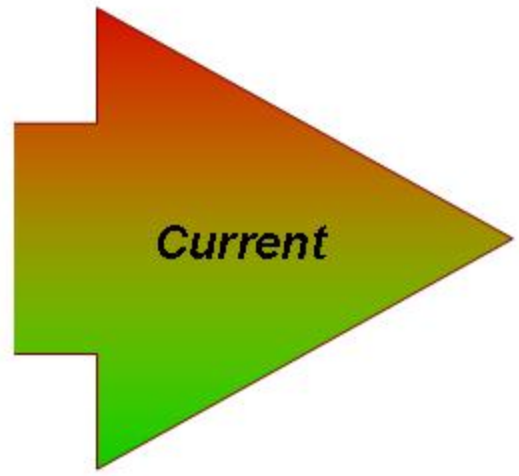
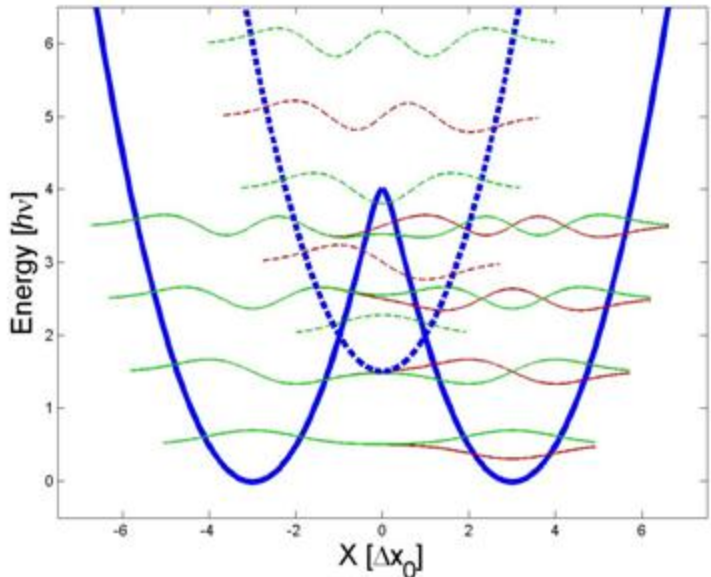




Dynamical symmetry breaking in transport through molecules

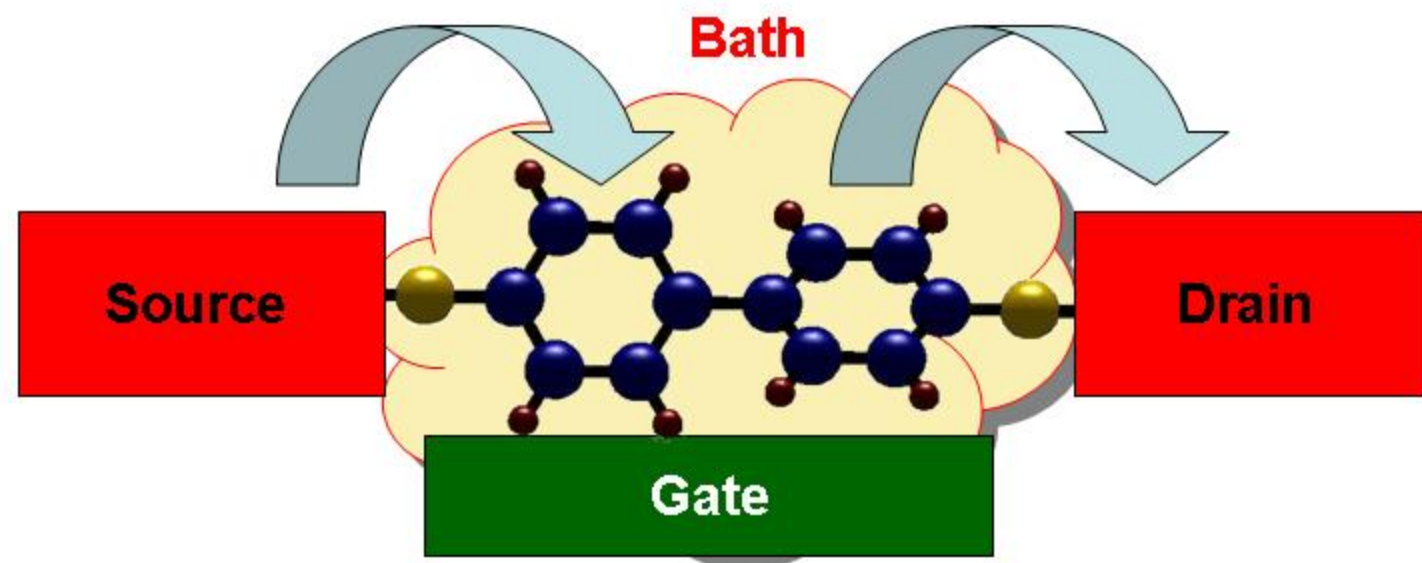
Andrea Donarini, Milena Grifoni, Klaus Richter

Even or Odd ?





The system



- Weak coupling to the leads + low temperature → Coulomb blockade
- Gate voltage: a three terminal device
- The molecule can move: we consider the softest mode.



