Fingerprints of symmetry in transport through Anderson molecules

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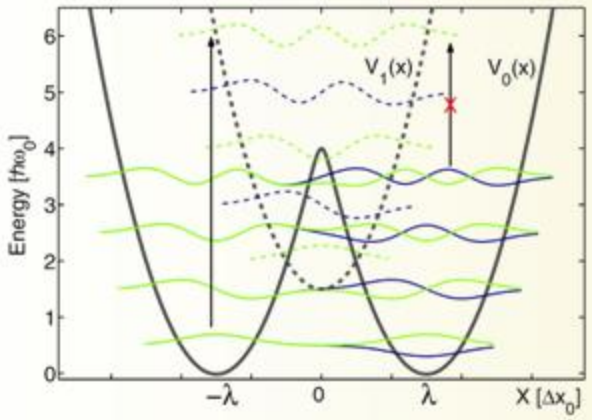
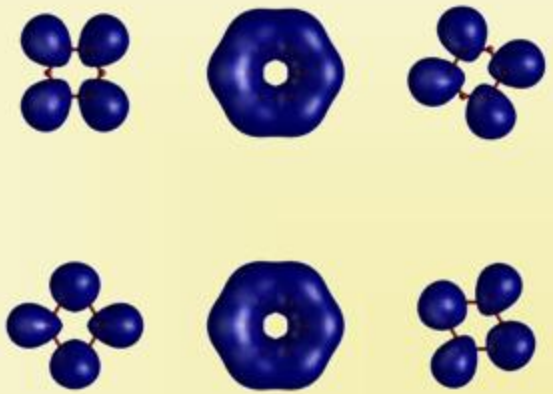
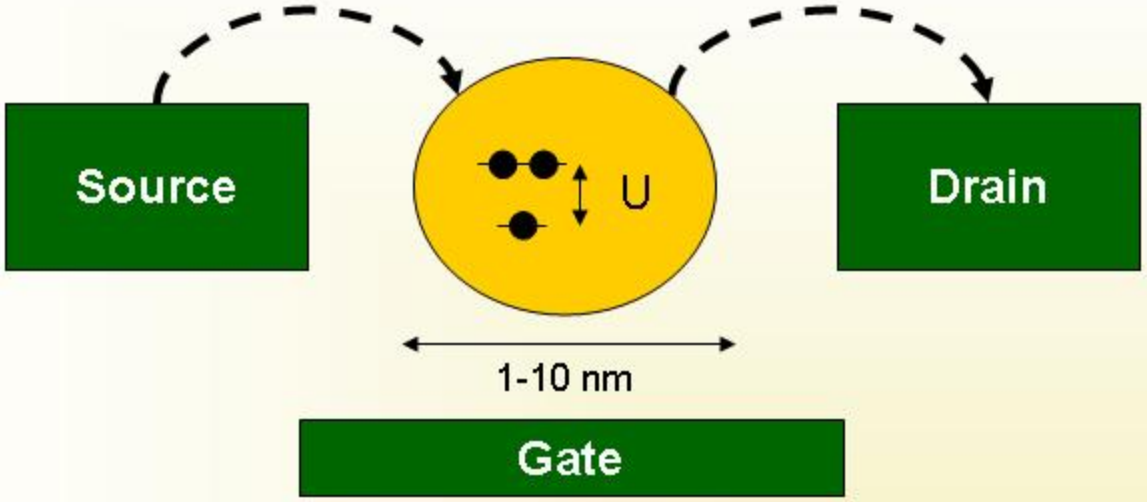




Outline

- What is an Anderson molecule ?
- A master equation WITH coherences
- Orbital symmetries in Benzene
- Electromechanical symmetries in Biphenyl

Anderson-impurity model



$$H = H_{\mathrm{dot}} + H_{\mathrm{leads}} + H_{\mathrm{tun}}$$

$$H_{\mathrm{dot}} = \sum_{\sigma} \xi_{\sigma} d_{\sigma}^{\dagger} d_{\sigma} + U \left(n_{\uparrow} - \frac{1}{2} \right) \left(n_{\downarrow} - \frac{1}{2} \right)$$

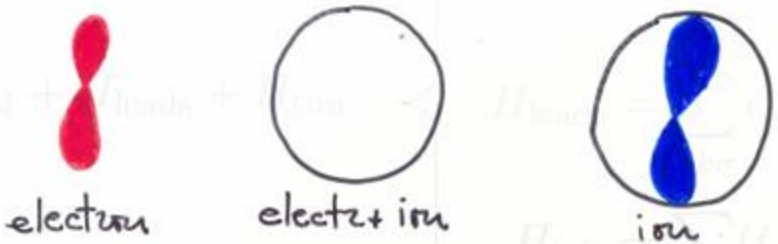
$$H_{\mathrm{leads}} = \sum_{\alpha k \sigma} \epsilon_{\alpha k \sigma} c_{\alpha k \sigma}^{\dagger} c_{\alpha k \sigma}$$

$$H_{\mathrm{tun}} = \sum_{\alpha k \sigma} (t_{\alpha k \sigma} c_{\alpha k \sigma}^{\dagger} d_{\sigma} + t_{\alpha k \sigma}^{*} d_{\sigma}^{\dagger} c_{\alpha k \sigma})$$

Anderson-molecule junction

$$H_{\mathrm{PPP}} = \sum_{i\sigma} \xi_\sigma d^\dagger_{i\sigma} d_{i\sigma} + b \sum_{i\sigma} (d^\dagger_{i\sigma} d_{i+1\sigma} + d^\dagger_{i+1\sigma} d_{i\sigma}) + U \sum_i \left(n_{i\uparrow} - \frac{1}{2}\right)\left(n_{i\downarrow} - \frac{1}{2}\right) + V \sum_{\langle i<j \rangle} (n_{i\uparrow} + n_{i\downarrow} - 1)(n_{j\uparrow} + n_{j\downarrow} - 1)$$

The **P**ariser-**P**arr-**P**ople is an **extended Hubbard** Hamiltonian introduced to describe interaction effects in **conjugated molecules**.



Only π-electrons are taken into account. Ions are assumed to have the **same spatial symmetry** of the relevant electrons.

Generalized Master Equation

1. Write the Liouville equation:

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[\mathcal{H}, \rho]$$

2. Restrict to 2nd order in the coupling to the electrical (and mechanical) baths. Make the standard Markov approximations and trace out the leads:

$$\dot{\tilde{\sigma}} = -\frac{1}{\hbar^2}\int_0^\infty d\tau \mathrm{Tr}_\mathrm{B}\{[\tilde{H}_\mathrm{I}(t), [\tilde{H}_\mathrm{I}(t-\tau), \tilde{\sigma}(t)\otimes\rho_\mathrm{B}]]\}$$

