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

Andrea Donarini

Sandra Sobczyk and Milena Grifoni

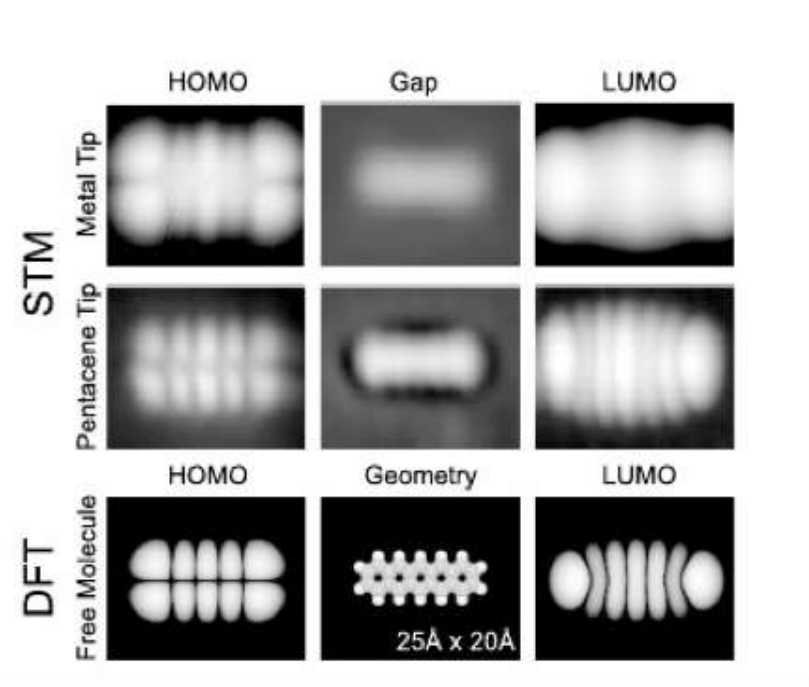
University of Regensburg, Germany

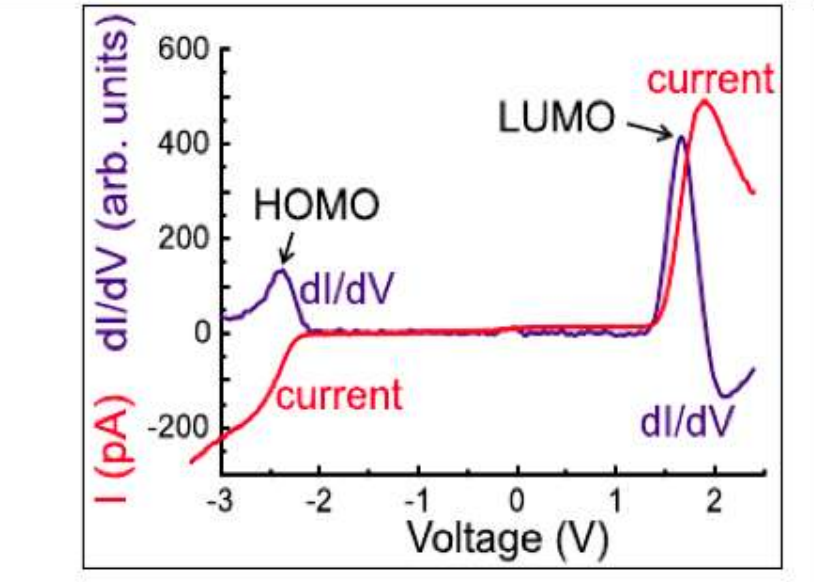
Theory Group Seminar - DTU - 05.03.2012

Visualization of molecular orbitals

Topography

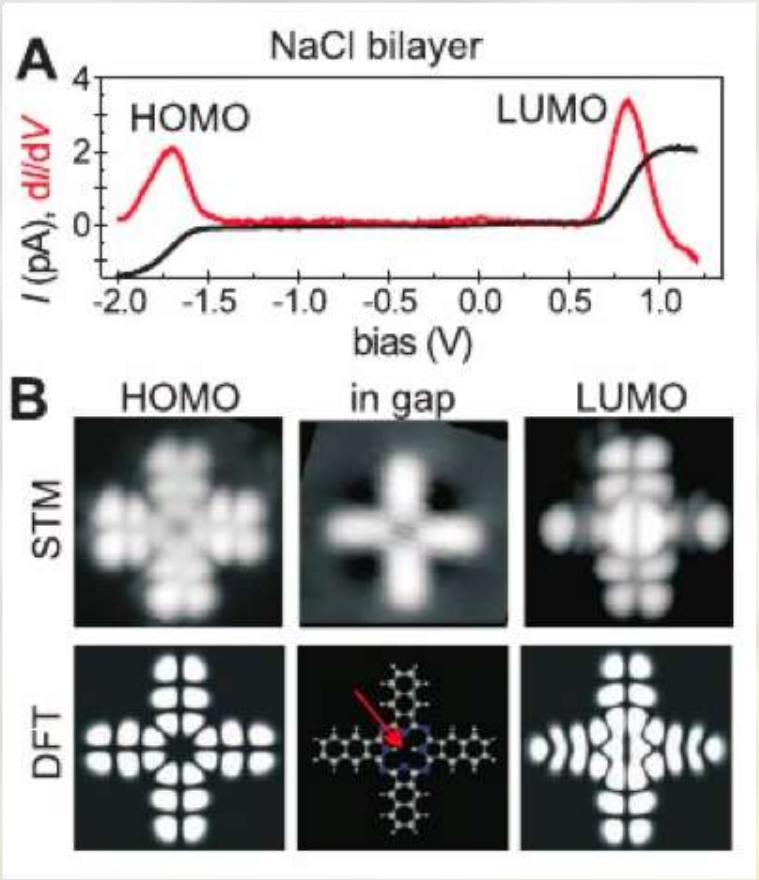
Spectroscopy

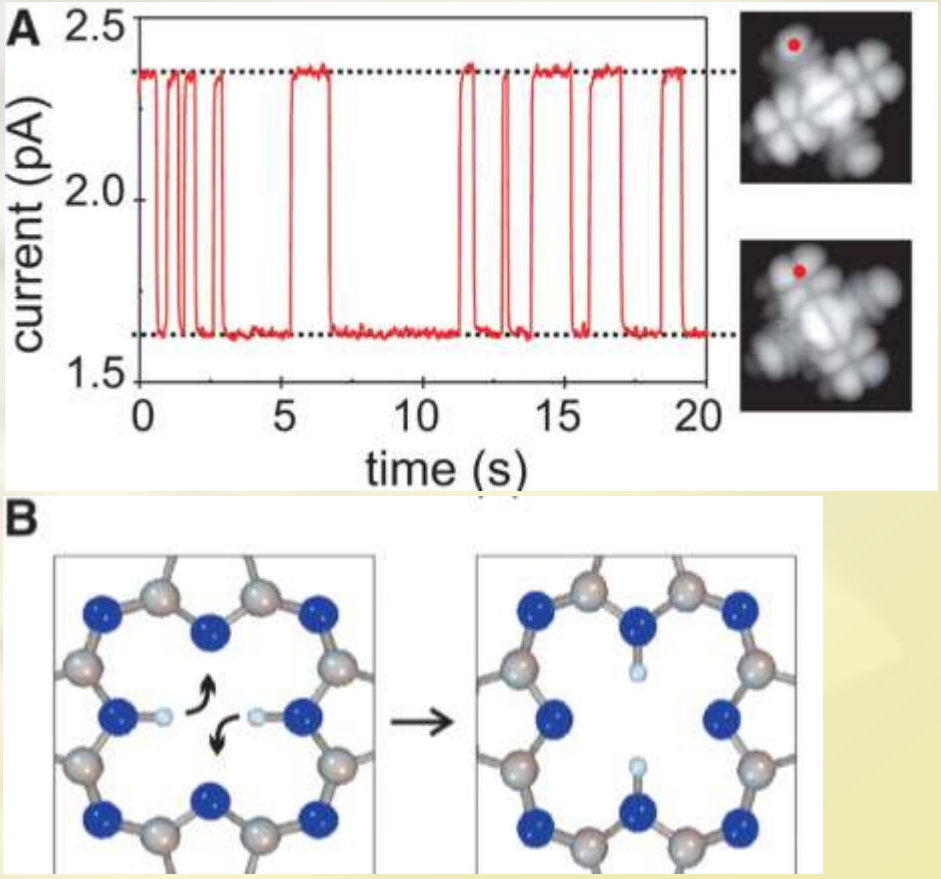




J. Repp and G. Meyer, Physical Review Letters **94**, 026803 (2005)

