Electromechanical properties of a biphenyl transistor

Andrea Donarini
The model

- Weak coupling to the leads + low temperature -> Coulomb blockade
- Gate voltage
- Torsional (the softest mechanical) degree of freedom of the molecule
The Hamiltonian

The Hamiltonian of the device can be written as

\[ H = H_{Mol} + H_{Leads} + V \]

Where

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

\[ H_{Leads} = \sum_{\alpha k \sigma} \epsilon_{k,\alpha} c_{\alpha k \sigma}^\dagger c_{\alpha k \sigma} \]

\[ V = t \sum_{\alpha k \sigma} (c_{\alpha k \sigma}^\dagger c_{\alpha 3 \sigma} + c_{\alpha 3 \sigma}^\dagger c_{\alpha k \sigma}) \]
Isolated biphenyl

- $H_{PPP}$ is the Pariser-Parr-Pople Hamiltonian

$$H_{PPP}(\theta) = \sum_{i\sigma} b_{ii+1}(\theta) (c_{i\sigma}^\dagger c_{i+1\sigma} + c_{i+1\sigma}^\dagger c_{i\sigma}) + \sum_i U_i \left( \hat{n}_{i\uparrow} - \frac{z_i}{2} \right) \left( \hat{n}_{i\downarrow} - \frac{z_i}{2} \right)$$

$$+ \sum_{\langle i<j \rangle} V_{ij}(\theta) (\hat{n}_i - z_i)(\hat{n}_j - z_j)$$

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

- Ground state electronic energy for the neutral molecule: four tilted equilibrium configurations

- Technique: Hartree-Fock approximation of the PPP Hamiltonian
Anionic state

- Planar equilibrium configuration for the anionic state
- The Hartree-Fock approximation fails for the anionic state

**CORRELATIONS!!!**
(work in progress to go beyond Hartree-Fock)

DFT calculations
With gaussian basis set
And B3LYP exchange potential

0.1 eV
Model ... of the model

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

\[ \alpha = \sqrt{\frac{\omega_1}{\omega_0}} \]
\[ \lambda = \frac{\Delta \theta}{\sqrt{\theta_{z0} \theta_{z1}}} \]
\[ \epsilon_a = \frac{EA}{\hbar \sqrt{\omega_0 \omega_1}} \]
Definition of Unity

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

\[ 1 = |N\rangle\langle N| (P_+ + P_-) + |N + 1\rangle\langle N + 1| P_0 \]

- where

\[ P_\pm = \sum_{n=0}^{N_\pm} |n_\pm\rangle\langle n_\pm|, \quad P_0 = \sum_{n=0}^{\infty} |n_0\rangle\langle n_0| \]

that define the effective Hilbert space.
Effective Hamiltonian

\[ H_{\text{eff}} = \sum_{\alpha k \sigma} \epsilon_{\alpha k} c_{\alpha k \sigma}^{\dagger} c_{\alpha k \sigma} + \]
\[ + \sum_{\alpha k \sigma, n, m} \left[ t_{n, m}^{(+)} c_{\alpha k \sigma}^{\dagger} c_{\sigma \sigma} |m_0\rangle \langle n_+| + t_{n, m}^{(-)} c_{\alpha k \sigma}^{\dagger} c_{\sigma \sigma} |m_0\rangle \langle n_-| \right] + \]
\[ + \left( 1 - \sum_{\sigma} c_{\sigma \sigma}^{\dagger} c_{\sigma \sigma} \right) \left\{ \epsilon_0 + \hat{\kappa}_\omega \left[ \mathcal{P}_+ \left( d_+^\dagger d_+ + \frac{1}{2} \right) \mathcal{P}_+ + \mathcal{P}_- \left( d_-^\dagger d_- + \frac{1}{2} \right) \mathcal{P}_- \right] \right\} + \]
\[ + \sum_{\sigma} c_{\sigma \sigma}^{\dagger} c_{\sigma \sigma} \left[ \epsilon_1 + \mathcal{P}_0 \left( d_+^\dagger d_+ + \frac{1}{2} \right) \mathcal{P}_0 \right] \]

where

\[ c_{d \sigma}^{\dagger} |N\rangle \equiv |N+1, \sigma\rangle \]

\[ t_{n, m}^{(\pm)} = \frac{t \langle N | c_{3\alpha} | N + 1 \rangle \langle n_{\pm} | m_0 \rangle}{\langle n_{\pm} | m_0 \rangle} \]

