STM theory for π-conjugated molecules on thin insulating films

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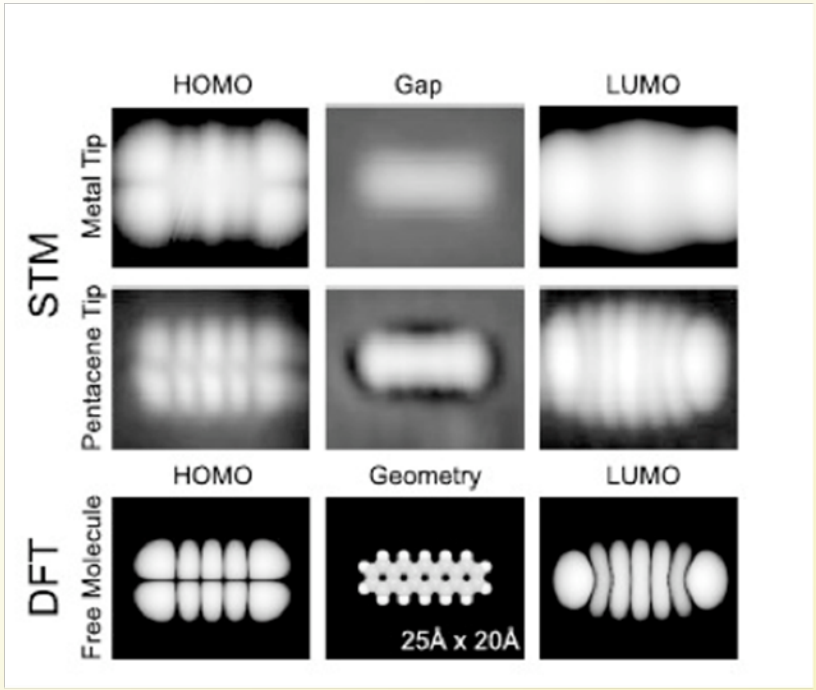
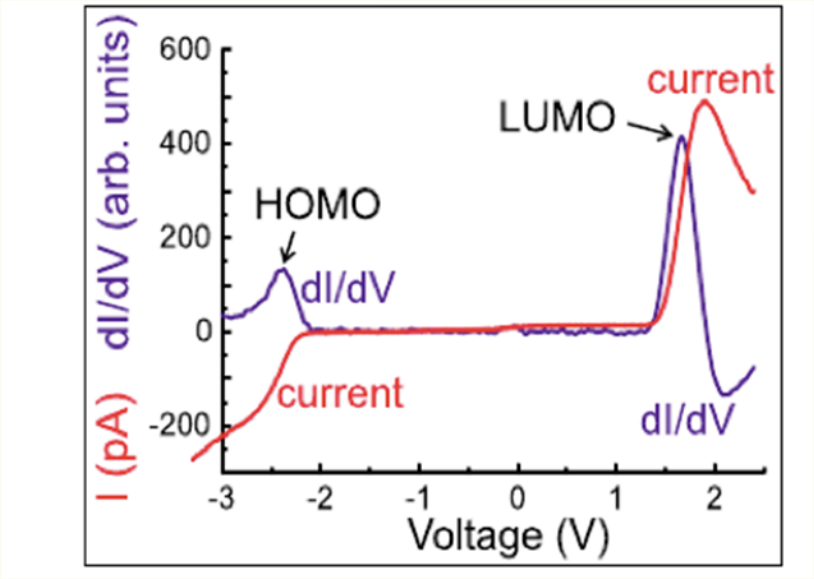
"Weak coupling" STM

Topography

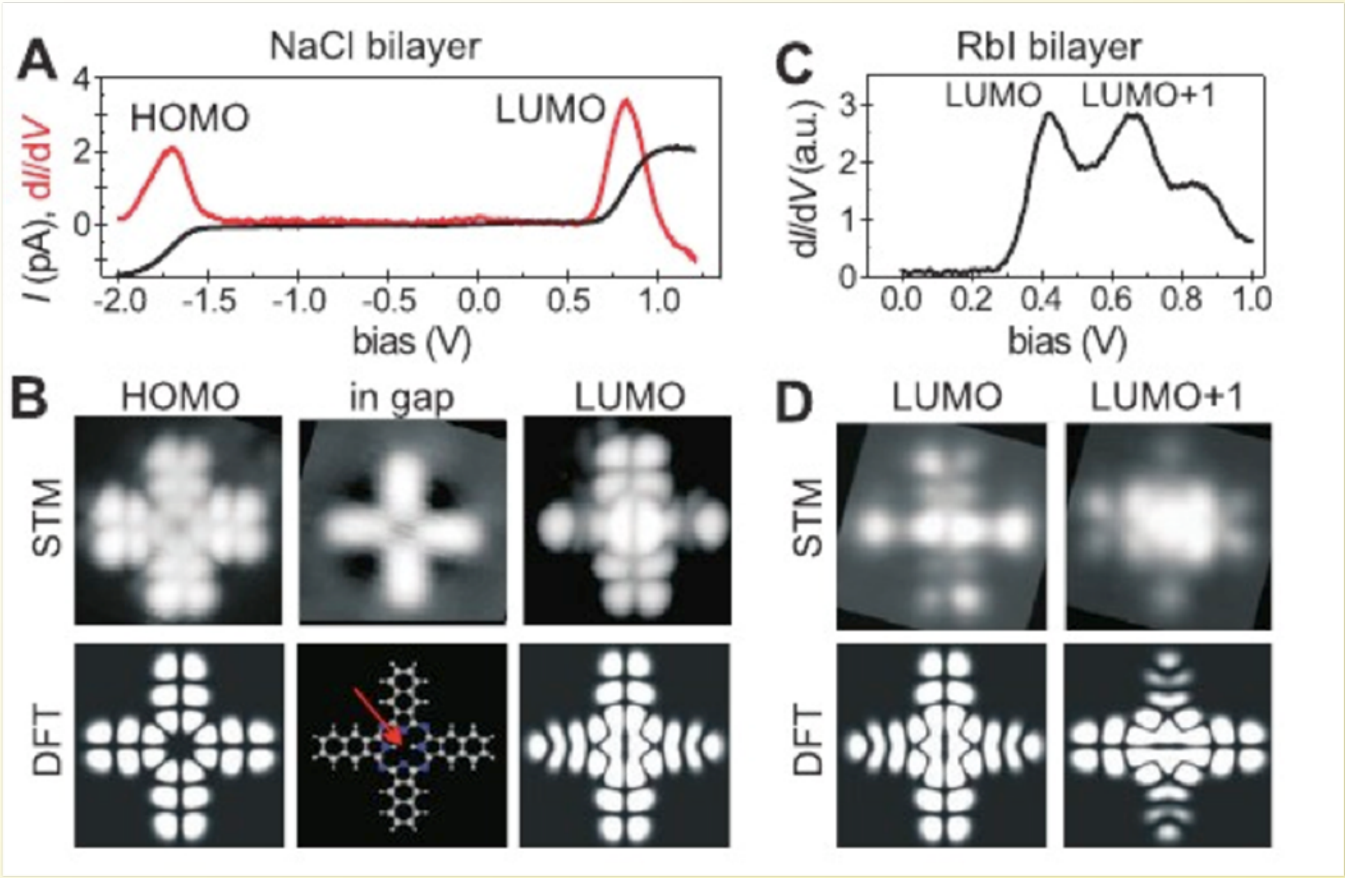
Spectroscopy





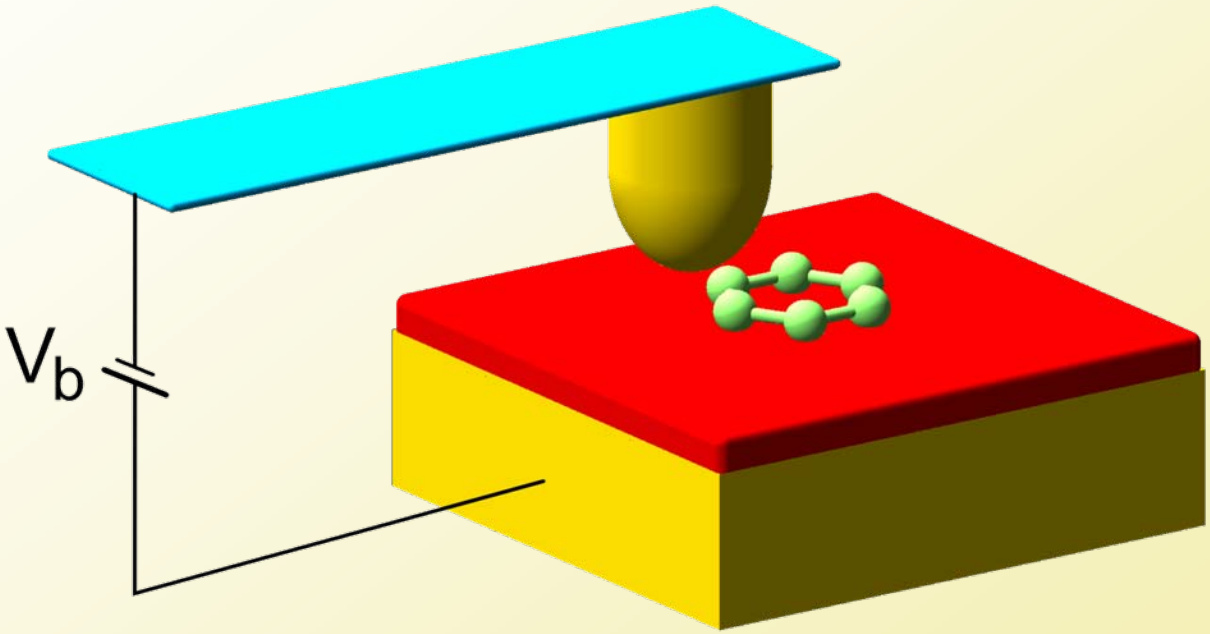
J. Repp and G. Meyer, Physical Review Letters **94**, 026803 (2005)

"Weak coupling" STM



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

STM in real space



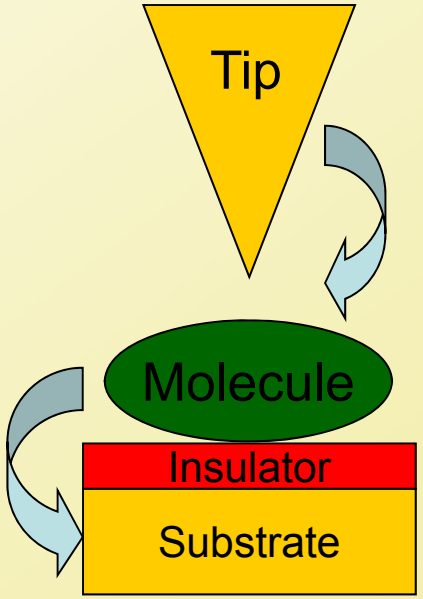
Some numbers

The temperature of the experiments is 5K.