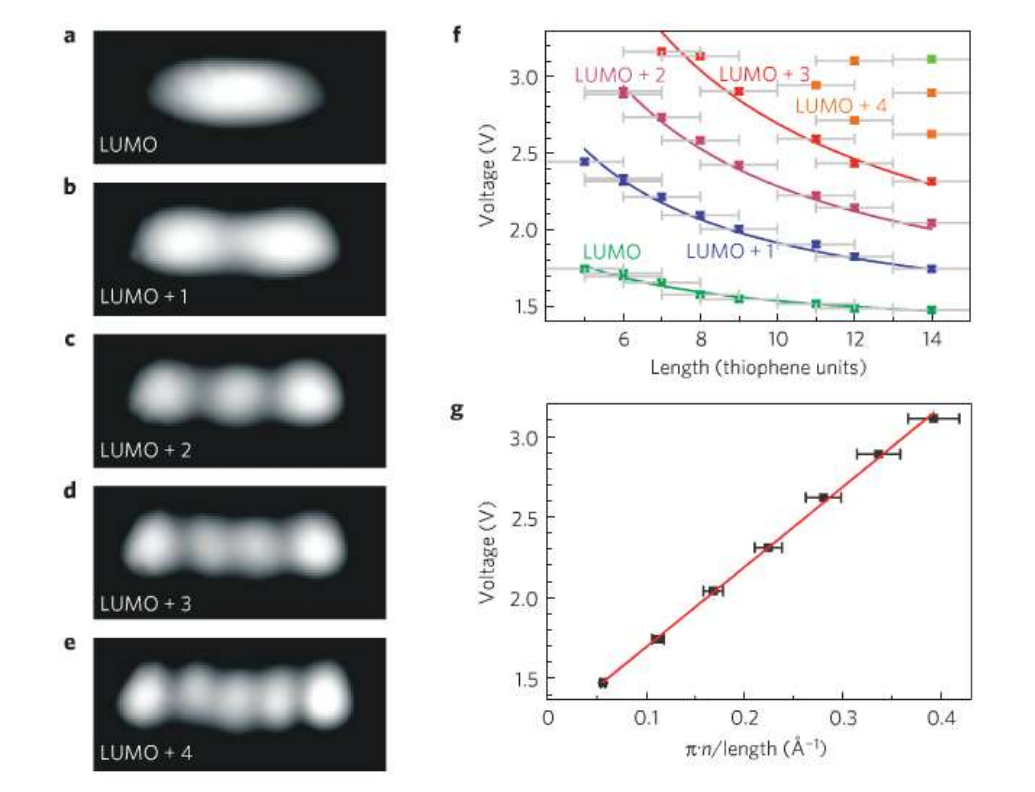
Tautomerization and switching

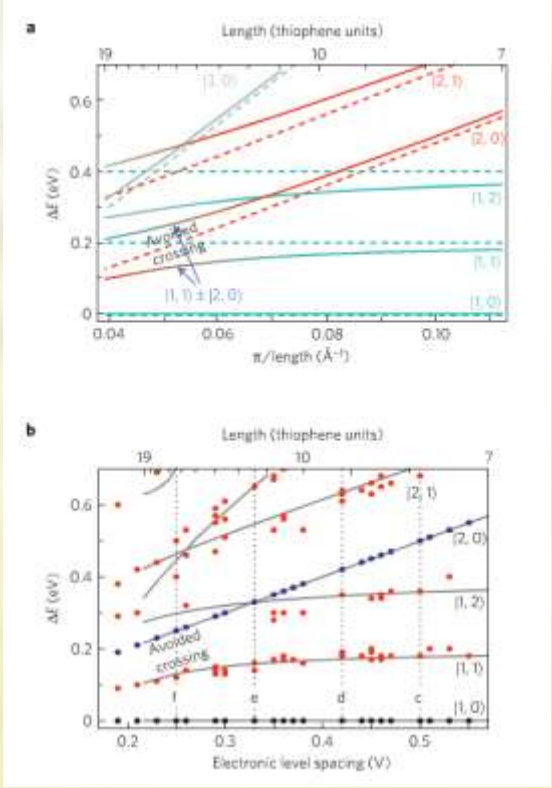




P. Liljeroth, J. Repp, G. Meyer, Science **317**, 1203 (2007)

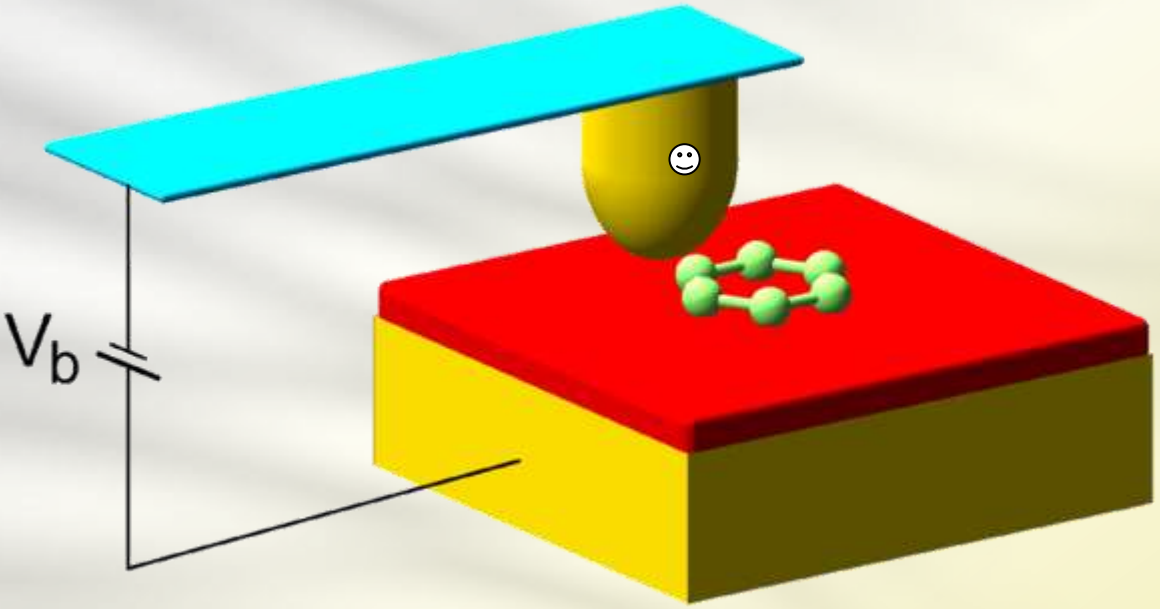
Coherent electron-nuclear coupling





J. Repp, P. Liljeroth, G. Meyer, Nature Physics **6**, 975 (2010)

Sequential tunnelling regime

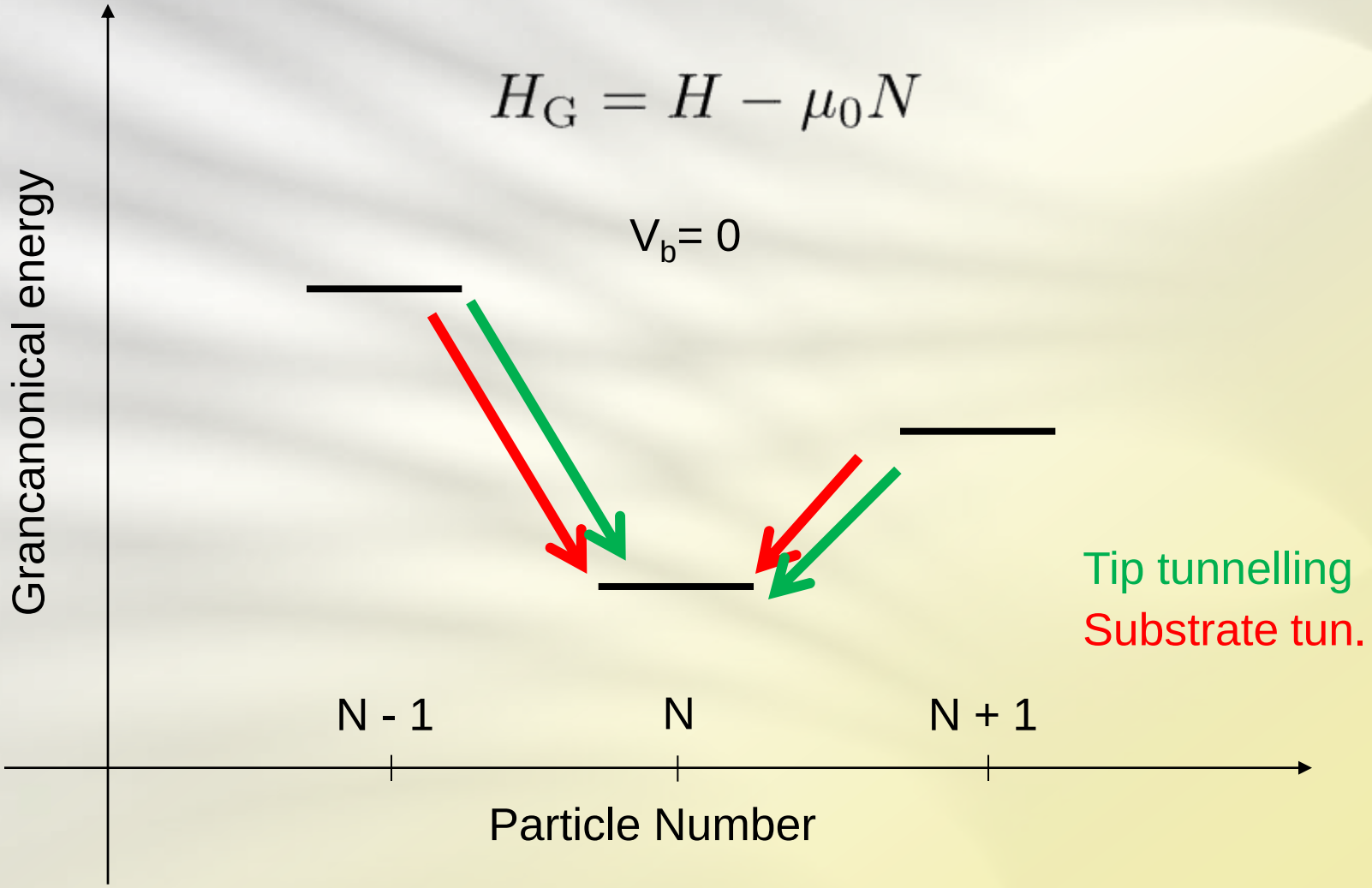


Weak tip-molecule **tunnelling coupling**
Low molecule-substrate **hybridization**

