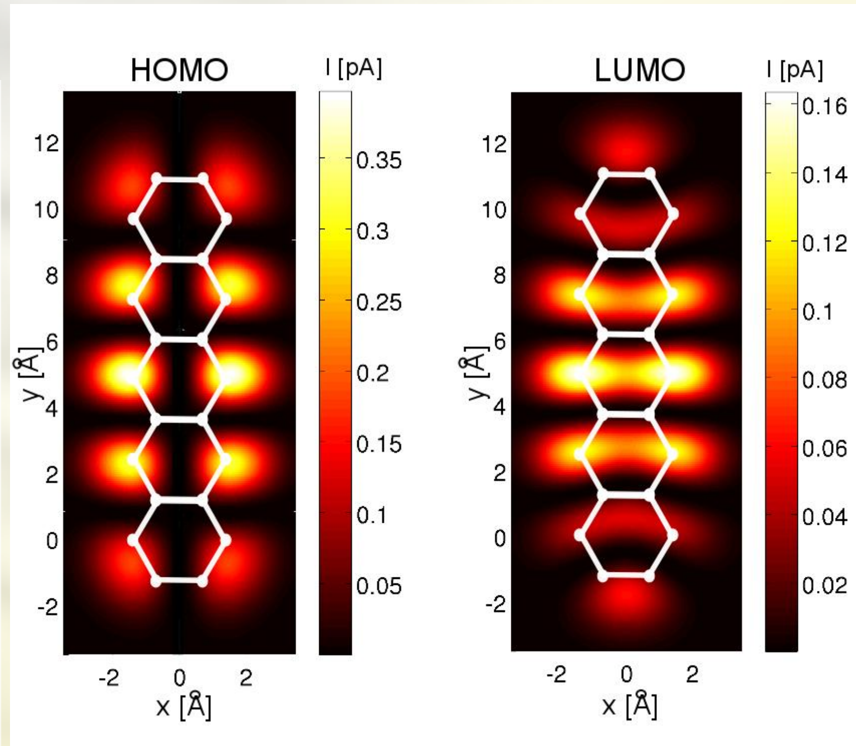
Tip tunnelling

Substrate tun.

Visualization of molecular orbitals

Topography



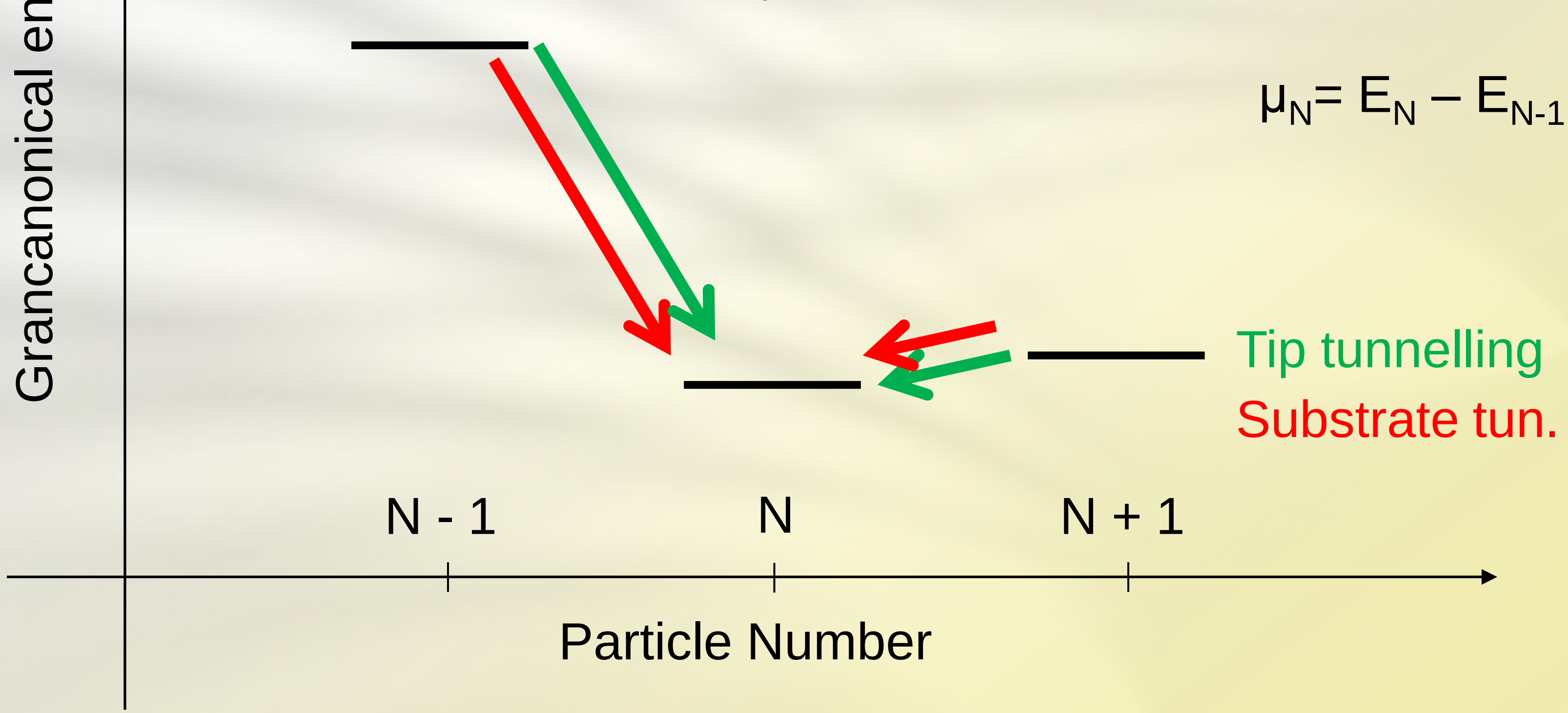


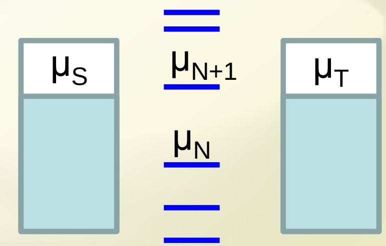
J. Repp and G. Meyer, Physical Review Letters **94**, 026803 (2005)

