Topographical fingerprints of many-body interference blocking in STM junctions on thin insulating films

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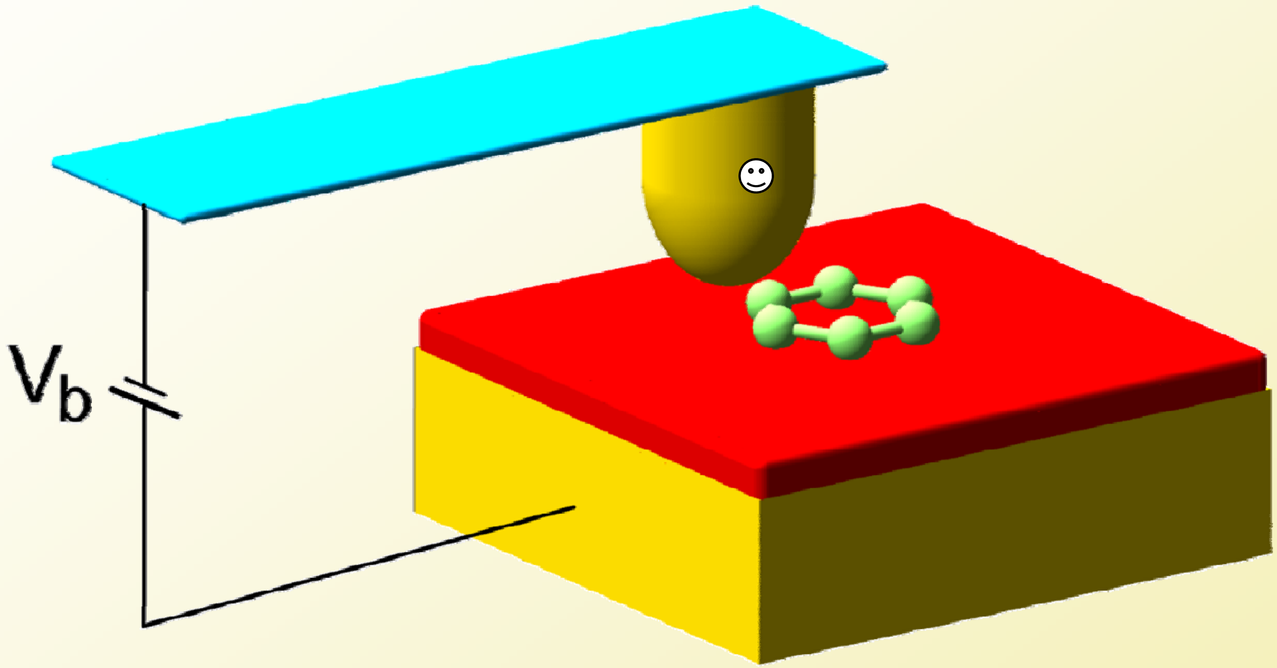
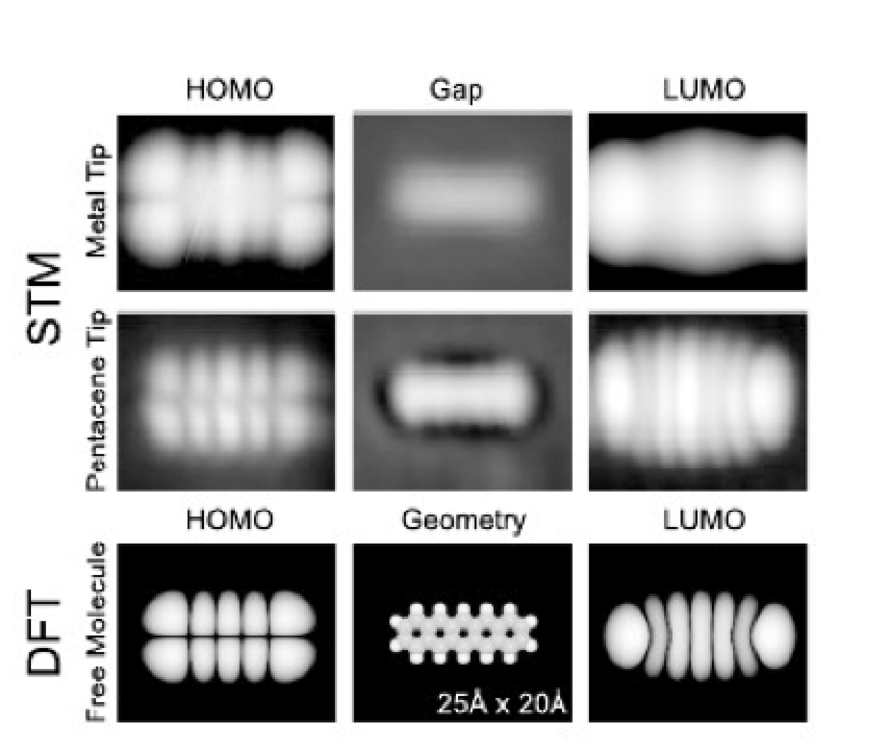
STM on thin insulating films



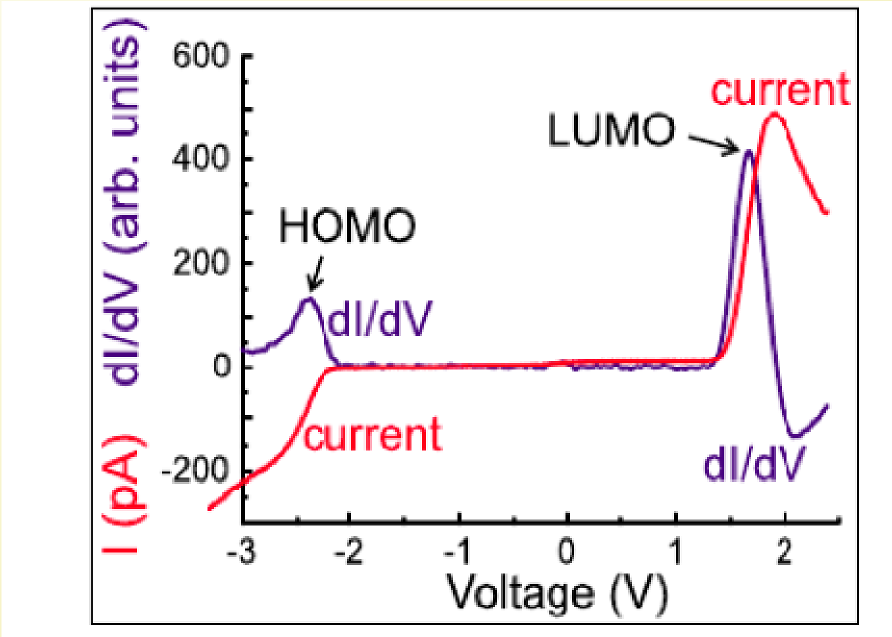
Weak tip-molecule **tunnelling coupling**
Low molecule-substrate **hybridization** ➡ **sequential tunnelling**