$5\ k_B T = 0.43$ meV

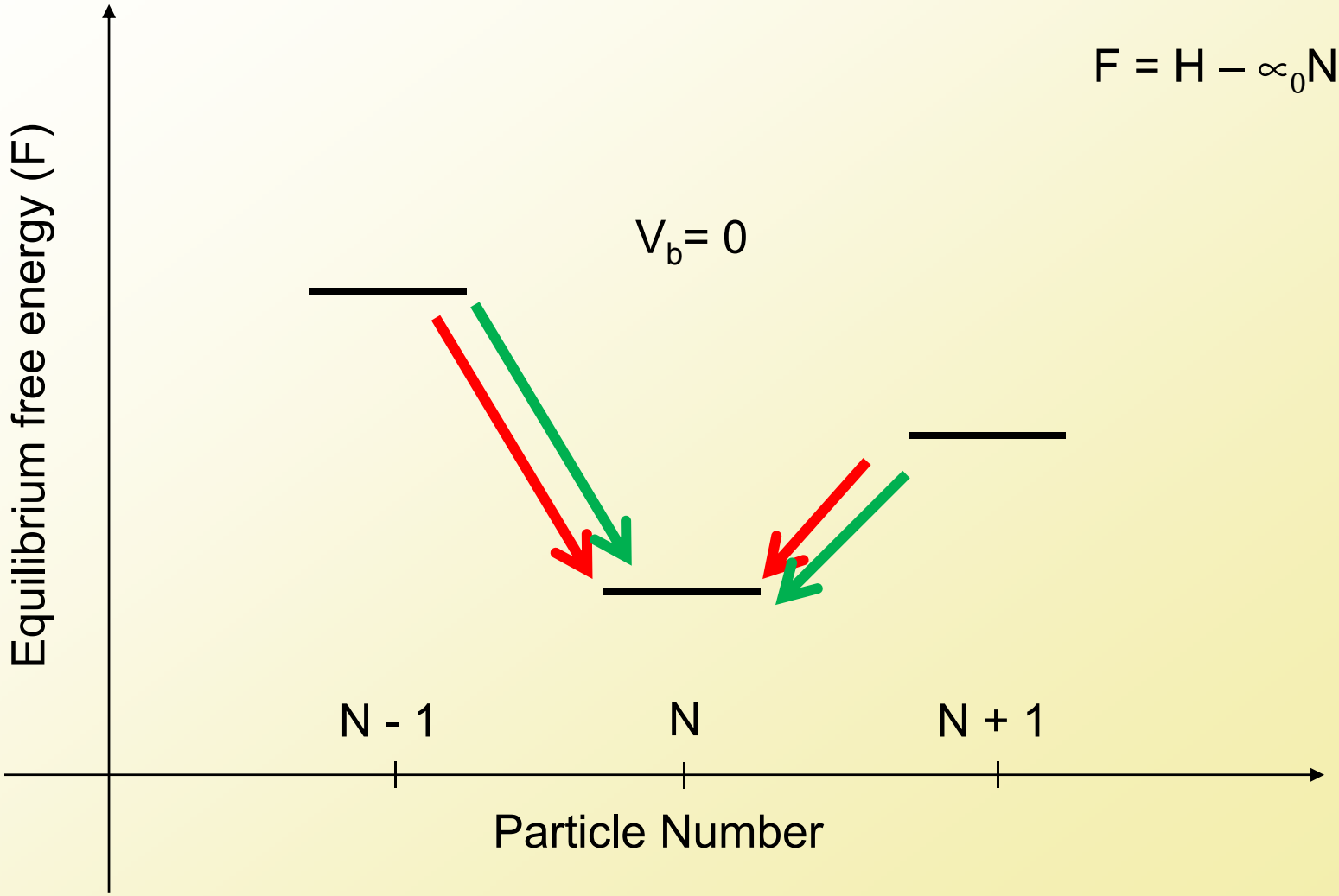
The tip-molecule coupling sets the current.

1 pA ⇨ $\Gamma_{tip} = 6 \times 10^6\ s^{-1}$ ⇨ $\hbar\Gamma_{tip} = 0.25 \propto$eV

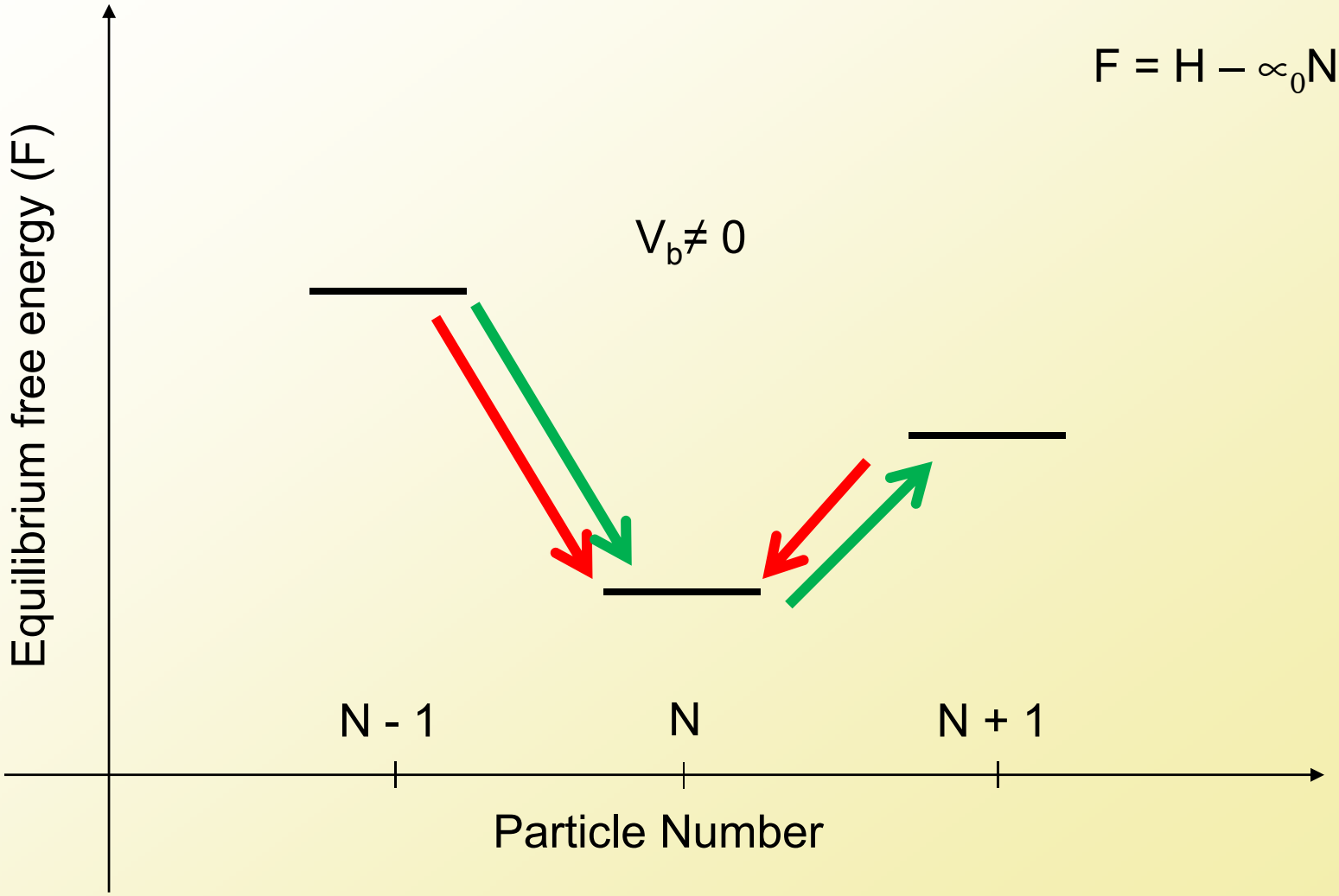


The molecule-substrate coupling = ??