➡ **sequential tunnelling**

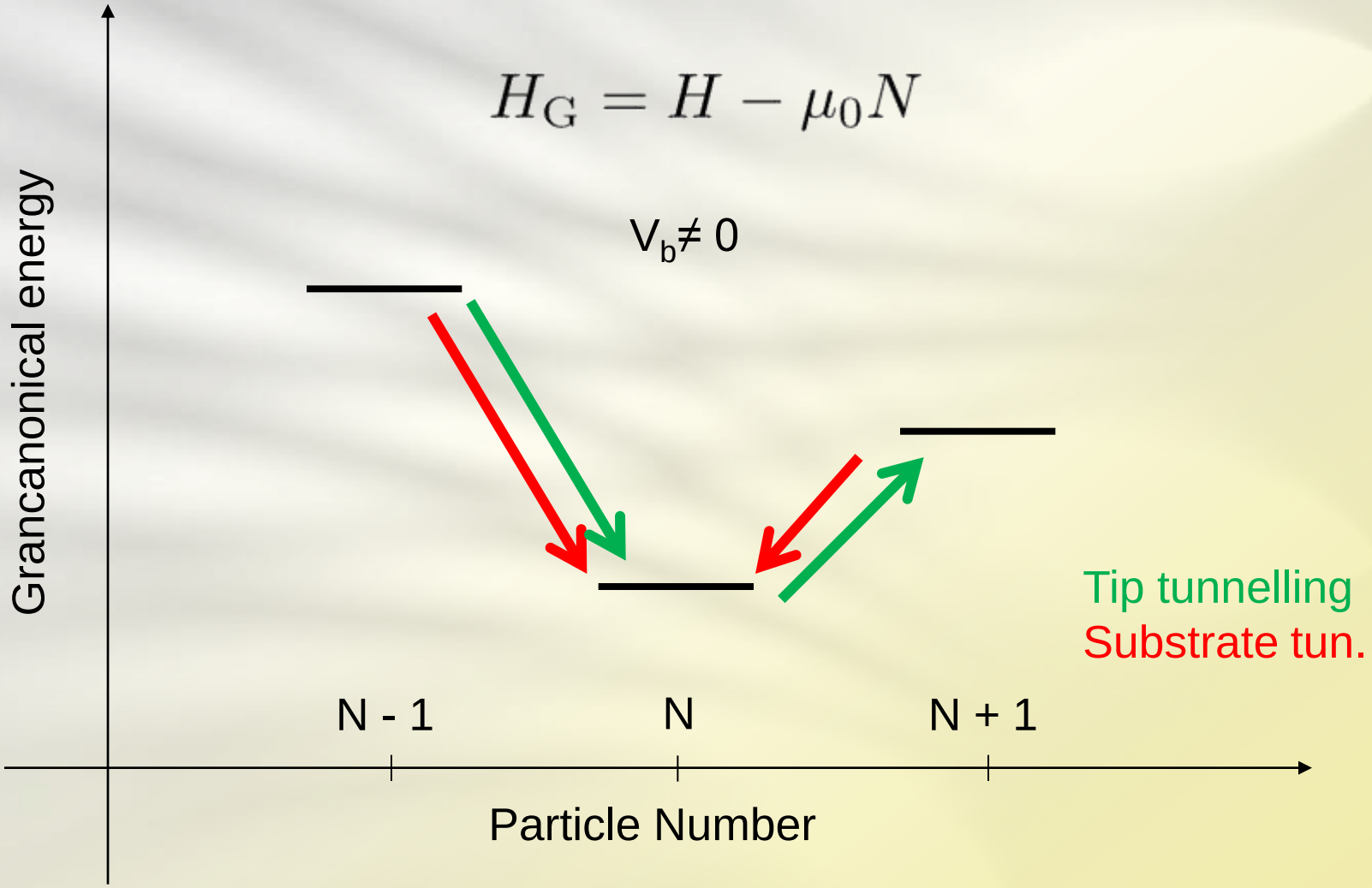
Dynamics in energy space

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



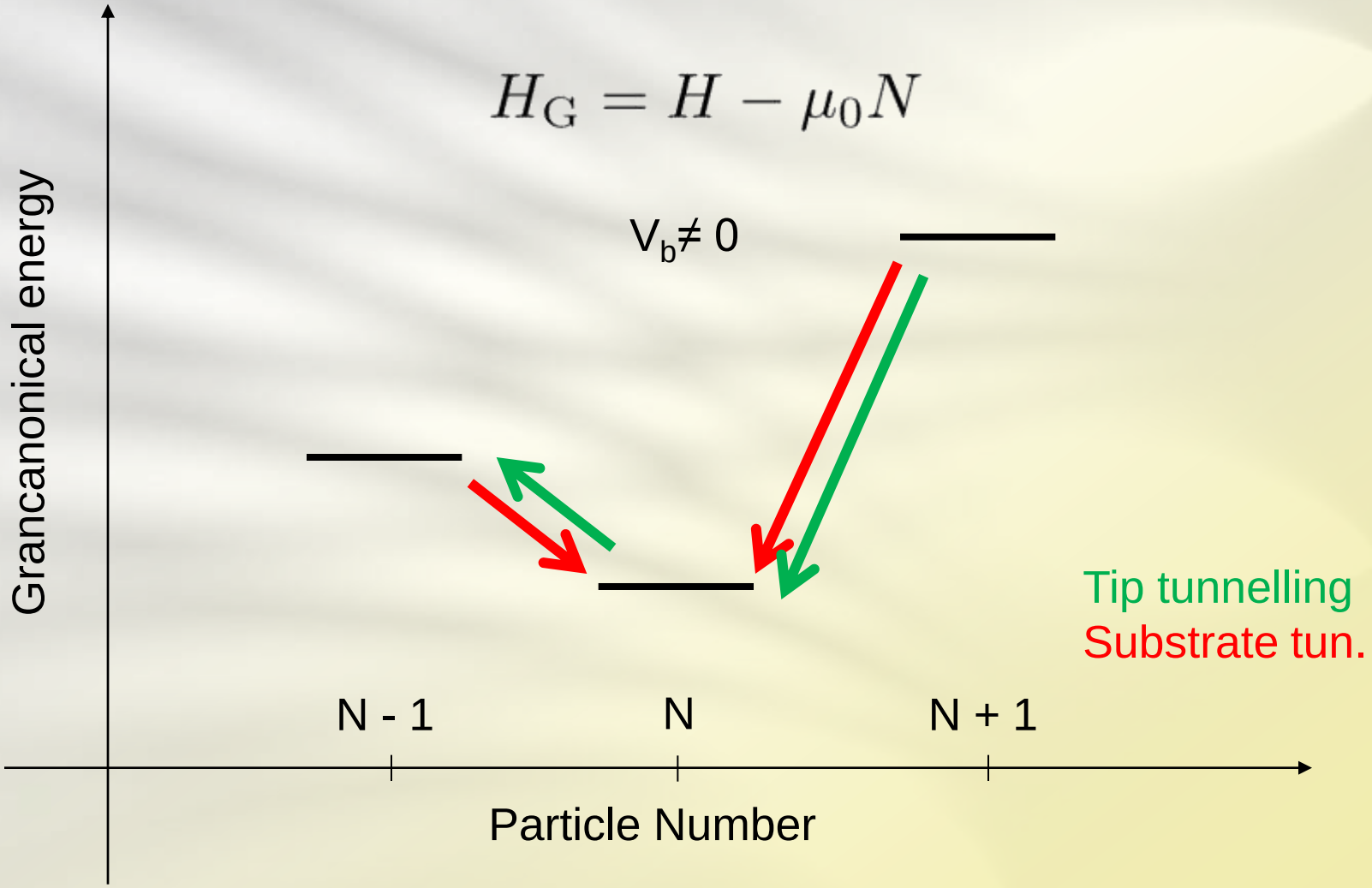
Dynamics in energy space

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



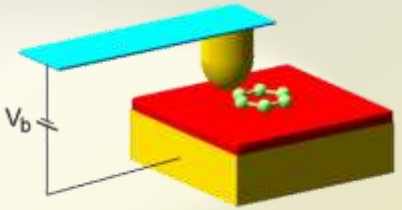
Dynamics in energy space

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



The total Hamiltonian

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



$$H_{\mathrm{m}} = \underbrace{\sum_{\alpha\sigma} a_\alpha d^\dagger_{\alpha\sigma} d_{\alpha\sigma}}_{\text{On-site}} + \underbrace{\sum_{\alpha\neq\beta\sigma} b_{\alpha\beta} d^\dagger_{\alpha\sigma} d_{\beta\sigma}}_{\text{Hopping}} + \underbrace{\frac{1}{2} U \left(N - N_0\right)^2}_{\text{Constant interaction}}$$

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