The Hamiltonian

The hamiltonian of the device can be written as

$$H = H_S + H_{EL} + H_B + V_T + V_{SB}$$

where

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

and

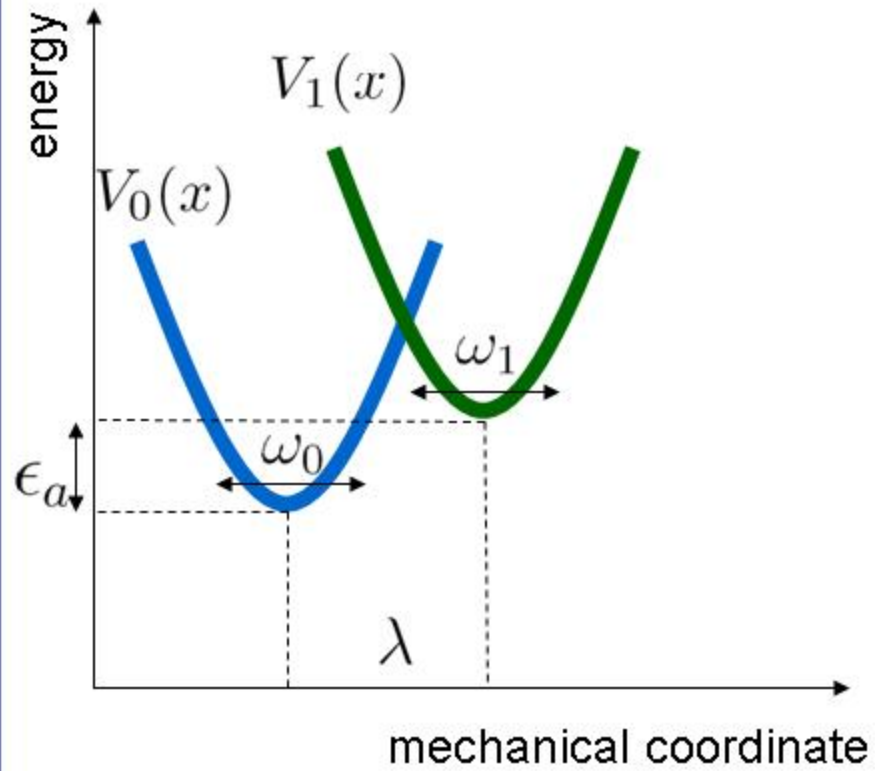
$$V_T = t \sum_{k;\alpha=L,R} \left(|0\rangle\langle 1| c_{k\alpha}^\dagger + |1\rangle\langle 0| c_{k\alpha} \right)$$

$$V_{SB} = \hbar\tilde{g} \sum_q \hat{x} (d_q + d_q^\dagger)$$

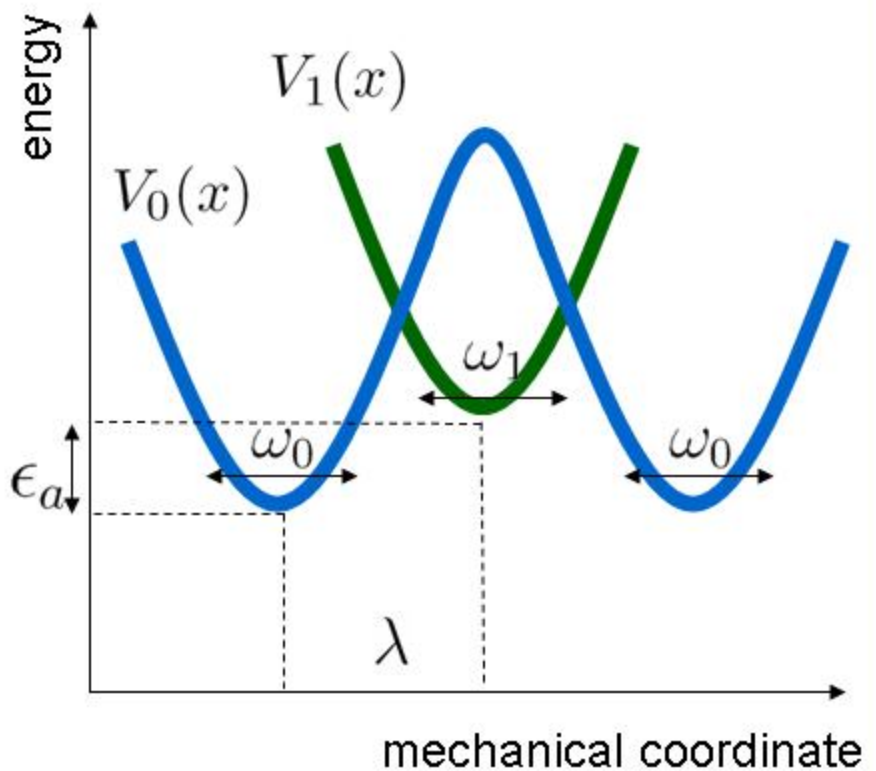


The adiabatic potentials

Simplest model

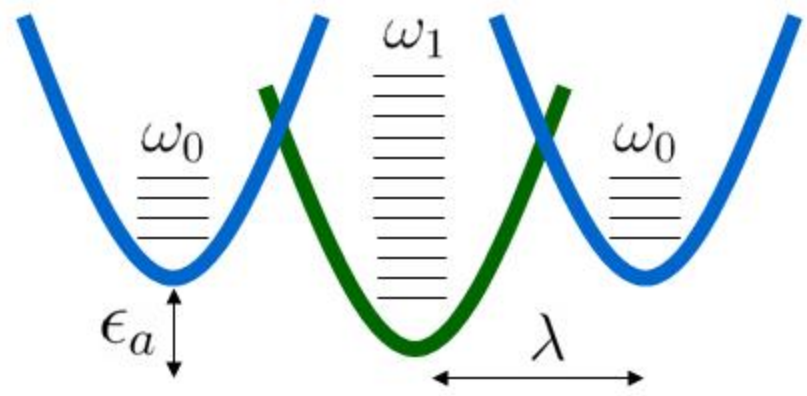


Bistable configurations are not so rare!





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:

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

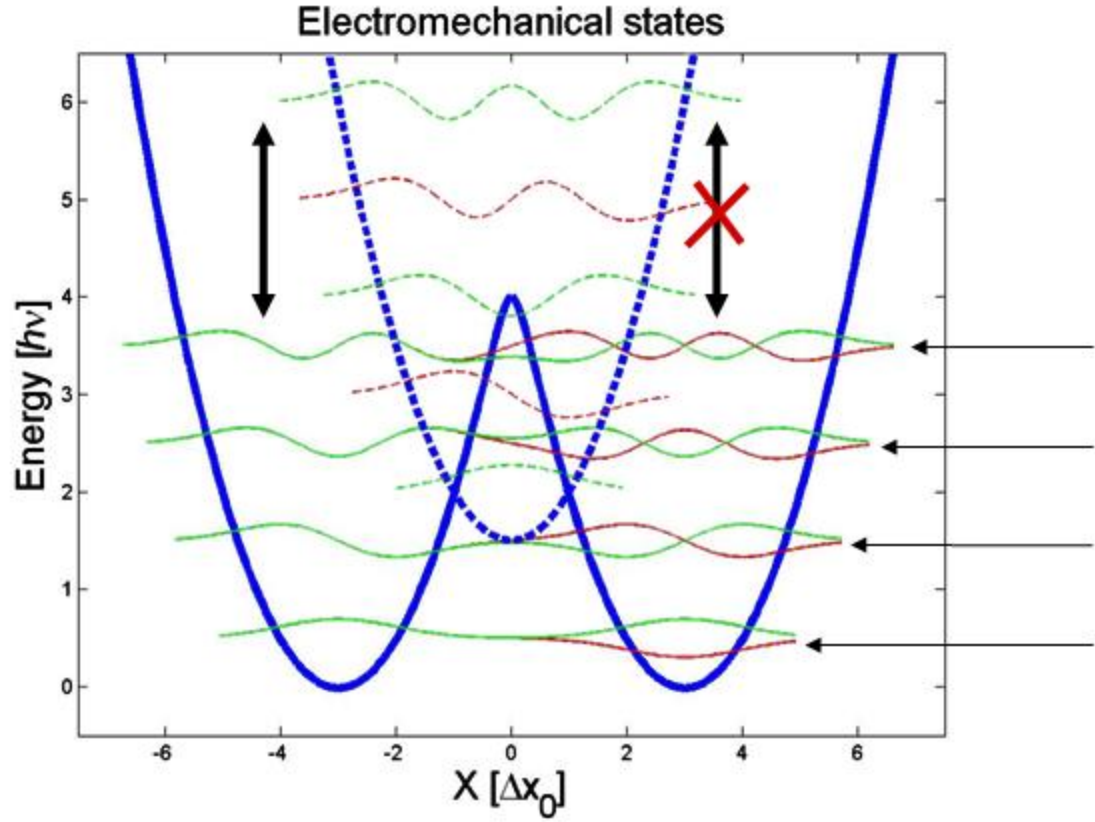
and

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

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



Symmetries



~~Quasi-degenerate doublets~~

- 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

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

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



Electrical leads

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

$$(\mathcal{L}_{\text{driv}} \sigma)_{00}^{\tau\tau'} = \sum_{\alpha} \mathcal{P}_{\tau} \left[\Gamma_{\text{out}}^{\alpha} \sigma_{11} + \sigma_{11} \Gamma_{\text{out}}^{\alpha \dagger} - 2(\Gamma_{\text{in}}^{\alpha} \sigma_{00} + \sigma_{00} \Gamma_{\text{in}}^{\alpha \dagger}) \right] \mathcal{P}_{\tau'}$$

where

bare tunneling rate

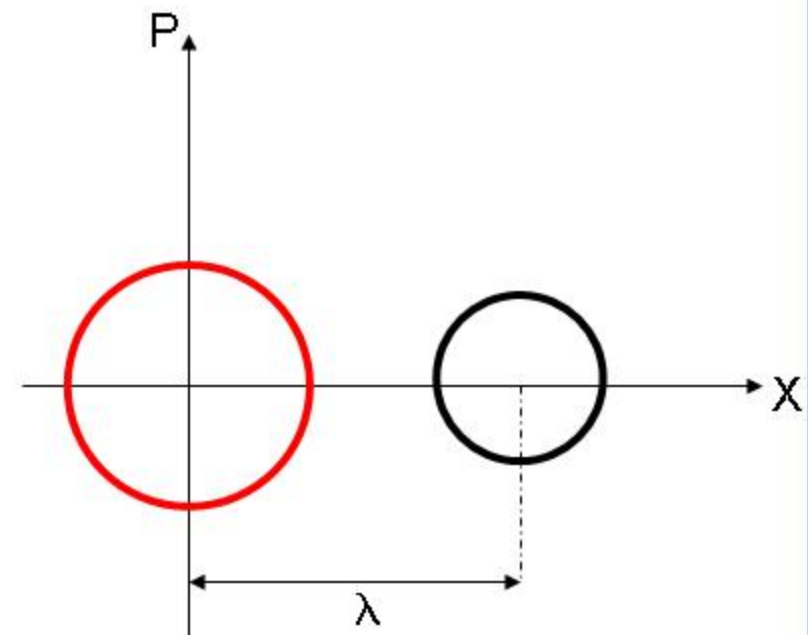
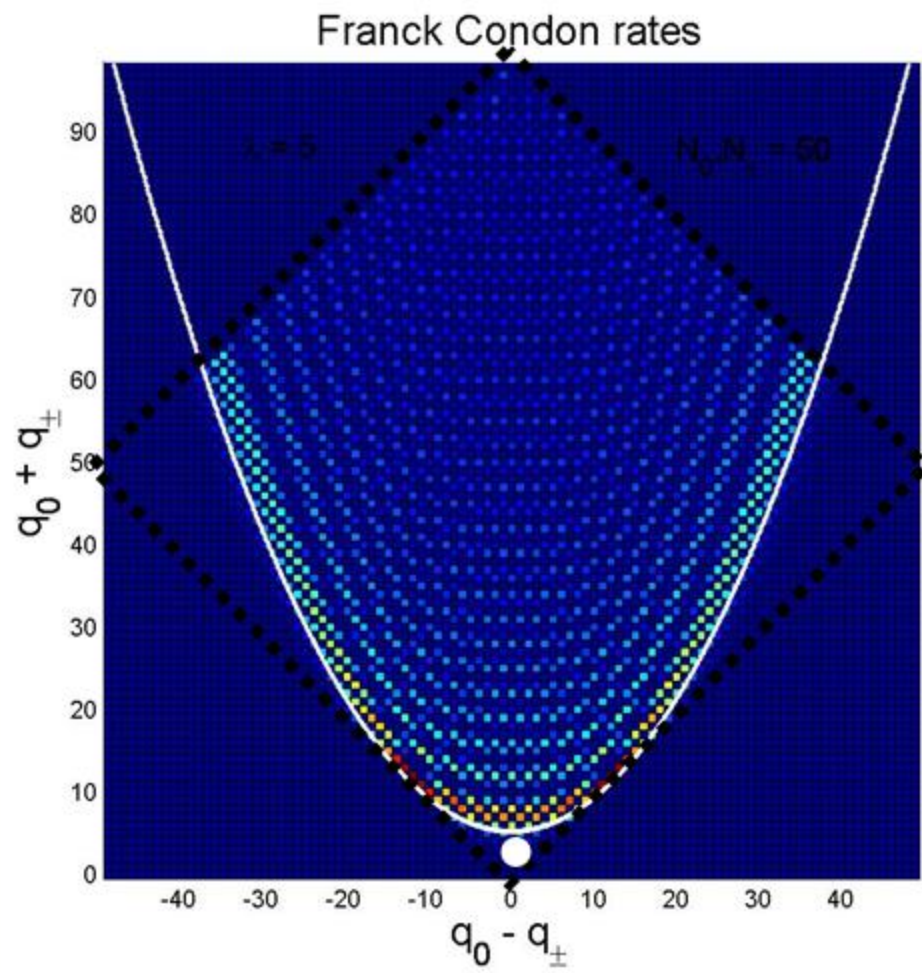
$$\Gamma_{\text{in}}^{\alpha} = \frac{\Gamma_{\alpha}}{2} \sum_{m, n\tau} |m\rangle \underbrace{\left\{ f_{\alpha}[eV_g - \epsilon_a + \hbar\omega(m - n)] \right\}}_{\text{Fermi factor}} \underbrace{\langle m|n, \tau\rangle}_{\text{Franck-Condon coefficient}} \langle n, \tau|$$

