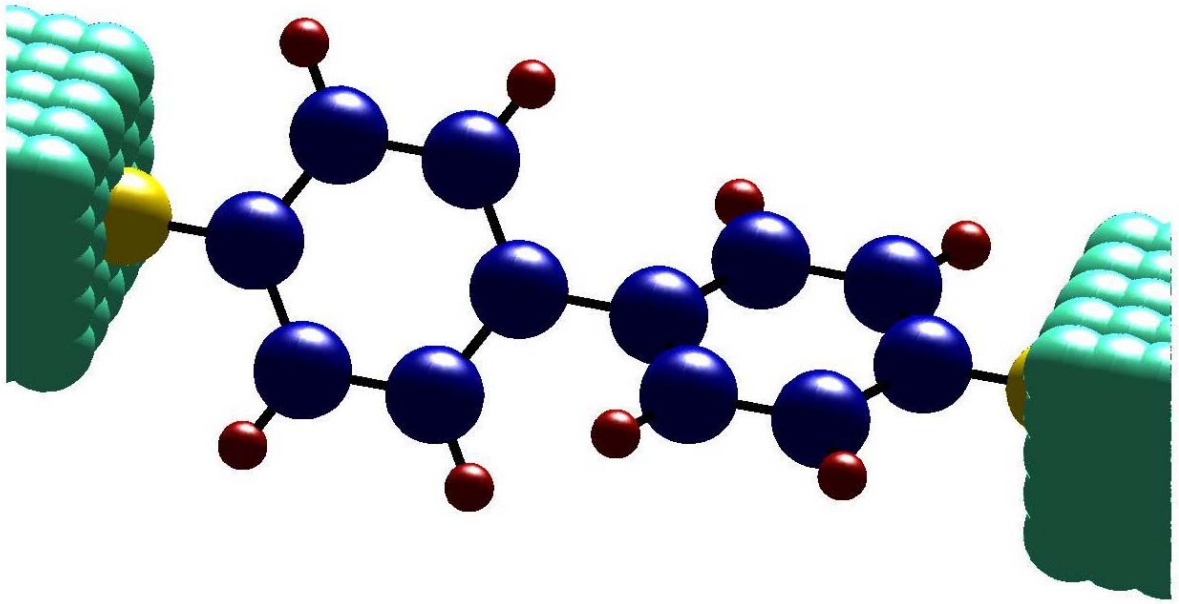
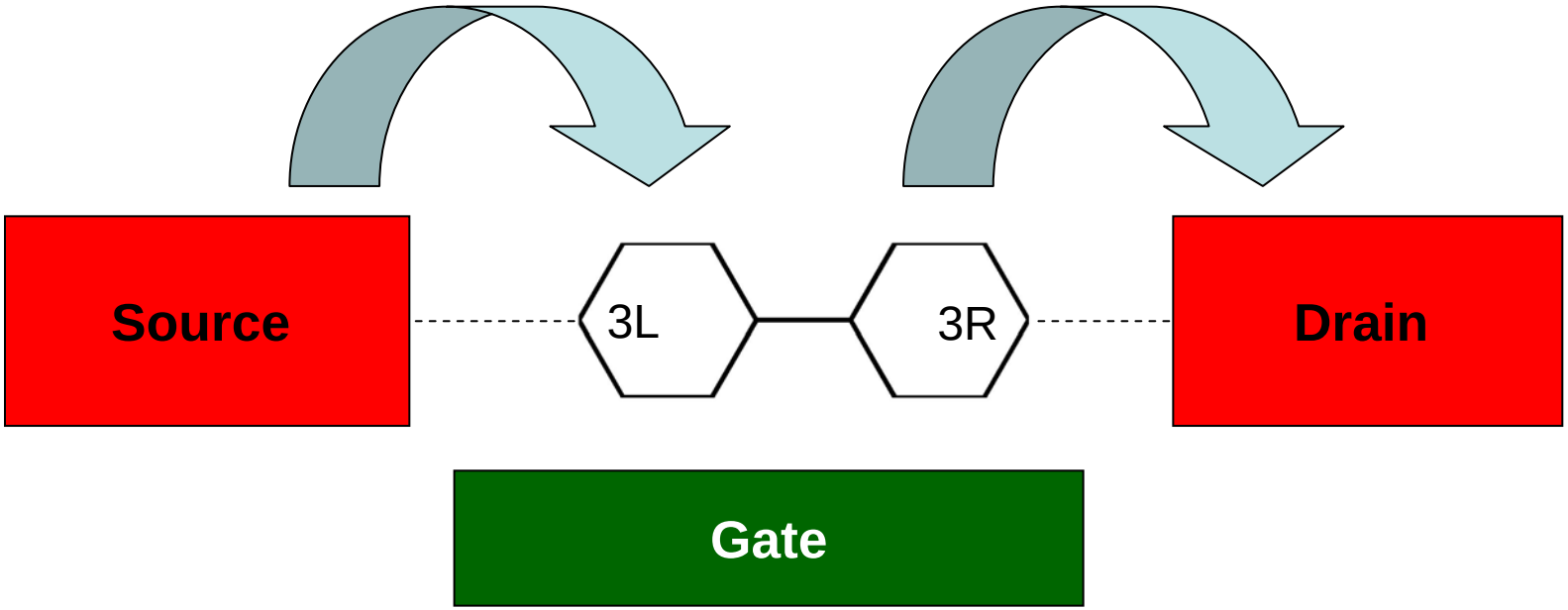
Electromechanical properties of a biphenyl transistor



The model



- Weak coupling to the leads + low temperature -> Coulomb blockade
- Gate voltage
- Torsional degree of freedom of the molecule

The Hamiltonian

The hamiltonian of the device can be written as

$$H = H_{Mol} + H_{Leads} + V$$

Where

$$H_{Mol} = T_\theta + H_{PPP}(\hat{\theta})$$

$$H_{Leads} = \sum_{\alpha k \sigma} \epsilon_{k,\alpha} c^\dagger_{\alpha k \sigma} c_{\alpha k \sigma}$$