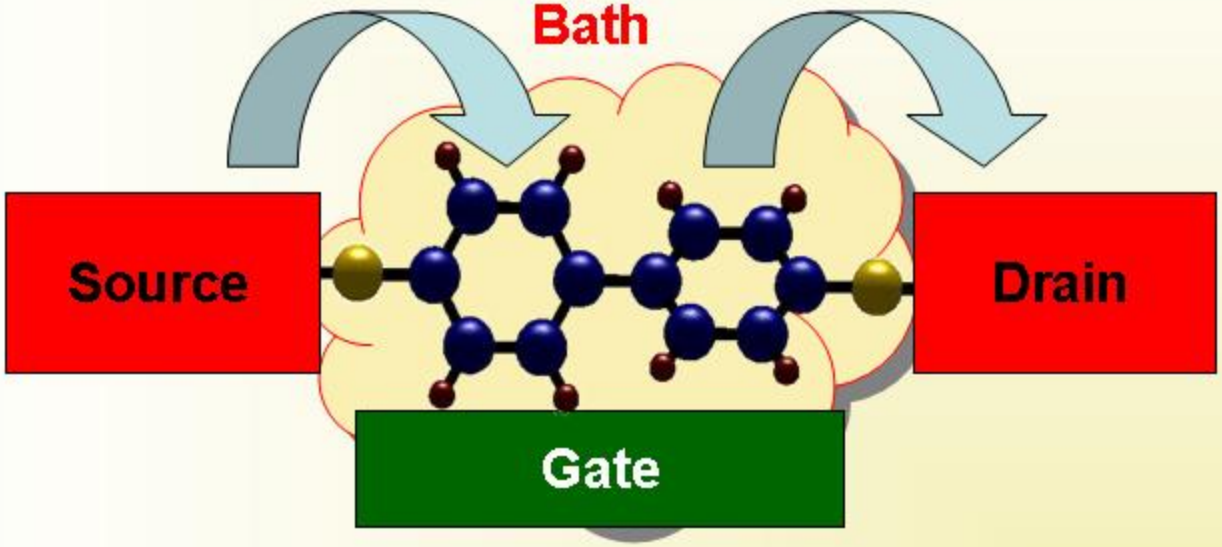
3. Neglect coherences between states with different number of particles in the system: they are decoupled and damped.

4. KEEP coherences between energy degenerate states (**Generalized Master Equation**). Any other choice is (in general) arbitrary!!

5. Calculate the stationary solution of the GME and evaluate the expectation values of relevant observables.

Electromechanical symmetries

Biphenyl junction



The Hamiltonian

The hamiltonian of the device can be written as

$$H = H_{\mathrm{S}} + H_{\mathrm{EL}} + H_{\mathrm{B}} + V_{\mathrm{T}} + V_{\mathrm{SB}}$$

where

$$H_{\mathrm{S}} = \frac{\hat{p}^2}{2m} + |0\rangle\langle 0|\, V_0(\hat{x}) + |1\rangle\langle 1|\, V_1(\hat{x})$$

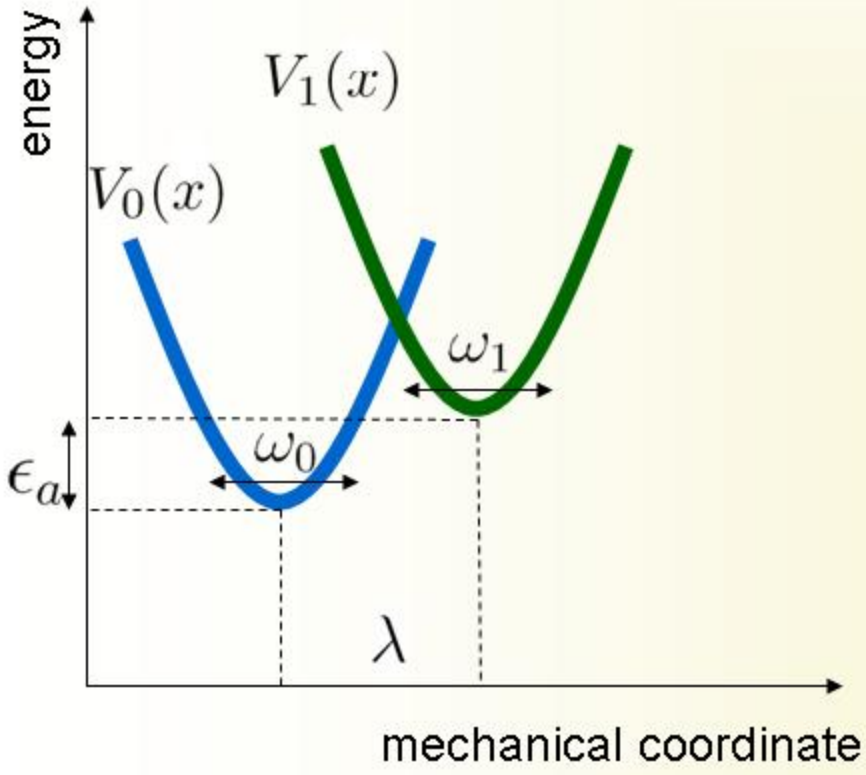
and

$$V_{\mathrm{T}} = t \sum_{k;\alpha=\mathrm{L,R}} \left(|0\rangle\langle 1| c^{\dagger}_{k\alpha} + |1\rangle\langle 0| c_{k\alpha} \right)$$

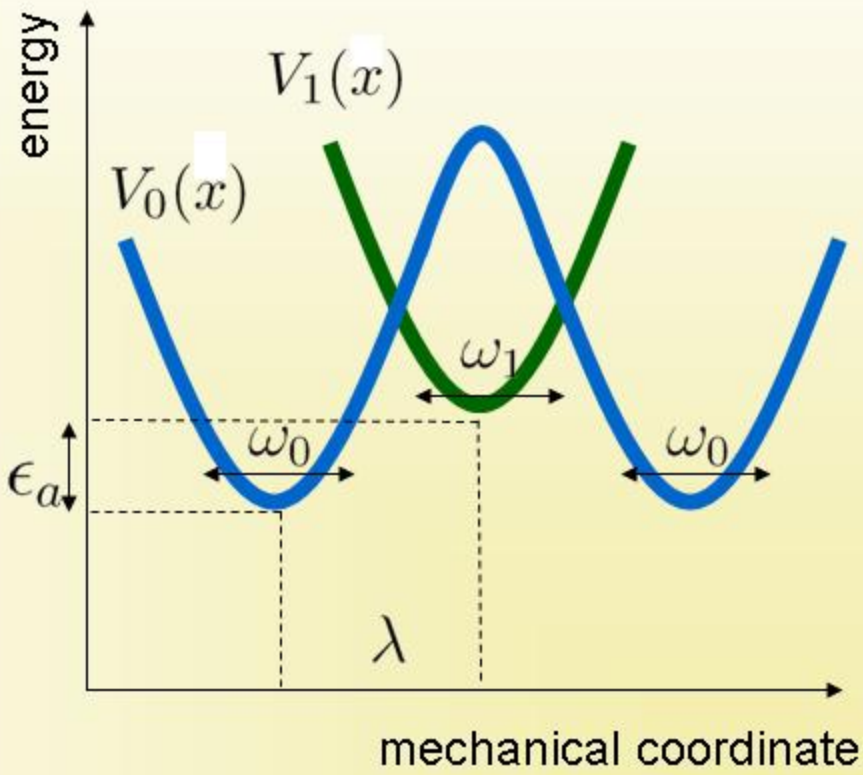
$$V_{\mathrm{SB}} = \hbar\tilde{g} \sum_{q} \hat{x}(d_q + d^{\dagger}_q)$$

The adiabatic potentials

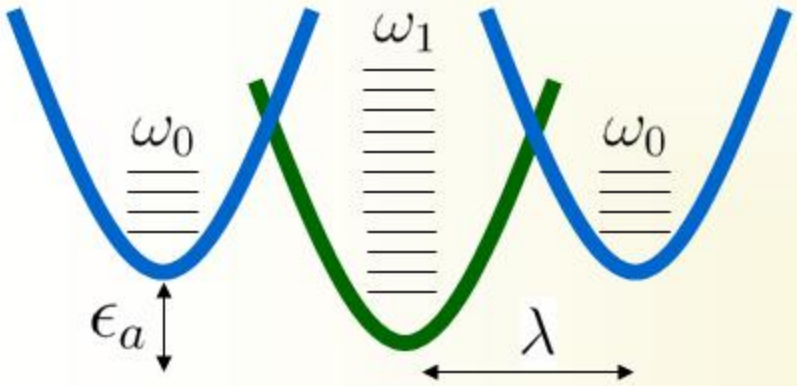
Simplest model



Bistable configurations are not so rare!