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

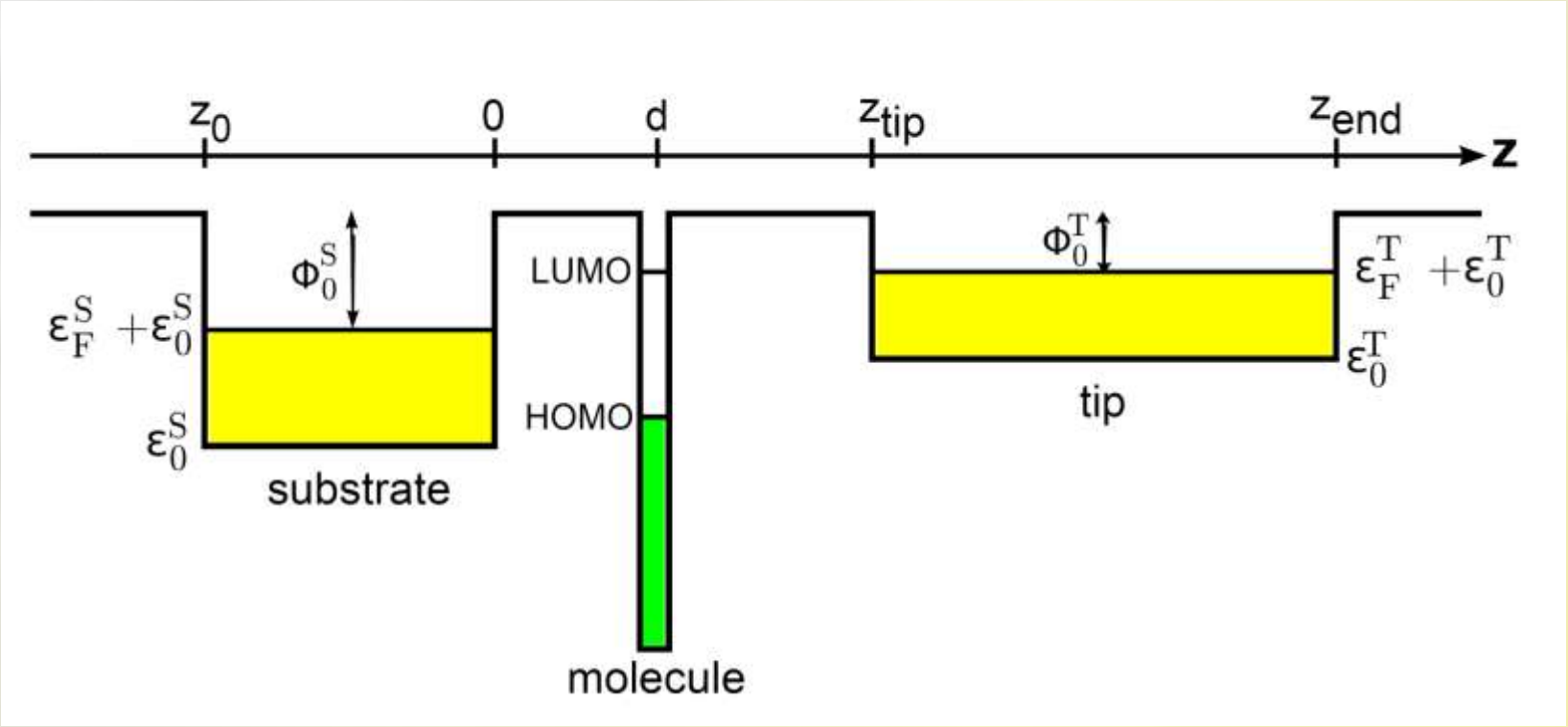
$$H_{\mathrm{tun}} = \sum_{\chi k i\sigma} t^\chi_{ki} c^\dagger_{\chi k\sigma} d_{i\sigma} + h.c.$$

It is a **single particle** operator

Molecular orbital

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)

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

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

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)

$$t_{ki}^{S} = \varepsilon_i \sum_{\alpha} \mathrm{e}^{-\mathrm{i}\vec{k}_{||}\cdot\vec{R}_\alpha} O_S(\vec{k}) \langle \alpha\sigma | i\sigma \rangle$$

Coherent superposition

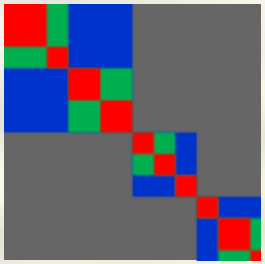
Molecular to atomic basis

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

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.