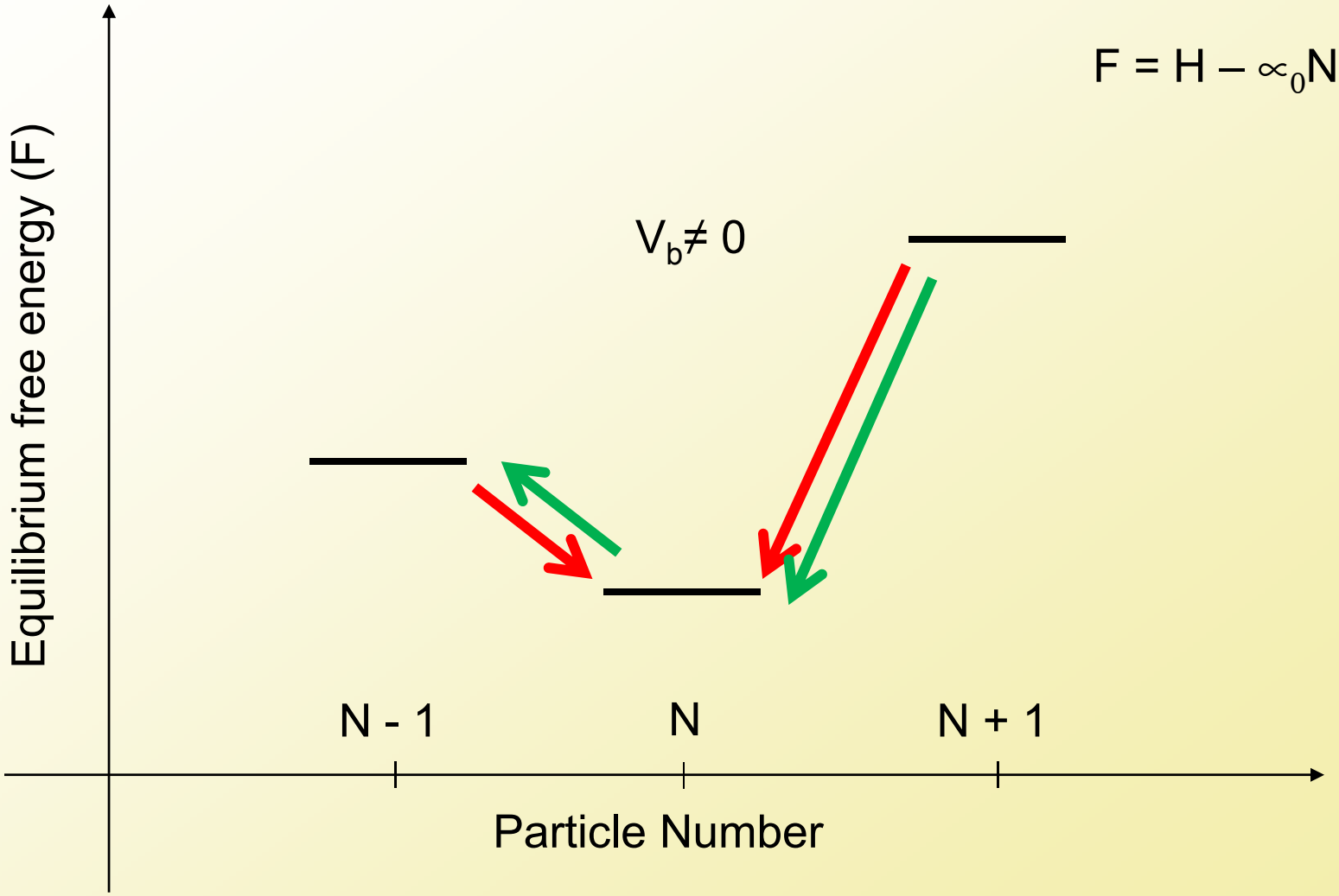
Dynamics in (free) energy space



Dynamics in (free) energy space

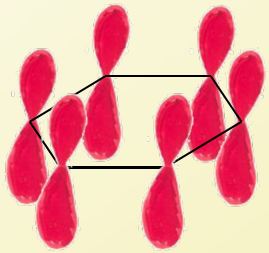


Dynamics in (free) energy space



The total Hamiltonian

$$H = H_m + H_{sub} + H_{tip} + H_T$$



$$H_m = \underbrace{a\sum_{\alpha\sigma} d^\dagger_{\alpha\sigma} d_{\alpha\sigma}}_{\text{On-site}} + \underbrace{b\sum_{\alpha\sigma}\left(d^\dagger_{\alpha\sigma} d_{\alpha+1\sigma} + d^\dagger_{\alpha+1\sigma} d_{\alpha\sigma}\right)}_{\text{Hopping}} + \underbrace{\frac{1}{2}U\left(\hat{N}-6\right)^2}_{\text{Constant interaction}}$$

$$H_{sub} = \sum_{\vec{k}\sigma}\left(\epsilon_{\vec{k}} - \mu_S\right) c^\dagger_{\vec{k}\sigma} c_{\vec{k}\sigma}$$

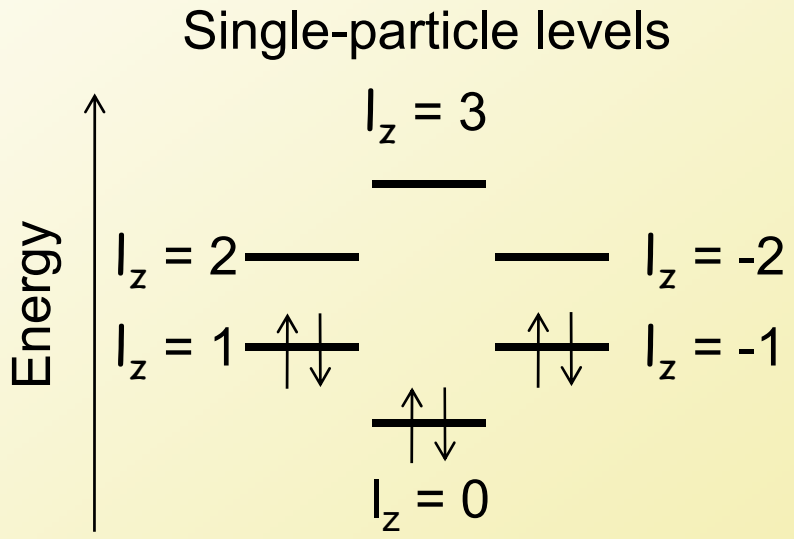
$$H_{tip} = \sum_{\vec{k}\sigma}\left(\epsilon_{\vec{k}} - \mu_T\right) a^\dagger_{\vec{k}\sigma} a_{\vec{k}\sigma}$$

$eV_b = \mu_S - \mu_T$ The applied bias

$$H_T = H_{mol-tip} + H_{mol-sub}$$ It is of single particle form

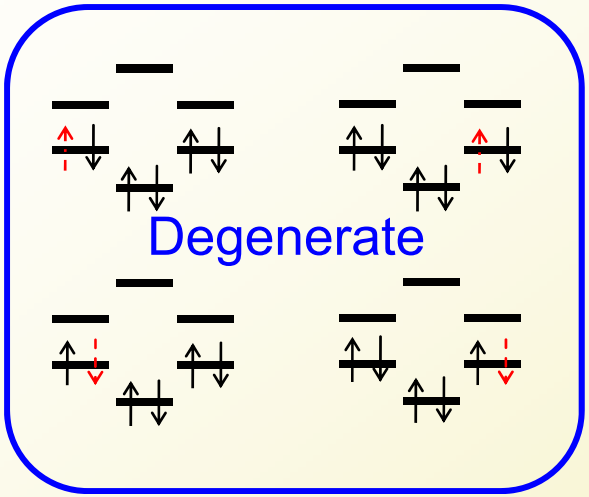
Symmetry and degeneracy

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

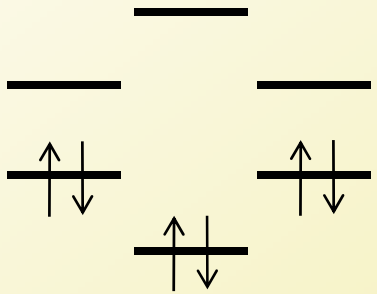


Symmetry and degeneracy

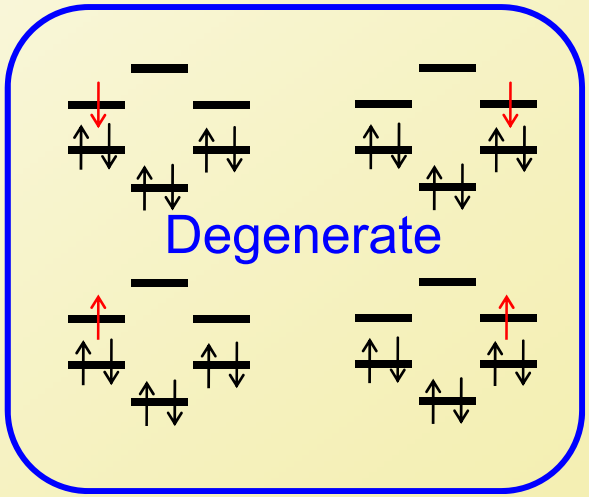
$$H_m = a\sum_{\alpha\sigma} d^{\dagger}_{\alpha\sigma} d_{\alpha\sigma} + b\sum_{\alpha\sigma}\left(d^{\dagger}_{\alpha\sigma} d_{\alpha+1\sigma} + d^{\dagger}_{\alpha+1\sigma} d_{\alpha\sigma}\right) + \frac{1}{2}U\left(\hat{N} - 6\right)^2$$