Visualization of molecular orbitals

Topography



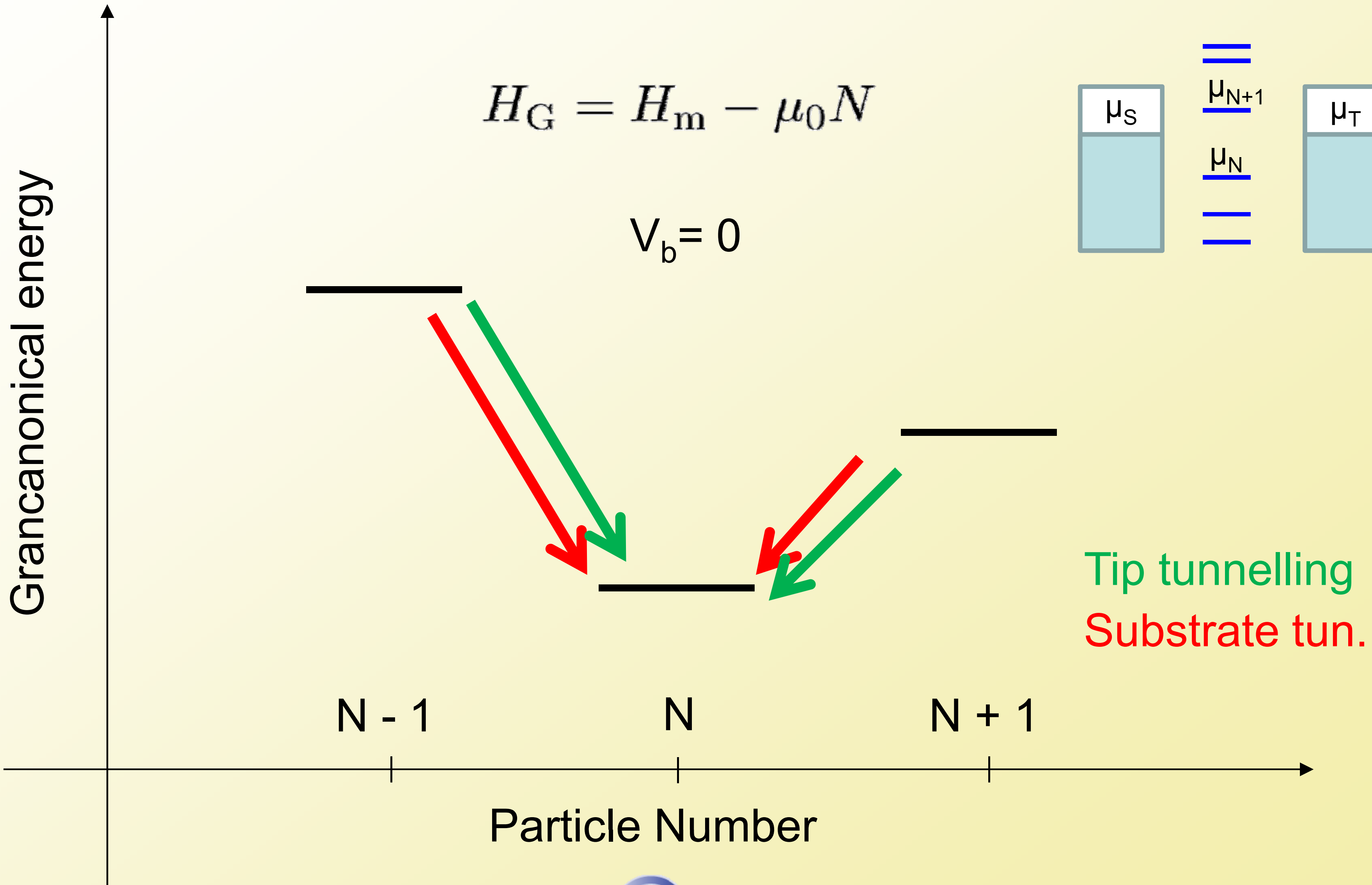
Spectroscopy



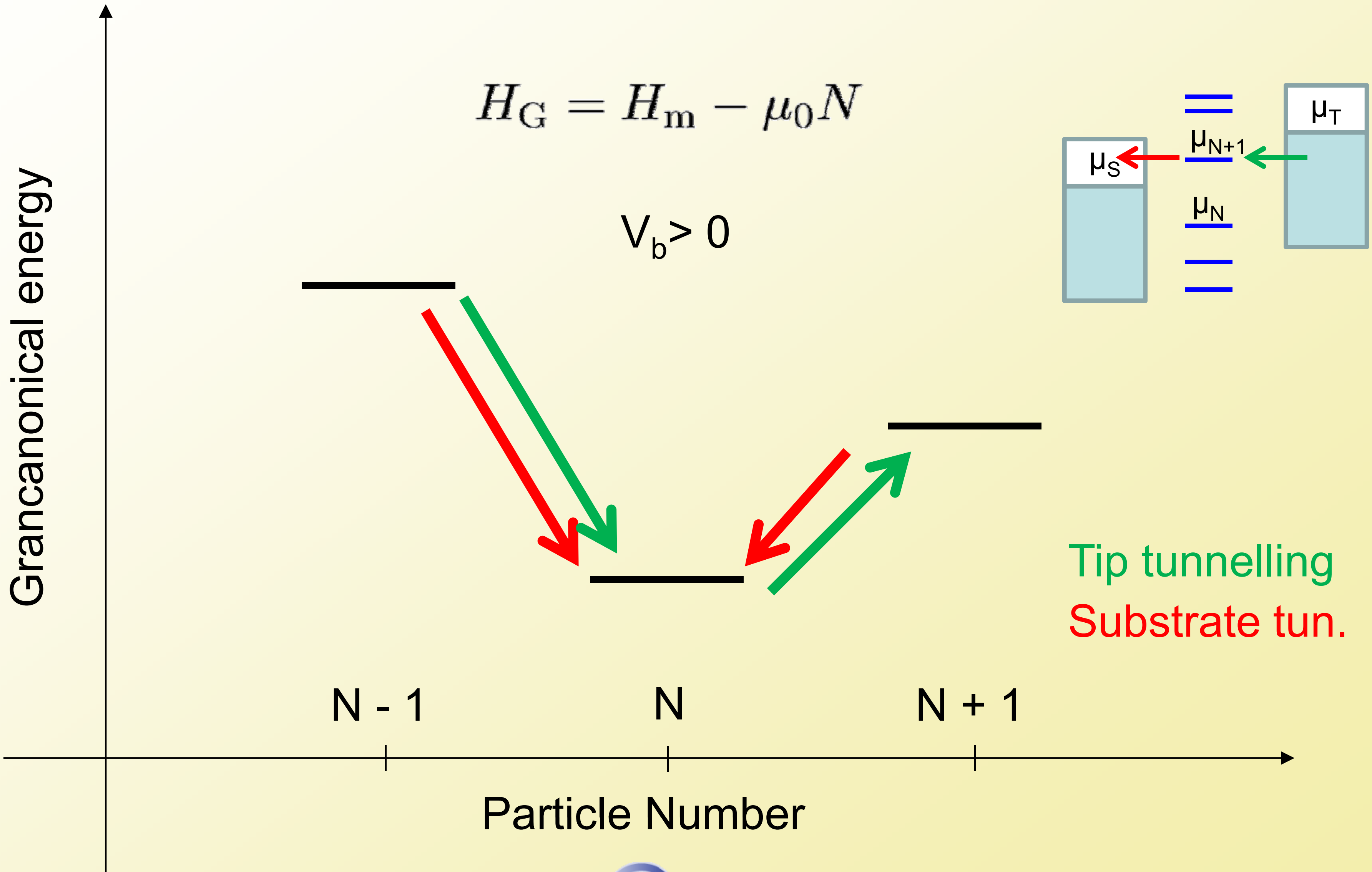
J. Repp and G. Meyer, Physical Review Letters **94**, 026803 (2005)