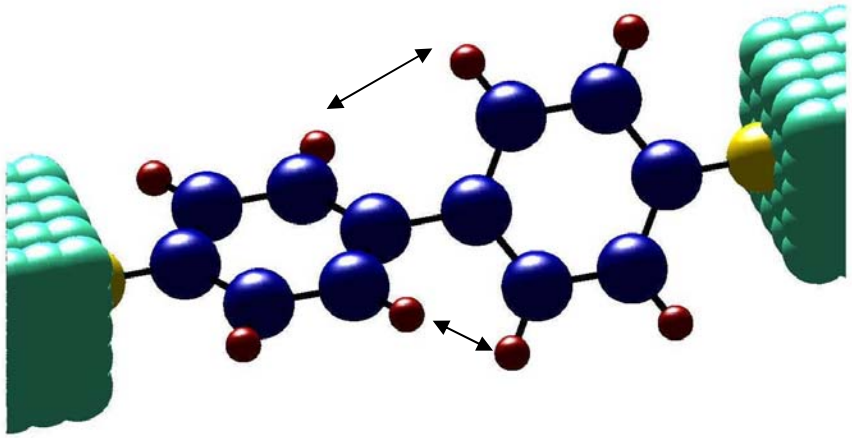
$$V = t \sum_{\alpha k \sigma} (c^\dagger_{\alpha k \sigma} c_{\alpha 3 \sigma} + c^\dagger_{\alpha 3 \sigma} c_{\alpha k \sigma})$$

Isolated biphenyl

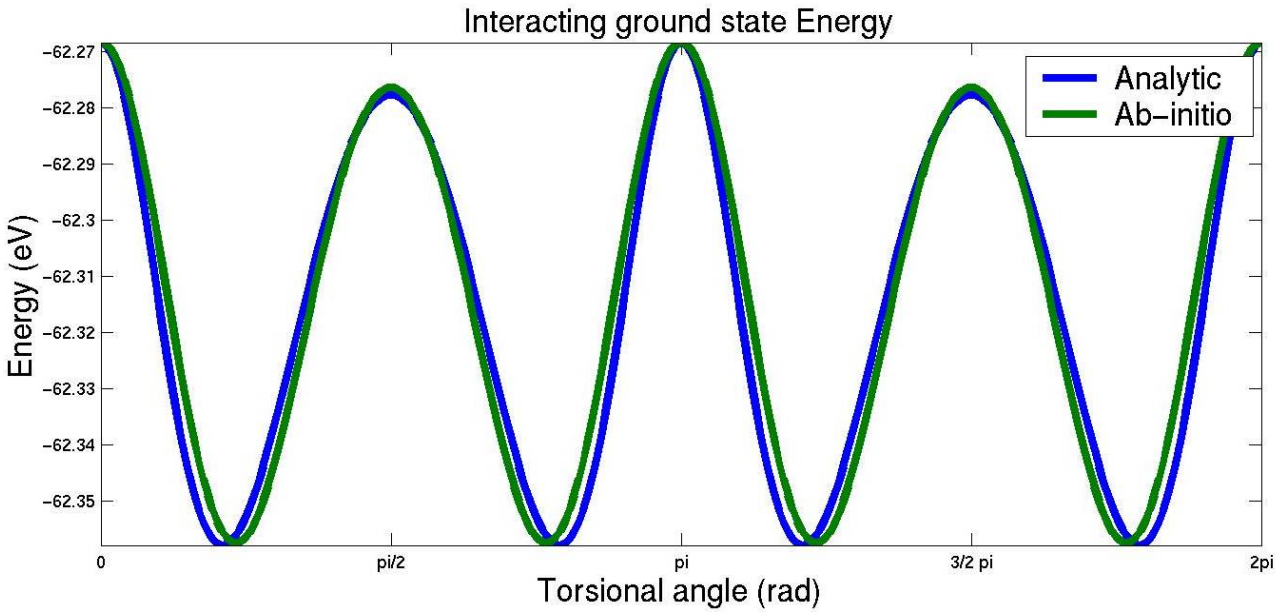
- H_{PPP} is the Pariser-Parr-Pople hamiltonian

$$H_{PPP}(\theta) = \sum_{i\sigma} b_{i\,i+1}(\theta)(c^{\dagger}_{i\sigma}c_{i+1\sigma} + c^{\dagger}_{i+1\sigma}c_{i\sigma}) + \sum_{i} U_i(\theta)\left(\hat{n}_{i\uparrow} - \frac{z_i}{2}\right)\left(\hat{n}_{i\downarrow} - \frac{z_i}{2}\right) + \sum_{\langle i<j\rangle} V_{ij}(\theta)(\hat{n}_i - z_i)(\hat{n}_j - z_j)$$

+ H-H steric repulsion (Lehnard-Jones potential)



Potential surfaces (I)



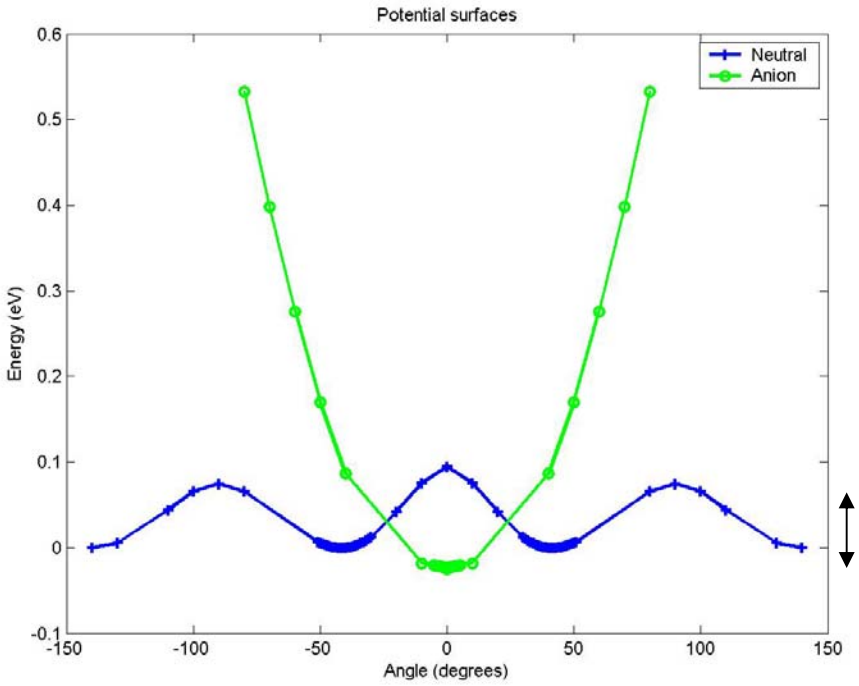
- ground state electronic energy
- neutral biphenyl molecule
- Hartree-Fock approximation of the PPP Hamiltonian

Potential surfaces (II)

The Hartree-Fock approximation fails for the anionic state

CORRELATIONS!!!