Dynamics in energy space

$$H_G = H_m - \mu_0 N$$

$V_b = 0$

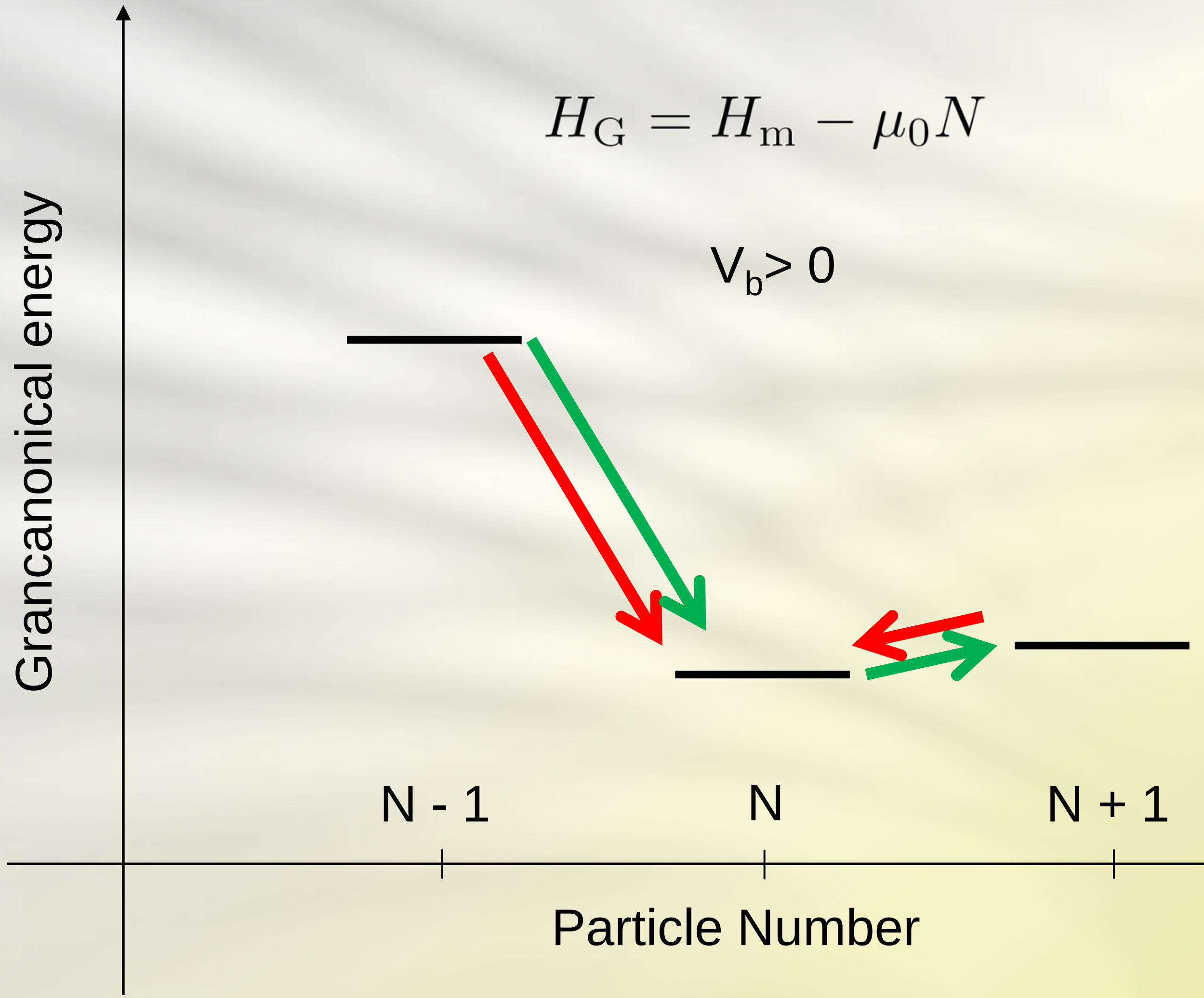


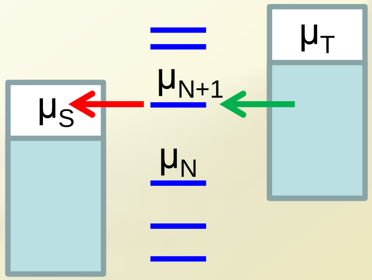


$$\mu_N = E_N - E_{N-1}$$

Dynamics in energy space

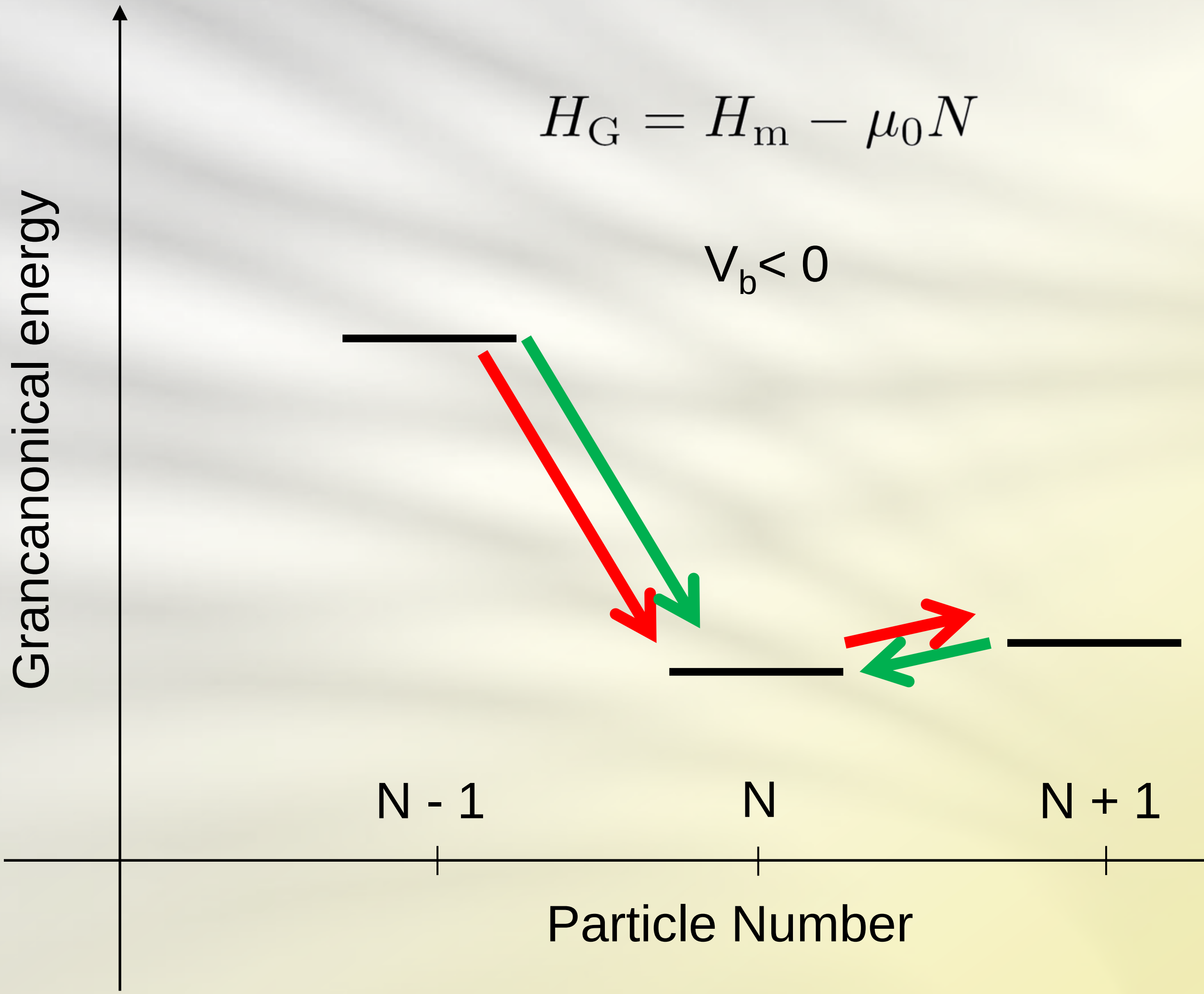
$$H_\mathrm{G} = H_\mathrm{m} - \mu_0 N$$