Dynamics in energy space

$$H_G = H_m - \mu_0 N$$



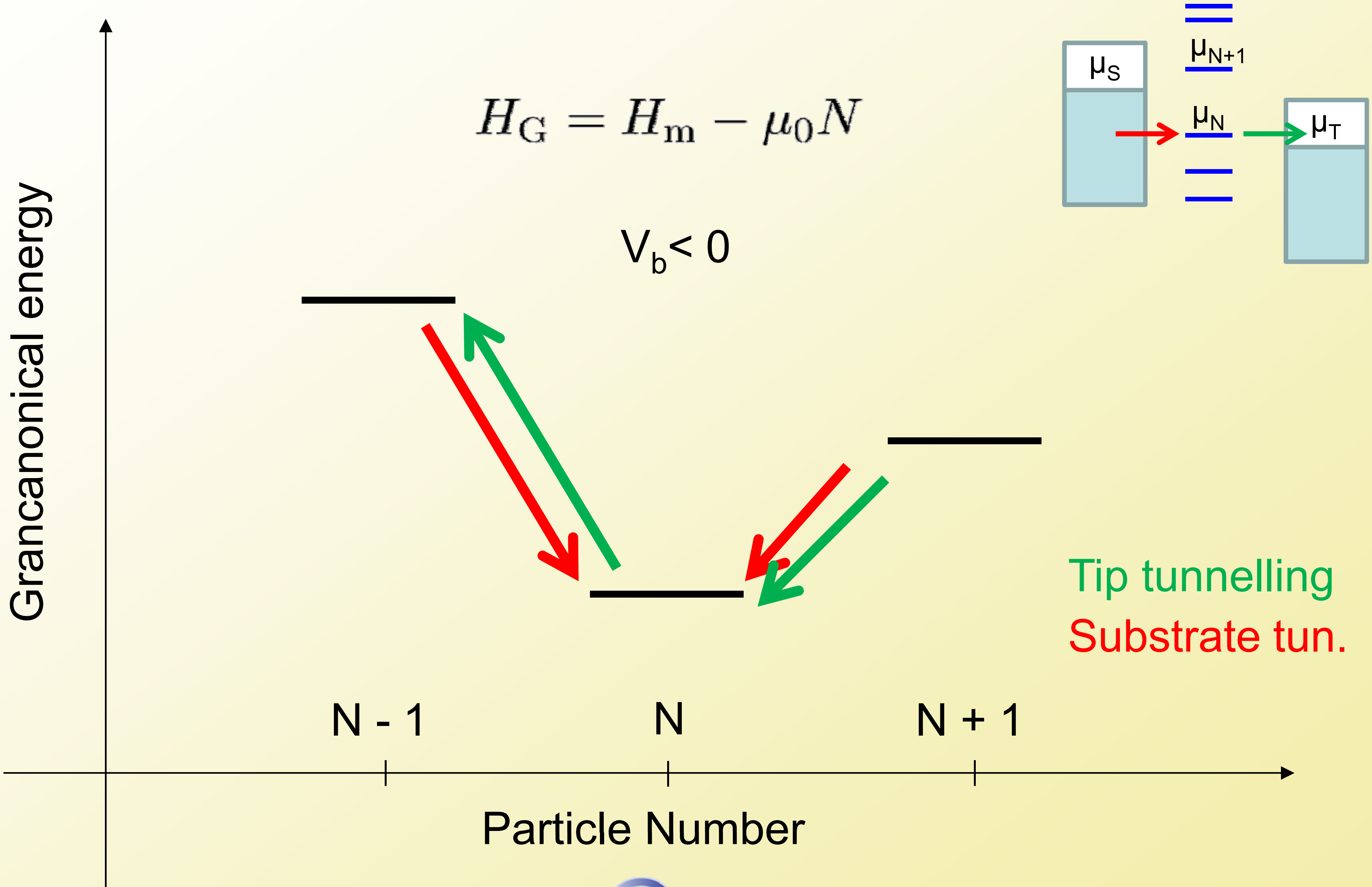
Dynamics in energy space



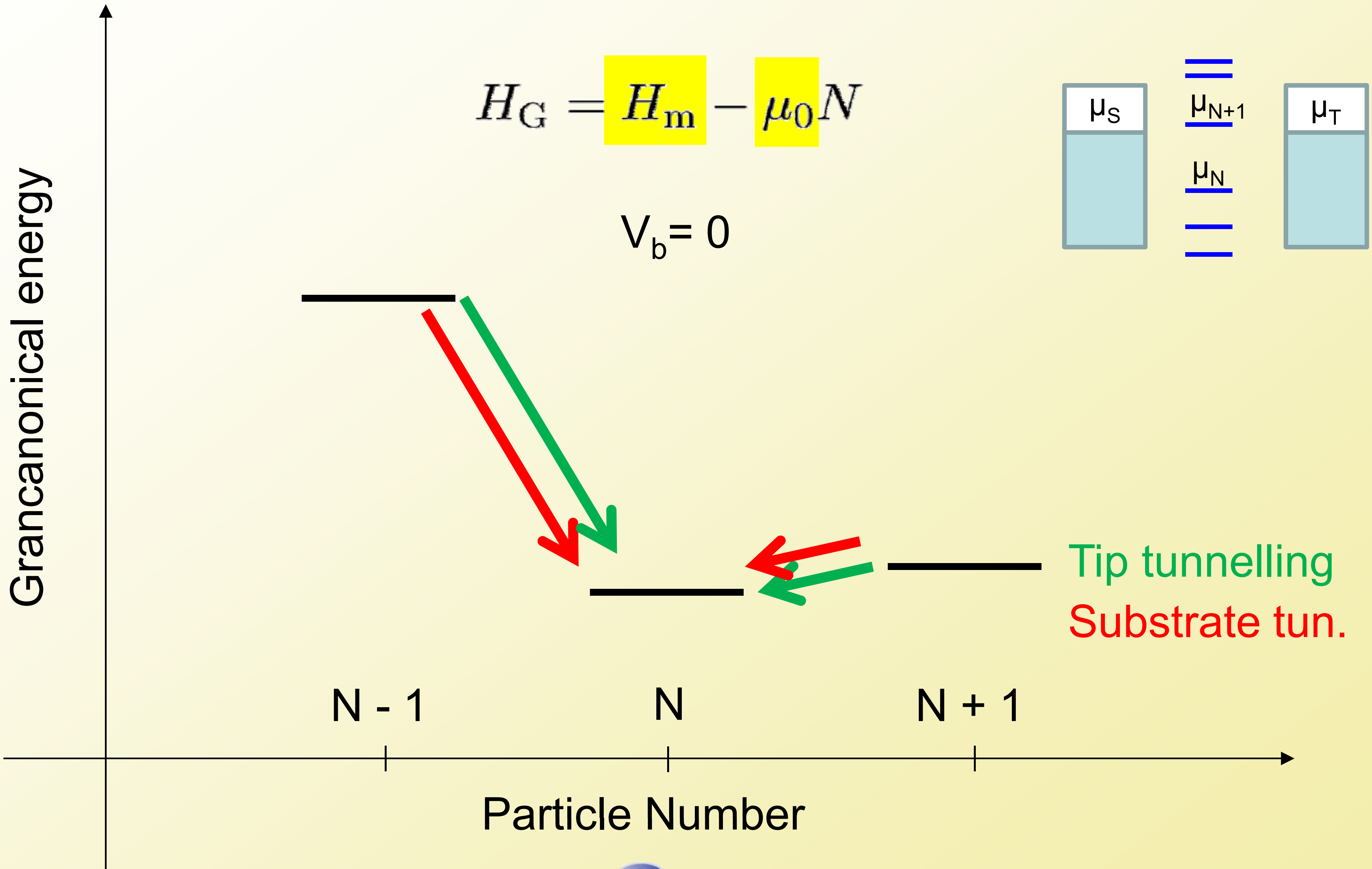
Dynamics in energy space

$$H_G = H_m - \mu_0 N$$