N = 5
$L_z = \pm 1$
$S_z = \pm 1/2$

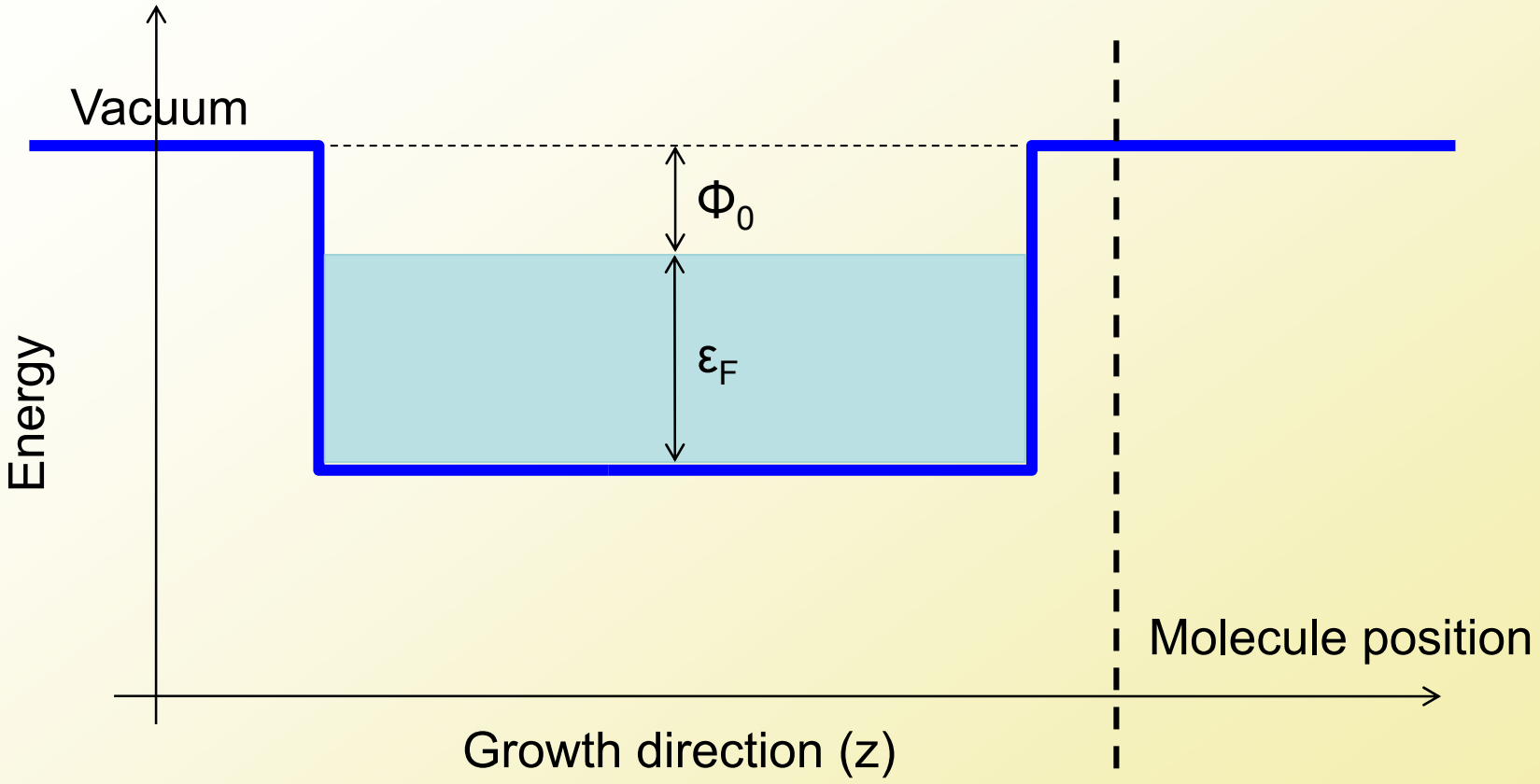


N = 6
$L_z = 0$
$S_z = 0$



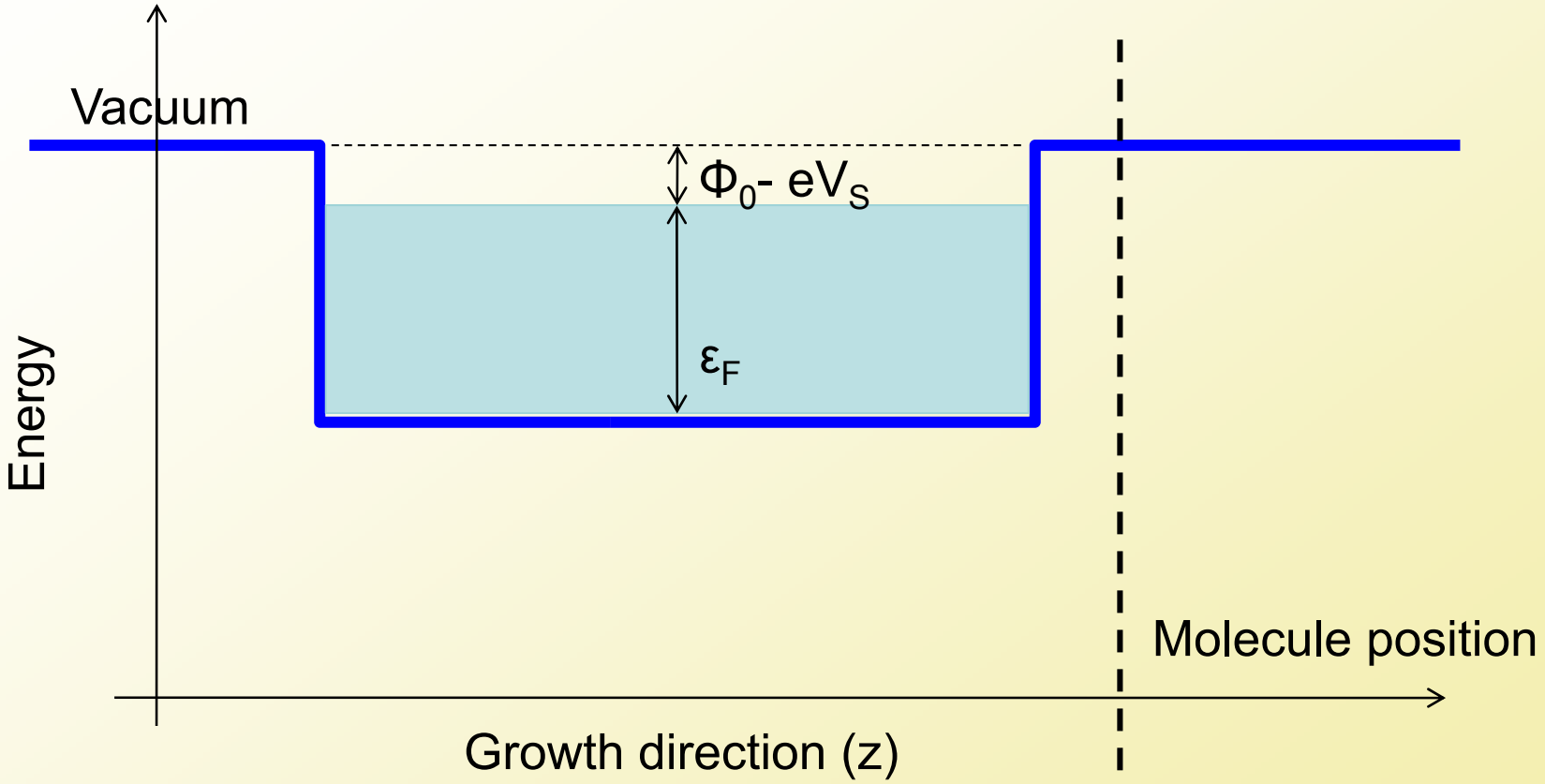
N = 7
$L_z = \pm 2$
$S_z = \pm 1/2$

The substrate



We assume no confining potential in the x and y direction.

The substrate

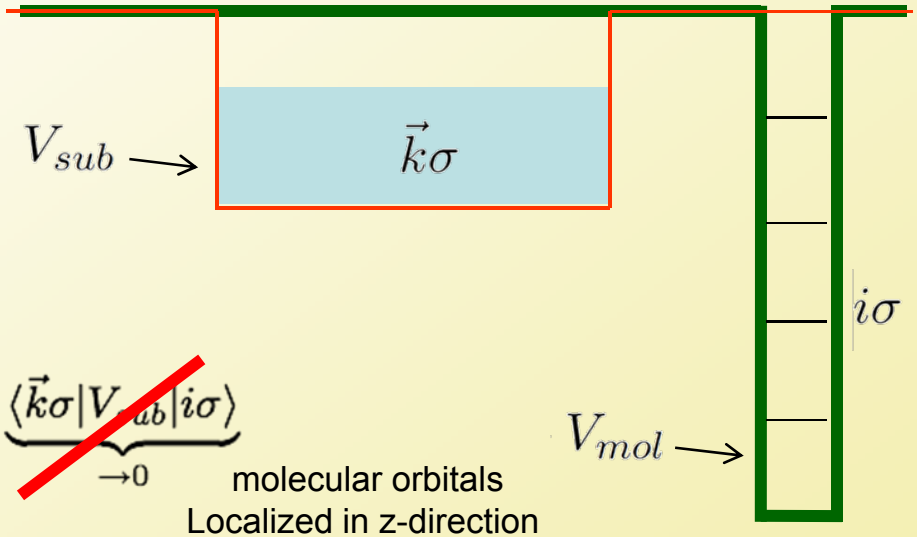


We assume no confining potential in the x and y direction.

Substrate-tunnelling

$$H_{mol-sub} = \sum_{\vec{k},i,\sigma} \langle \vec{k}\sigma | h | i\sigma \rangle c^{\dagger}_{\vec{k}\sigma} d_{i\sigma} + h.c.$$

$$h = T + V = T + V_{mol} + V_{sub}$$



$$\langle \vec{k}\sigma | T + V_{mol} + V_{sub} | i\sigma \rangle = \langle \vec{k}\sigma | \overbrace{T + V_{mol}}^{=:h_{mol}} | i\sigma \rangle + \underbrace{\langle \vec{k}\sigma | V_{sub} | i\sigma \rangle}_{\to 0}$$

molecular orbitals
Localized in z-direction

using the eigevalue equation: $h_{mol}|i\sigma\rangle = \epsilon_i |i\sigma\rangle$

$$\langle \vec{k}\sigma | h | i\sigma \rangle = \epsilon_i \langle \vec{k}\sigma | i\sigma \rangle = \epsilon_i \sum_{\alpha} \langle \vec{k}\sigma | \alpha\sigma \rangle \langle \alpha\sigma | i\sigma \rangle$$

overlap of the substrate and the p_z-orbital

change of the basis: from the molecular orbital to the carbon's p_z-orbital

Angular momentum channels (i)

$$H_{mol-sub} = \sum_{\vec{k},i,\sigma} \langle \vec{k}\sigma|h|i\sigma\rangle c^{\dagger}_{\vec{k}\sigma} d_{i\sigma} + h.c. = \sum_{\vec{k},i,\sigma} \underbrace{\epsilon_i \sum_{\alpha} \mathrm{e}^{-\mathrm{i}\vec{k}_{||}\cdot\vec{R}_{\alpha}} F\left(k_{||},\kappa,d\right) \langle \alpha\sigma|i\sigma\rangle}_{=:t^{S}_{\vec{k}i}} c^{\dagger}_{\vec{k}\sigma} d_{i\sigma} + h.c.$$

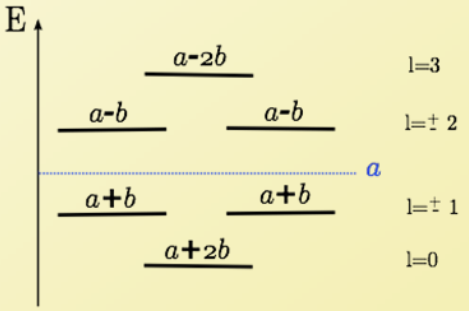
The single particle states of benzene labelled by their angular momentum

we change $i \rightarrow l$ ⇒ $\langle \alpha\sigma|l\sigma\rangle = \frac{1}{\sqrt{6}} \mathrm{e}^{\mathrm{i}\frac{2\pi}{6}\alpha l}$

$\epsilon_i \rightarrow \epsilon_l$ ⇒ $\epsilon_l = a + 2b\cos\left(\frac{2\pi}{6} l\right)$

onsite energy of the p_z-orbital

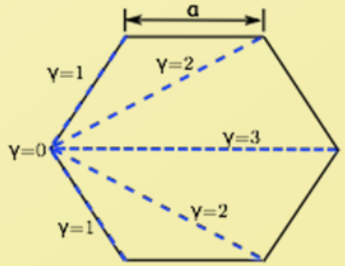
hopping integral



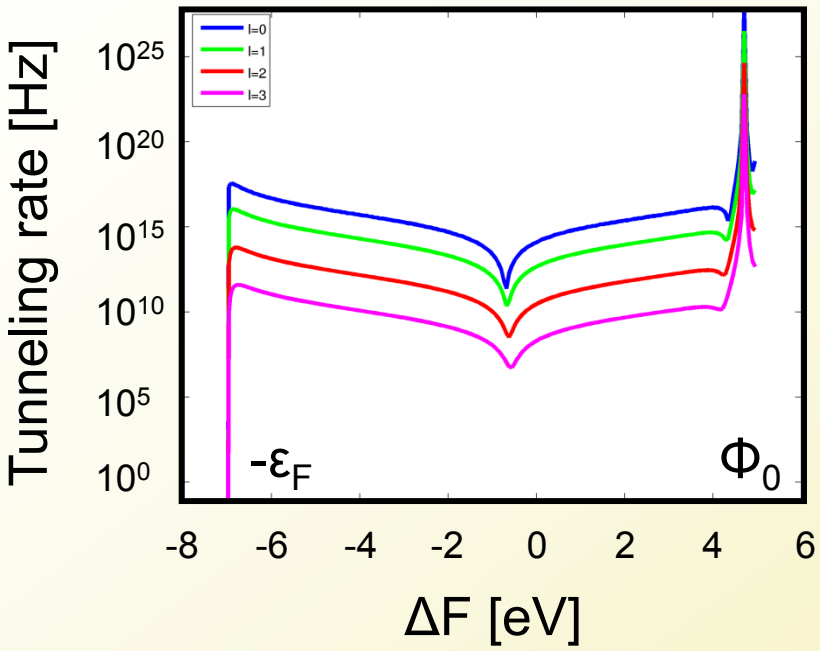
$$t^{S}_{\vec{k}l}\left(t^{S}_{\vec{k}l'}\right)^{*} = \epsilon_l \epsilon'_l \sum_{\alpha\alpha'} \mathrm{e}^{-\mathrm{i}\vec{k}_{||}\cdot\left(\vec{R}_{\alpha}-\vec{R}_{\alpha'}\right)} F\left(k_{||},\kappa,d\right) F^{*}\left(k_{||},\kappa,d\right) \mathrm{e}^{\mathrm{i}\frac{2\pi}{6}(\alpha l-\alpha' l')}$$