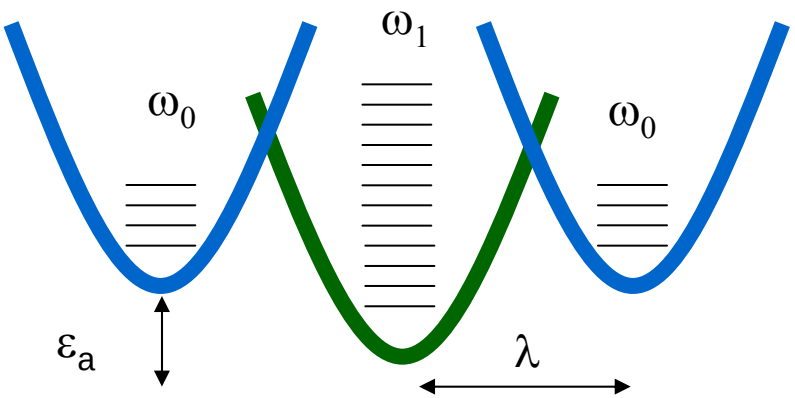
(work in progress to go beyond Hartree-Fock)



0.1 eV

DFT calculations
With gaussian basis set
And B3LYP exchange potential

Model ... of the model



- Harmonic approximation for the anionic state
- Low lying states of a double (harmonic) well potential for the neutral state
- The model is identifyed by three parameters:

$$\alpha = \sqrt{\frac{\omega_1}{\omega_0}} \qquad \lambda = \frac{\Delta\theta}{\sqrt{\theta_{z0}\theta_{z1}}} \qquad \epsilon_a = \frac{EA}{\hbar\sqrt{\omega_0\omega_1}}$$

Definition of Unity

- We write the previous approximation in terms of unity operator:

$$1 = |N\rangle\langle N|(\mathcal{P}_+ + \mathcal{P}_-) + |N+1\rangle\langle N+1|\mathcal{P}_0$$

- where $\mathcal{P}_\pm = \sum_{n=0}^{N_\pm} |n_\pm\rangle\langle n_\pm|$, $\mathcal{P}_0 = \sum_{n=0}^{\infty} |n_0\rangle\langle n_0|$

that define the effective Hilbert space.

Effective Hamiltonian

$$
\begin{aligned}
H_{eff} = & \sum_{\alpha k\sigma} \epsilon_{k,\alpha} c^{\dagger}_{\alpha k\sigma} c_{\alpha k\sigma} + \\
& + \sum_{\alpha k\sigma,n,m} \left[t^{(+)}_{n,m} c^{\dagger}_{\alpha k\sigma} c_{d\sigma} |n_+\rangle\langle m_0| + t^{(-)}_{n,m} c^{\dagger}_{\alpha k\sigma} c_{d\sigma} |n_-\rangle\langle m_0| + t^{(+)}_{n,m} c^{\dagger}_{d\sigma} c_{\alpha k\sigma} |m_0\rangle\langle n_+| + t^{(-)}_{n,m} c^{\dagger}_{d\sigma} c_{\alpha k\sigma} |m_0\rangle\langle n_-| \right] + \\
& + \left(1 - \sum_{\sigma} c^{\dagger}_{d\sigma} c_{d\sigma} \right) \left\{ \epsilon_0 + \hbar\omega_0 \left[\mathcal{P}_+ \left(d^{\dagger}_+ d_+ + \frac{1}{2} \right) \mathcal{P}_+ + \mathcal{P}_- \left(d^{\dagger}_- d_- + \frac{1}{2} \right) \mathcal{P}_- \right] \right\} + \\
& + \sum_{\sigma} c^{\dagger}_{d\sigma} c_{d\sigma} \left[\epsilon_1 + \mathcal{P}_0 \left(d^{\dagger} d + \frac{1}{2} \right) \mathcal{P}_0 \right]
\end{aligned}
$$

where

$$c^{\dagger}_{d\sigma} |N\rangle \equiv |N+1, \sigma\rangle$$

$$t^{(\pm)}_{n,m} = t \underbrace{\langle N | c_{3\alpha} | N+1 \rangle} \langle n_{\pm} | m_0 \rangle$$

We assume it independent of θ

Franck-Condon coefficient

Generalized Master Equation (I)

The density matrix evolves according to the Liouville-von Neumann equation:

$$\dot{\rho} = -\frac{i}{\hbar}[H, \rho]$$

We define the reduced density matrix:

$$\sigma = \mathrm{Tr}_{Leads}\{\rho\}$$

To second order in the coupling to the leads and in the Markov approximation:

$$\dot{\sigma} = -\frac{i}{\hbar}[H_{Mol}, \sigma] - \frac{1}{\hbar^2}\int_0^\infty \mathrm{d}\tau \mathrm{Tr}_{Leads}\{[V, [\tilde{V}_I(-\tau), \sigma]] \otimes \rho_{Leads}\}$$

GME (II)

- coherencies between different charge states vanish

- due to the mechanical degeneracies of the neutral state we MUST keep coherencies between displaced mechanical states

- we write the GME in the basis that diagonalize the molecule hamiltonian (Bloch-Redfield form)