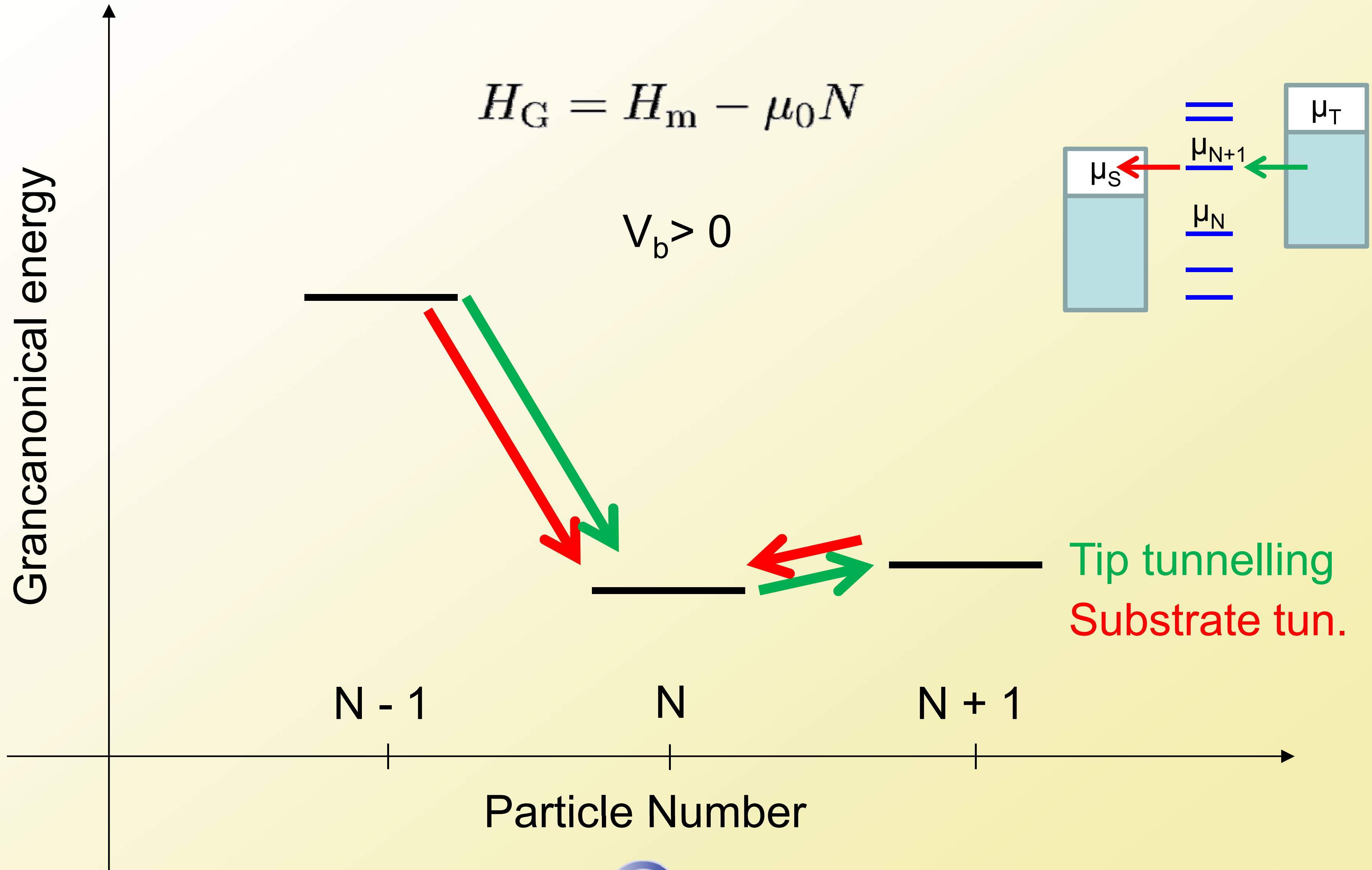
$V_b < 0$



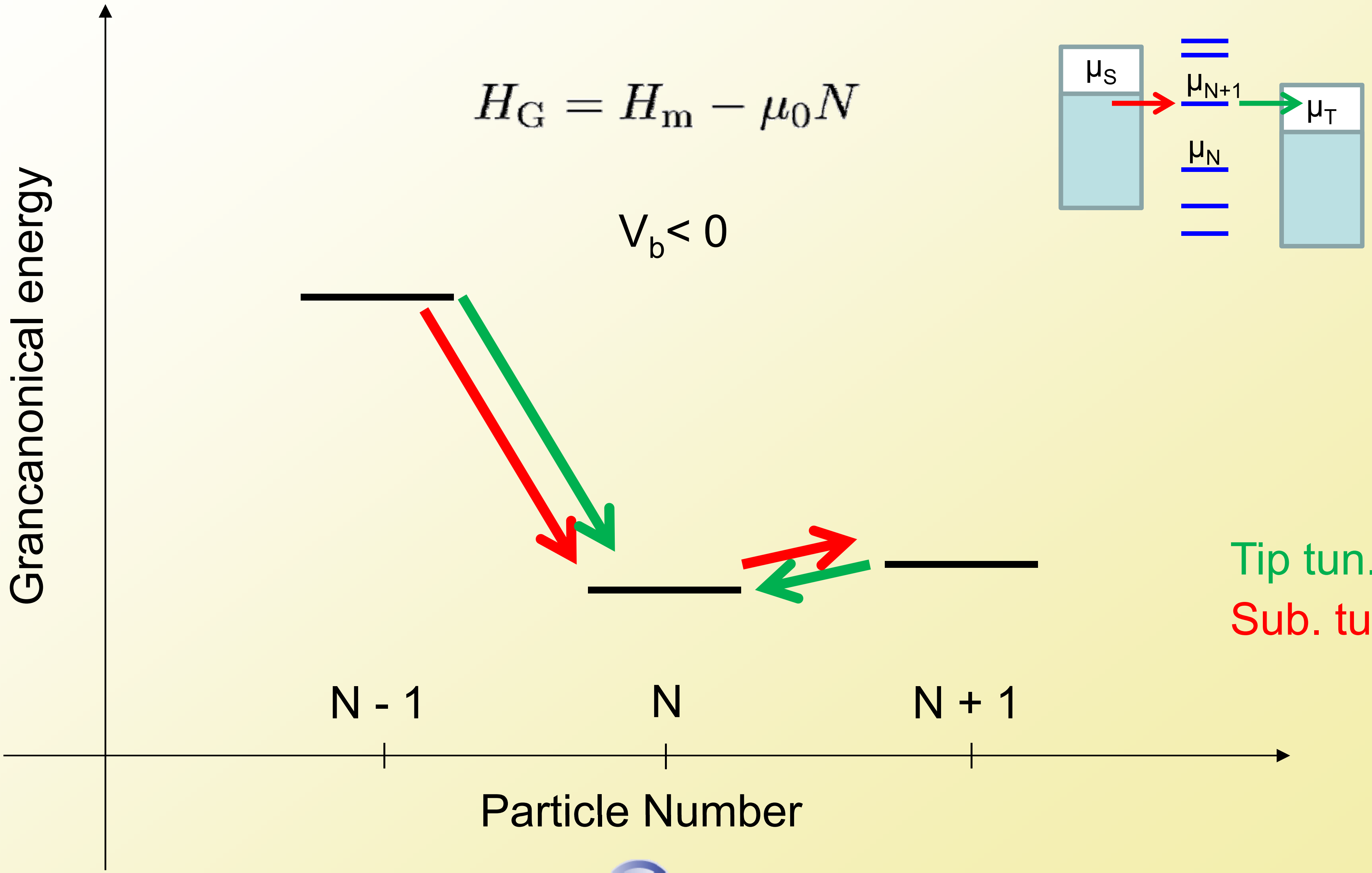
Dynamics in energy space



Dynamics in energy space



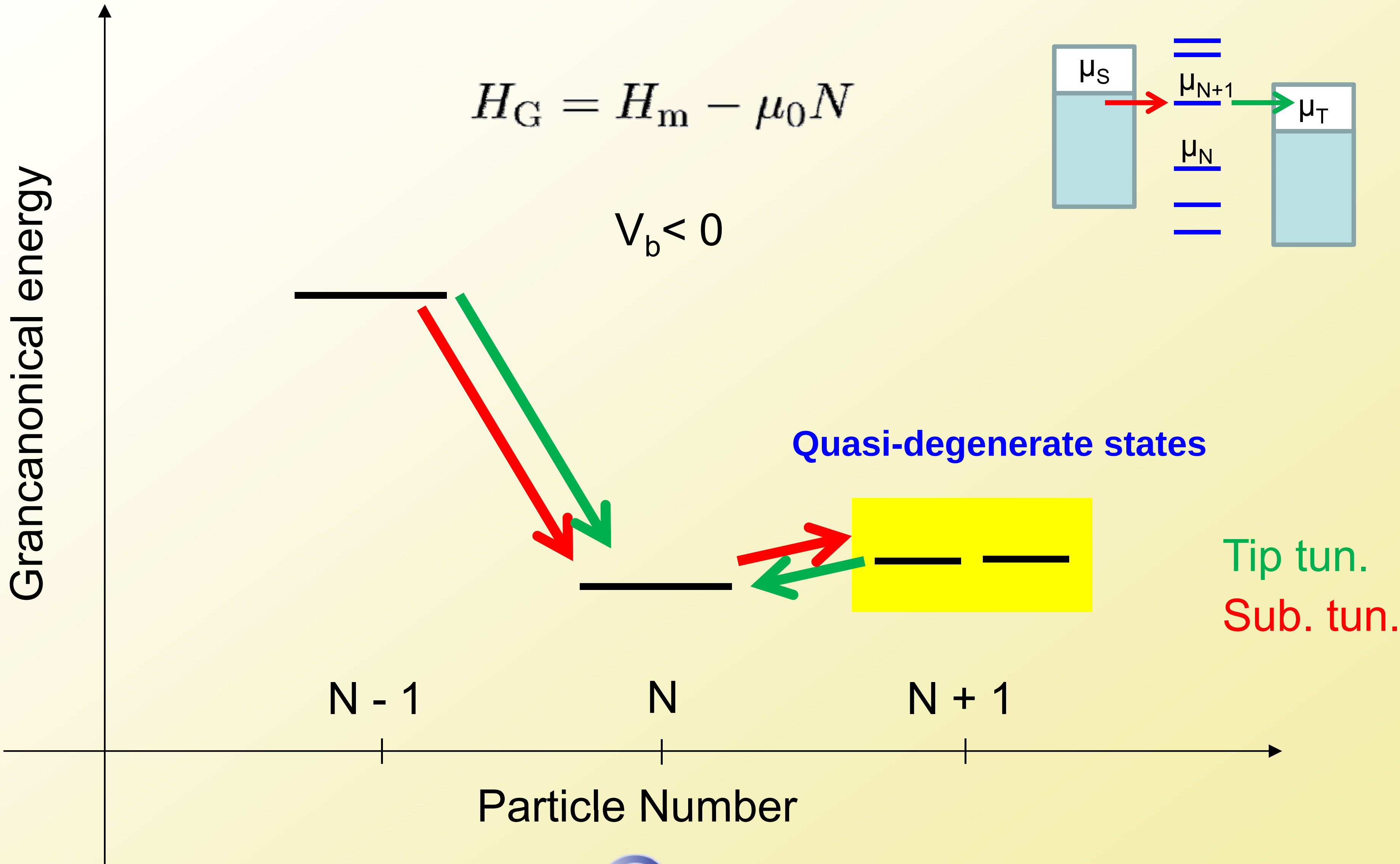
Dynamics in energy space



Tip tun.
Sub. tun.