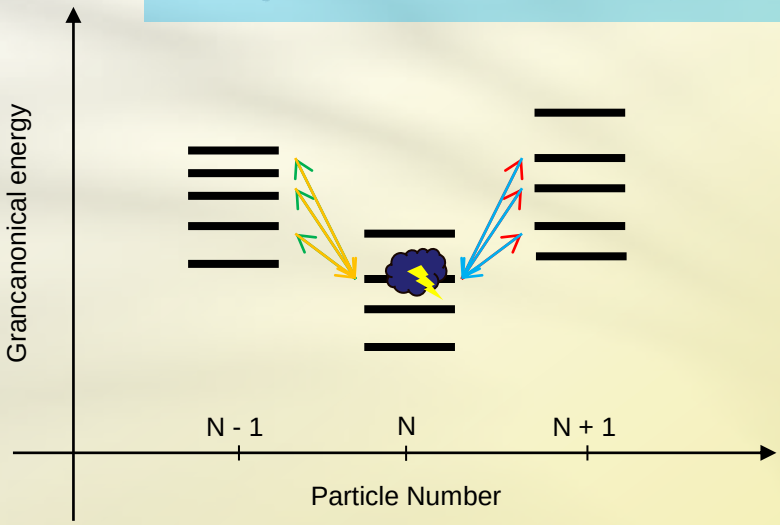
- The **Generalized Master Equation** is the equation of motion for σ :

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

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

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

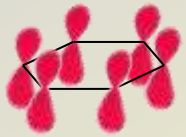
Effective Hamiltonian

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

Current operator

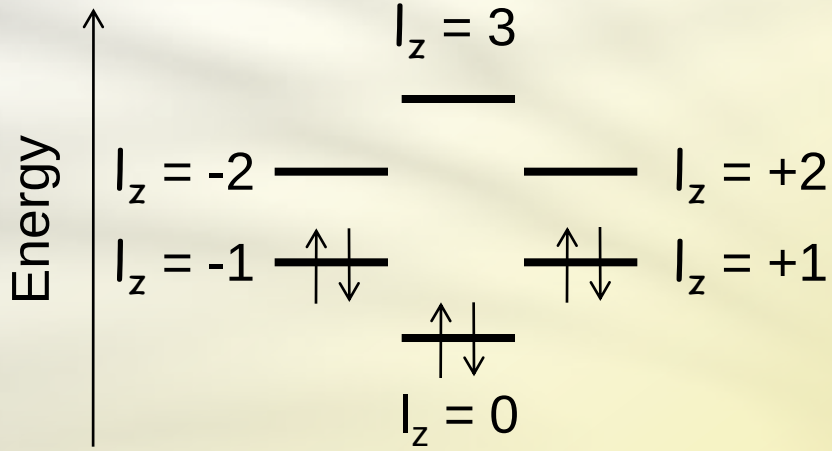
$$\Gamma^{\chi}_{ij}(\Delta E) = \frac{2\pi}{\hbar} \sum_{k} (t^{\chi}_{ki})^{*} \, t^{\chi}_{kj} \, \delta(\varepsilon^{\chi}_{k} - \Delta E)$$

Special example: benzene



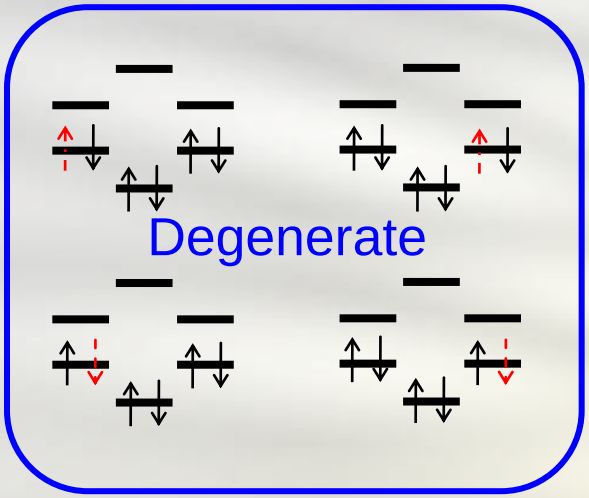
$$H_m = a\sum_{\alpha\sigma} d^{\dagger}_{\alpha\sigma} d_{\alpha\sigma} + b\sum_{\alpha\sigma}\left(d^{\dagger}_{\alpha\sigma} d_{\alpha+1\sigma} + d^{\dagger}_{\alpha+1\sigma} d_{\alpha\sigma}\right) + \frac{1}{2}U\left(\hat{N} - 6\right)^2$$

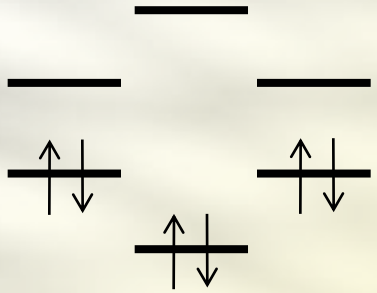
Single-particle levels

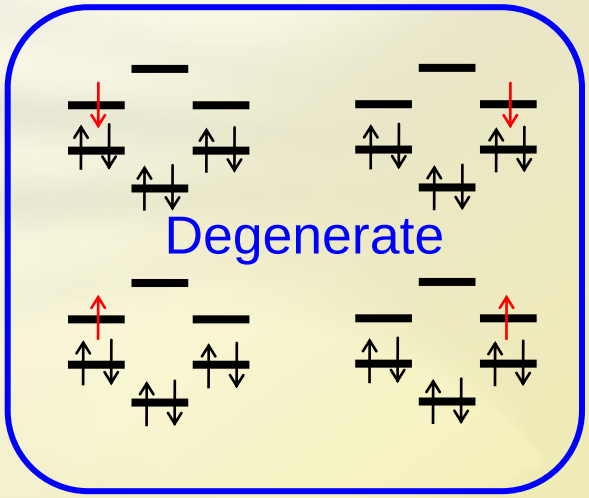


Symmetry and degeneracy

$$H_m = a\sum_{\alpha\sigma} d^{\dagger}_{\alpha\sigma} d_{\alpha\sigma} + b\sum_{\alpha\sigma}\left(d^{\dagger}_{\alpha\sigma} d_{\alpha+1\sigma} + d^{\dagger}_{\alpha+1\sigma} d_{\alpha\sigma}\right) + \frac{1}{2}U\left(\hat{N} - 6\right)^2$$







N = 5
L_z = 1
S_z = 1/2

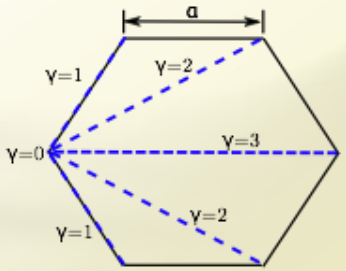
N = 6
L_z = 0
S_z = 0

N = 7
L_z = 2
S_z = 1/2

The **same symmetry properties** are maintained also by the eigenstates of **more sofisticated interaction Hamiltonians** (e.g. PPP models)

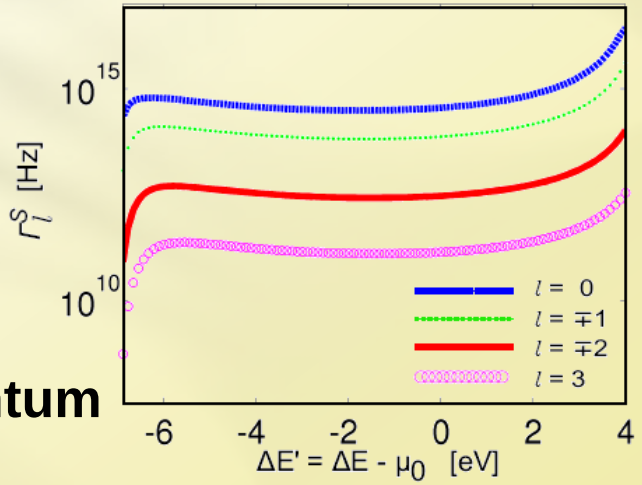
Angular momentum channels (i)

$$\Gamma^S_{ll'}(\Delta E) = \delta_{ll'} \frac{\pi^2}{\hbar^4} m^{\frac{3}{2}} \sqrt{2}\, \varepsilon_l^2 \int_0^{\varepsilon_F^S + \Phi_0^S} \mathrm{d}\varepsilon_z \frac{V}{\sqrt{\varepsilon_z}}$$
$$\times \sum_\gamma J_0 \left(\sqrt{\frac{2m}{\hbar} \left(\Delta E - \varepsilon_z - \varepsilon_0^S\right)} |\Delta \vec{R}_\gamma| \right) \mathrm{e}^{-\mathrm{i}\frac{2\pi}{6} l\gamma}$$
$$\times |O_S(\Delta E - \varepsilon_z - \varepsilon_0^S, \varepsilon_z)|^2$$
$$\times \Theta\left(\Delta E - \varepsilon_z - \varepsilon_0^S\right) \Theta\left(\varepsilon_z - \Delta E\right) \ .$$