The low energy limit



- Harmonic approximation for the anionic state
- Low lying states of a double (harmonic) well potential for the neutral state

- The effective Hilbert space is defined by the unity operator:

$$\mathbb{1} = |1\rangle\langle 1| + |0\rangle\langle 0|(\mathcal{P}_+ + \mathcal{P}_-)$$

where

$$\mathcal{P}_\pm = \sum_{n=0}^{N} |n,\pm\rangle\langle n,\pm|$$

Effective Hamiltonian

The only components of the Hamiltonian modified by the projection are:

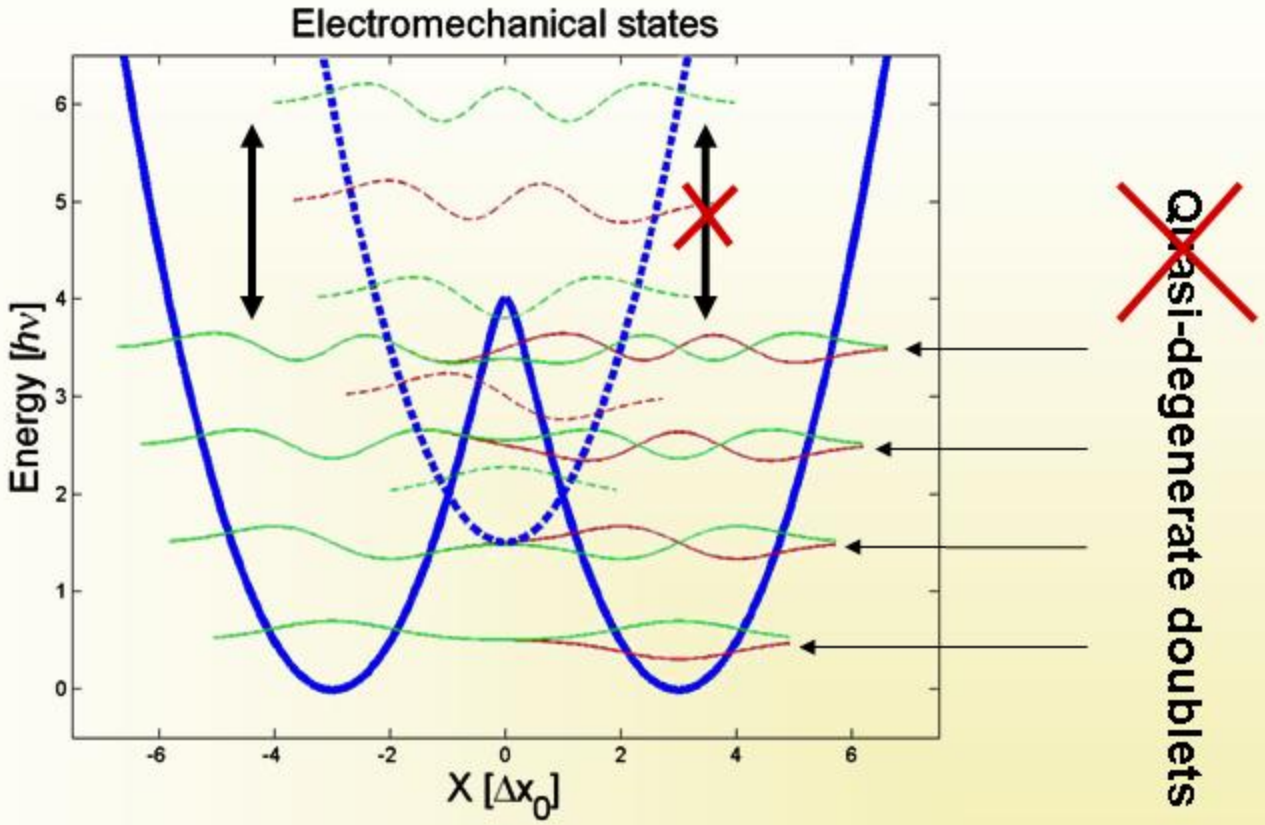
$$H_{\mathrm{S}}^{eff} = |0\rangle\langle 0| \sum_{\tau=+,-} \left[\mathcal{P}_\tau(\tfrac{1}{2} + d_\tau^\dagger d_\tau)\mathcal{P}_\tau\right] \hbar\omega_0 + |1\rangle\langle 1| \left[(\tfrac{1}{2} + d^\dagger d)\hbar\omega_1 + eV_g - \epsilon_a\right]$$

and

$$V_{\mathrm{T}}^{eff} = \sum_{k;\alpha=\mathrm{L,R}} \left[t|0\rangle\langle 1|c_{k\alpha}^\dagger(\mathcal{P}_+ + \mathcal{P}_-) + h.c.\right]$$

$$V_{\mathrm{SB}}^{eff} = \hbar g \sum_q (d_q + d_q^\dagger)\left\{|1\rangle\langle 1|(d + d^\dagger) + |0\rangle\langle 0| \sum_{\tau=-,+} [\mathcal{P}_\tau(d_\tau + d_\tau^\dagger + \tau 2\lambda)\mathcal{P}_\tau]\right\}$$

Symmetries



- We neglect the inter-well tunneling coupling: $\mathcal{P}_- \mathcal{P}_+ = 0$
- Electron tunneling in and off the molecule preserves mechanical parity.

Generalized Master Equation

$$\dot{\sigma}(t) = \mathcal{L}\,\sigma(t) = (\mathcal{L}_{\rm coh} + \mathcal{L}_{\rm driv} + \mathcal{L}_{\rm damp})\,\sigma(t)$$

- The Generalized Master Equation is derived in second order perturbation in the interaction Hamiltonians $V_{\rm T}^{eff}$ and $V_{\rm SB}^{eff}$
- Coherences between different charge states vanish
- Due to the mechanical (quasi-)degenerate neutral states we MUST keep coherences between displaced mechanical states