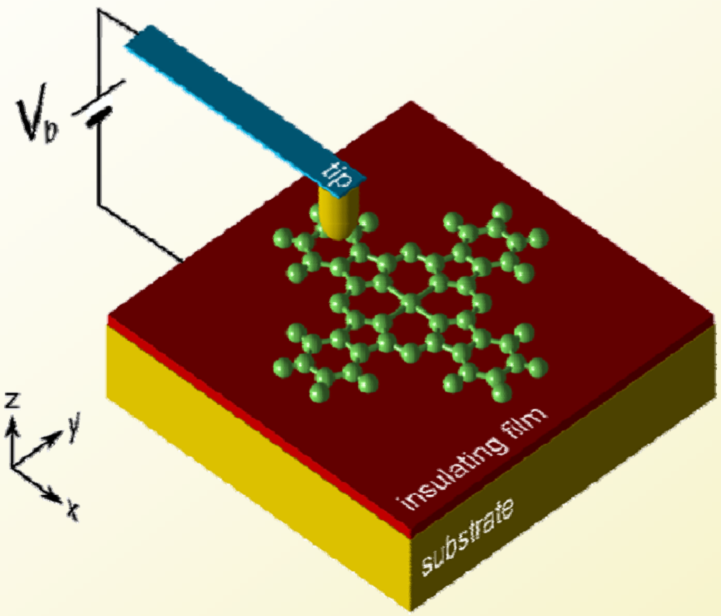
Dynamics in energy space

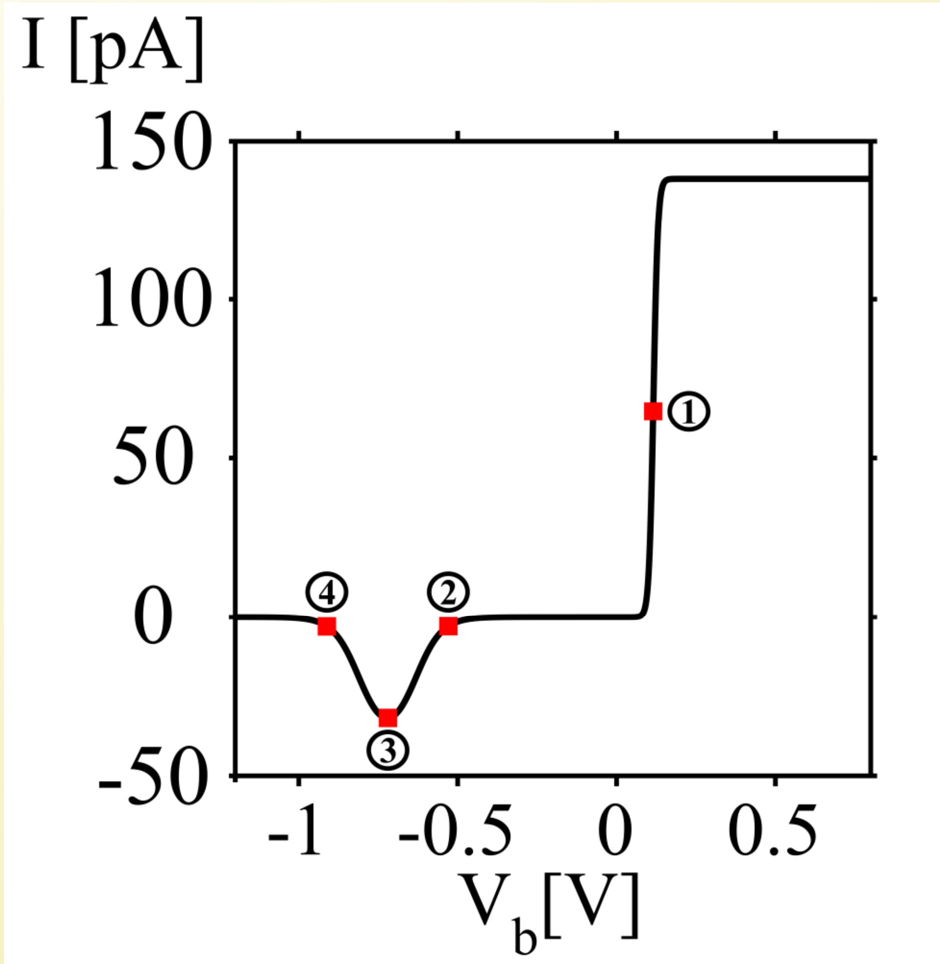
$$H_{\mathrm{G}} = H_{\mathrm{m}} - \mu_0 N$$