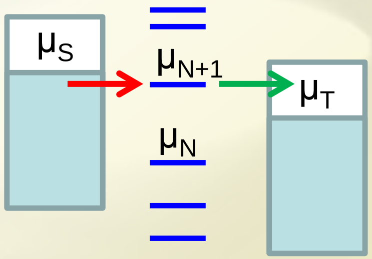




$$\mu_{N+1} = E_{N+1} - E_N$$

Dynamics in energy space



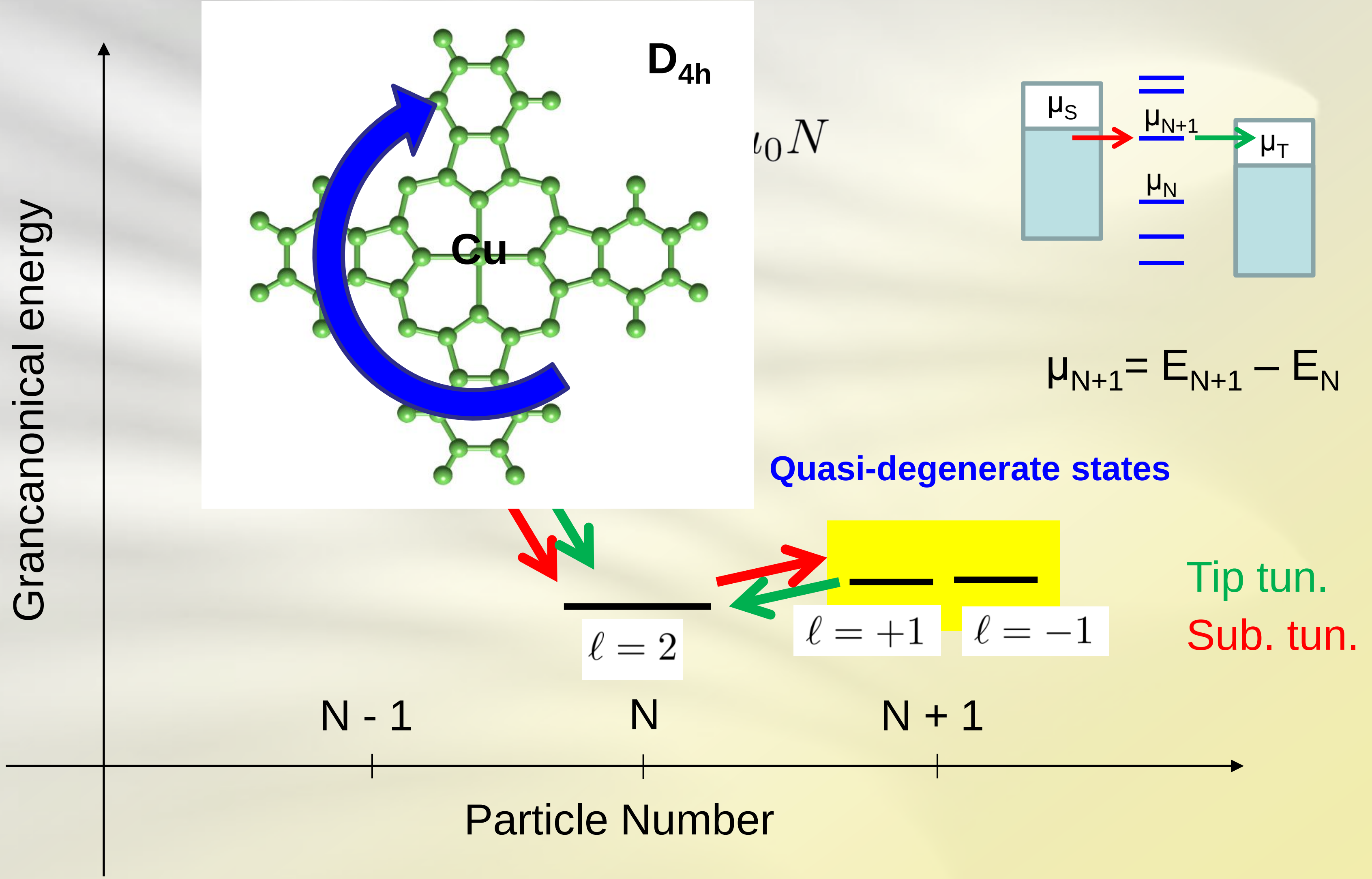


$\mu_{N+1} = E_{N+1} - E_N$

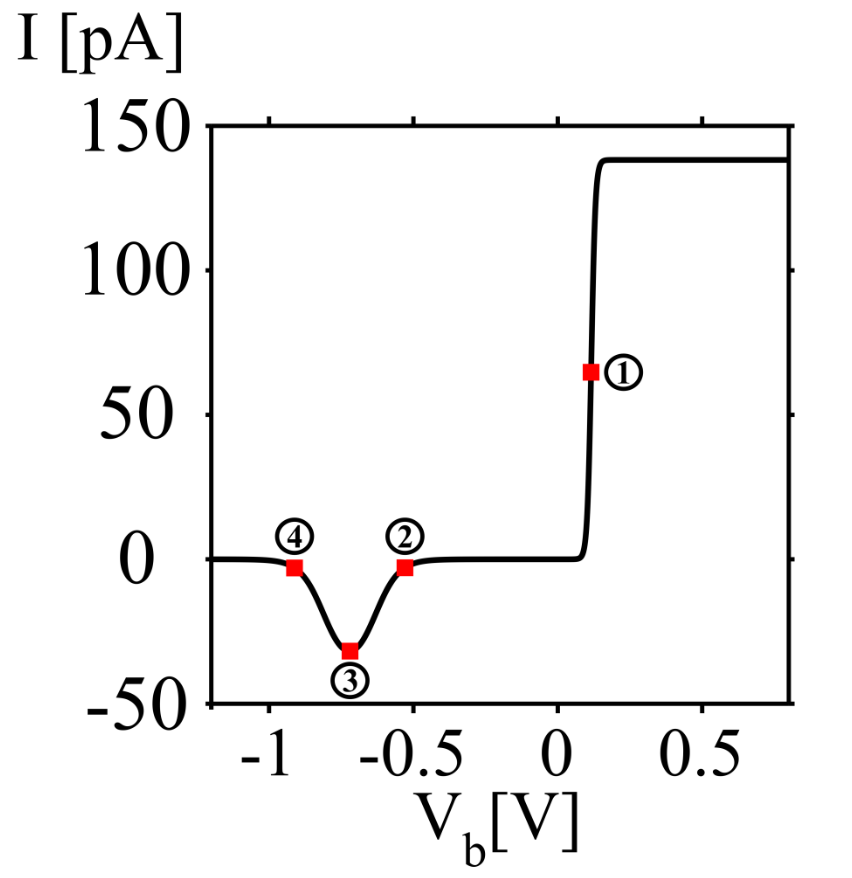
Tip tun.

Sub. tun.