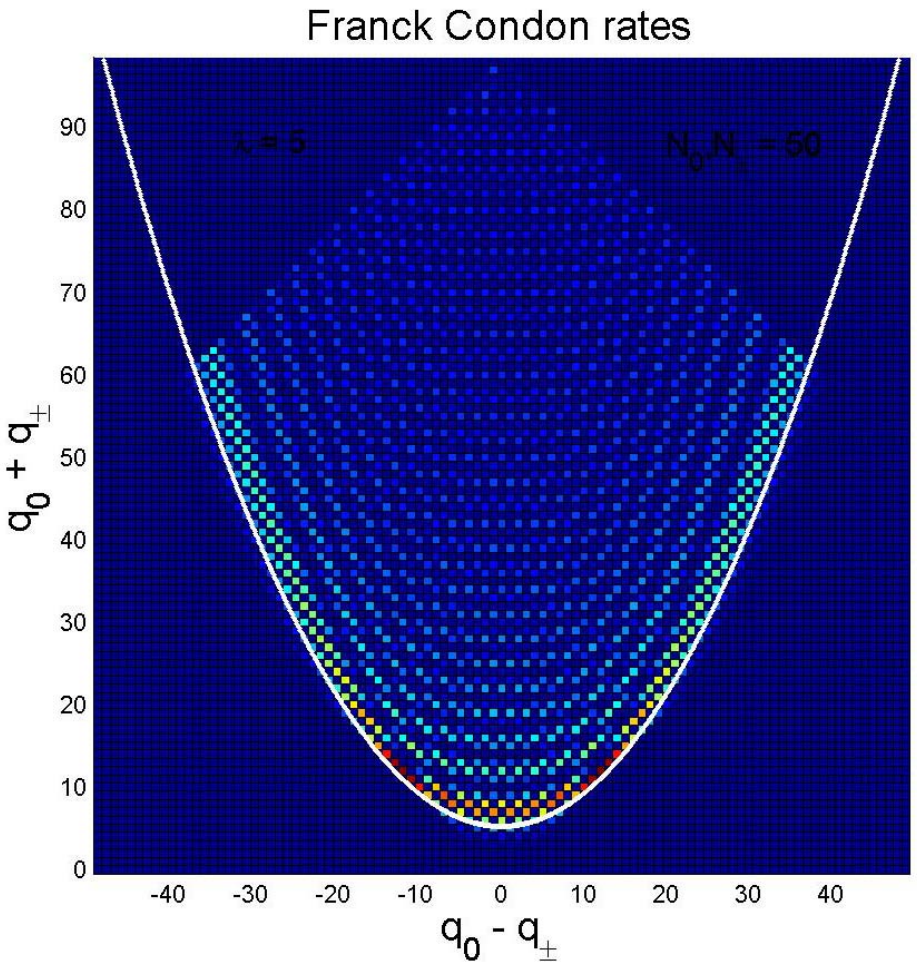
$$\dot{\sigma}_{ij} = \sum_{mn} R_{ijmn}\sigma_{mn}$$

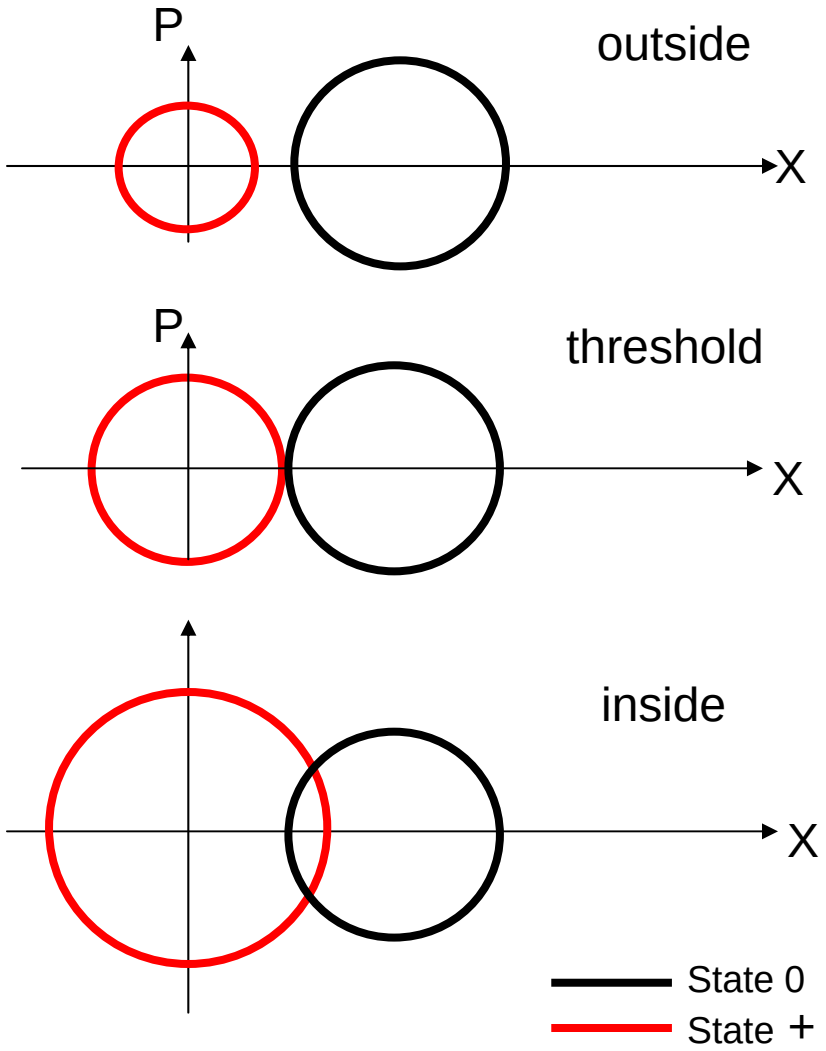
GME (III)

The elements of the Redfield tensor R_{ijmn} depend on

- Fermi factors - the Pauli esclusion principle prevents some transitions to occur
- Bare tunneling rates - given by the density of states in the leads times the electrical coupling leads-molecule
- Franck-Condon coefficients – each state transition in the system is electromechanical

The Franck-Condon parabola





GME (IV)

$$\dot{\sigma}_{00}^{r\tau\, s\tau'} = -\frac{i}{\hbar}\sum_{l\rho}\left[H^{(0)}_{r\tau\, l\rho}\sigma_{00}^{l\rho\, s\tau'} - \sigma_{00}^{r\tau\, l\rho}H^{(0)}_{l\rho\, s\tau'}\right] - \sum_{l\rho\,\alpha}\left[W^{\alpha}_{r\tau\, l\rho}\sigma_{00}^{l\rho\, s\tau'} - \sigma_{00}^{r\tau\, l\rho}W^{\alpha}_{l\rho\, s\tau'}\right] + \sum_{m\,m'\,\alpha}\left[R^{\alpha}_{r\tau\, s\tau'\, m'\, m} + R^{\alpha}_{s\tau'\, r\tau\, m\, m'}\right]\sigma_{11}^{m'\, m}$$

$$\dot{\sigma}_{11}^{k,k'} = -\frac{i}{\hbar}\sum_{l}\left[H^{(1)}_{k\,l}\sigma_{11}^{l\,k'} - \sigma_{11}^{k\,l}H^{(1)}_{l\,k'}\right] - \sum_{l\,\alpha}\left[W^{\alpha}_{k\,l}\sigma_{11}^{l\,k'} - \sigma_{11}^{k\,l\rho}W^{\alpha}_{l\,k'}\right] + \sum_{n'\tau'\,n\tau\,\alpha}\left[R^{\alpha}_{k\,k'\,n'\tau'\,n\tau} + R^{\alpha}_{k'\,k\,n\tau\,n'\tau'}\right]\sigma_{00}^{n'\tau'\,n\tau}$$