Interference blocking

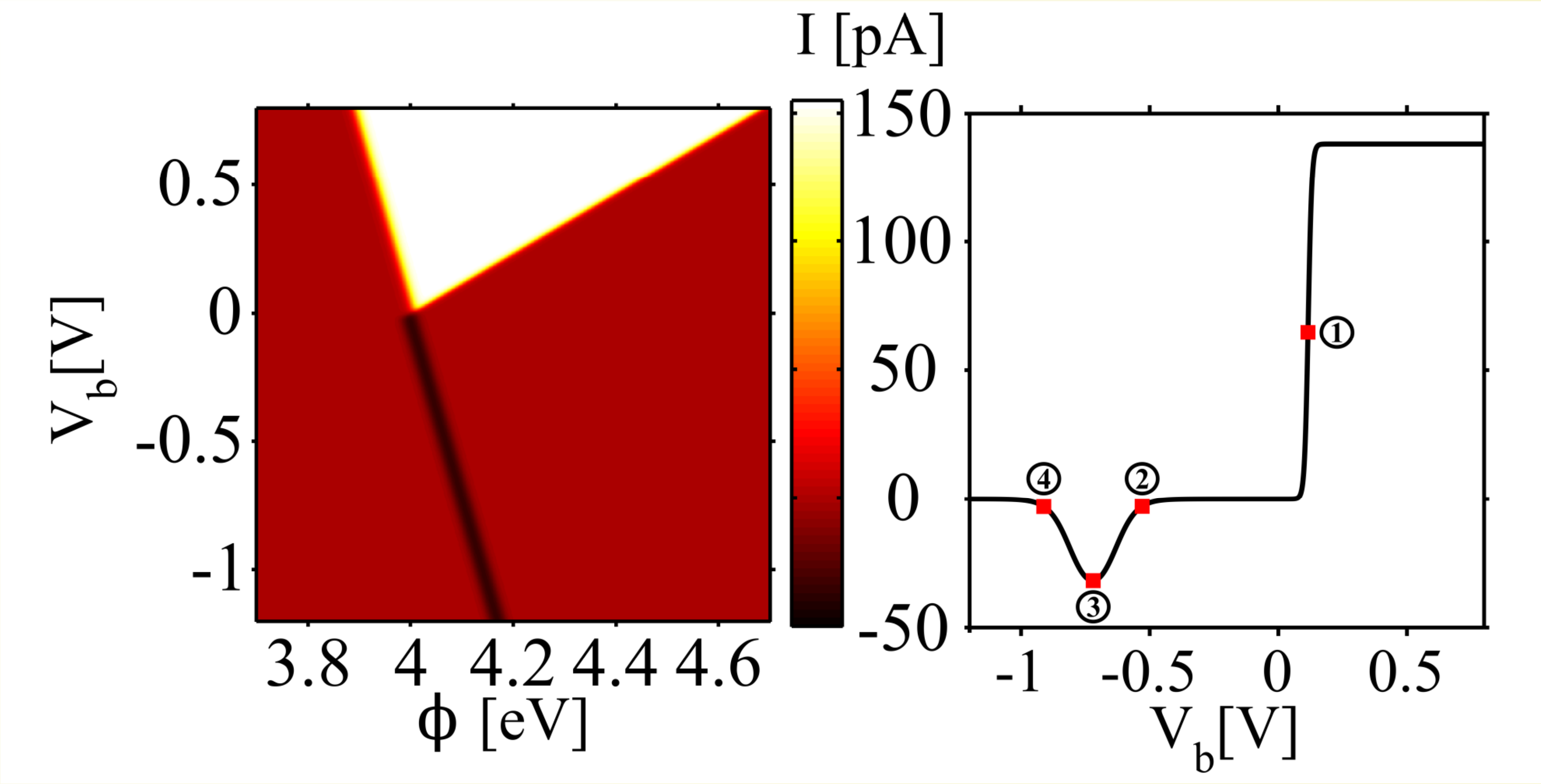
Cu - Phthalocyanine





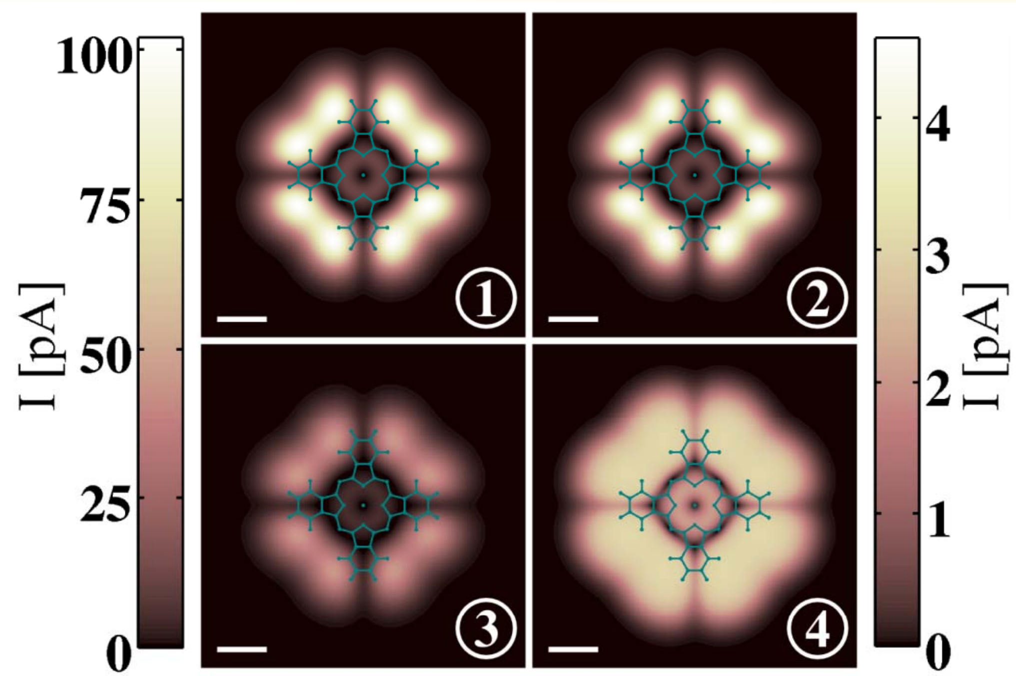
Donarini, Sobczyk, Siegert, and Grifoni **arXiv:1206.2664 (2012)**

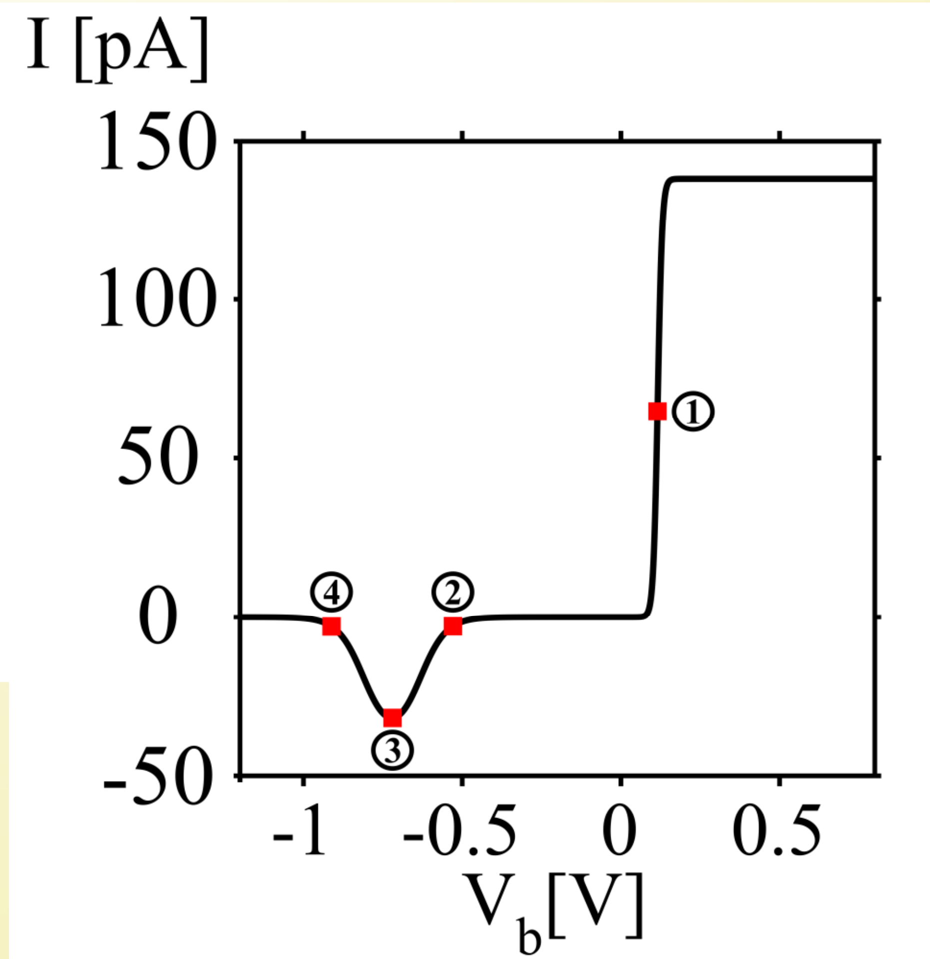
Interference blocking

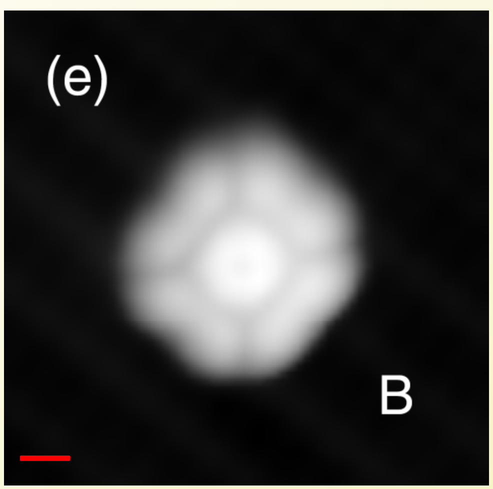


Donarini, Sobczyk, Siegert, and Grifoni **arXiv:1206.2664 (2012)**

Topographical fingerprint







Experiment:
Cu-Pc on t
wo-atomic-layer NaBr

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

Donarini, Sobczyk, Siegert, and Grifoni
arXiv:1206.2664 (2012)

Interference blocking

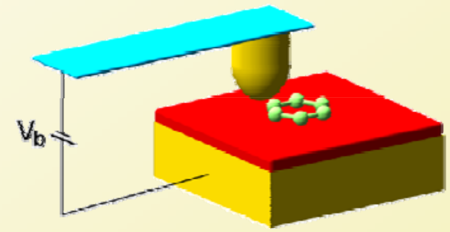
Necessary conditions:

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.