Dynamics in energy space

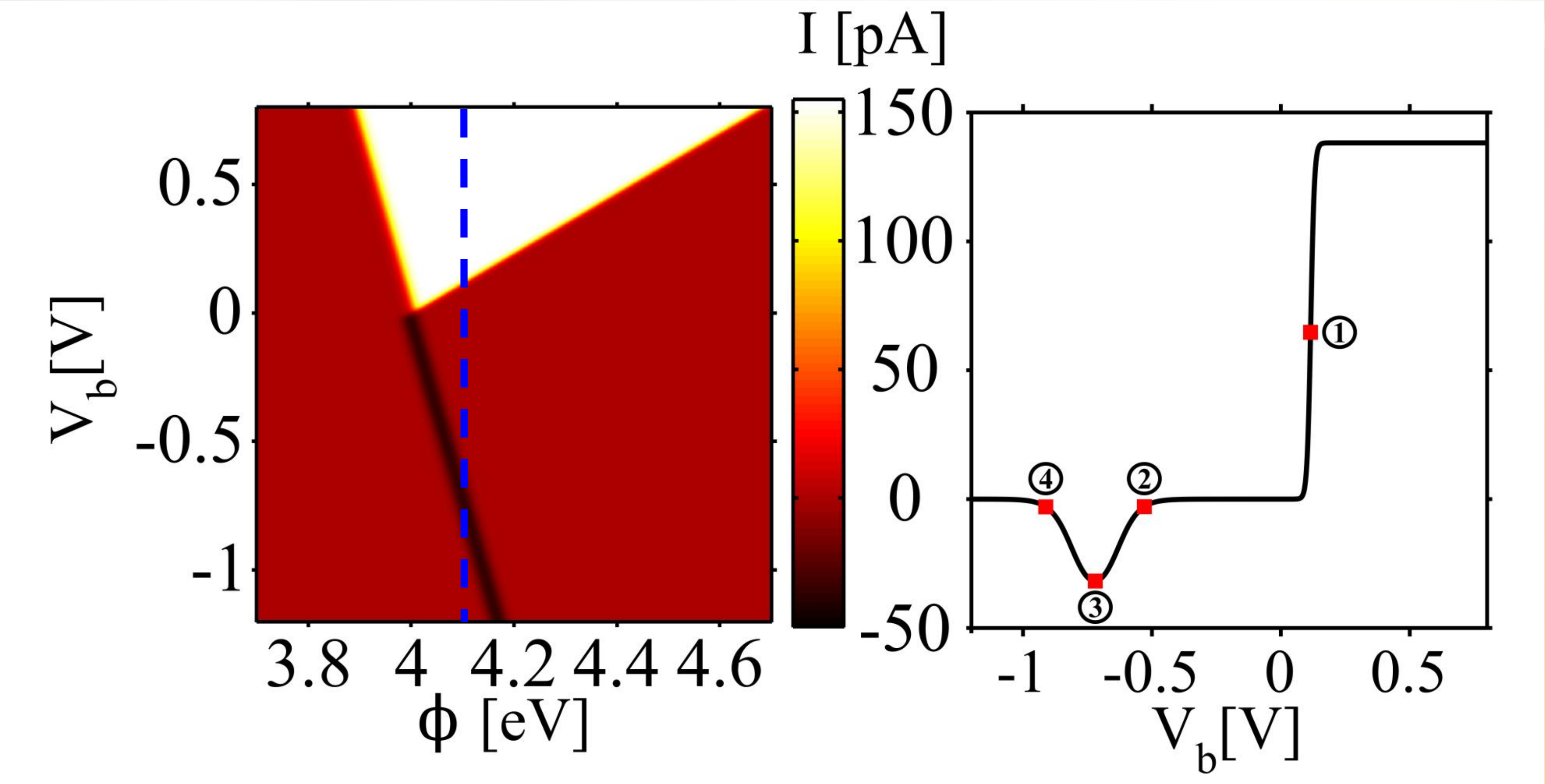


Interference blocking



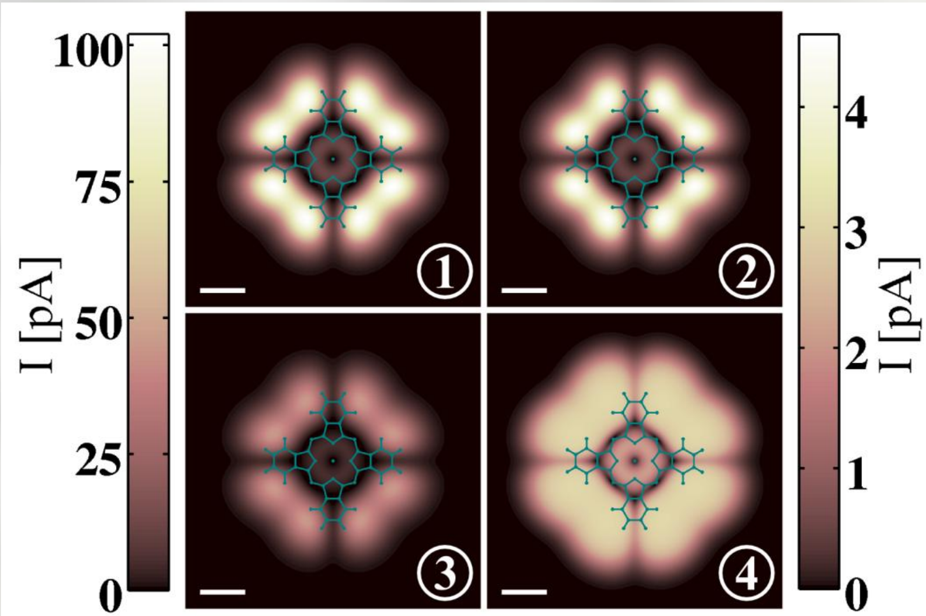
Donarini, Siegert, Sobczyk and Grifoni **Phys. Rev. B 86, 155451 (2012)**

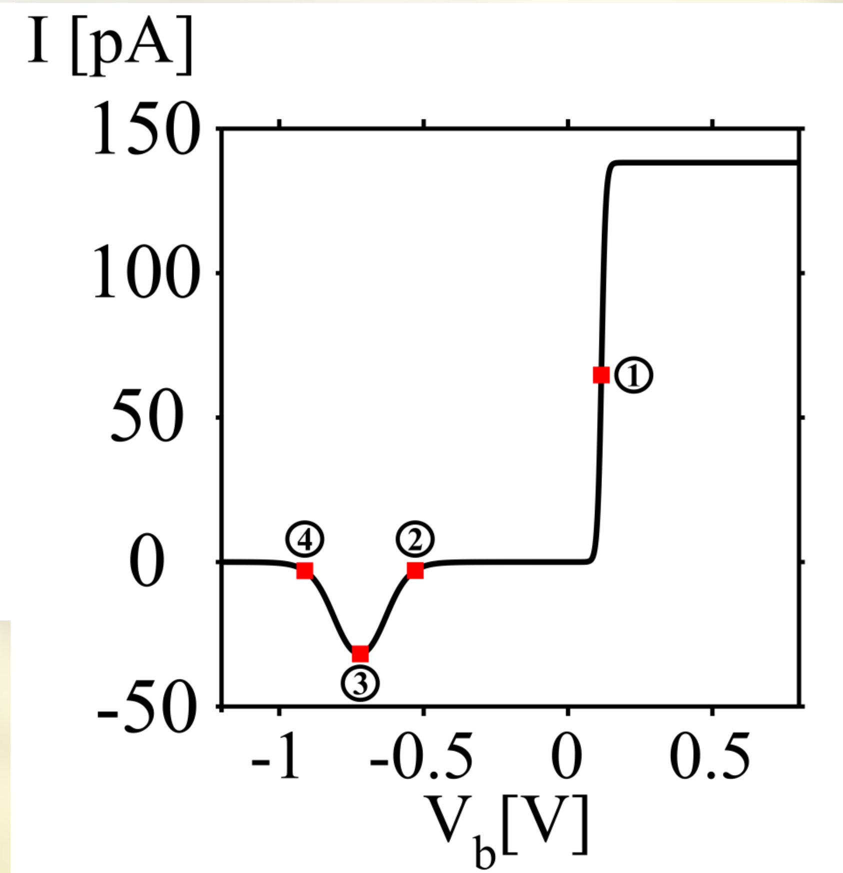
Interference blocking

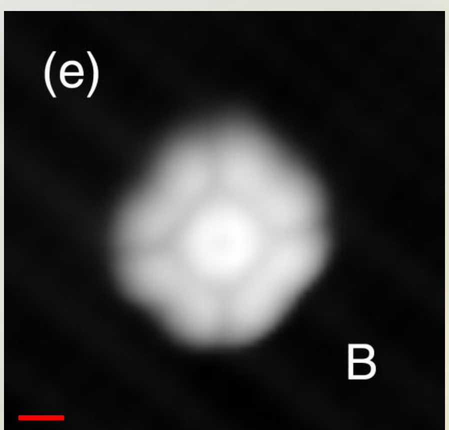


Donarini, Siegert, Sobczyk and Grifoni **Phys. Rev. B 86, 155451 (2012)**

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.