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

$$\left(\mathcal{L}_{\text{coh}} \sigma = -\frac{i}{\hbar} [H_S^{\text{eff}}, \sigma] \right)$$



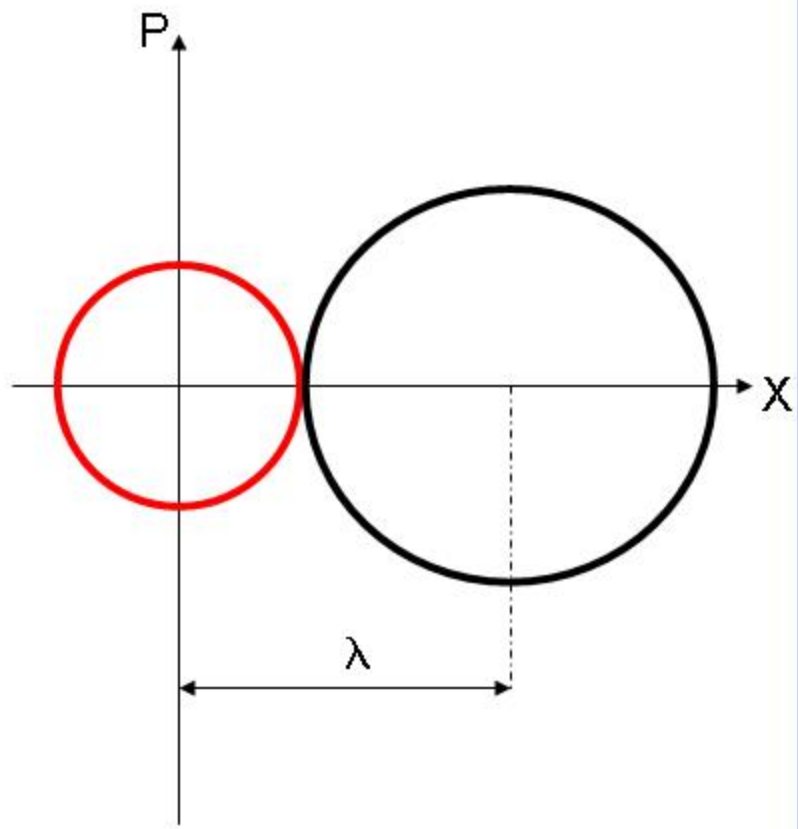
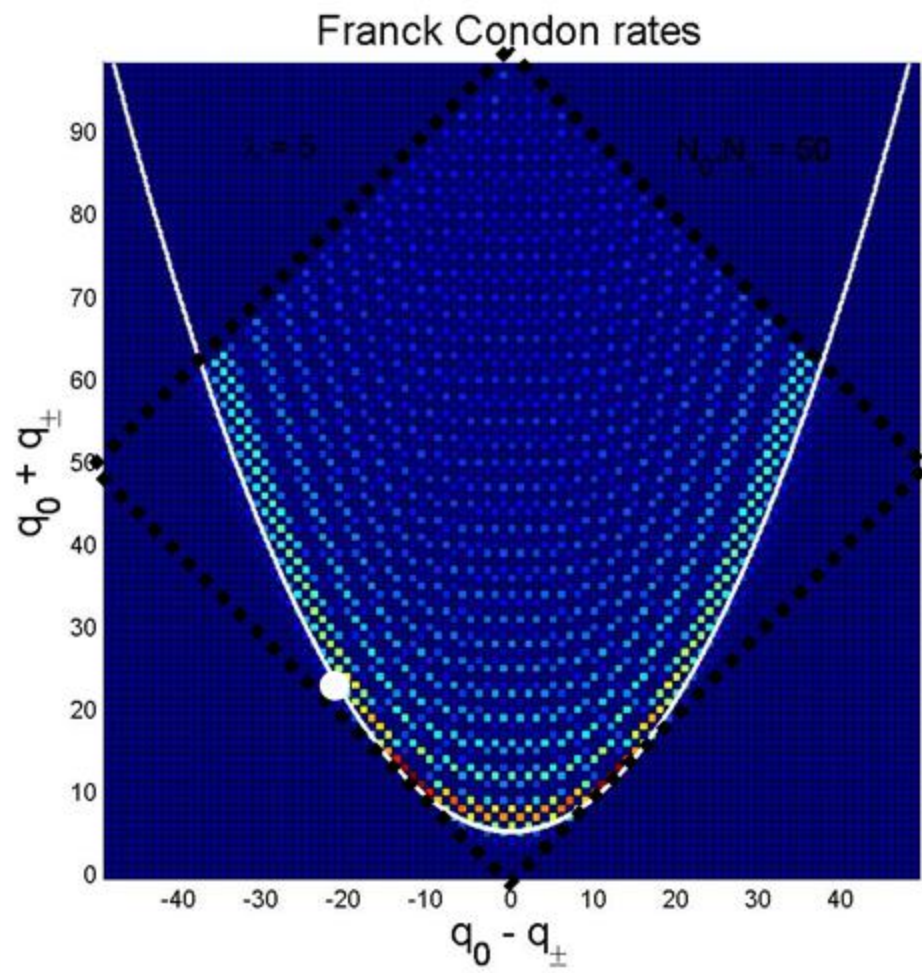
The Franck-Condon parabola