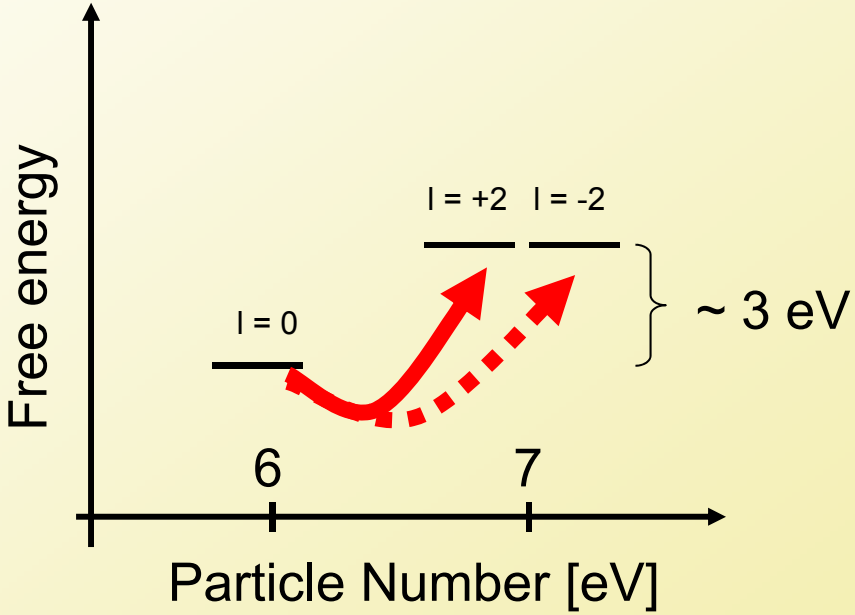
$$= \epsilon_l^2 \sum_{\gamma} \mathrm{e}^{-\mathrm{i}|\vec{k}_{||}||\Delta\vec{R}_{\gamma}|\cos\Theta} |F\left(k_{||},\kappa,d\right)|^2 \mathrm{e}^{\mathrm{i}\frac{2\pi}{6}l\gamma} \delta_{ll'}$$

$\Delta R_0 = 0$, $\Delta R_1 = a$,
$\Delta R_2 = \sqrt{3}a$, $\Delta R_3 = 2a$.



Angular momentum channels (ii)





In the tunnelling the molecule changes free energy F and angular momentum l

The tunnelling rate changes of several orders of magnitude depending on ΔF and Δl

Tip-tunnelling

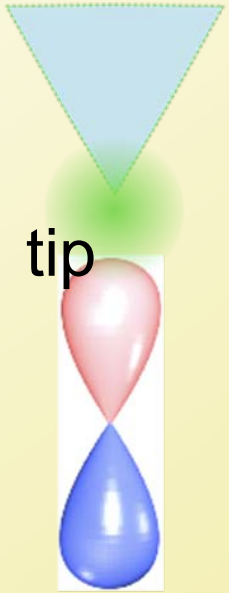
$$H_{mol-tip} = \sum_{\vec{k}i\sigma} \langle \vec{k}\sigma | h | i\sigma \rangle a^{\dagger}_{\vec{k}\sigma} d_{i\sigma} + h.c \quad \text{with} \quad h = T + V_{mol} + V_{tip}$$

$$\langle \vec{k}\sigma | T+V_{mol}+V_{tip} | i\sigma \rangle = \langle \vec{k}\sigma | T+V_{mol} | i\sigma \rangle + \underbrace{\langle \vec{k}\sigma | V_{tip} | i\sigma \rangle}_{\to 0} = \epsilon_i \langle \vec{k}\sigma | i\sigma \rangle$$

$$= \epsilon_i \sum_{\alpha} \langle \vec{k}\sigma | \alpha\sigma \rangle \langle \alpha\sigma | i\sigma \rangle$$

← from molecular to atomic orbitals

overlap



→ the tip: $|\vec{k}\sigma\rangle = \frac{1}{\sqrt{N_{cell}}} \sum_{\vec{R}_j} e^{i\vec{k}\cdot\vec{R}_j} \Phi_n(\vec{r} - \vec{R}_j)$ →

Closest atom in the tip
+
δ approximation

$$\langle \vec{k}\sigma | \alpha\sigma \rangle = \frac{1}{\sqrt{N_{cell}}} e^{-i\vec{k}\cdot\vec{R}_{tip}} p_z(\vec{R}_{tip} - \vec{r}_\alpha)$$

$$t^T_{\vec{k}l} (t^T_{\vec{k}l'})^* = \epsilon_l \epsilon_{l'} \sum_{\beta\beta'} p_z(\vec{R}_{tip} - \vec{R}_\beta) p_z(\vec{R}_{tip} - \vec{R}_{\beta'}) \frac{1}{6} e^{i\frac{2\pi}{6} l\beta} e^{-i\frac{2\pi}{6} l'\beta'}$$