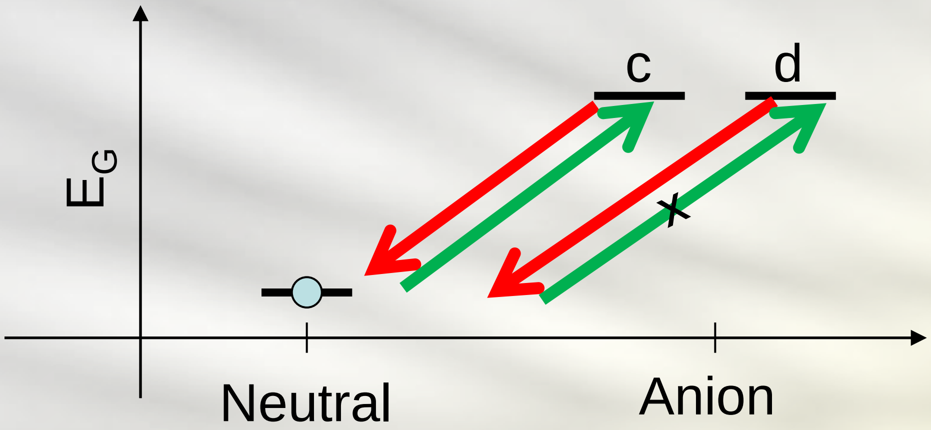
Interference: decoupling basis

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	$\ell = +1$, $\ell = -1$ $\mathbf{R}^T = R_0^T \begin{pmatrix} 1 & e^{-2i\phi} \\ e^{+2i\phi} & 1 \end{pmatrix}$ **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	$\tilde{\mathbf{R}}^S = R_0^S \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$

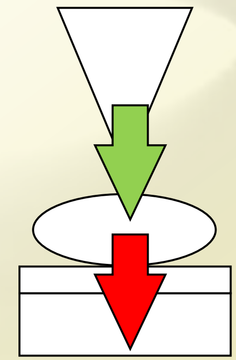
Notice that the decoupling basis **depends** on the **tip position**.