Electrical leads

$$(\mathcal{L}_{\rm driv}\,\sigma)_{11} = \sum_{\alpha,\tau}\Big[2(\Gamma^{\alpha}_{\rm in}\,\sigma_{00}\,\mathcal{P}_{\tau} + \mathcal{P}_{\tau}\,\sigma_{00}\,\Gamma^{\alpha\,\dagger}_{\rm in}) - (\mathcal{P}_{\tau}\,\Gamma^{\alpha}_{\rm out}\,\sigma_{11} + \sigma_{11}\,\Gamma^{\alpha}_{\rm out}{}^{\dagger}\mathcal{P}_{\tau})\Big]$$

$$(\mathcal{L}_{\rm driv}\,\sigma)^{\tau\tau'}_{00} = \sum_{\alpha}\mathcal{P}_{\tau}\Big[\Gamma^{\alpha}_{\rm out}\,\sigma_{11} + \sigma_{11}\,\Gamma^{\alpha}_{\rm out}{}^{\dagger} - 2(\Gamma^{\alpha}_{\rm in}\,\sigma_{00} + \sigma_{00}\,\Gamma^{\alpha\,\dagger}_{\rm in})\Big]\,\mathcal{P}_{\tau'}$$

where

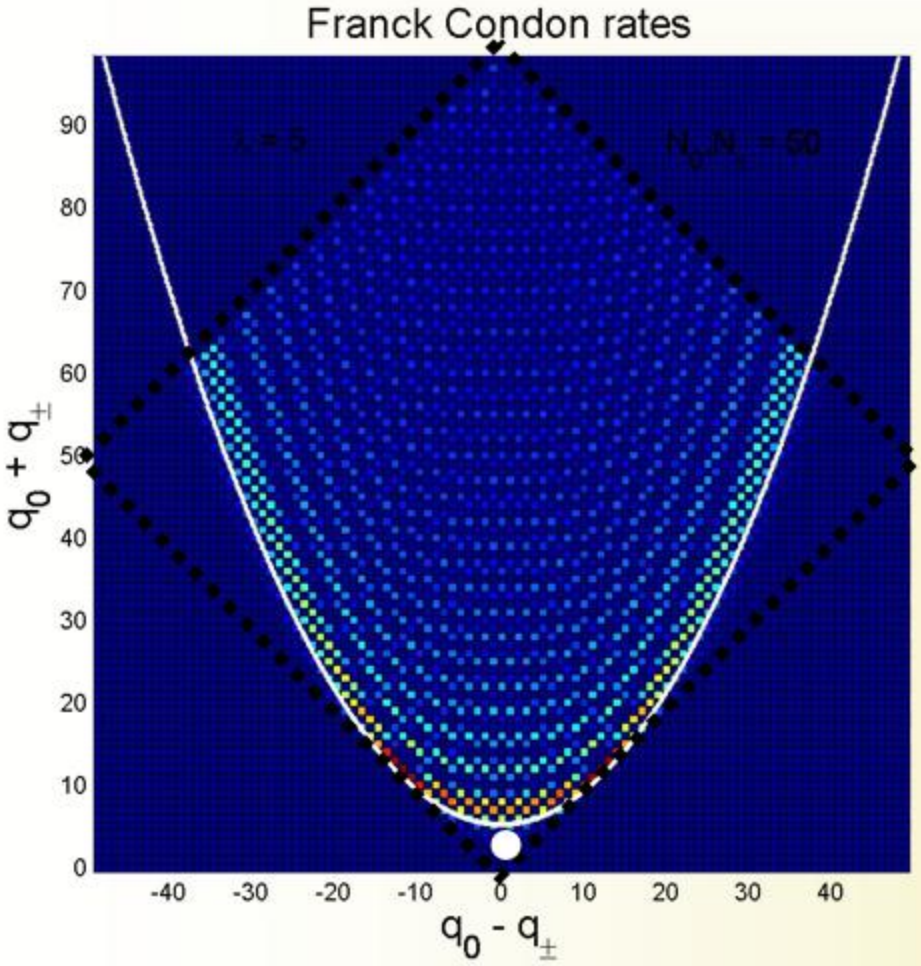
bare tunneling rate

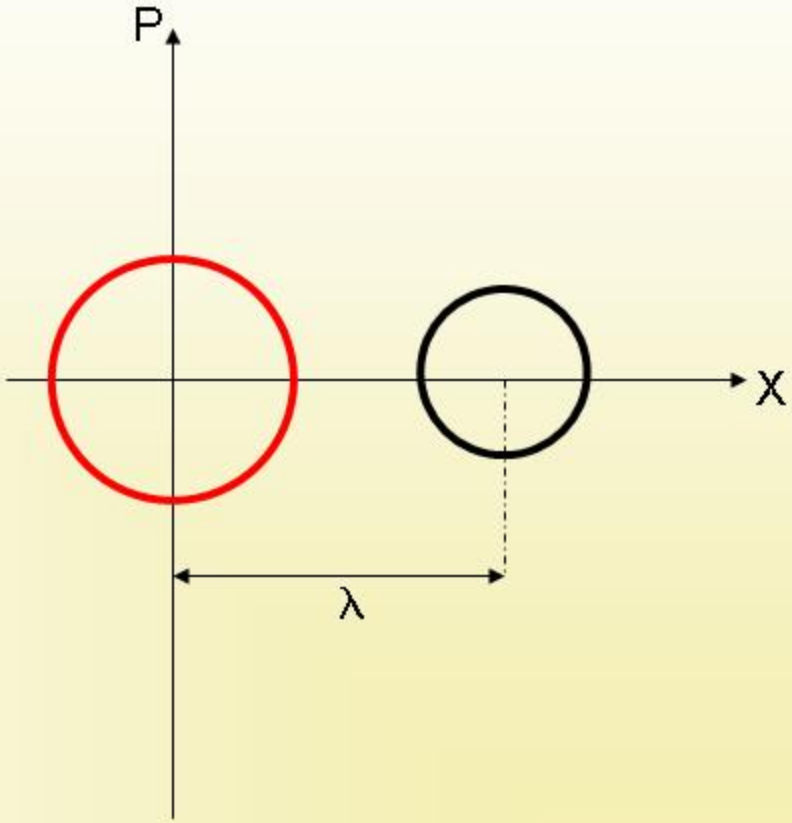
$$\Gamma^{\alpha}_{\rm in} = \frac{\Gamma_{\alpha}}{2}\sum_{m,n\tau}|m\rangle\Big\{\underbrace{f_{\alpha}[eV_g - \epsilon_a + \hbar\omega(m-n)]}_{\text{Fermi factor}}\underbrace{\langle m|n,\tau\rangle}_{\text{Franck-Condon coefficient}}\Big\}\langle n,\tau|$$

$$\Gamma^{\alpha}_{\rm out} = \frac{\Gamma_{\alpha}}{2}\sum_{m,n\tau}|n,\tau\rangle\langle m| - \Gamma^{\alpha\,\dagger}_{\rm in}$$