The total Hamiltonian



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

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

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

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

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

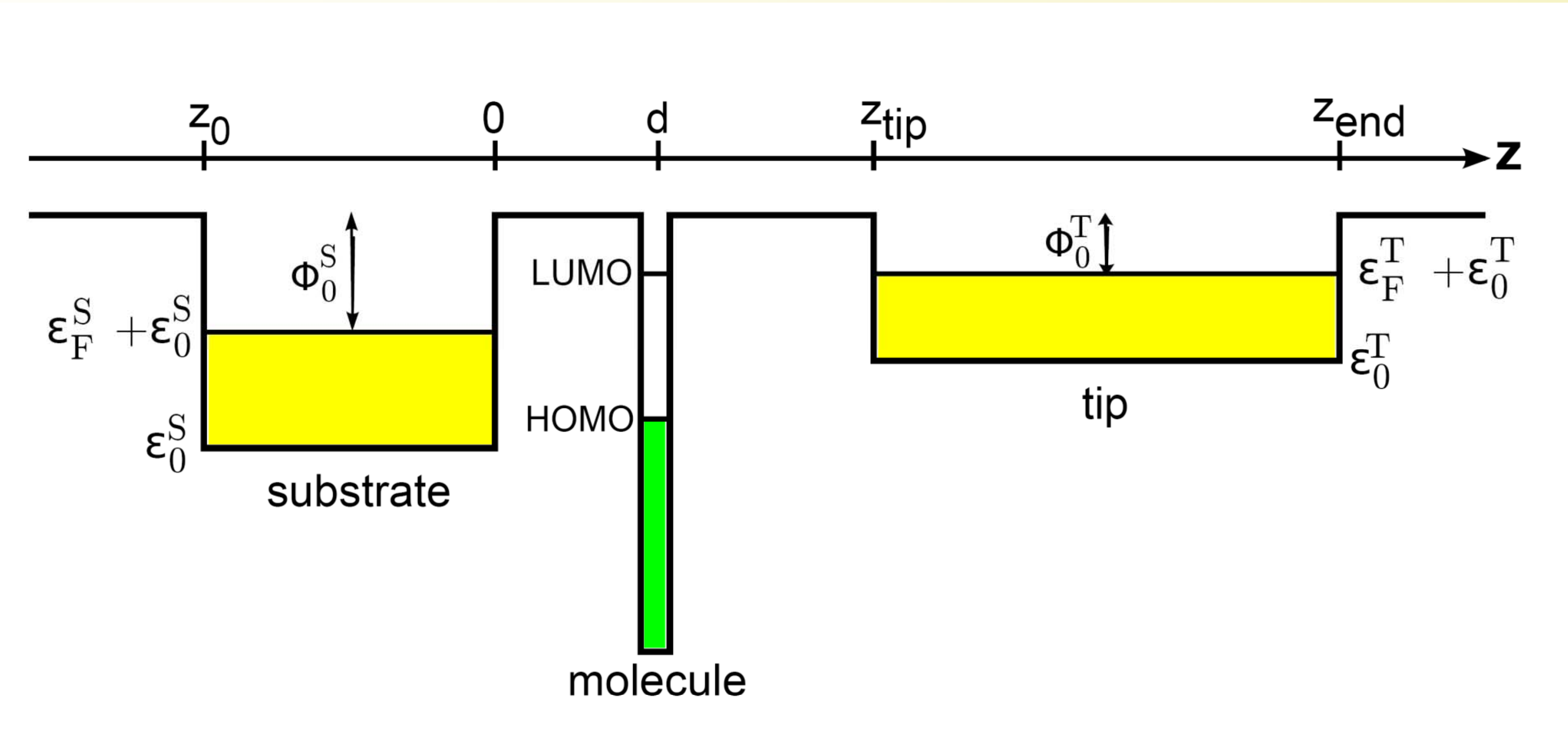
It is a **single particle** operator

Molecular orbital

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

Tunnelling amplitudes

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



Tunnelling amplitudes (ii)

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

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

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 molecule

Tunnelling amplitudes (iii)

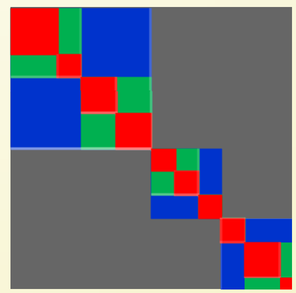
$$t^S_{ki} = \varepsilon_i \underbrace{\sum_\alpha \mathrm{e}^{-\mathrm{i}\vec{k}_{||}\cdot\vec{R}_\alpha}}_{\text{Coherent superposition}} O_S(\vec{k}) \underbrace{\langle\alpha\sigma|i\sigma\rangle}_{\text{Molecular to atomic basis}}$$

$$t^T_{ki} = \varepsilon_i \sum_\alpha O_T(k_z, \vec{R}_{\mathrm{tip}} - \vec{R}_\alpha)\langle\alpha\sigma|i\sigma\rangle$$

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

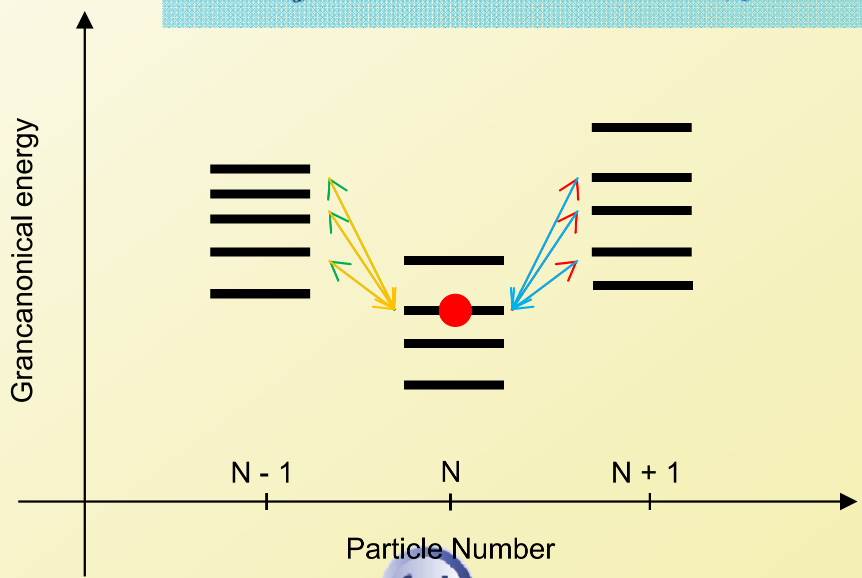
- We keep the coherences between orbitally degenerate states.

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

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

Tunnelling Liouvillean

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



Tunnelling rate matrix

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

Effective Hamiltonian

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

Current operator

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

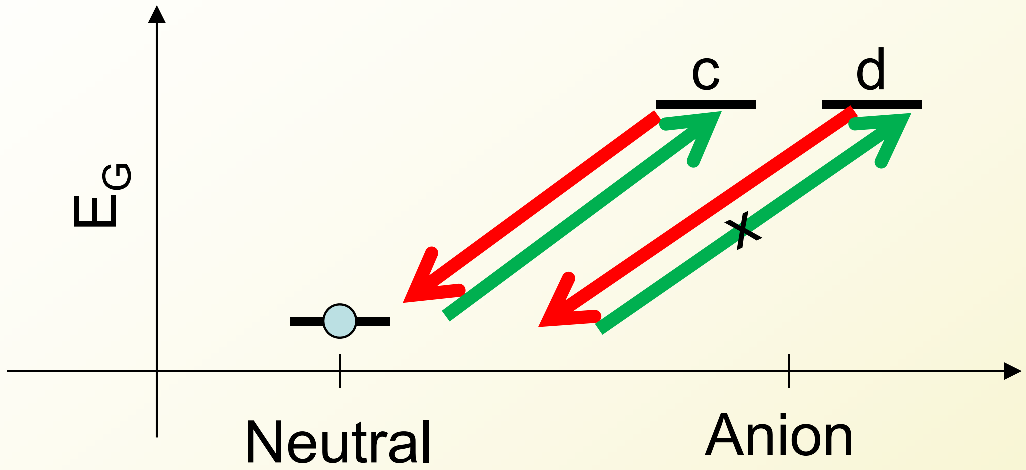
Interference: decoupling basis

Let us concentrate on the Neutral $\leftrightarrow$ Anion transition (Neglecting spin) of a Cu-Phthalocyanine molecule (rotationally symmetric)

	Angular momentum basis	Decoupling basis
Tip	$\mathbf{\Gamma}^T = \Gamma_l^T \begin{pmatrix} 1 & e^{-2i\phi_l} \\ e^{+2i\phi_l} & 1 \end{pmatrix}$	$\tilde{\mathbf{\Gamma}}^T = \Gamma_l^T \begin{pmatrix} 2 & 0 \\ 0 & 0 \end{pmatrix}$
Substrate	$\mathbf{\Gamma}^S = \Gamma_l^S \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\tilde{\mathbf{\Gamma}}^S = \Gamma_l^S \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$

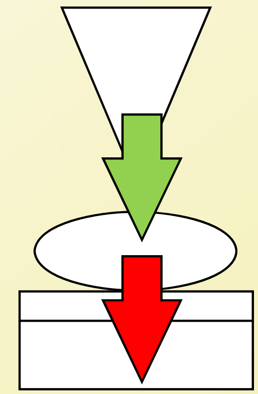
Notice that the decoupling basis depends on the position of the tip!