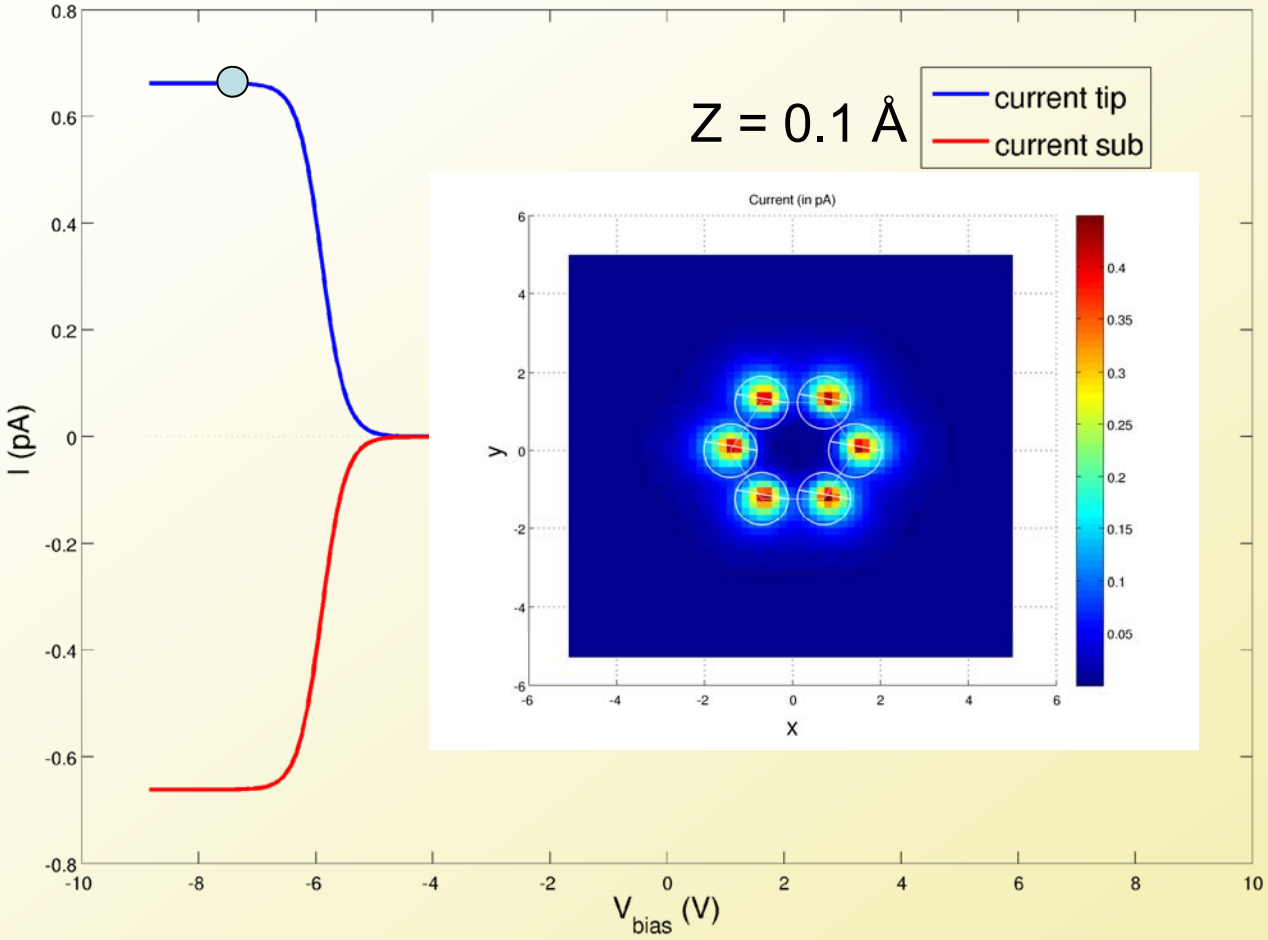
← Mixing of momentum channels

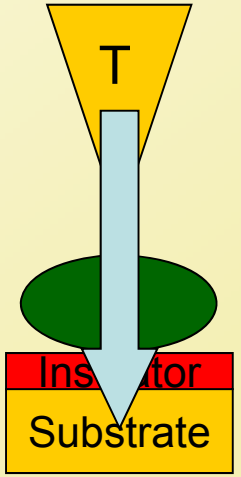
Interference: decoupling basis

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

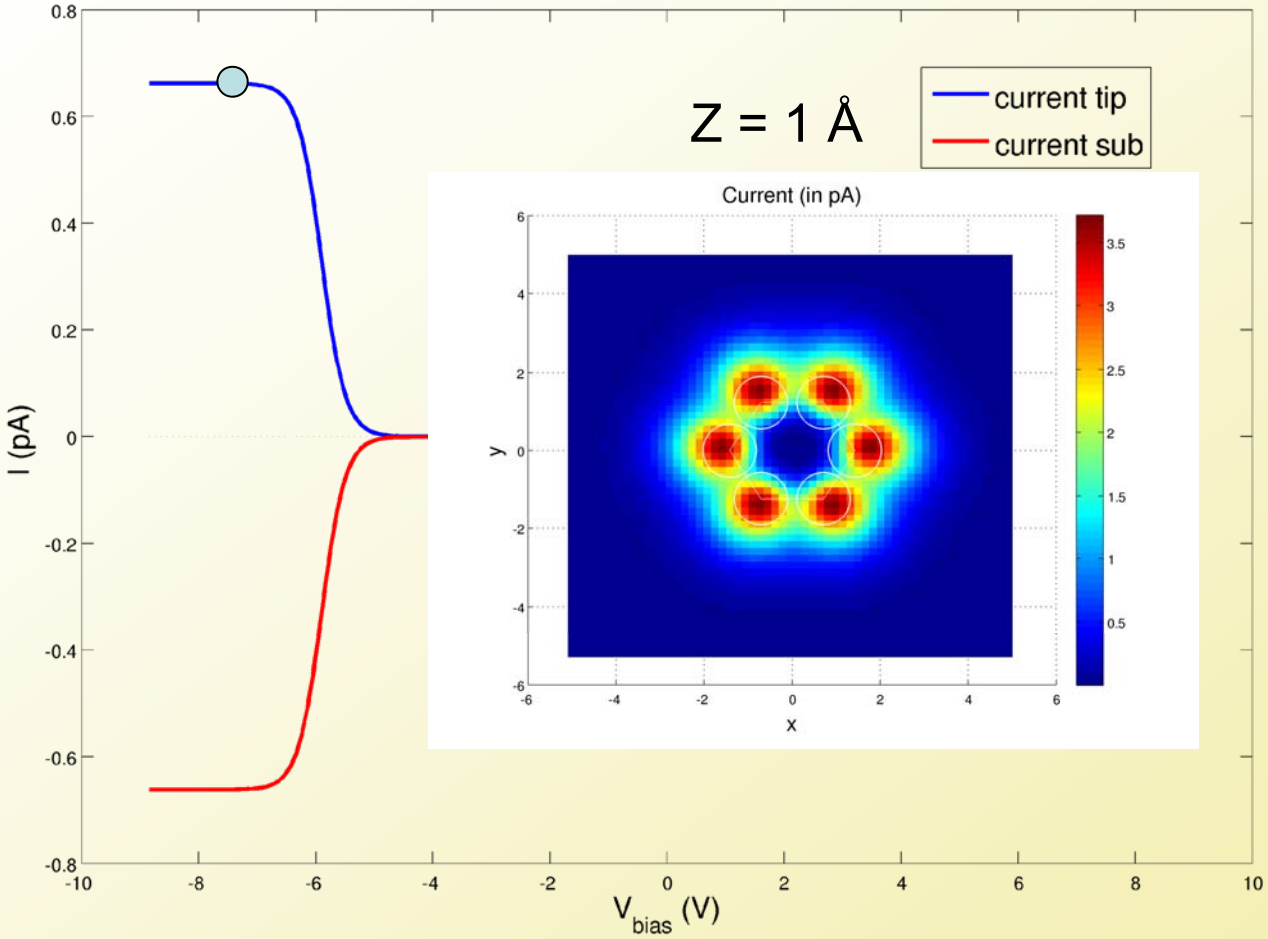
	Angular momentum basis	Decoupling basis
Tip	$\Gamma_T = \Gamma_T^0 \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}$	$\tilde{\Gamma}_T = \Gamma_T^0 \begin{pmatrix} 2 & 0 \\ 0 & 0 \end{pmatrix}$
Substrate	$\Gamma_S = \Gamma_S^0 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\tilde{\Gamma}_S = \Gamma_S^0 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$

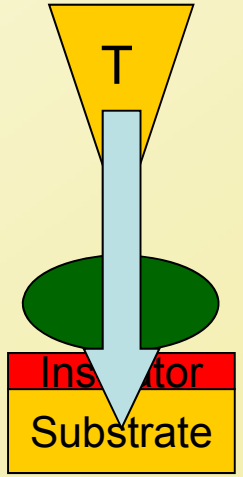
Current voltage characteristics (i)





Current voltage characteristics (i)





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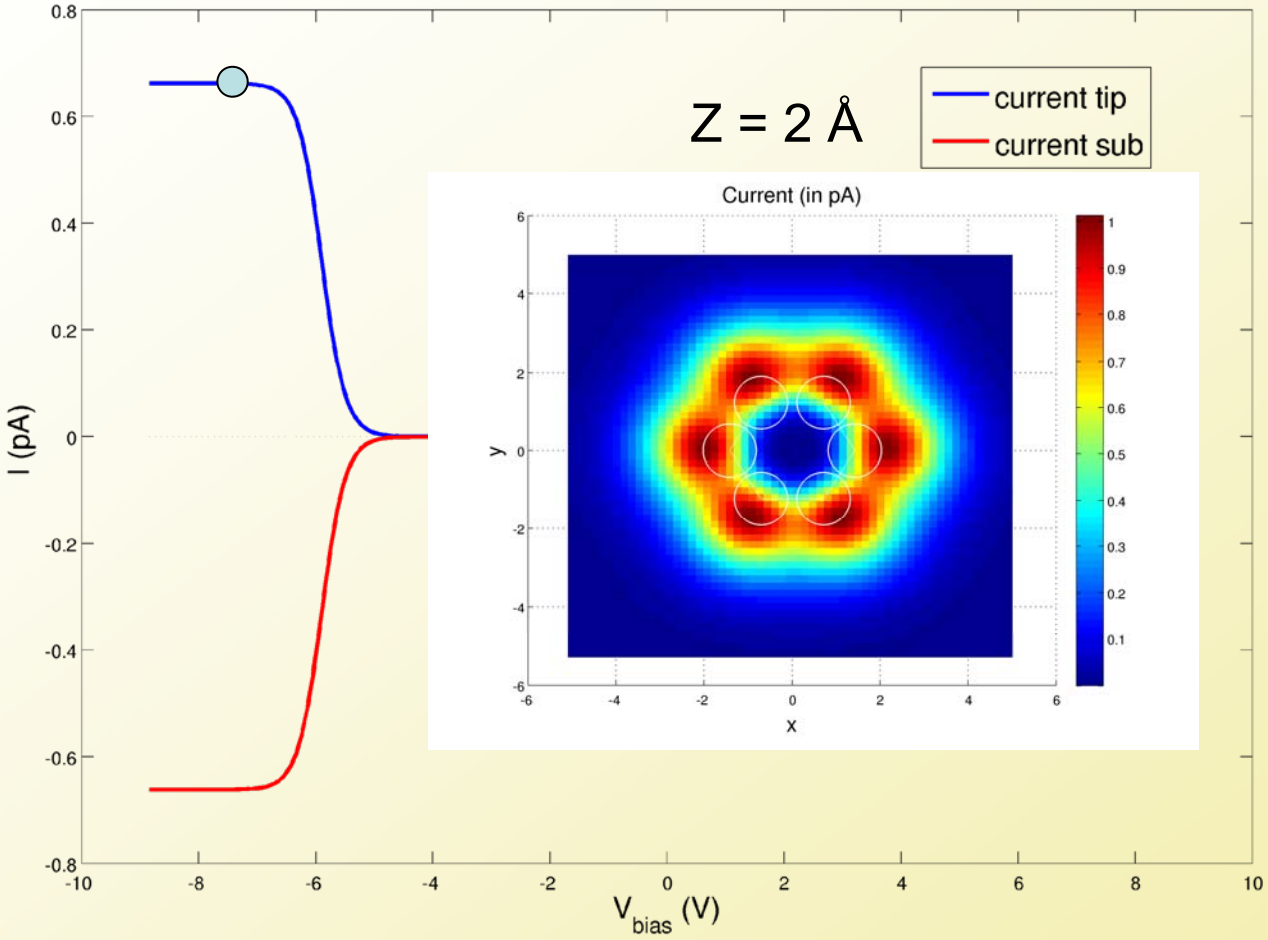

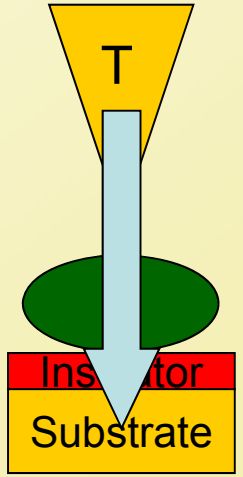

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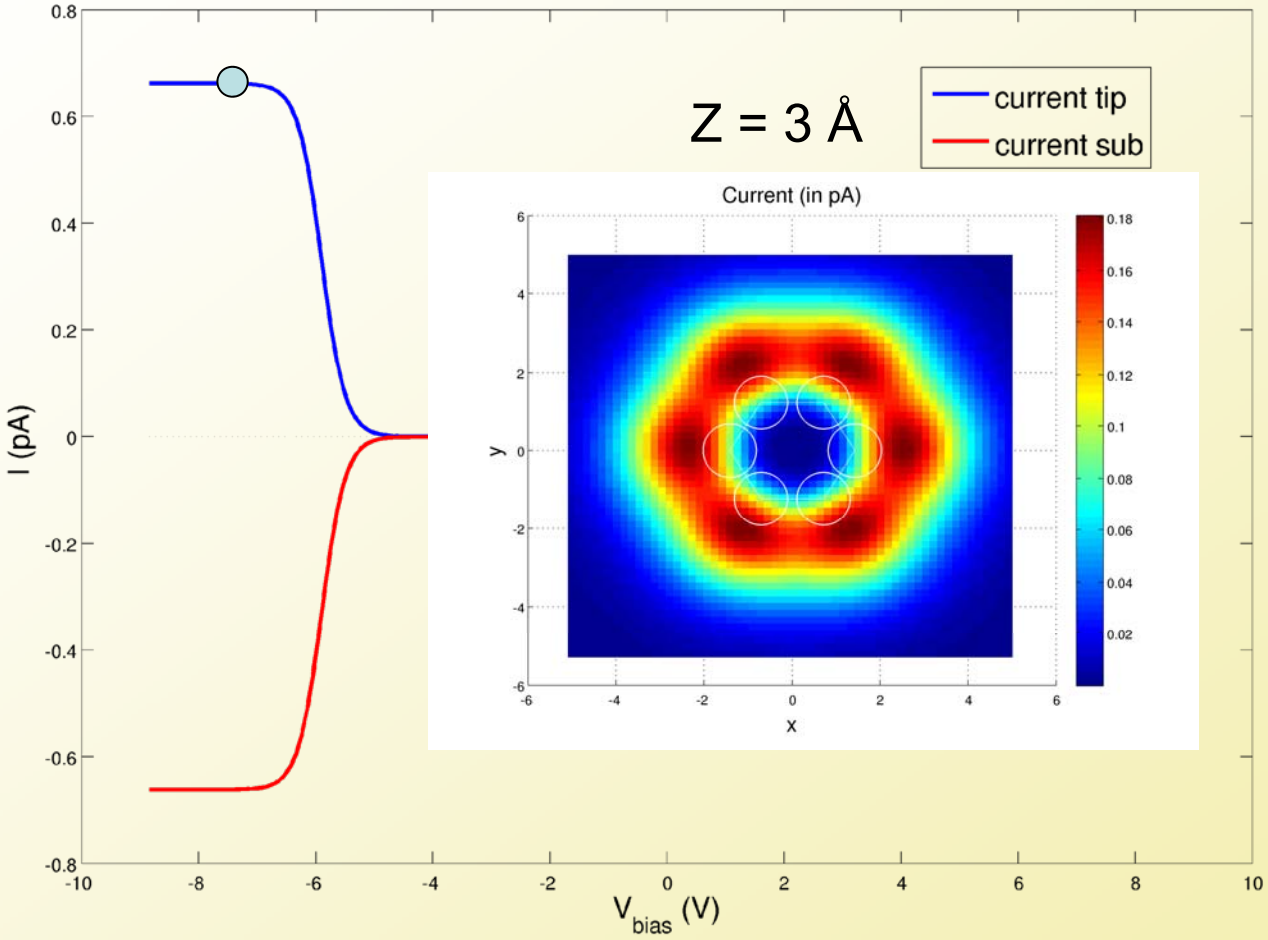