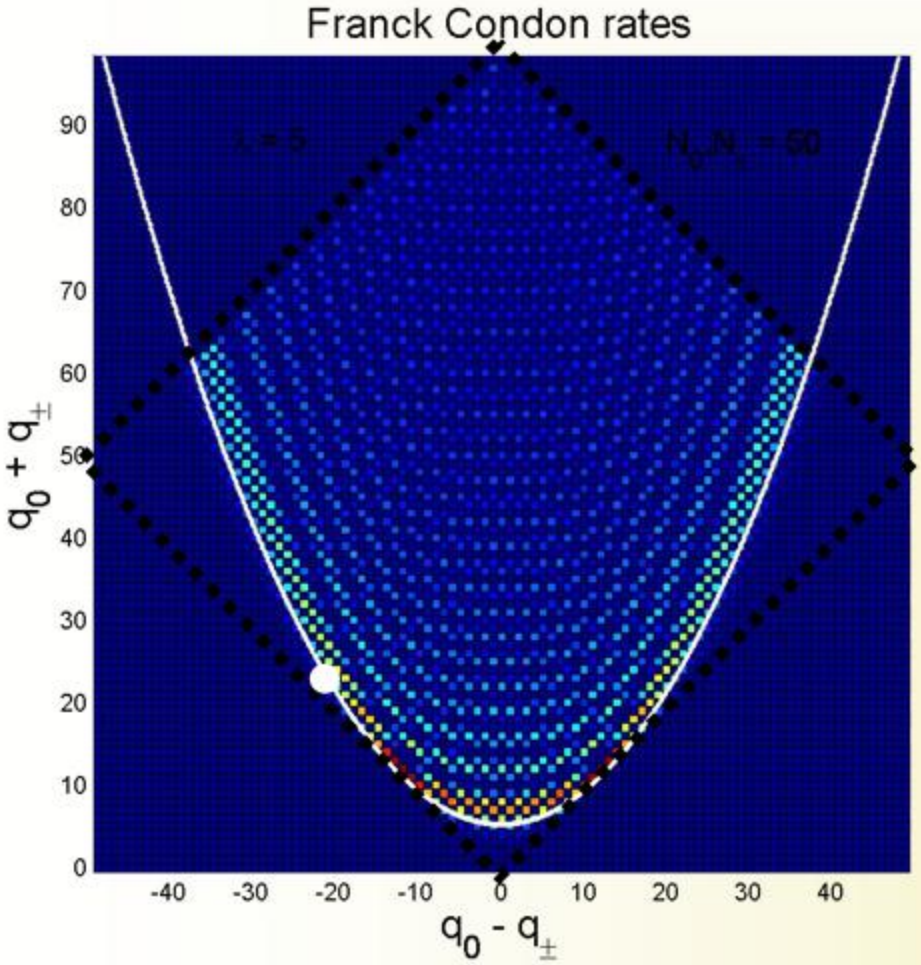
$$\Big(\ \mathcal{L}_{\rm coh}\,\sigma = -\frac{i}{\hbar}[H^{eff}_{\rm S},\sigma]\ \Big)$$