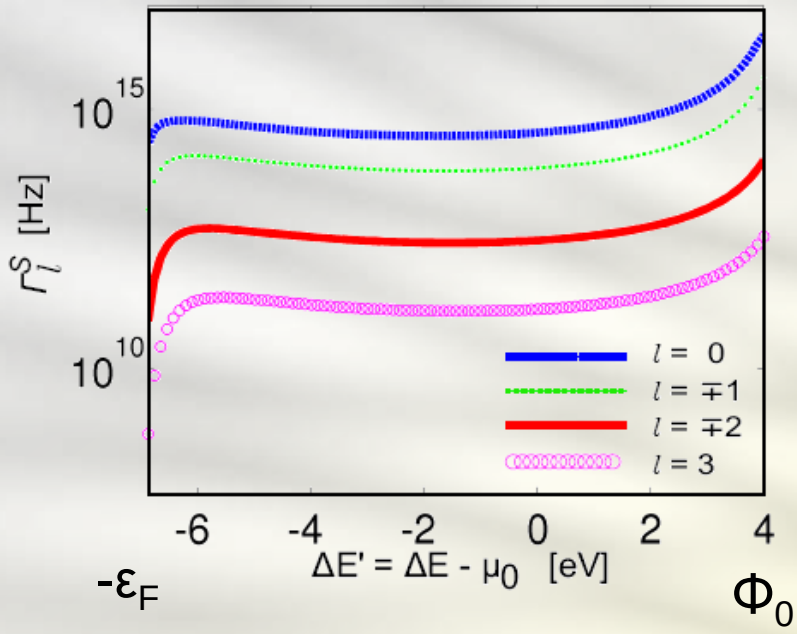


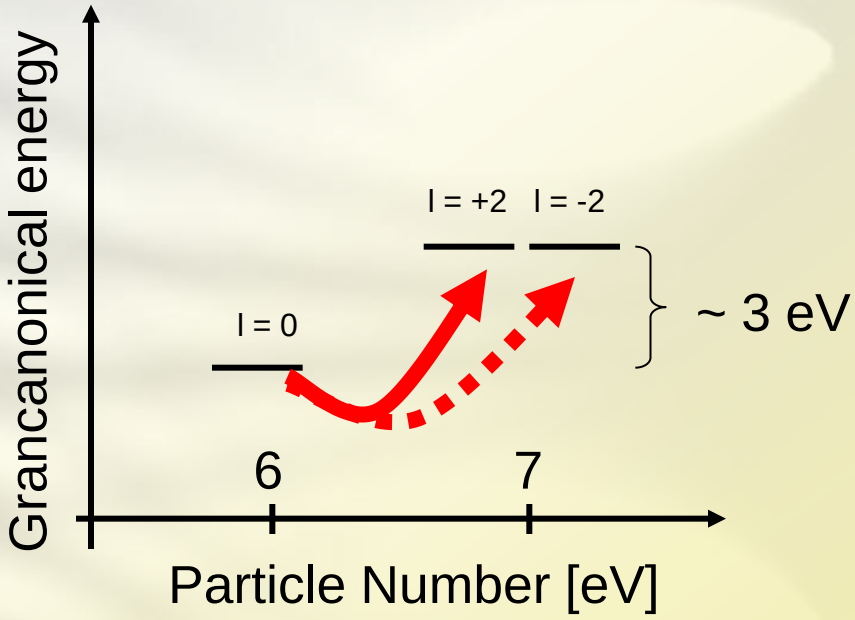
The substrate tunnelling rate matrix:

- Is **diagonal** in the **angular momentum**
- **Decreases** of several order of magnitude with the **increase** of the **angular momentum**



Angular momentum channels (ii)





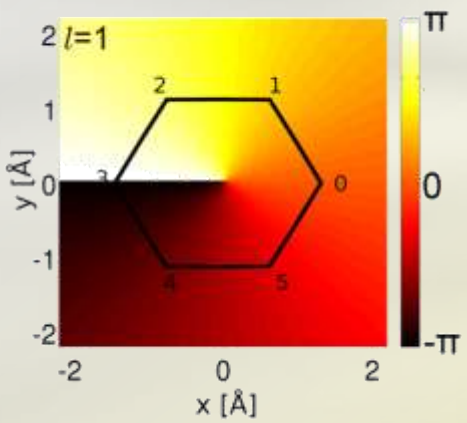
In the tunnelling **the molecule changes** its energy and angular momentum

Tip-tunnelling

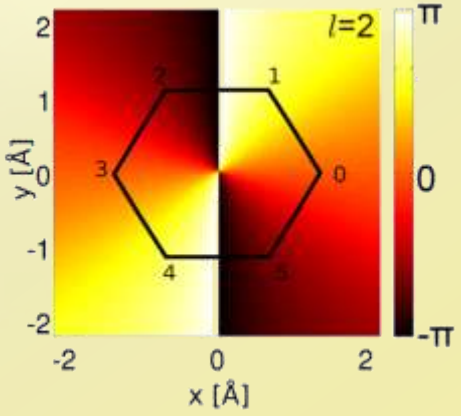
$$\Gamma_{ll'}{}^{T}(\Delta E, \vec{R}_{\rm tip}) = \frac{\pi}{6\hbar^2}\sqrt{\frac{m}{2}}\sum_{\alpha\alpha'}\varepsilon_l\varepsilon_{l'}\mathrm{e}^{-\mathrm{i}\frac{2\pi}{6}(\alpha l-\alpha' l')}$$
$$\times O_T^*(\tilde{k}, \vec{R}_{\rm tip}-\vec{R}_\alpha)O_T(\tilde{k}, \vec{R}_{\rm tip}-\vec{R}'_\alpha)\frac{|z_{end}-z_{\rm tip}|}{\sqrt{\Delta E-\varepsilon_0^T-\hbar\omega}}$$
$$\times\,\Theta(\Delta E-\hbar\omega-\varepsilon_0^T)\Theta(2\hbar\omega-\Delta E+\varepsilon_0^T)\ ,$$

The angular momentum channels are **mixed**

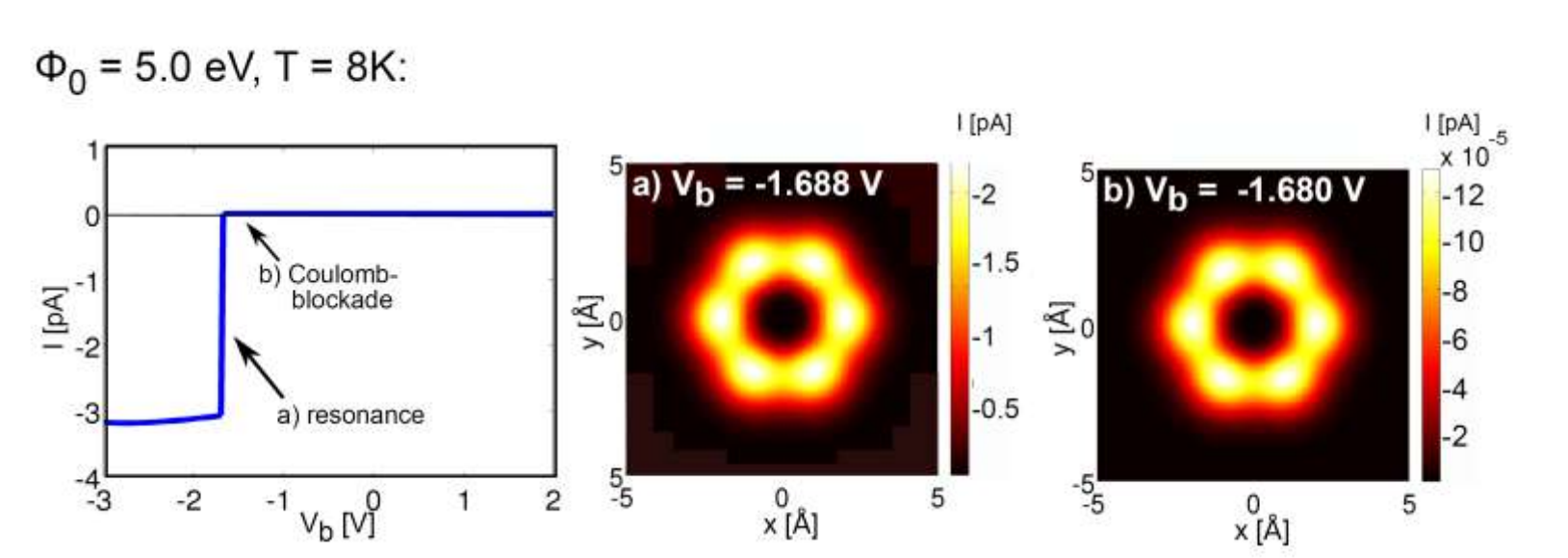
In particular:



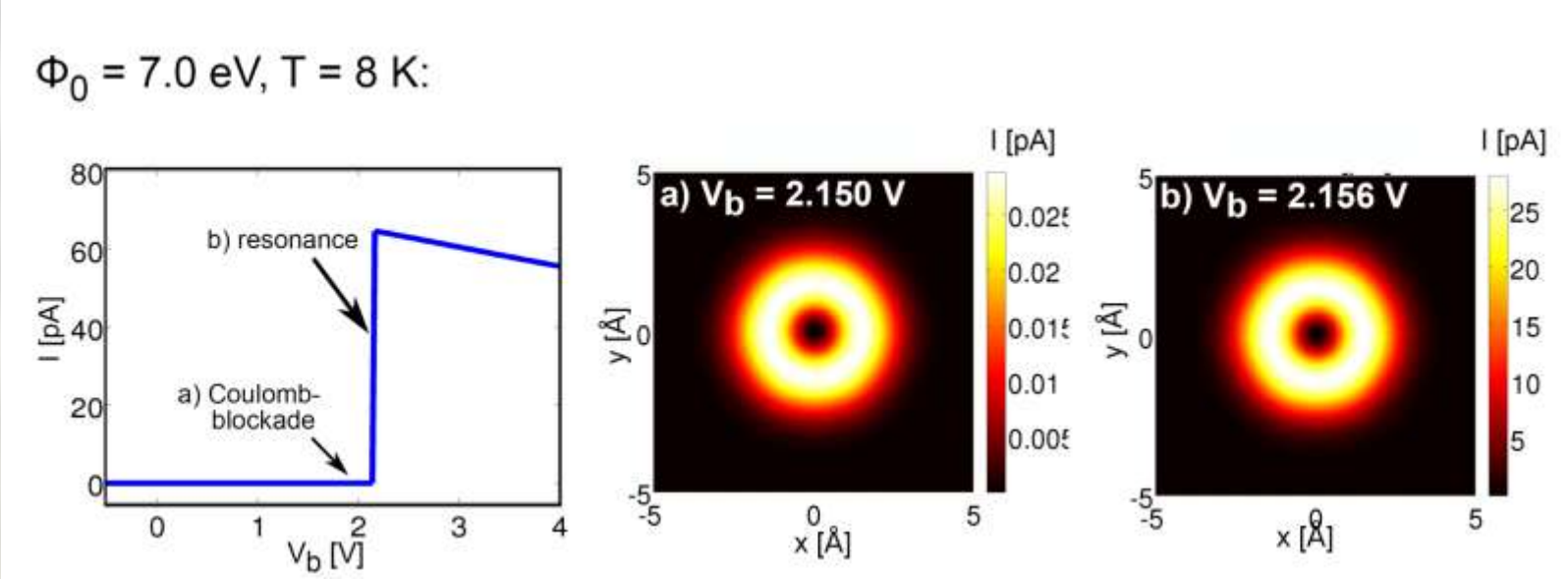
$$\mathbf{\Gamma}^T = \Gamma_l^T\begin{pmatrix}1 & \mathrm{e}^{-2\mathrm{i}\phi_l(\vec{R}_{\rm tip})}\\ \mathrm{e}^{+2\mathrm{i}\phi_l(\vec{R}_{\rm tip})} & 1\end{pmatrix}$$



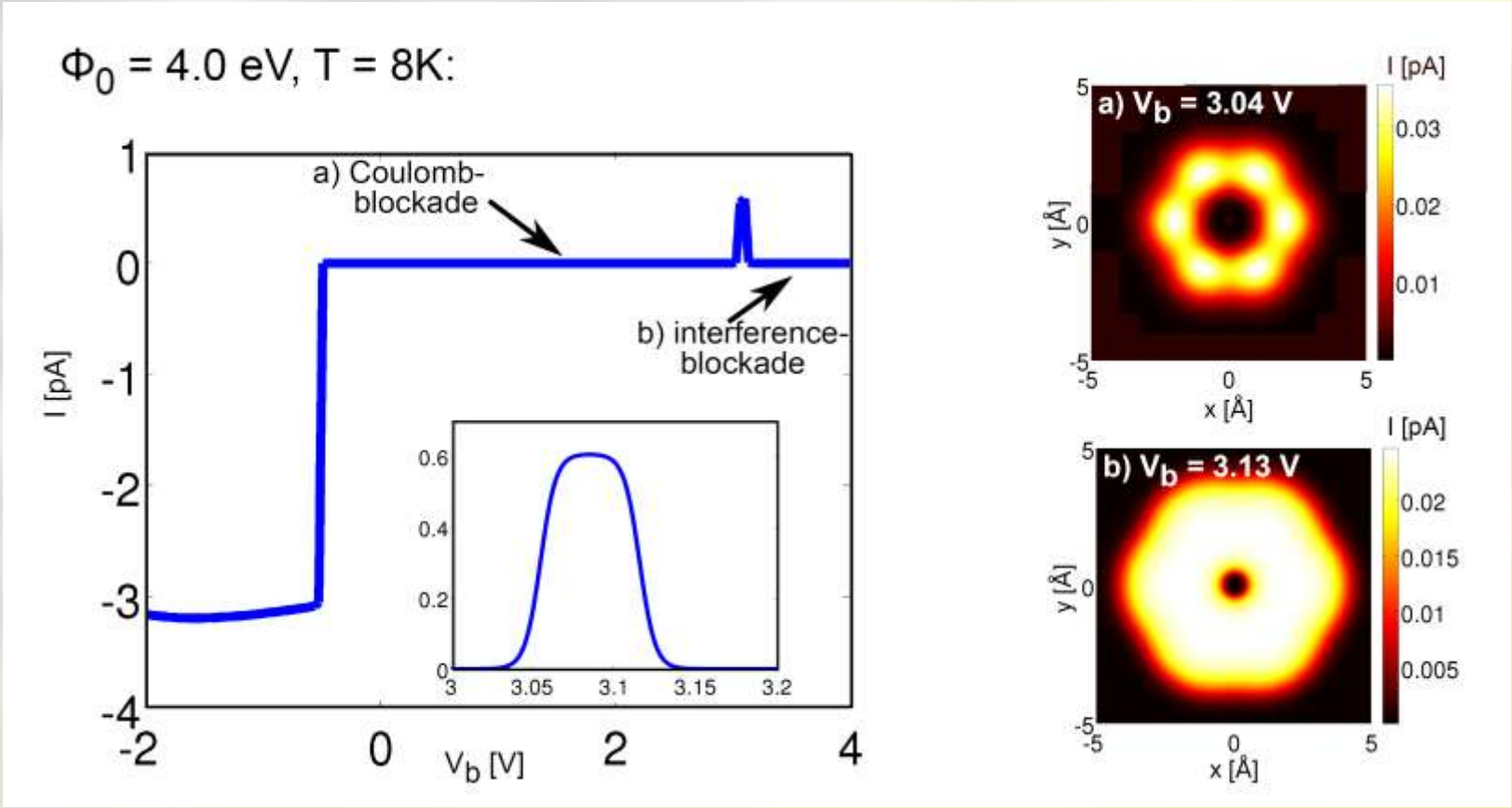
Negative ion resonance (6<->7)