— State +
— State 0



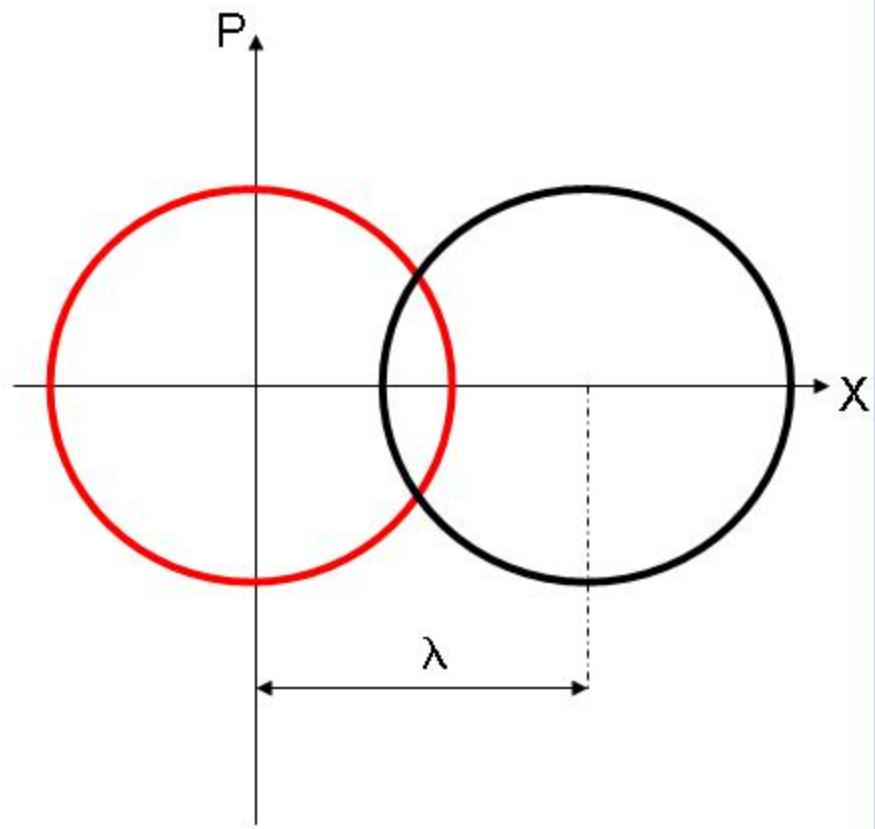
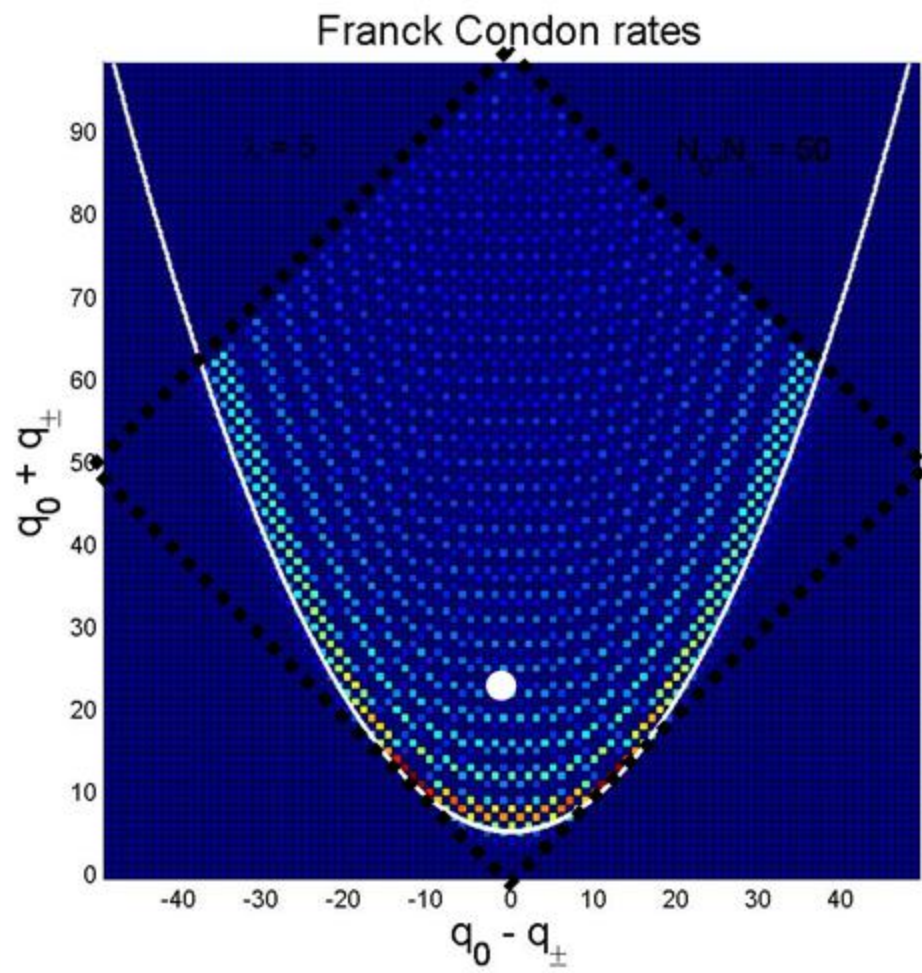
The Franck-Condon parabola