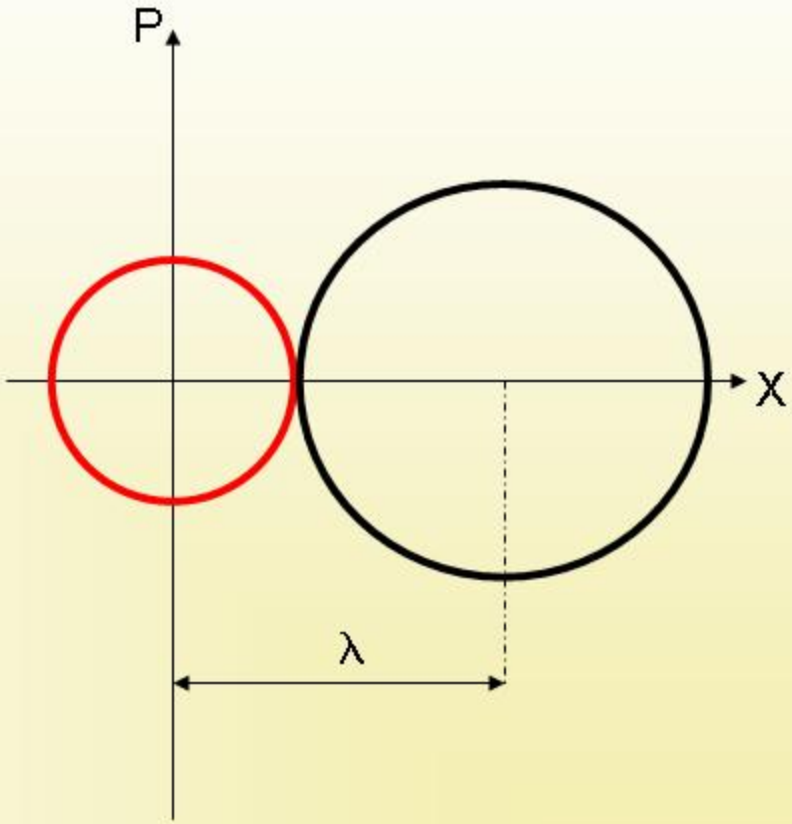
The Franck-Condon parabola



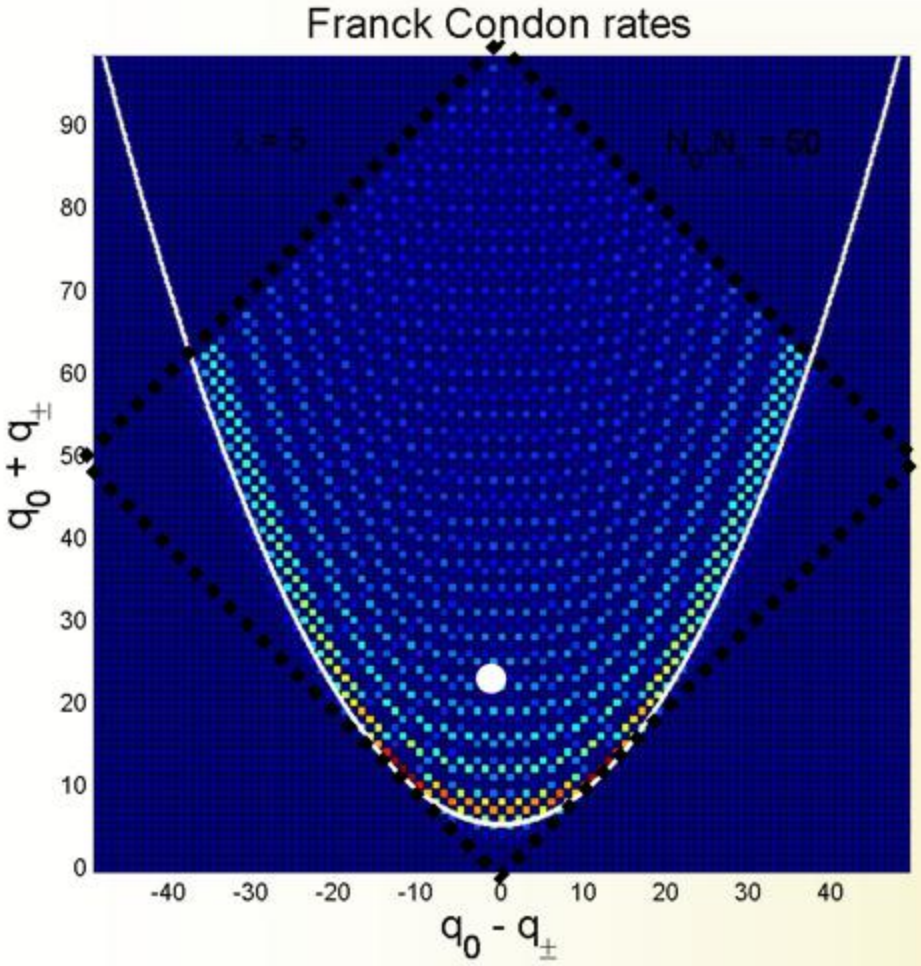


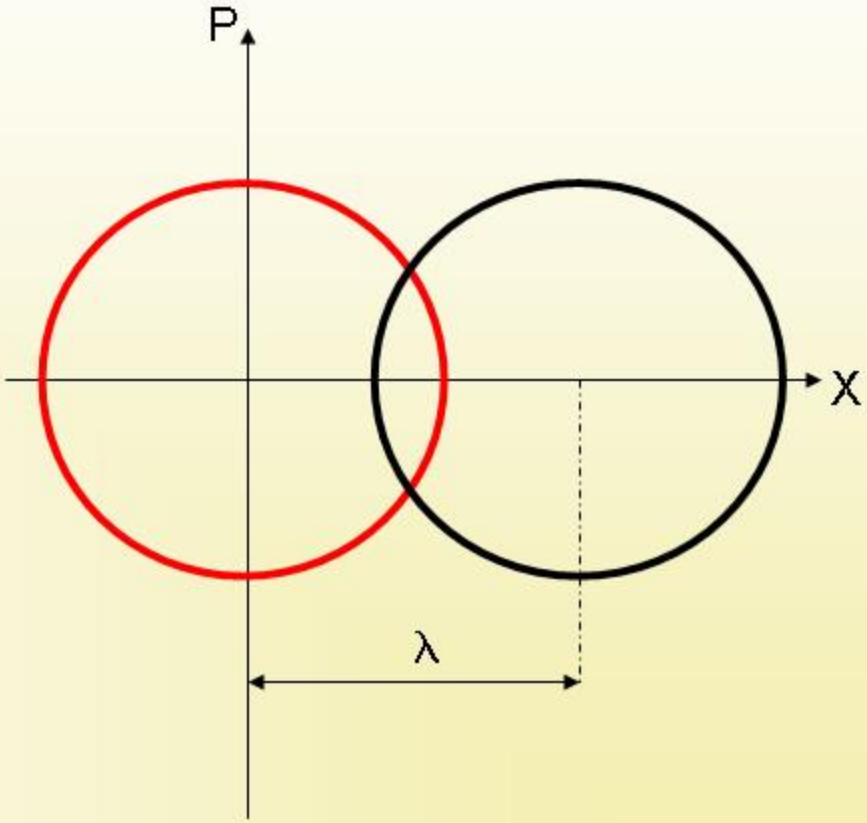
The Franck-Condon parabola





The Franck-Condon parabola

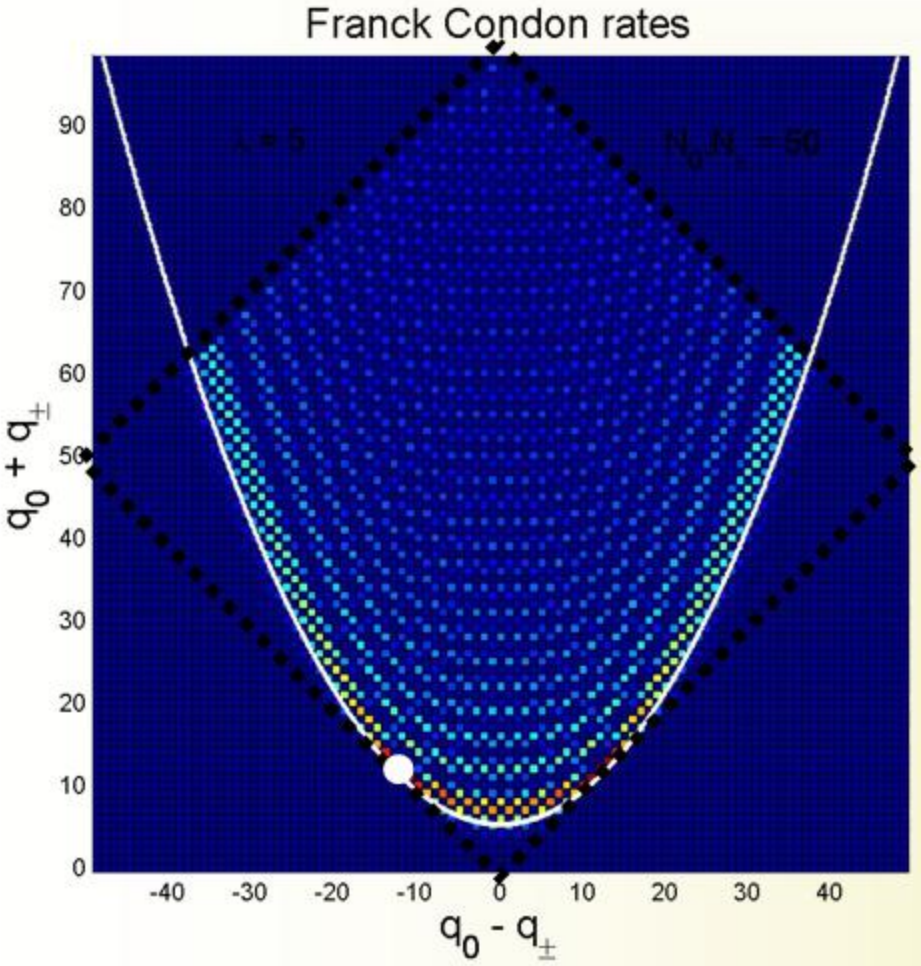


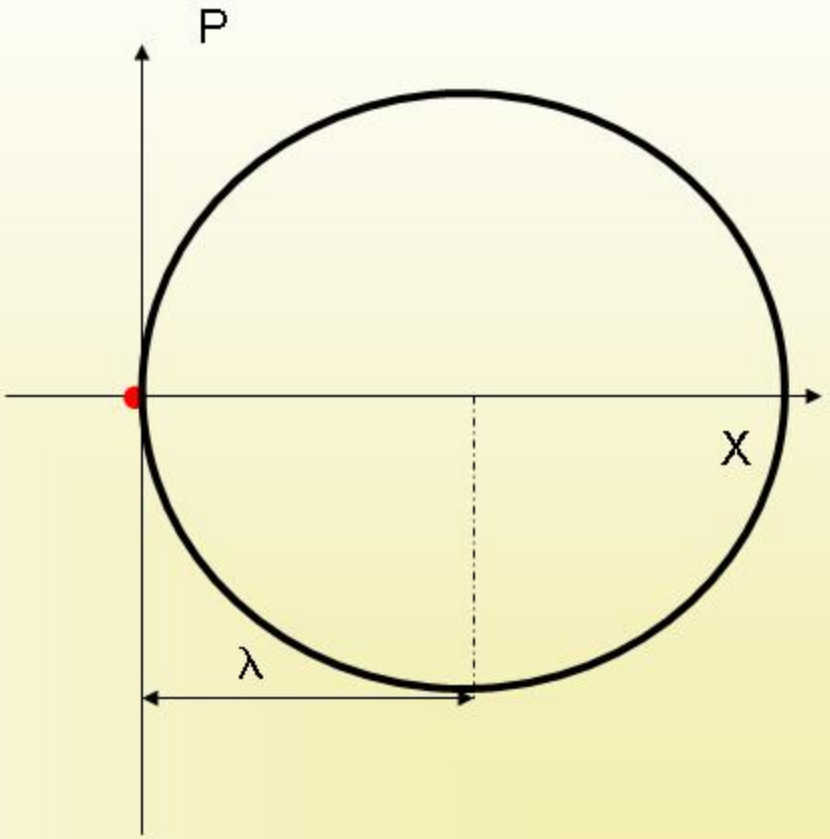


State +

State 0

The Franck-Condon parabola





Mechanical bath

$$(\mathcal{L}_{\rm damp}\,\sigma)_{11} = -\frac{i\gamma}{2\hbar}[\hat{x},\{\hat{p},\sigma_{11}\}] - \frac{\gamma m\omega}{\hbar}(\bar{N}+\tfrac{1}{2})[\hat{x},[\hat{x},\sigma_{11}]]$$