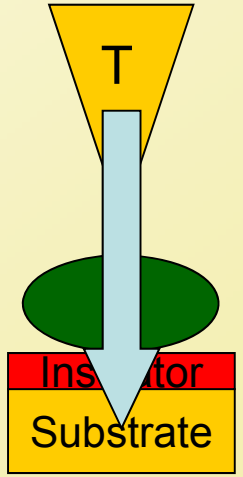

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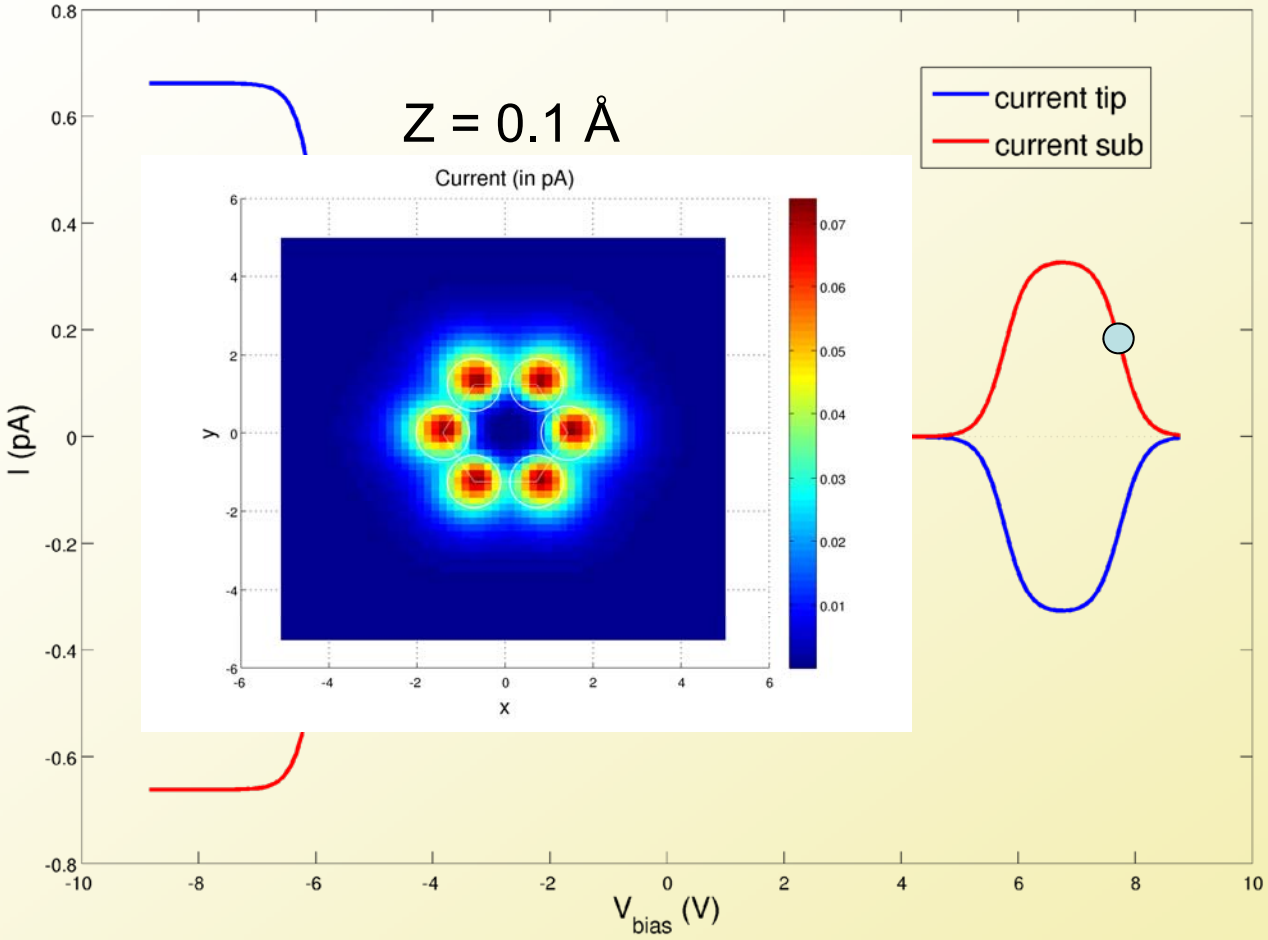

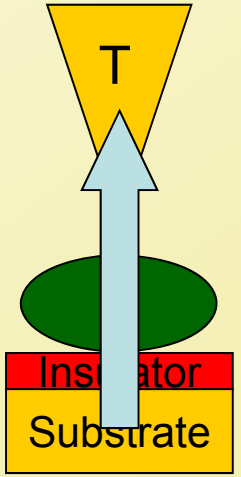

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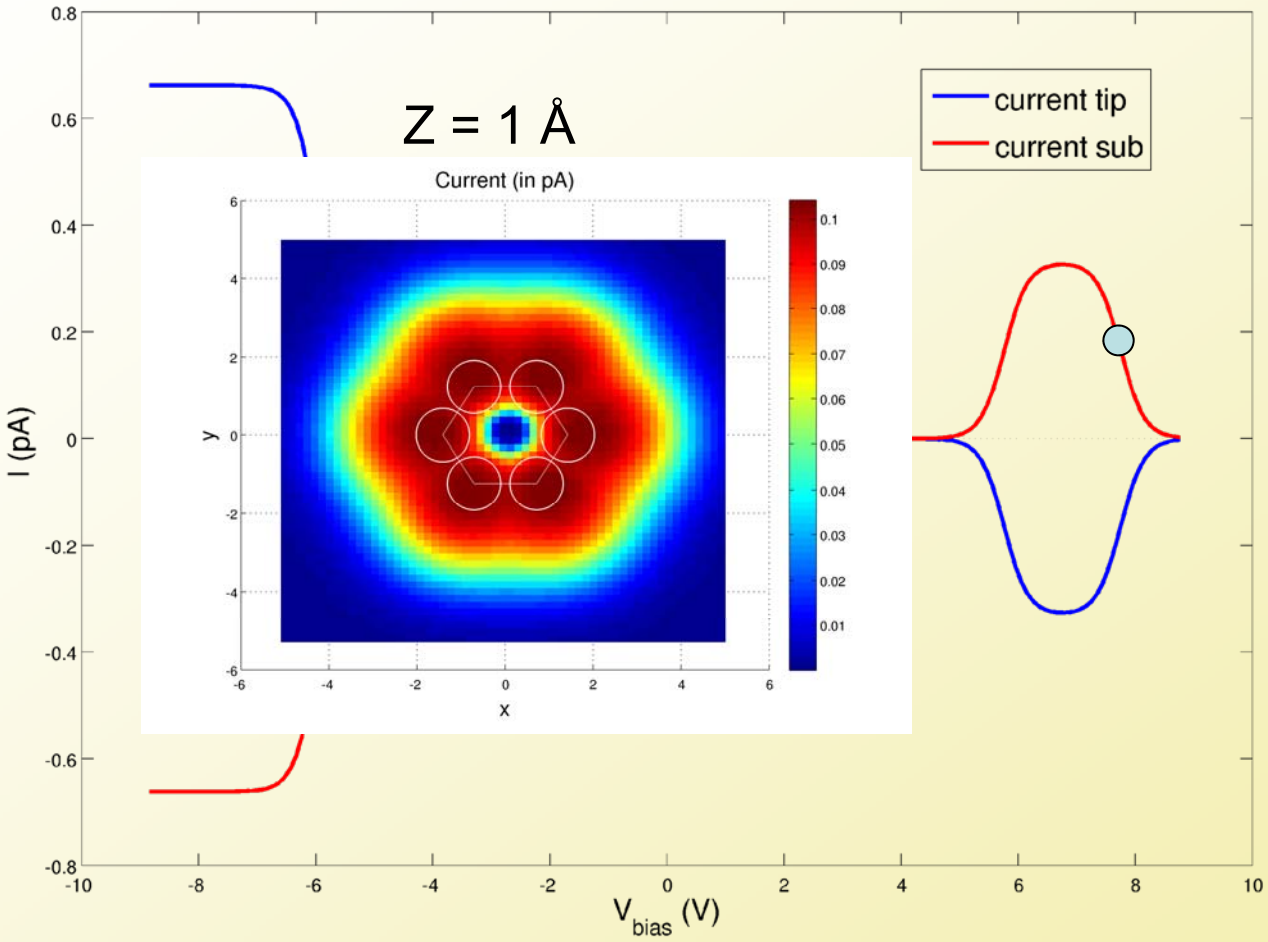