where

$$W^{\alpha}_{r\tau\, l\rho} = \sum_{m}\Gamma^{0}_{\alpha} f_{\alpha}(\epsilon_c + \hbar\omega_1(m+1/2) - \hbar\omega_0(l+1/2))C_{r\tau\, m}C_{l\rho\, m}$$

$$R^{\alpha}_{r\tau\, s\tau'\, m'\, m} = \frac{\Gamma^{0}_{\alpha}}{2}[1 - f_{\alpha}(\epsilon_c + \hbar\omega_1(m+1/2) - \hbar\omega_0(s+1/2))]C_{r\tau\, m'}C_{s\tau'\, m}$$

$$W^{\alpha}_{k\,l} = \sum_{n\tau}\frac{\Gamma^{0}_{\alpha}}{2}[1 - f_{\alpha}(\epsilon_c + \hbar\omega_1(l+1/2) - \hbar\omega_0(n+1/2))]C_{n\tau\, k}C_{n\tau\, l}$$

$$R^{\alpha}_{k\,k'\,n'\tau'\,n\tau} = \Gamma^{0}_{\alpha} f_{\alpha}(\epsilon_c + \hbar\omega_1(k+1/2) - \hbar\omega_0(n+1/2))C_{n'\tau'\, k}C_{n\tau\, k'}$$

The current calculation

1. Computation of the stationary reduced density matrix σ^{stat}

2. Identification of the current operators:

$$
\begin{aligned}
I =& \frac{dQ}{dt} = \sum_m \dot{\sigma}_{11}^{m\,m} \\
=& -\sum_{k\,l\,\alpha} \left(W_{k\,l}^{\alpha} \sigma_{11}^{l\,k} + \sigma_{11}^{k\,l} W_{l\,k}^{\alpha} \right) + \sum_{k\,n'\tau'\,n\tau\,\alpha} \left(R_{k\,k\,n'\tau'\,n\tau}^{\alpha} + R_{k\,k\,n\tau\,n'\tau'}^{\alpha} \right) \sigma_{00}^{n'\tau'\,n\tau} \\
=& -2\mathrm{Tr}_{Mech}\{W_1^L \sigma_{11}\} + 2\mathrm{Tr}_{Mech}\{W_0^L \sigma_{00}\} - 2\mathrm{Tr}_{Mech}\{W_1^R \sigma_{11}\} + 2\mathrm{Tr}_{Mech}\{W_0^R \sigma_{00}\} \\
=& \langle \hat{I}_L \rangle - \langle \hat{I}_R \rangle
\end{aligned}
$$

3. Calculation of the stationary current:

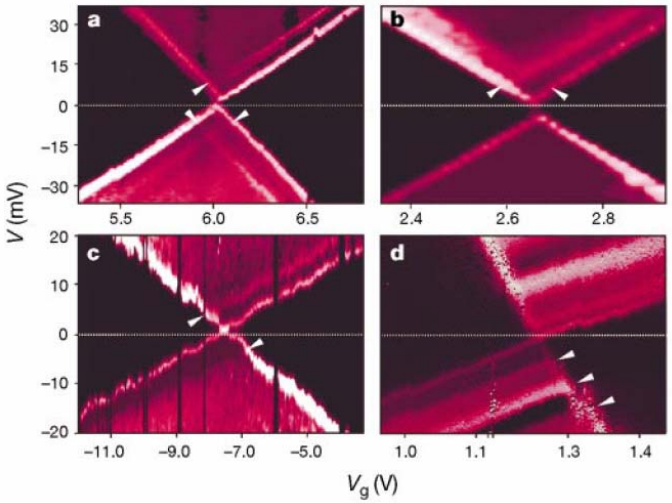
$$
\begin{aligned}
I_L^{stat} &= \mathrm{Tr}_{Mech}\{\sigma^{stat} \hat{I}_L\} \\
I_R^{stat} &= \mathrm{Tr}_{Mech}\{\sigma^{stat} \hat{I}_R\}
\end{aligned}
$$

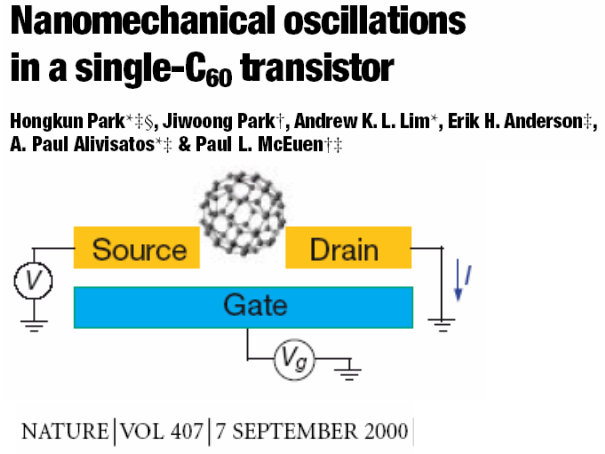
Stability diagrams

- Plot of differential conductance as a function of bias and gate voltage:

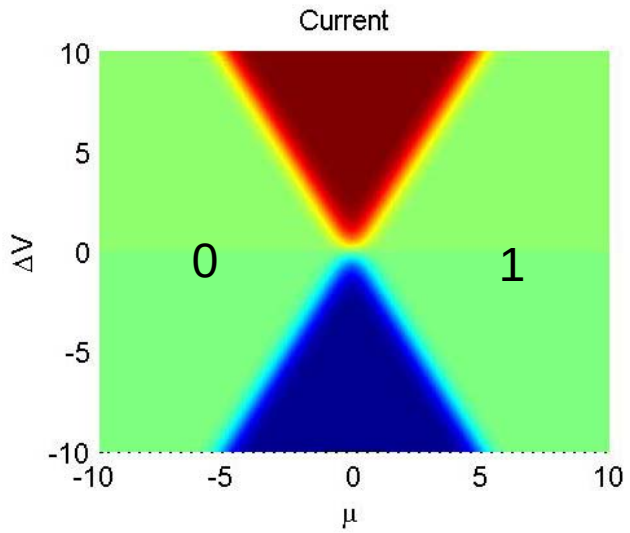
$$G = \frac{dI}{dV_b}(V_b, V_g)$$

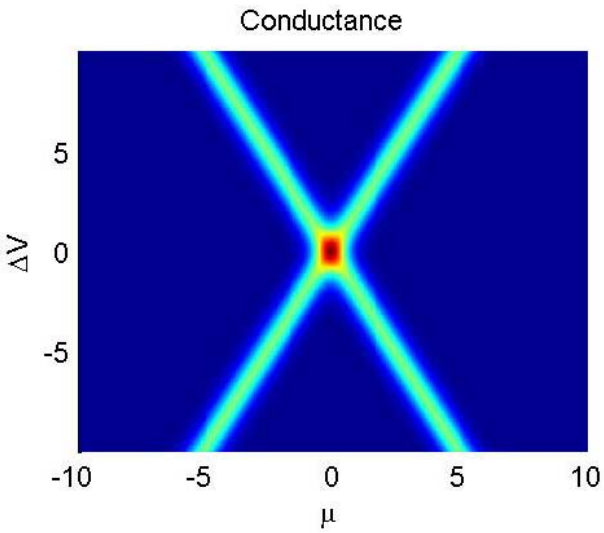
- Helpful representation of tunneling spectroscopy:

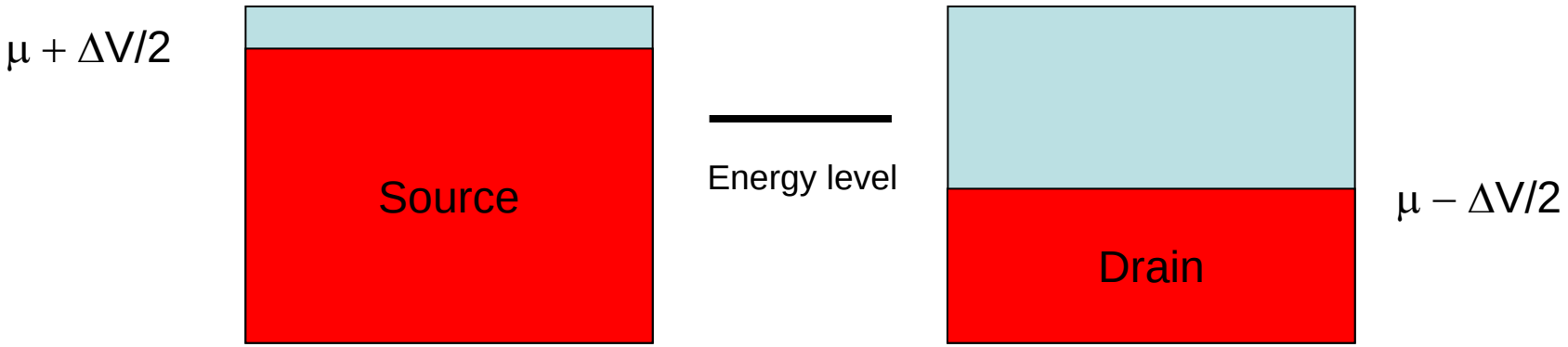




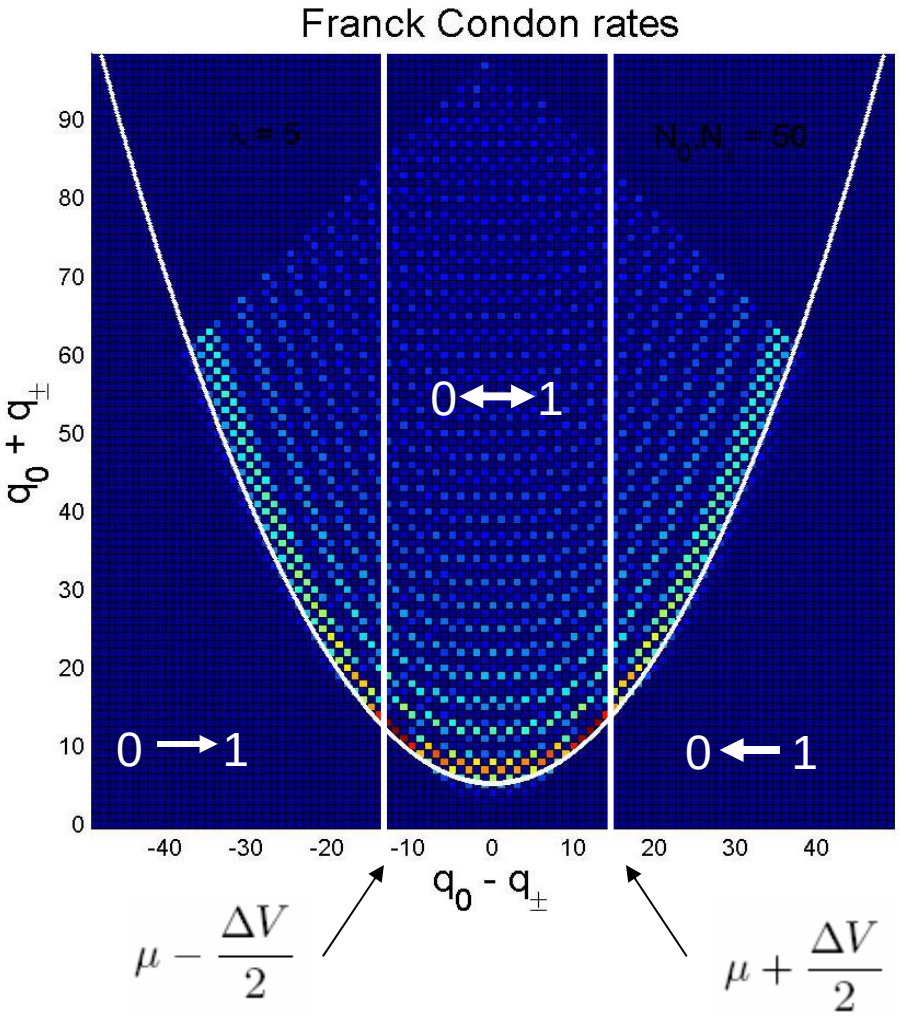
Single level







Franck-Condon parabola (II)