Positive ion resonance (6<->5)



Interference blocking



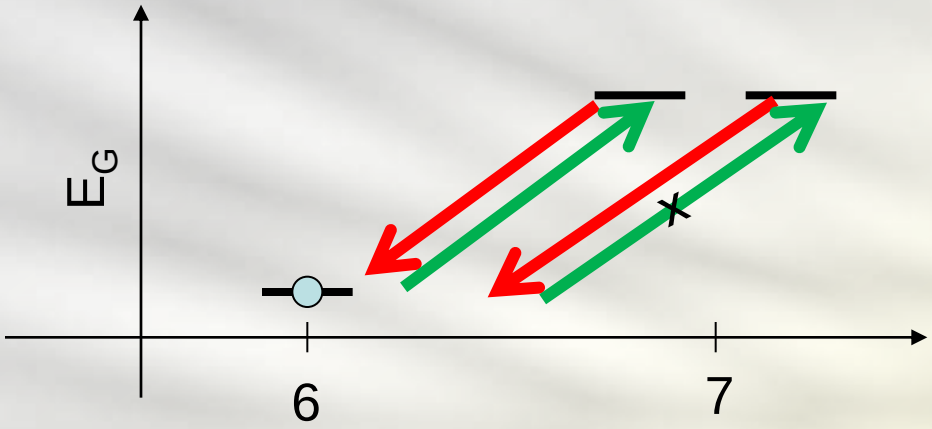
Interference: decoupling basis

Let‘s now concentrate on the transition $6_g \leftrightarrow 7_g$ (Neglecting the spin)

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

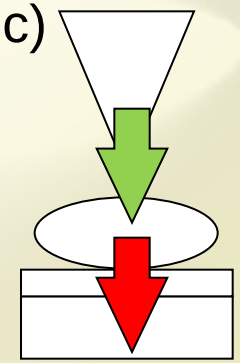
Notice that the decoupling basis depends on the position of the tip!

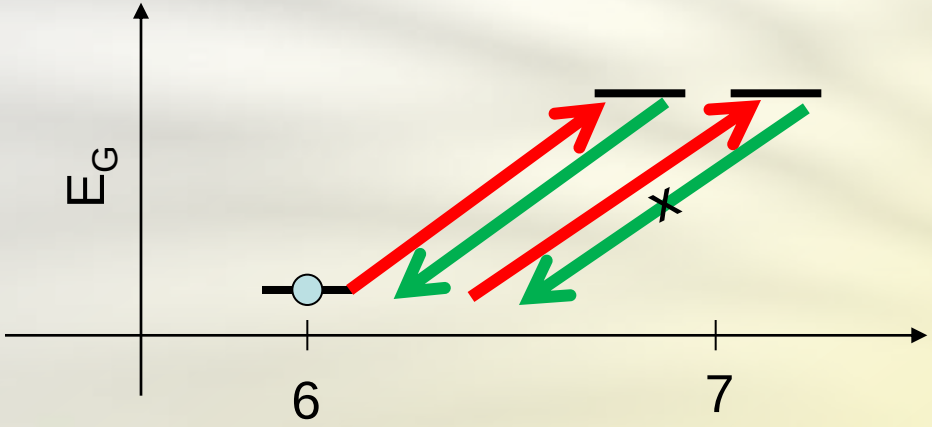
Interference: current blocking



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

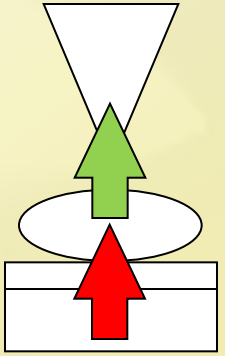
Current





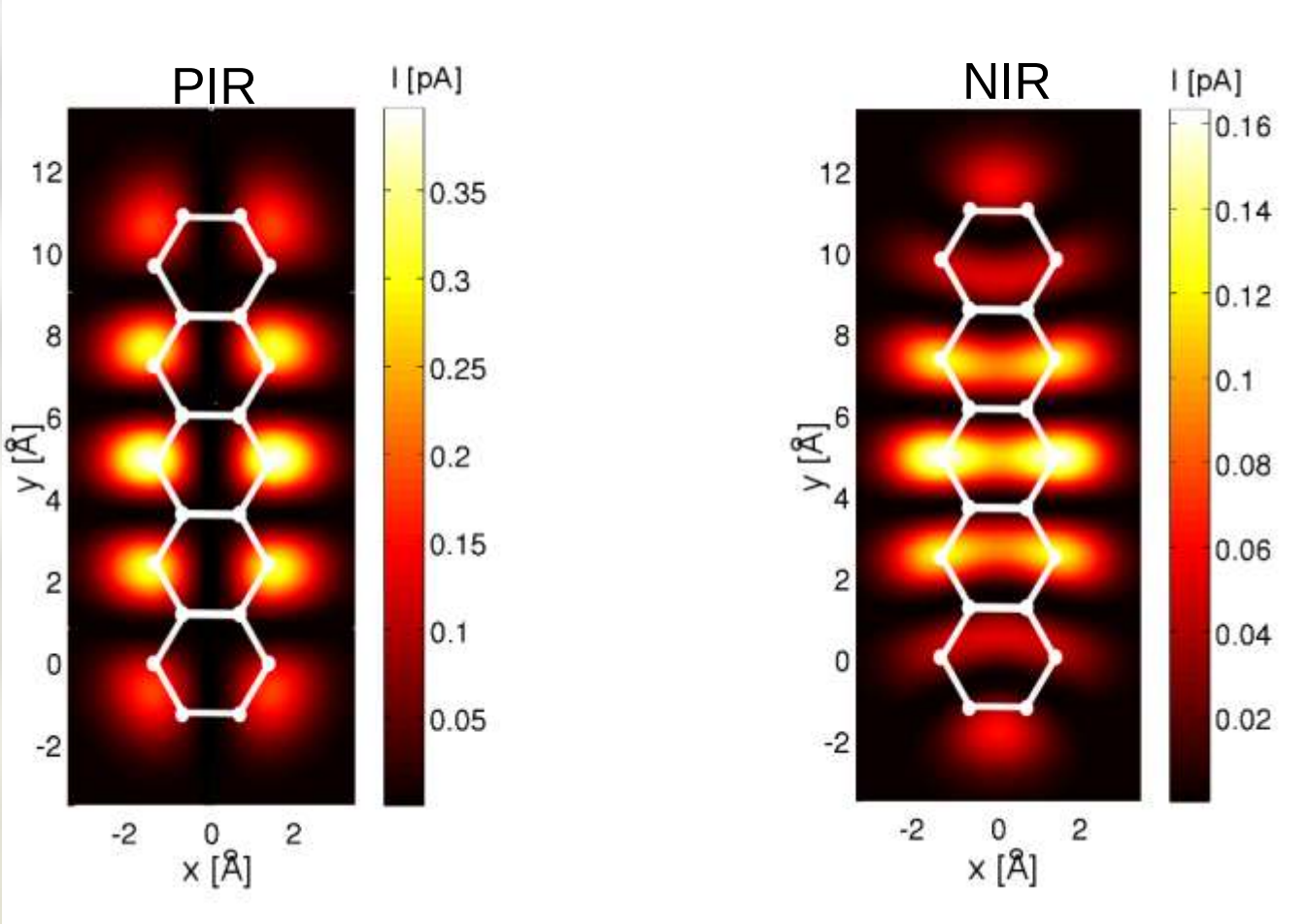
$eV_b > |\Delta E_G|/c$

No current



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

Pentacene


PIR
I [pA]
0.35
0.3
0.25
0.2
0.15
0.1
0.05
12
10
8
6
4
2
0
-2
y [Å]
-2
0
2
x [Å]
NIR
I [pA]
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
12
10
8
6
4
2
0
-2
y [Å]
-2
0
2
x [Å]

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
- In the case of rotationally symmetric molecules the substrate-tunnelling goes via angular momentum channels. The rate varies over order of magnitudes with different angular momenta.
- Transport through degenerate states can generate electron interference blockade depending on the sign of the current. This blocking phenomenon has a characteristic topographic signature.

Thank you for your attention…