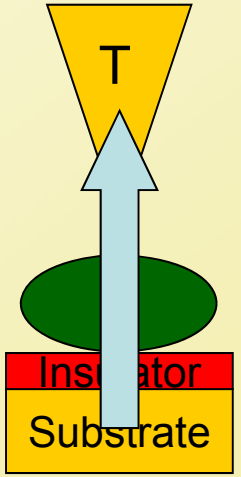

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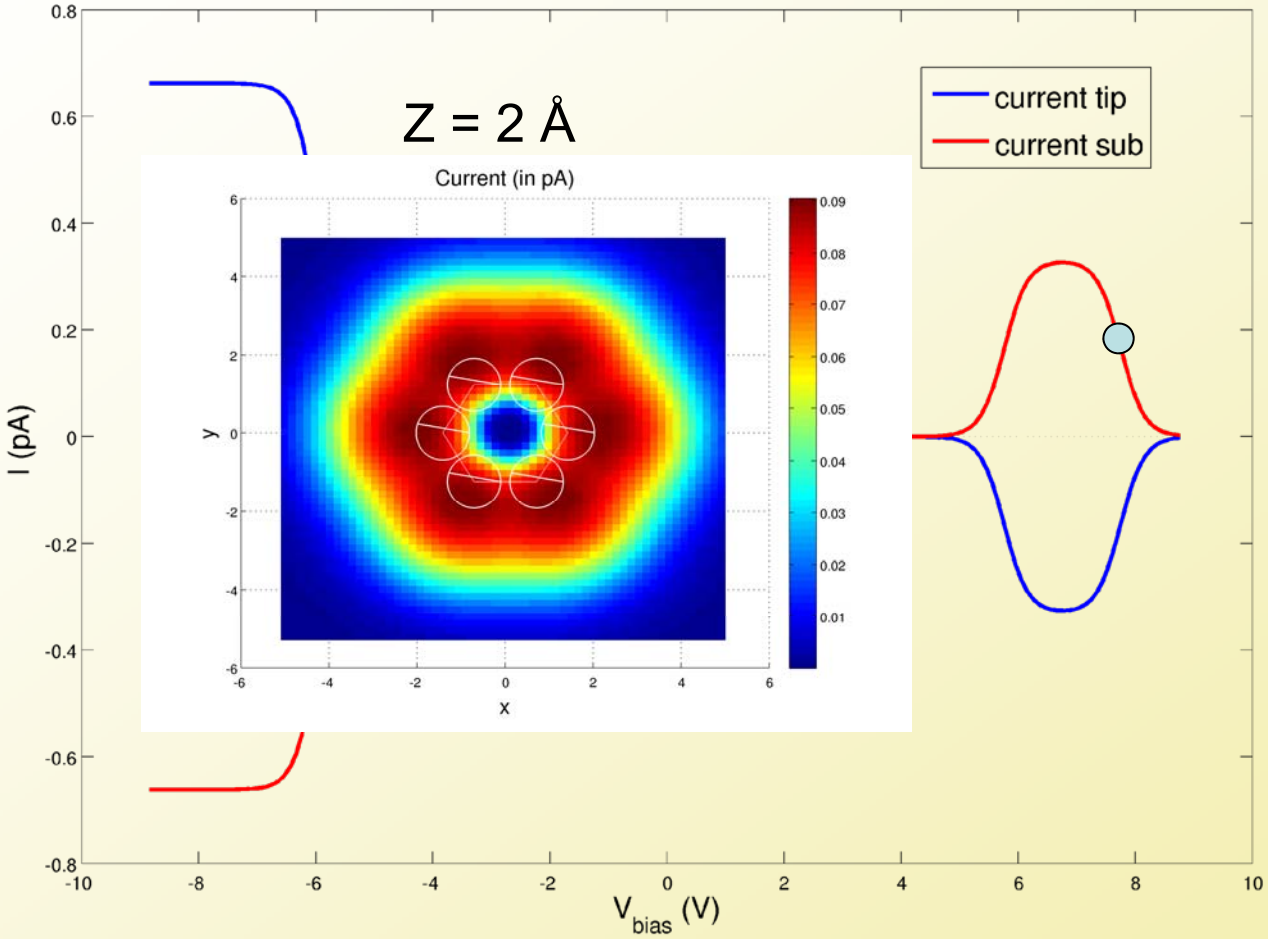

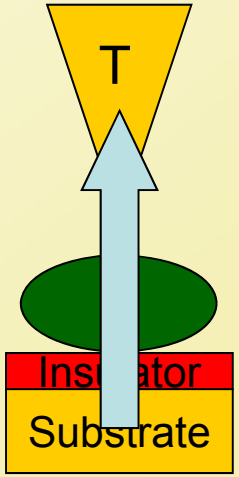

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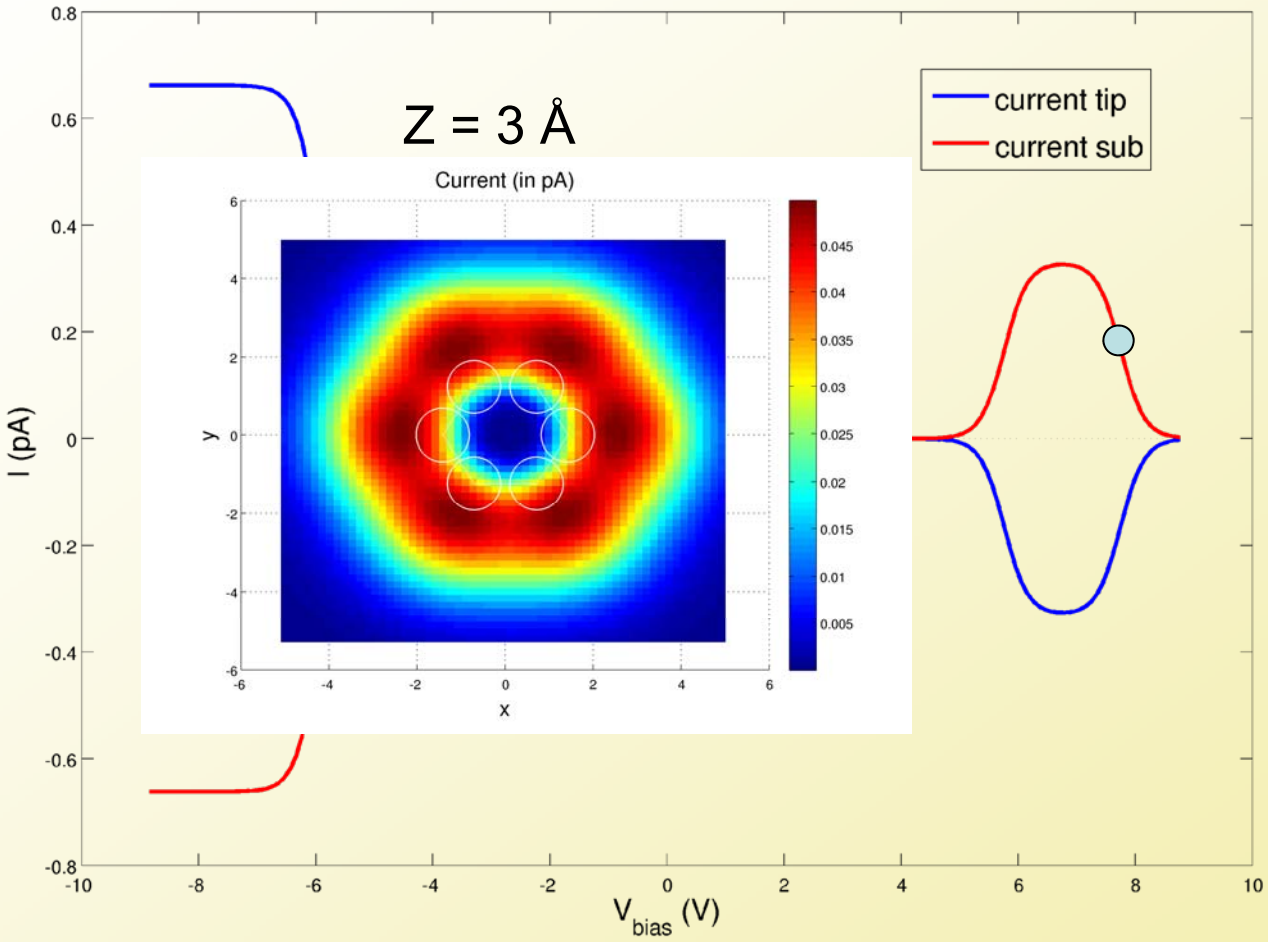
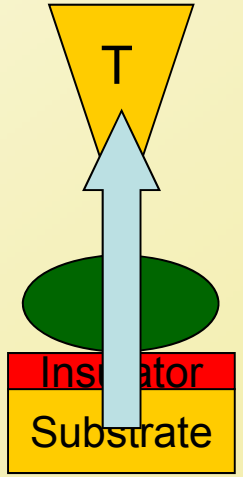
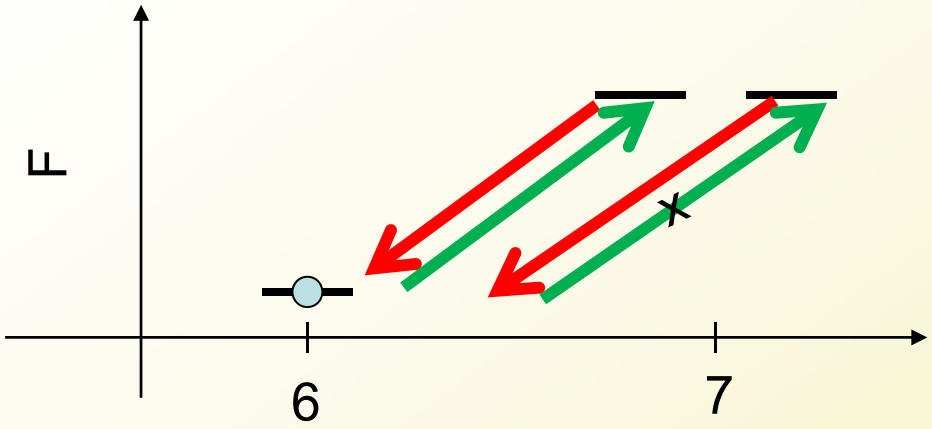


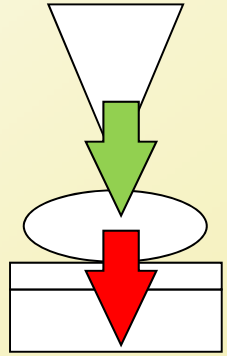


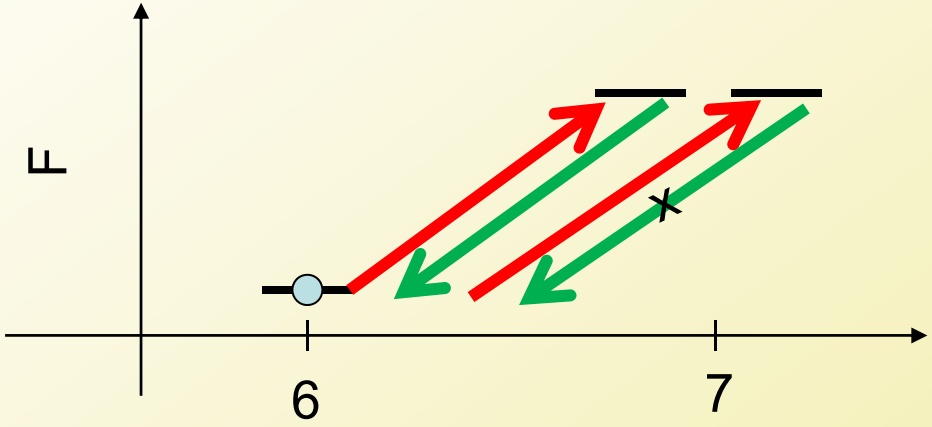
Interference: current blocking



$eV_b < -2|\Delta F|$

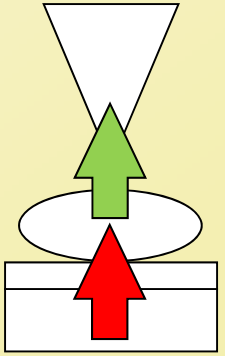
Current





$eV_b > 2|\Delta F|$

No current



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
- 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.

Thank you for your attention…