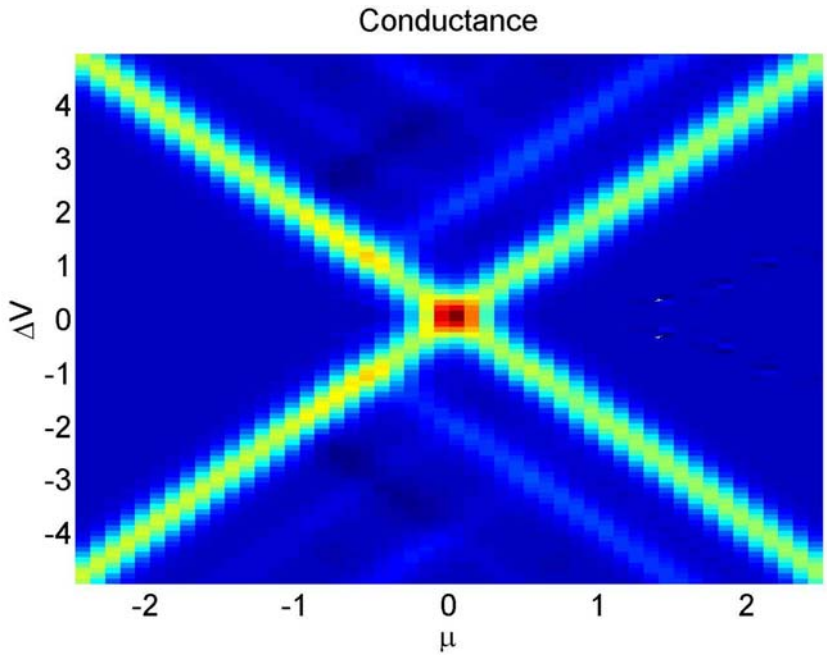
Incoming electrons

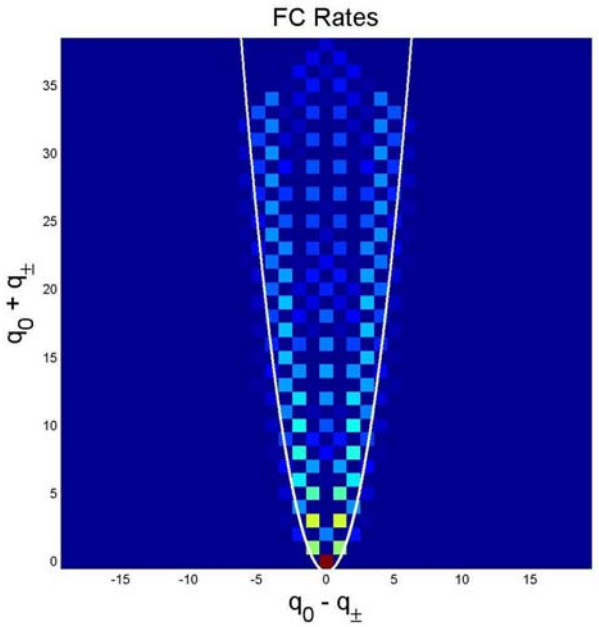
$$\mu_L = \mu + \frac{\Delta V}{2} \geq \epsilon_1 - \epsilon_0 + (q_0 - q_\pm)\hbar\omega$$

$$\mu_R = \mu - \frac{\Delta V}{2} \leq \epsilon_1 - \epsilon_0 + (q_0 - q_\pm)\hbar\omega$$