— State +
— State 0



The Franck-Condon parabola

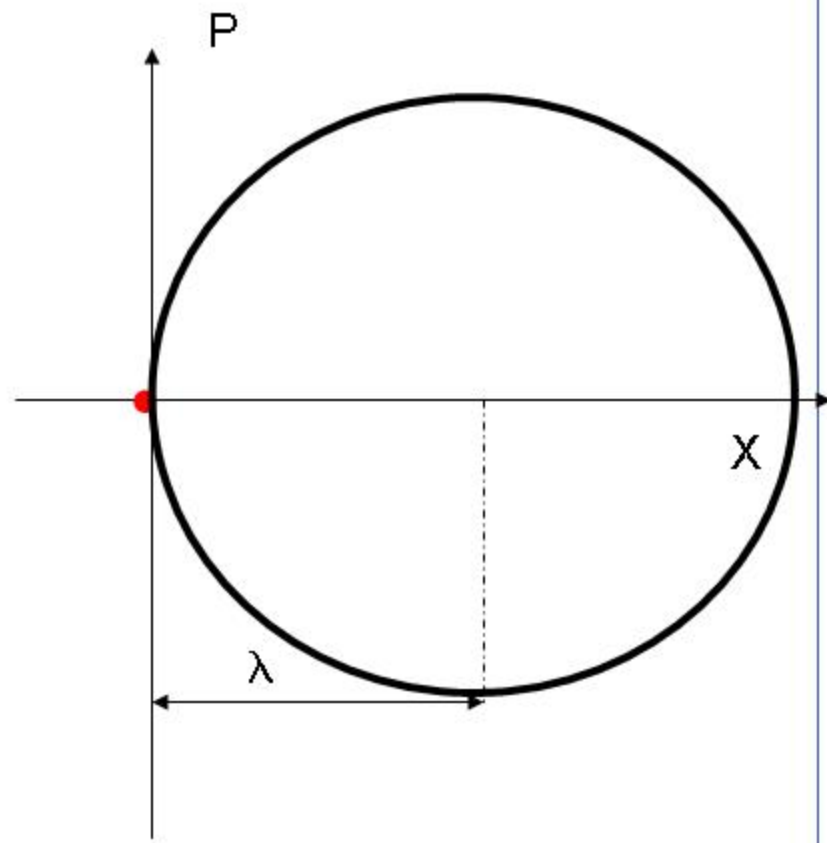
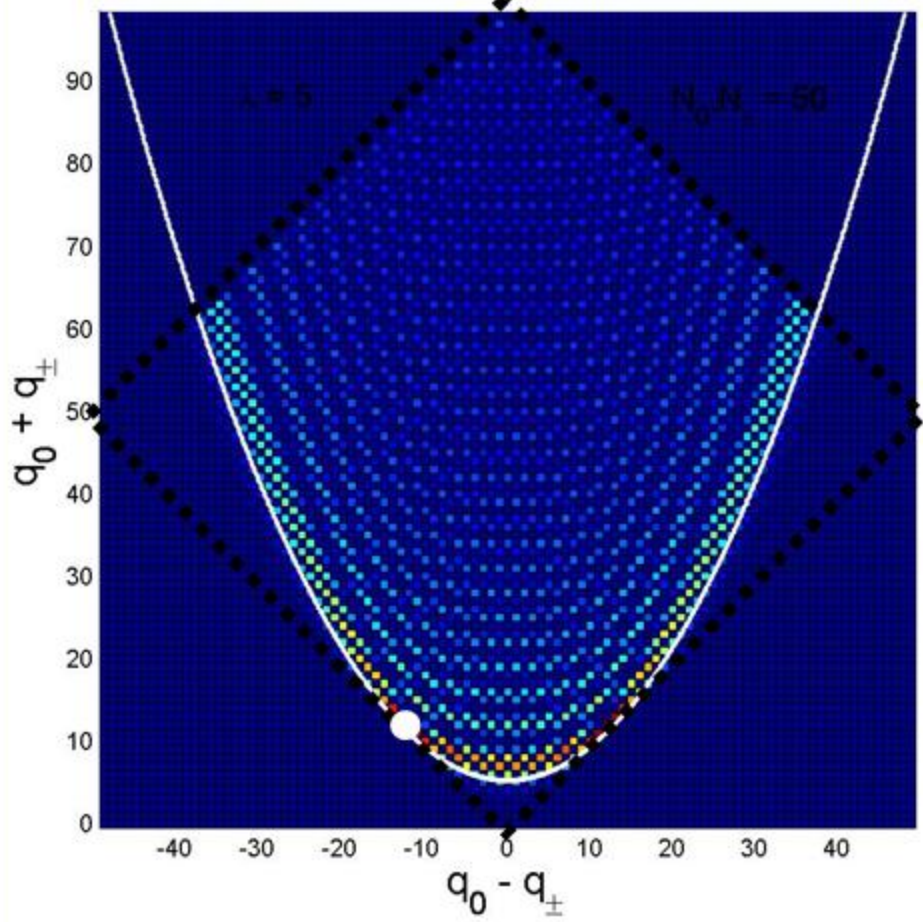