Franck-Condon coefficient

We assume it independent of \( \theta \)
Generalized Master Equation

We study the dynamics of the system with the Generalized Master Equation:

\[
\dot{\sigma} = -\frac{i}{\hbar} [H_{\text{mol}}, \sigma] - \frac{1}{\hbar^2} \int_0^\infty d\tau \Tr_{\text{Leads}} \{ [V, \tilde{V}_{\text{I}}(-\tau), \sigma] \otimes \rho_{\text{Leads}} \}
\]

- coherences between different charge states vanish
- due to the mechanical degeneracies of the neutral state we MUST keep coherences between displaced mechanical states
- we write the GME in the basis that diagonalize the molecule hamiltonian (Bloch-Redfield form)

\[
\dot{\sigma}_{ij} = \sum_{mn} R_{ijmn} \sigma_{mn}
\]
The Redfield tensor $R_{ijmn}$ depends on

- **Fermi factors** - the Pauli exclusion 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
The Franck-Condon parabola
The Franck-Condon parabola
The Franck-Condor parabola
The current calculation

1. Computation of the stationary reduced density matrix $\sigma^{stat}$

2. Identification of the current operators:

$$I = \frac{dQ}{dt} = \sum_m \hat{\sigma}^{mm}_{11}$$

$$= - \sum_{kl\alpha} \left( W^\alpha_{kl} \sigma^{kl}_{11} + \sigma^{kl}_{11} W^\alpha_{lk} \right) + \sum_{k'\tau' n\tau} \left( R^\alpha_{k'k} \sigma_{n'\tau' n\tau} + R^\alpha_{k'k} \sigma_{n'\tau' n\tau} \right) \sigma^{n'\tau' n\tau}_{00}$$

$$= - 2 \text{Tr}_{Mech} \{ W^L_1 \sigma_{11} \} + 2 \text{Tr}_{Mech} \{ W^L_0 \sigma_{00} \} - 2 \text{Tr}_{Mech} \{ W^R_1 \sigma_{11} \} + 2 \text{Tr}_{Mech} \{ W^R_0 \sigma_{00} \}$$

$$= \langle \hat{I}_L \rangle - \langle \hat{I}_R \rangle$$

3. Calculation of the stationary current:

$$I_{stat}^L = \text{Tr}_{Mech} \{ \sigma^{stat} \hat{I}_L \}$$

$$I_{stat}^R = \text{Tr}_{Mech} \{ \sigma^{stat} \hat{I}_R \}$$
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

Current

\[ \Delta V \]

\[ \mu \]

\( 0 \)

\( 1 \)

Conductance

\[ \Delta V \]

\[ \mu \]

\( \mu + \Delta V/2 \)

Source

Energy level

\( \mu - \Delta V/2 \)

Drain

Lancaster, 9.1.2006

NANO ELECTRONICS 2006
Franck-Condon parabola (II)

Incoming electrons

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

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

Outgoing electrons
Weak coupling $\lambda = 1$
\[ \lambda = 2 \]
\[ \lambda = 3 \]

Fraunck-Condon Blockade
Coherences...examples

\[ \lambda = 1 \quad \Delta V = 5, \quad \mu = -1 \]

Conductance evaluated neglecting coherences
Coherences...proof

- Tunneling preserves parity of the mechanical state

- In the even and odd sector degeneracies are lifted and a the stationary reduced density matrix is diagonal

- Franck-Condon coefficients are different in the even and odd sectors and give different stationary solutions

- Thus in the + / - basis we must have coherences
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 coherences 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 **coherences** in transport through biphenyl
- Use **realistic values** for the electron-vibron coupling in biphenyl ($\lambda \sim 50$)
- Investigate the role of the **mechanical bath**

**Thanks for your attention!**
\[ \lambda = 5 \]
Bath ($\lambda = 3$)
Lambda scaling

Scaling

Maxima

Abs max
Rel max
\[ \exp(-\lambda^2/2) \]
\[ 1/(1+\lambda)^{1.2} \]
\[ 1/(1+\lambda)^{1.5} \]