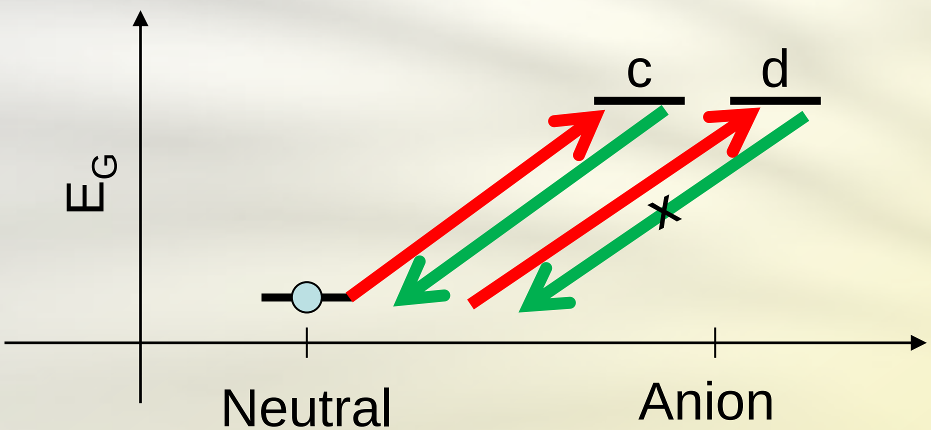
Interference: current blocking



$$V_b > -\Delta E_G/ec$$

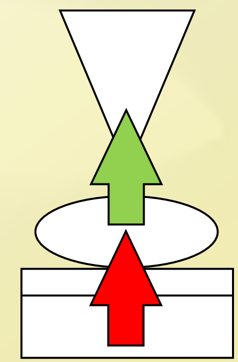
Current





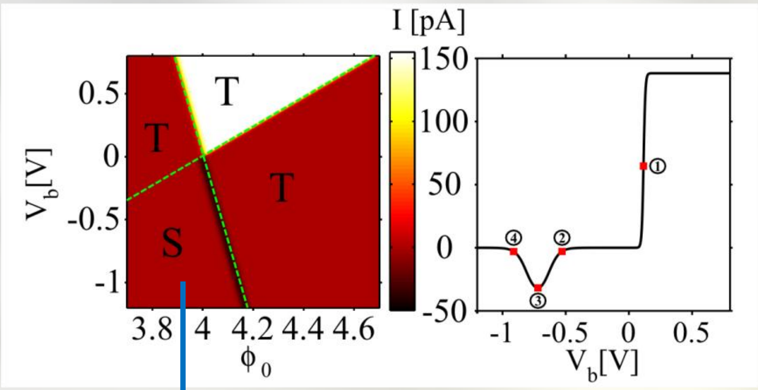
$$V_b < \Delta E_G/e(1-c)$$

No current

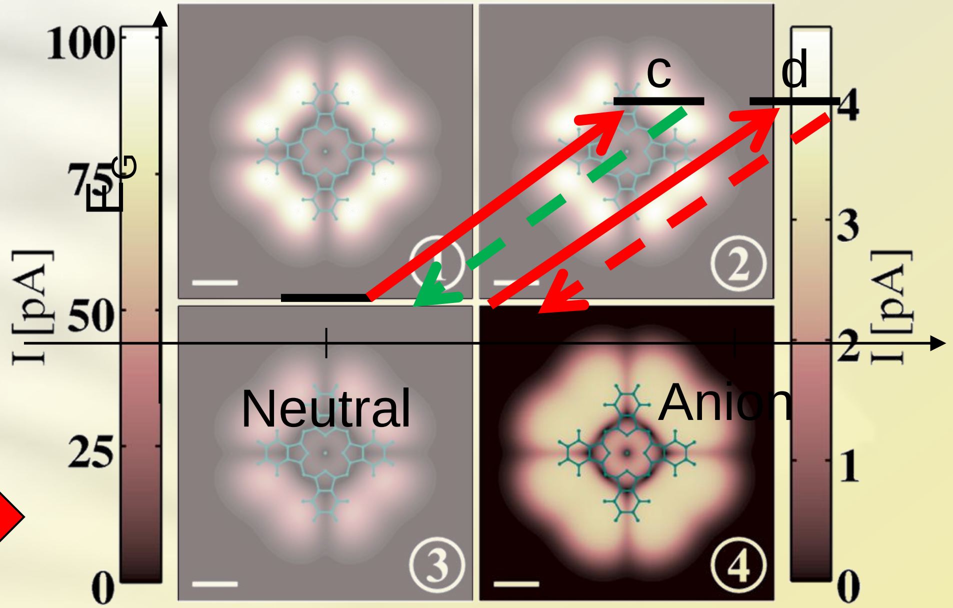


$$\mu_T = \mu_0 - c\,eV_b \qquad \mu_S = \mu_0 + (1-c)eV_b \qquad c \approx 0.9$$

A new bottle-neck process

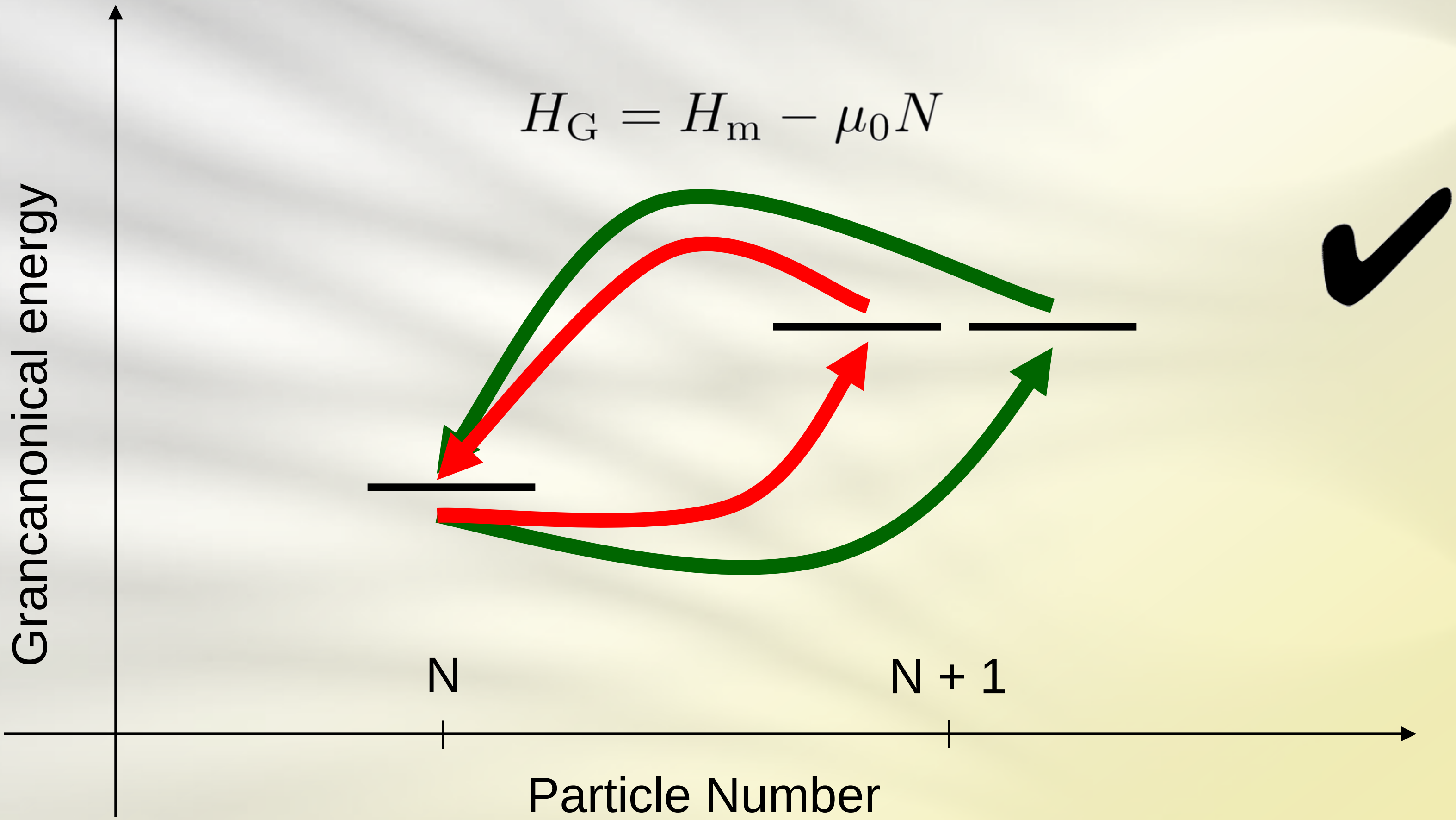


$$I_{\mathrm{IB}} = e\frac{R_0^S f_S^- R_0^T f_T^-}{R_0^S f_S^- + R_0^T f_T^-}$$



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

Interfernce + weak coupling



Donarini, Begemann, and Grifoni, *Phys. Rev. B* **82,** 125451 (2010)

Conclusions

- Interference effects survive in weakly coupled correlated systems in presence of **spatial symmetries** with associated **degenerate many-body states**.

- In STM single molecule junctions we identify two correlated fingerprints of many-body interference:

1. strong **negative differential conductance** and **current blocking** at negative sample biases.

2. **flat constant height current maps** in the vicinity of the interference blocking, indicating that the substrate tunnelling event becomes the new bottle-neck transport process.