$$(\mathcal{L}_{\rm damp}\,\sigma)^{\tau\tau'}_{00} = -\frac{i\gamma}{2\hbar}\mathcal{P}_\tau[\hat{x},\{\hat{p},\sigma^{\tau\tau'}_{00}\}]\mathcal{P}_{\tau'}$$

$$-\frac{\gamma m\omega}{\hbar}(\bar{N}+\tfrac{1}{2})\mathcal{P}_\tau[\hat{x},[\hat{x},\sigma^{\tau\tau'}_{00}]]\mathcal{P}_{\tau'}$$

$$\boxed{-8\gamma\frac{k_{\rm B}T}{\hbar\omega}\lambda^2(\mathcal{P}_+\,\sigma^{\tau\tau'}_{00}\,\mathcal{P}_- + \mathcal{P}_-\,\sigma^{\tau\tau'}_{00}\,\mathcal{P}_+)}$$

Interwell dephasing term

Observables

- Current:

$$I^{stat} = \mathrm{Tr}_S[\sigma^{stat}\hat{I}_L]$$

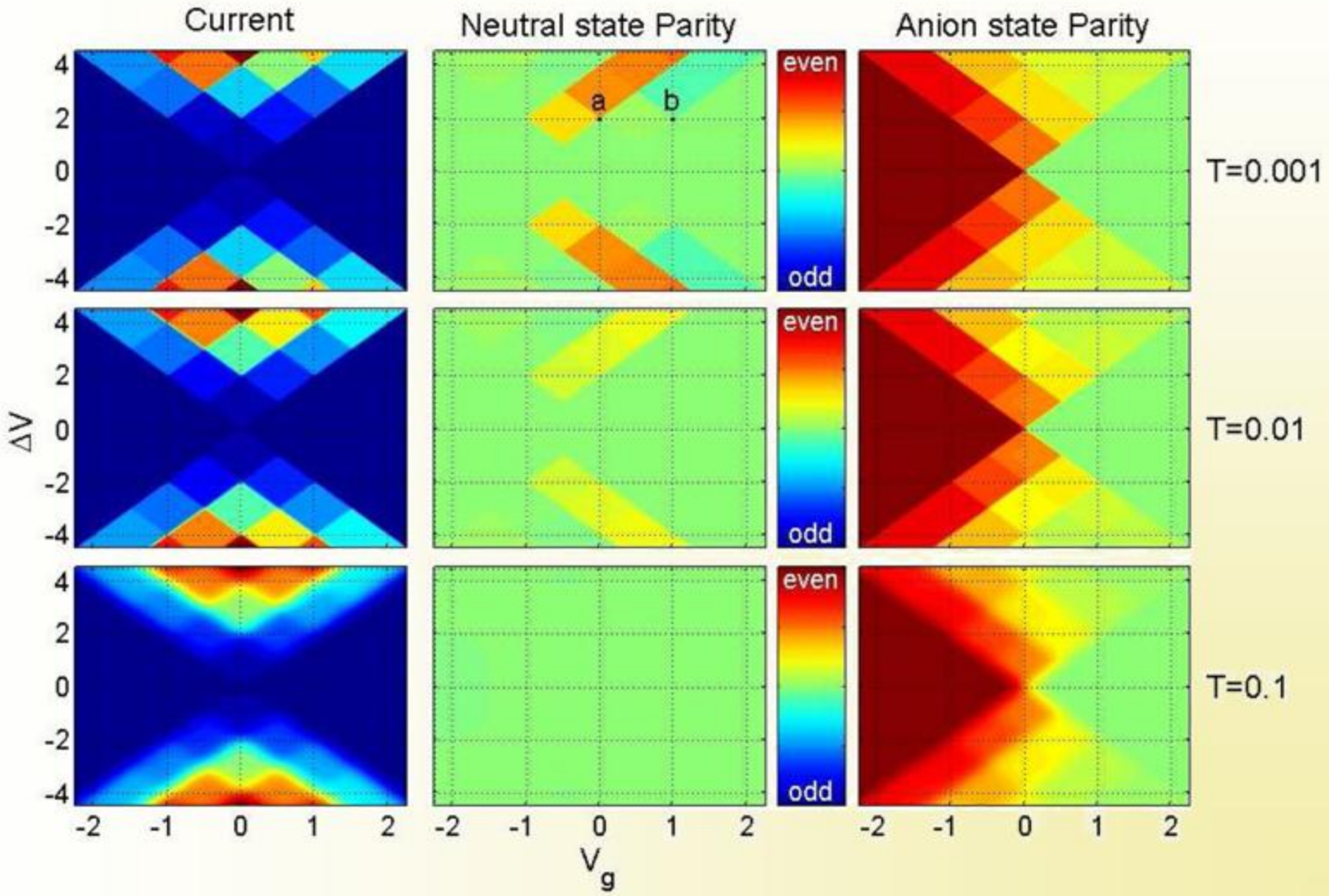
$$\hat{I}_L = \sum_\tau \left[2|0\rangle\langle 0|(\mathcal{P}_\tau \Gamma^L_{in} + \Gamma^{L\,\dagger}_{in}\mathcal{P}_\tau) - |1\rangle\langle 1|(\mathcal{P}_\tau \Gamma^L_{out} + \Gamma^{L\,\dagger}_{out}\mathcal{P}_\tau)\right]$$

- Parity:

$$P_0 = \sum_{n=0}^{N} \langle 0,e,n|\sigma^{stat}|0,e,n\rangle - \langle 0,o,n|\sigma^{stat}|0,o,n\rangle$$

$$P_1 = \sum_{n=0}^{\infty} \langle 1,2n|\sigma^{stat}|1,2n\rangle - \langle 1,2n+1|\sigma^{stat}|1,2n+1\rangle$$