— State +
— State 0



The Franck-Condon parabola

Franck Condon rates



— State +
— State 0



Mechanical bath

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

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

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

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

Interwell dephasing term



Observables

- **Current:**

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

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

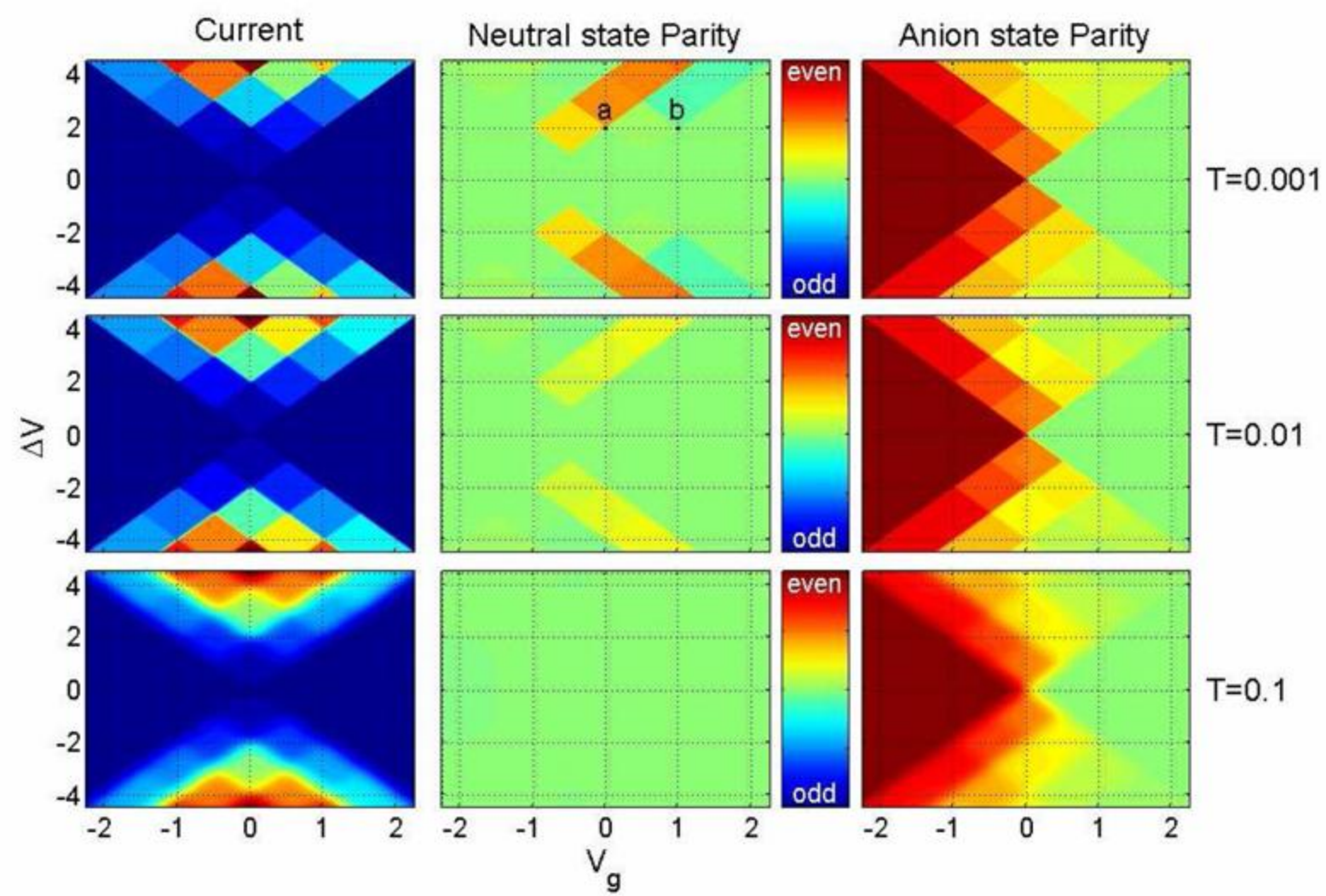
- **Parity:**

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

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

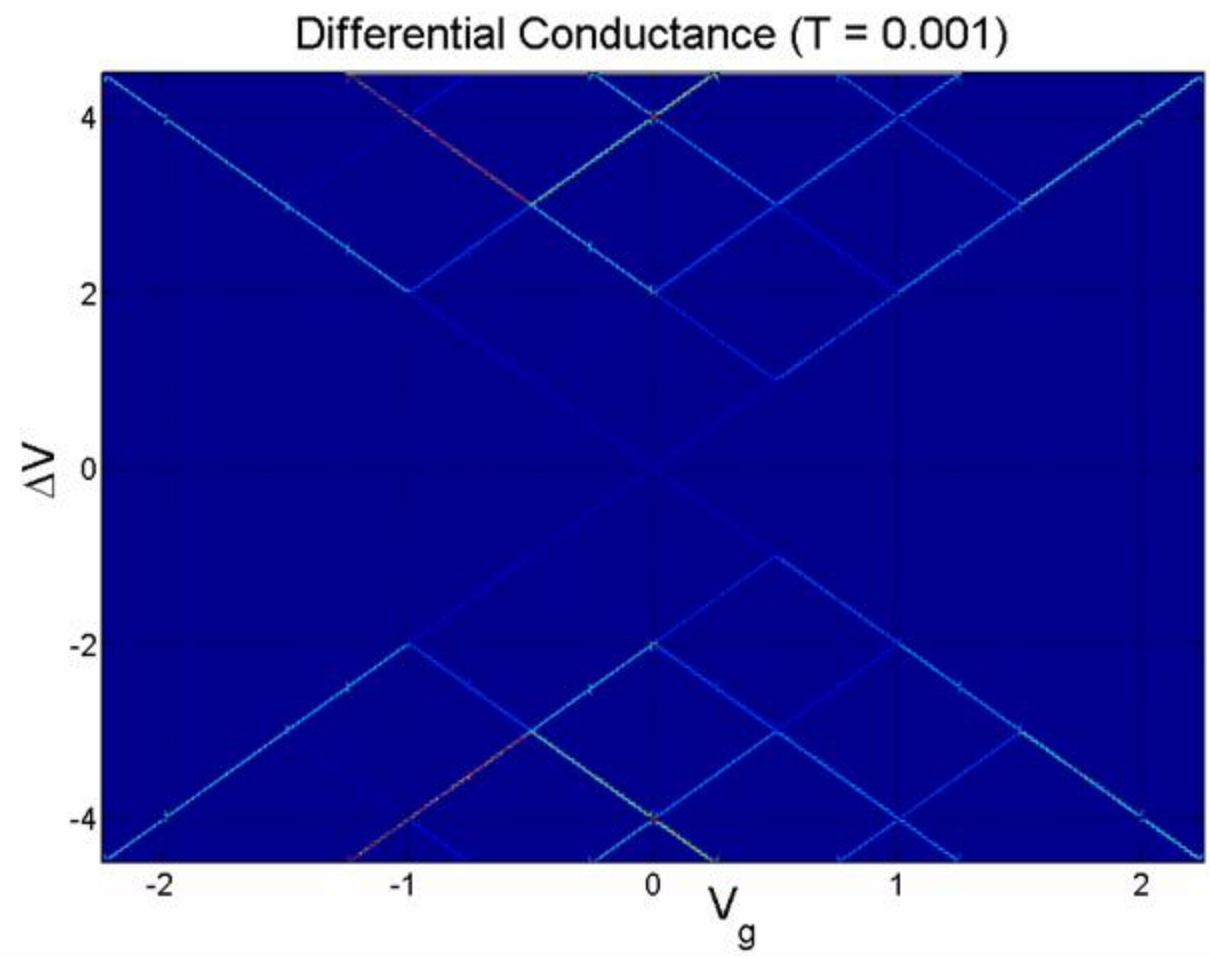


Symmetry breaking



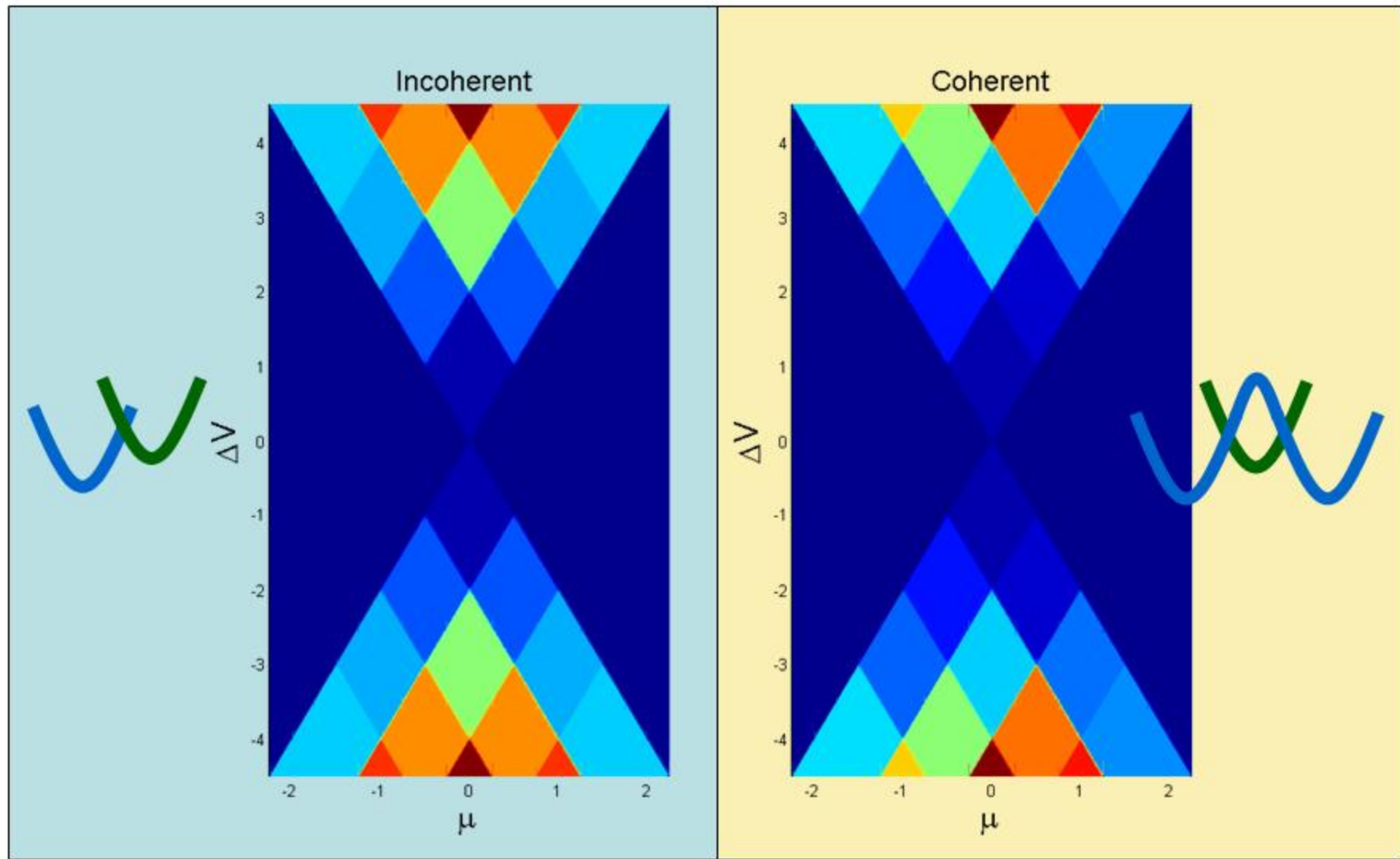