Thanks

Milena Grifoni

Benjamin Siegert

Sandra Sobczyk

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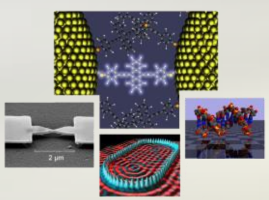


SPP 1243 Quantum Transport at the molecular scale

SFB 689

SFB 689 Spinphenomena in reduced dimensions

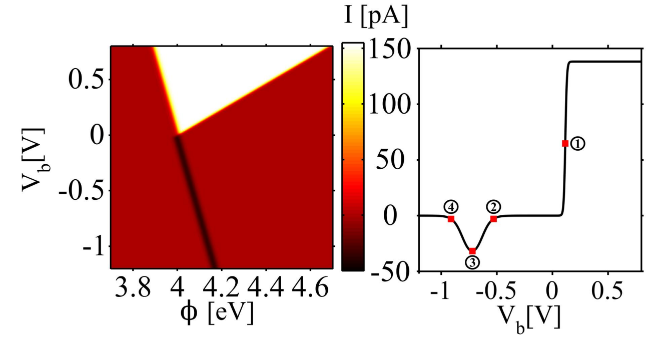
Thank you for your attention...

Regensburg, 10.04.2013

Dynamics in a reduced space

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

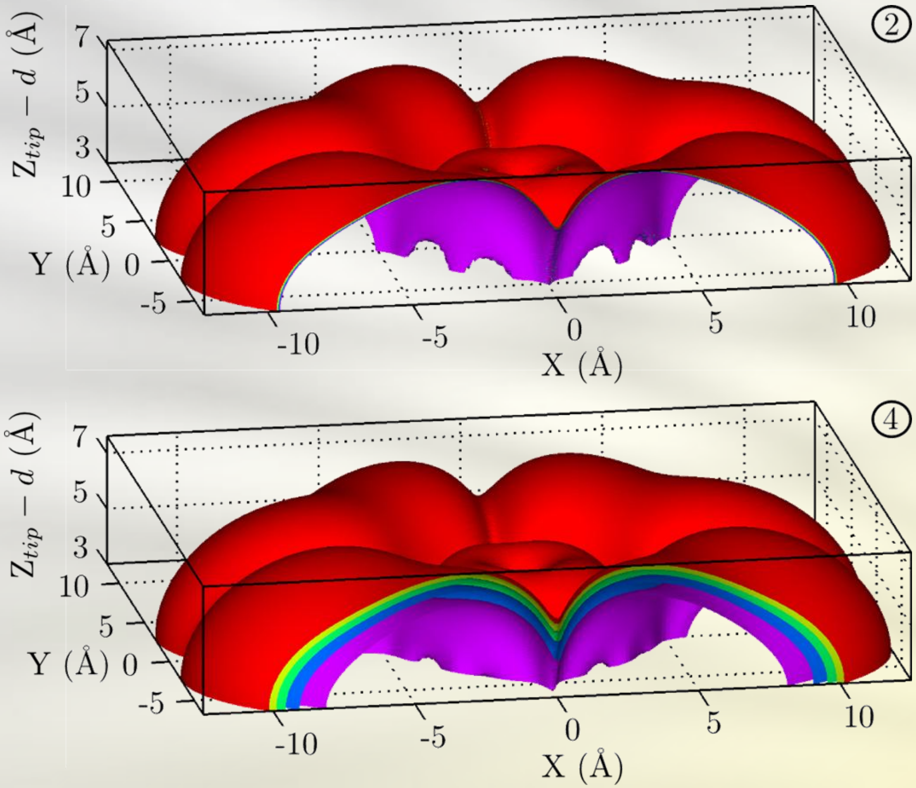
$$I(\vec{R}_{\mathrm{tip}}, V_{\mathrm{b}}) = 2eR^S f_S^+ \sigma^N \left(1 - \frac{\sigma_{\mathrm{c}}^{N+1\tau}}{\sigma_{\mathrm{d}}^{N+1\tau}} \right)$$

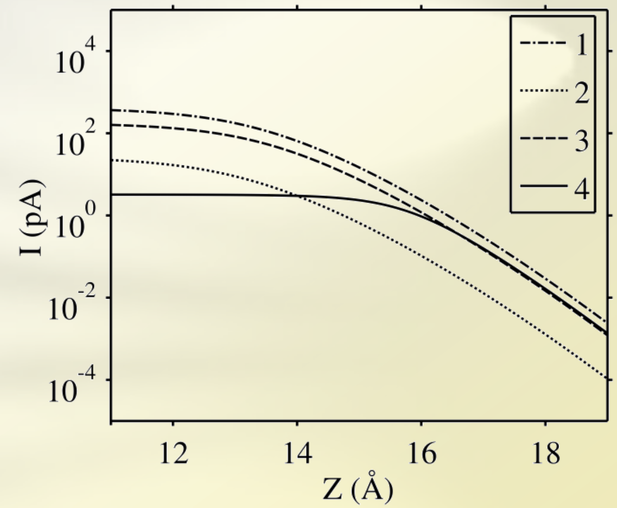


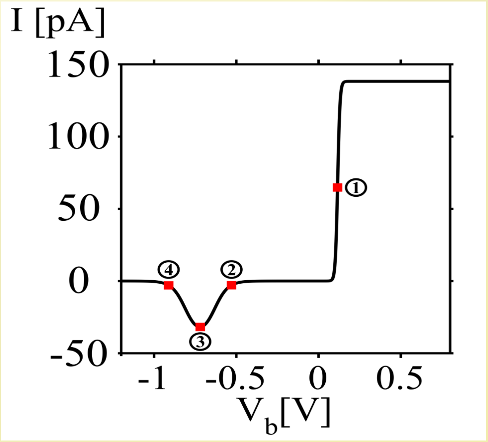
$$\sigma^N = \left(1 + 2\frac{R^S f_S^+ + 2R^T f_T^+}{R^S f_S^- + 2R^T f_T^-} + 2\frac{f_S^+}{f_S^-} \right)^{-1}$$

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

Constant current maps







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