Symmetry breaking



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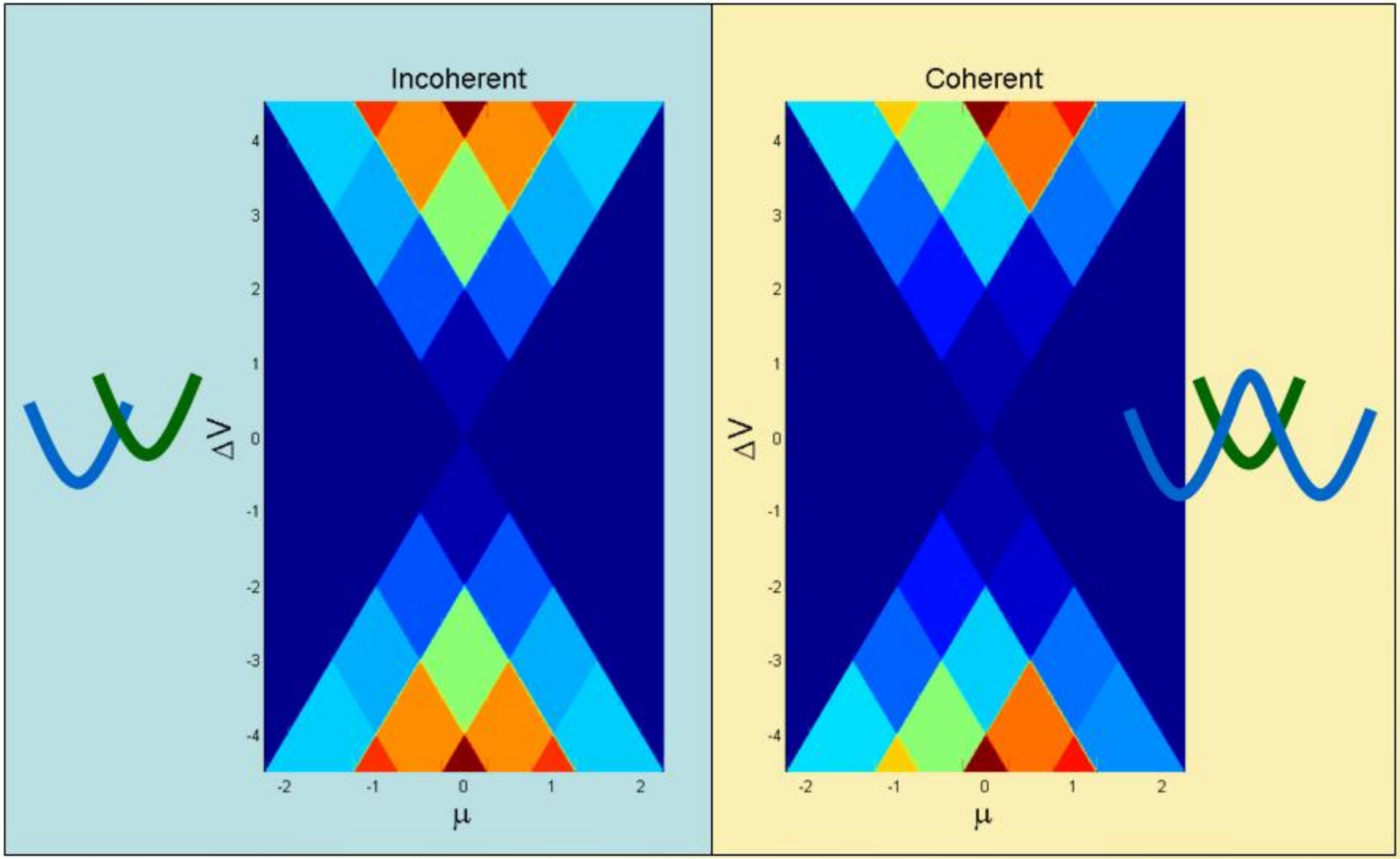
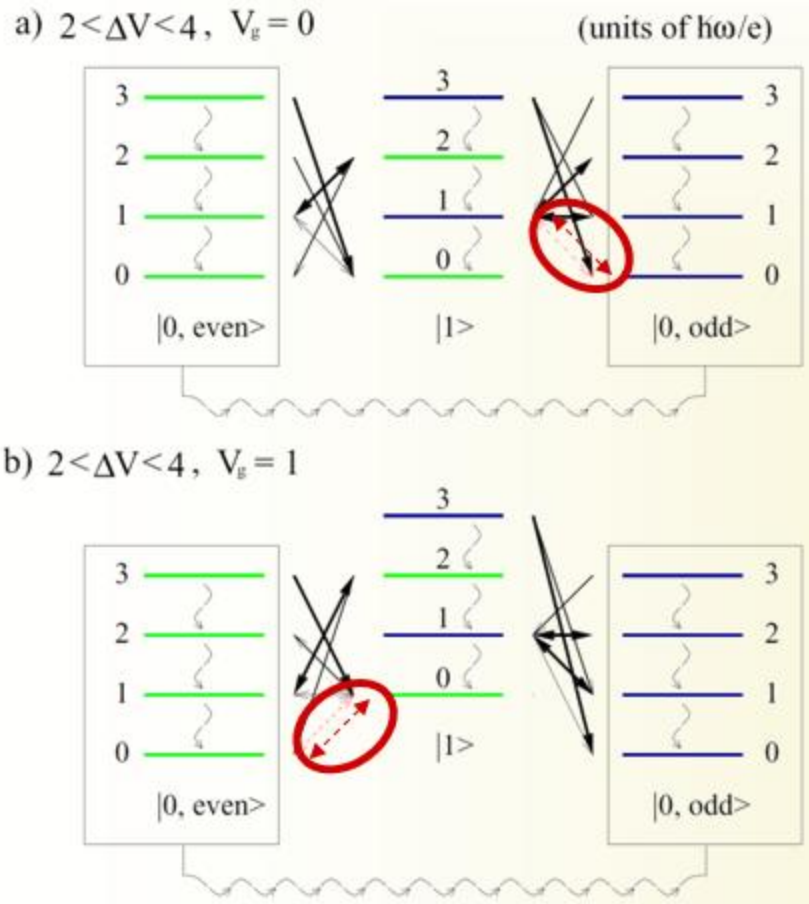
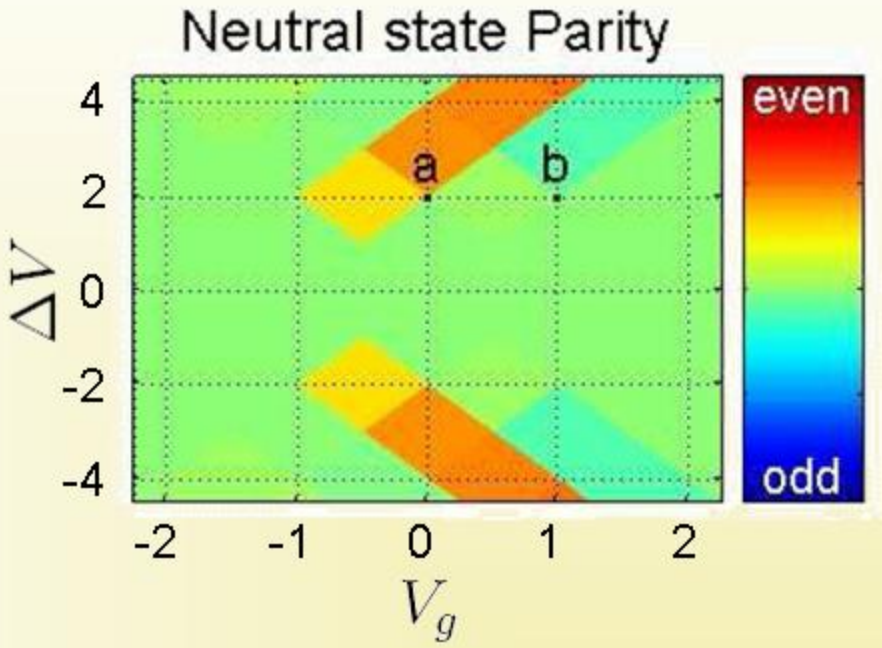
Incoherent vs. coherent



Un-blocking rates





Conclusions

- electron-electron **interaction** and orbital **symmetry** are important to understand transport through weakly coupled molecular junctions

- **semiempirical models** are usefull tool study molecular electronics at an analytical level.

- **coherences** between degenerate states play a crucial role in the generalized master equation approach to transport in molecular junctions.

Thanks!

Georg Begemann

Dana Darau

Milena Grifoni

quasi angular momentum = 2