Gate voltage asymmetry





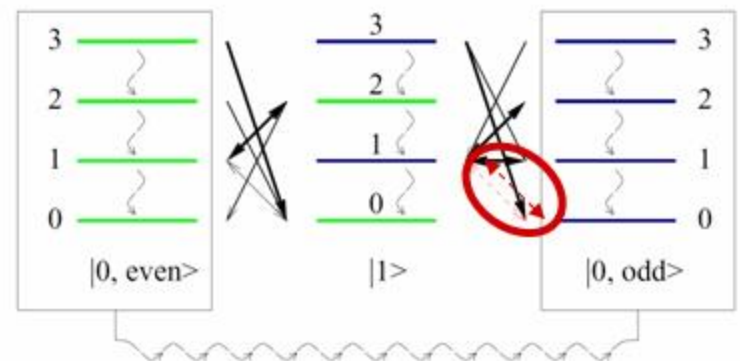
Incoherent vs. coherent



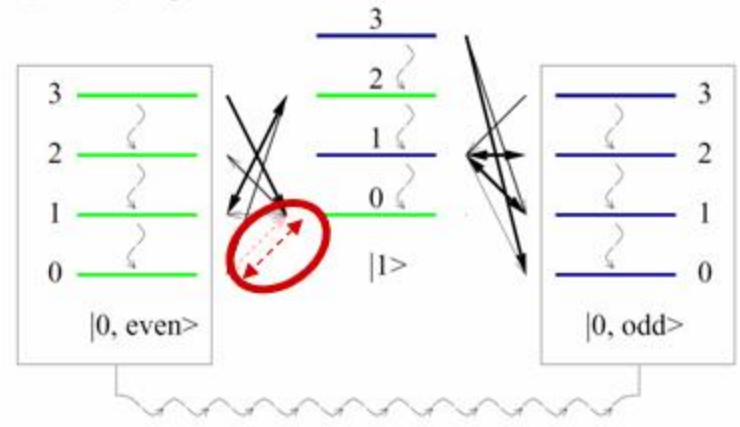


Un-blocking rates

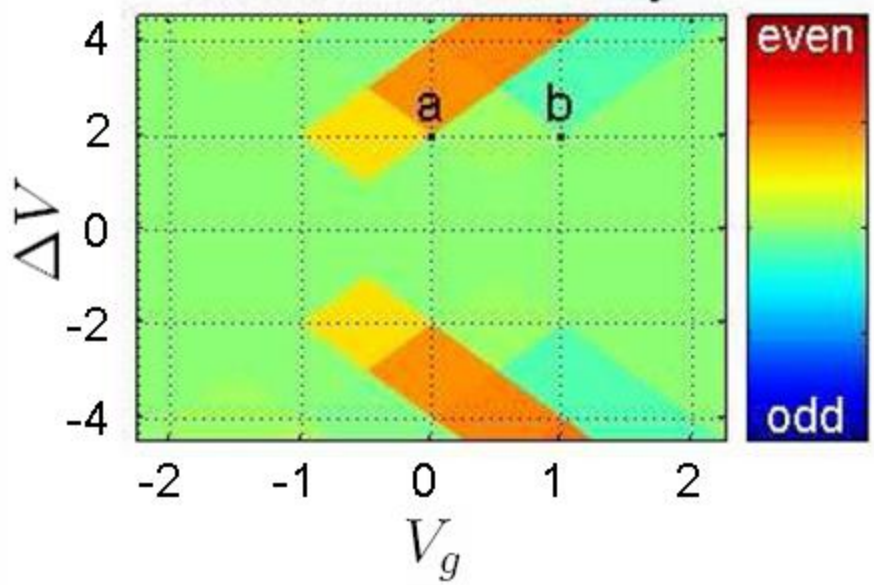
a) $2 < \Delta V < 4, V_g = 0$



b) $2 < \Delta V < 4, V_g = 1$



Neutral state Parity





Summary

- We derived an **effective Hamiltonian** for a molecule with bistable neutral potential
- We obtained the description of the electromechanical dynamics in terms of a **GME**
- We observed the parity **dynamical symmetry-breaking** in different bias and gating conditions
- We investigated the relevance of the **mechanical coherences** in the transport mechanism: i.e. gate voltage asymmetry of the current.

Thanks for your attention...