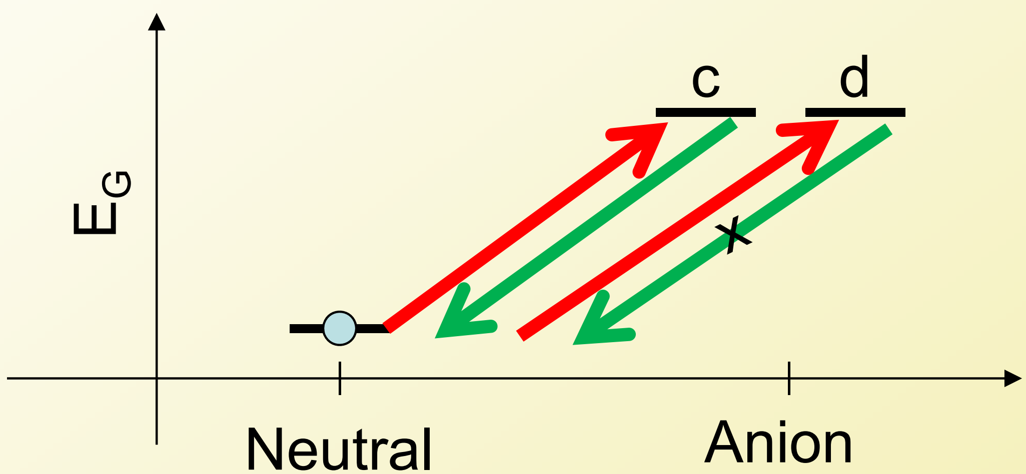
Interference: current blocking



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

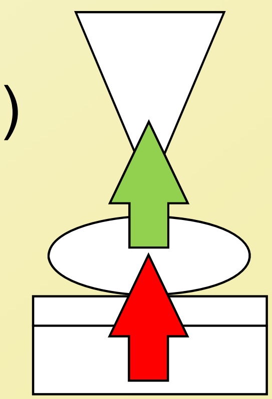
Current





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

No current



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

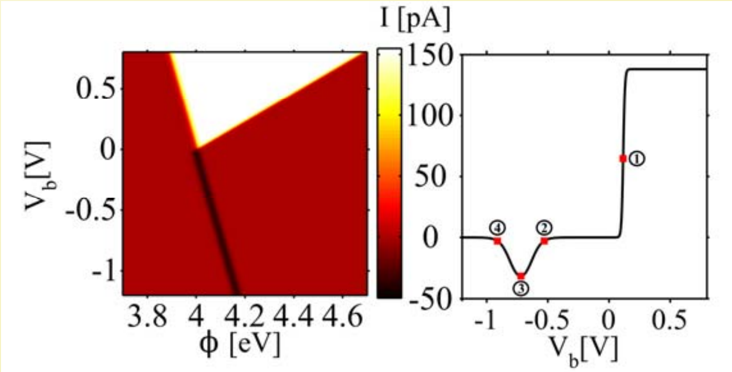
Dynamics in a reduced space

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

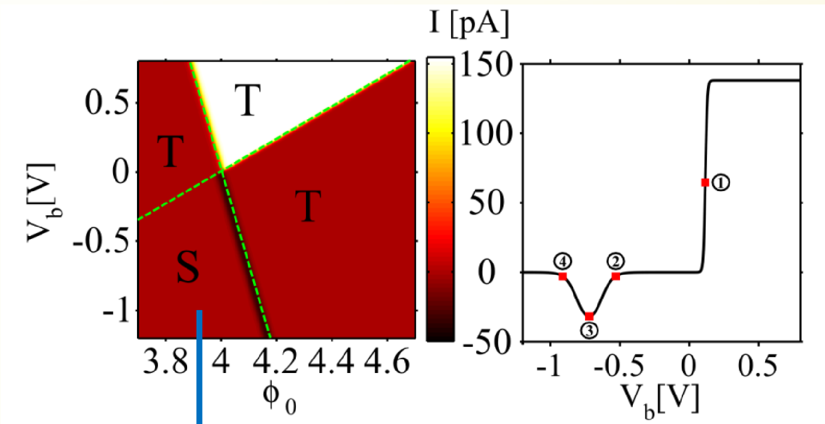
$$I(\vec{R}_{\mathrm{tip}}, V_{\mathrm{b}}) = 2eR^S f_S^+ \sigma^N \left(1 - \frac{\sigma_{\mathrm{c}}^{N+1\tau}}{\sigma_{\mathrm{d}}^{N+1\tau}}\right)$$

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

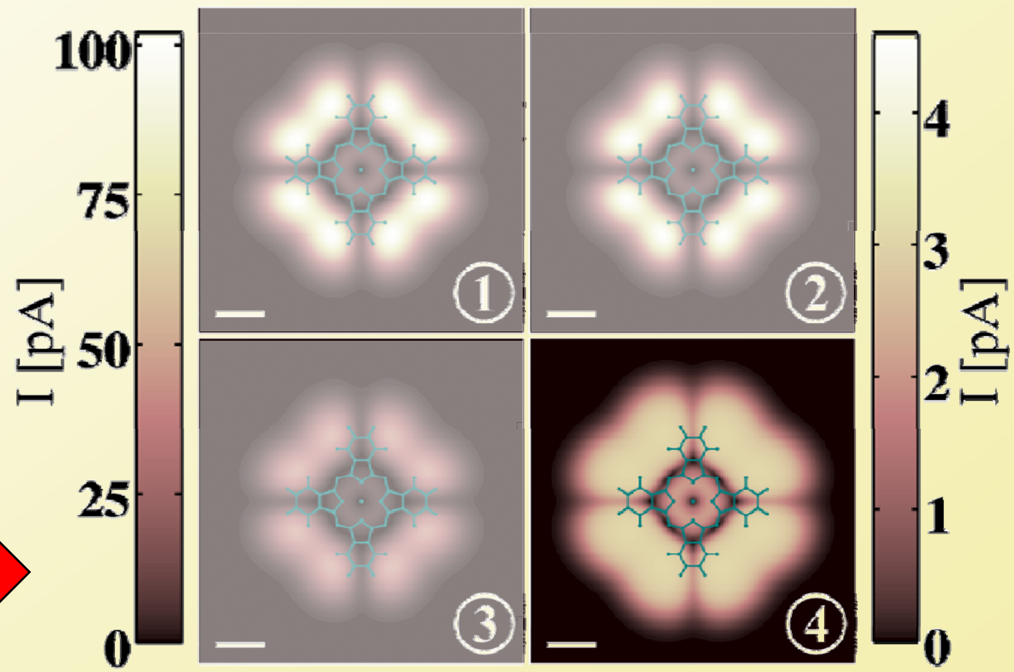
$$\frac{\sigma_{\mathrm{c}}^{N+1\tau}}{\sigma_{\mathrm{d}}^{N+1\tau}} = \frac{R^S f_S^+ + 2R^T f_T^+}{R^S f_S^- + 2R^T f_T^-} \cdot \frac{f_S^-}{f_S^+}.$$



A new bottle-neck process



$$I = \boxed{R^S f_S^-} \left(1 + \frac{R^S}{2R^T}\frac{f_S^-}{f_S^+}\right)^{-2}$$



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

Conclusions

- We developed a **semi-quantitative model** for the description of "weakly coupled" STM junctions with pi-conjugated molecules.
- The tunnelling dynamics is described in terms of tunnelling events connecting many-body states
- 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.

Thank you for your attention…