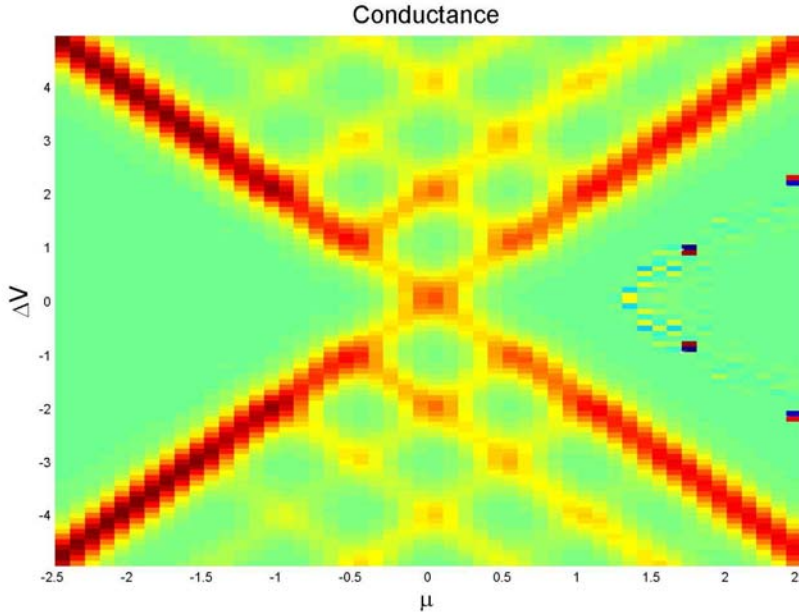
Outgoing electrons

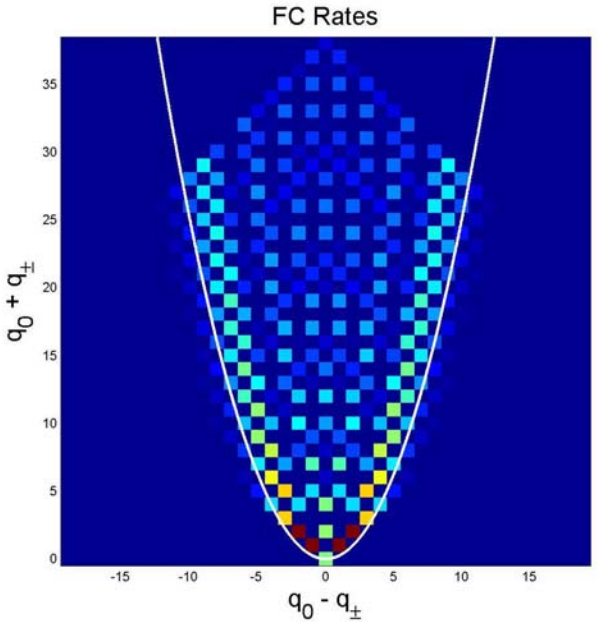
Preliminary results $\lambda = 1$



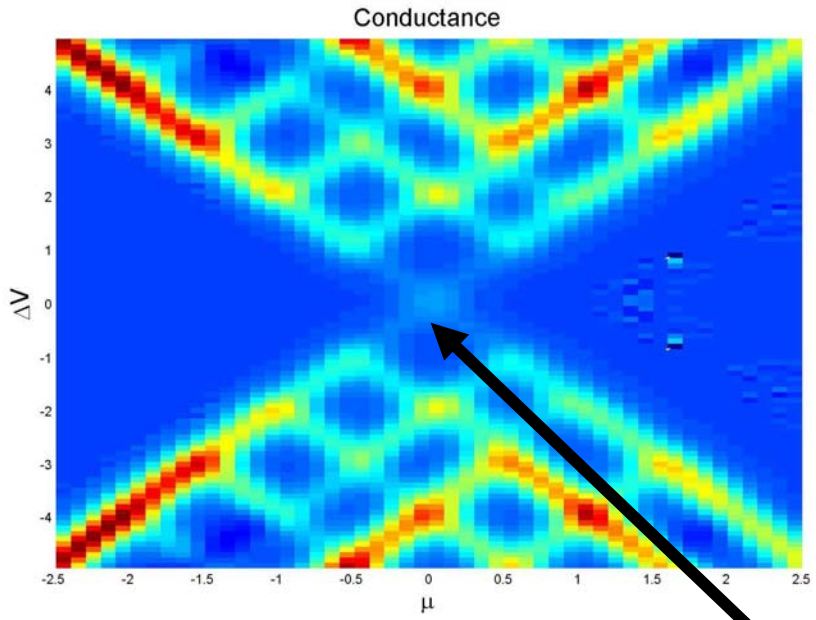


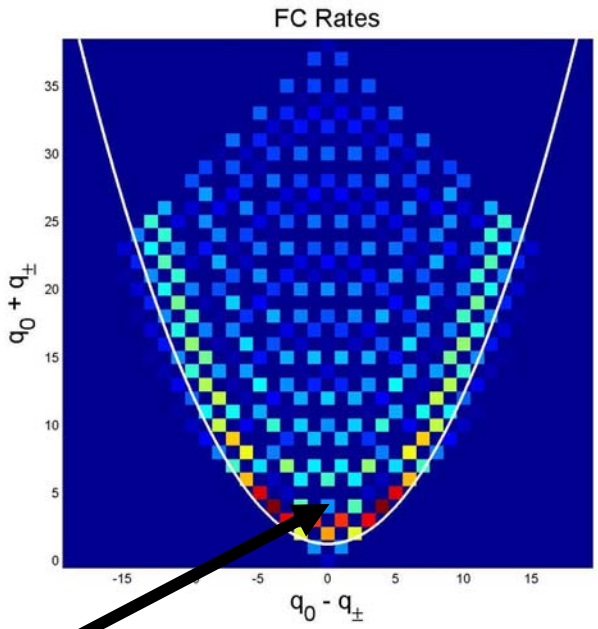
Preliminary results $\lambda = 2$





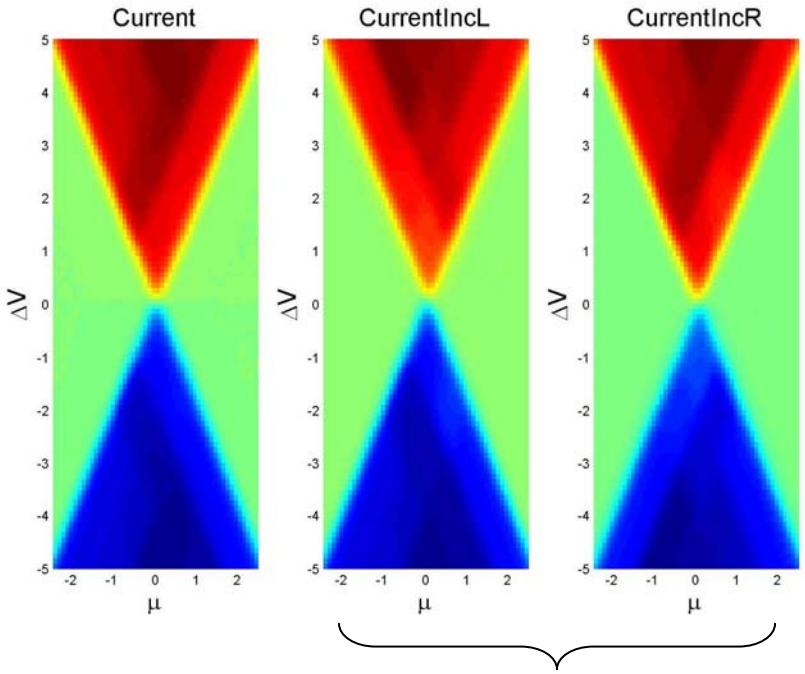
Preliminary results $\lambda = 3$





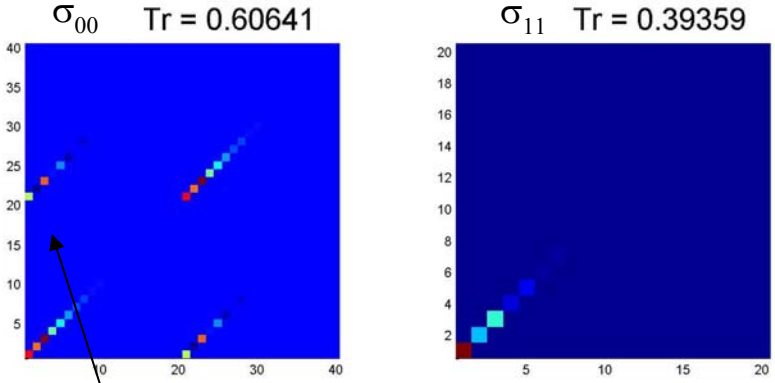
Franck Condon Blockade

Coherencies...examples



Current evaluated neglecting coherencies

$\lambda = 1$ **ΔV = 5, μ = -1**



coherencies

Summary

- We derived an effective Hamiltonian for the biphenyl transistor
- We obtained the description of the electromechanical dynamics in terms of a GME
- We observed the Franck-Condon blockade and gave an interpretation in terms of the Franck-Condon rates
- We observed the relevance of the mechanical coherencies in the transport mechanism

Still (a lot) to do!

- Understand the anionic potential surface in terms of the PPP Hamiltonian;
- Understand the role of mechanical coherencies in transport through biphenyl;
- Use realistic values for the electron-vibron coupling in biphenyl ($\lambda \sim 50$);
- Calculate the current noise

Thanks for your attention!