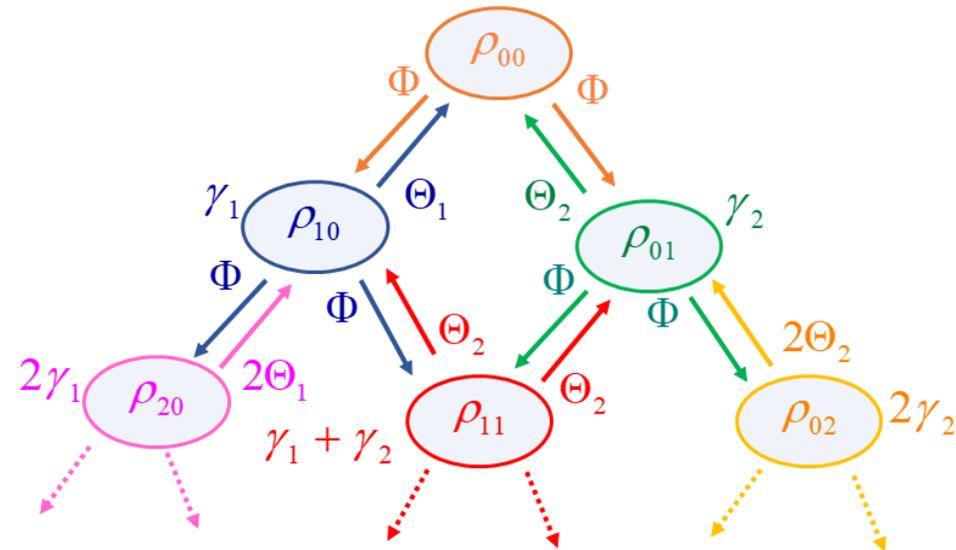
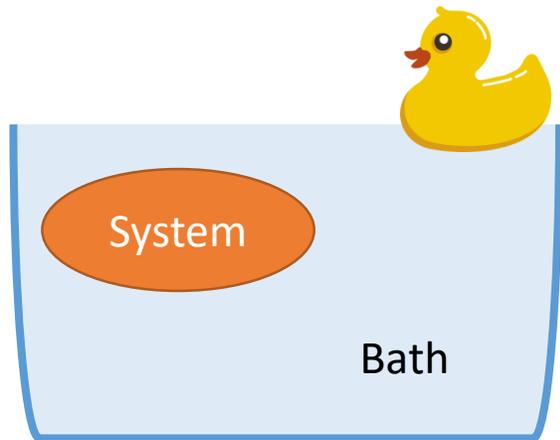


Hierarchical equations of motion: formalism and applications



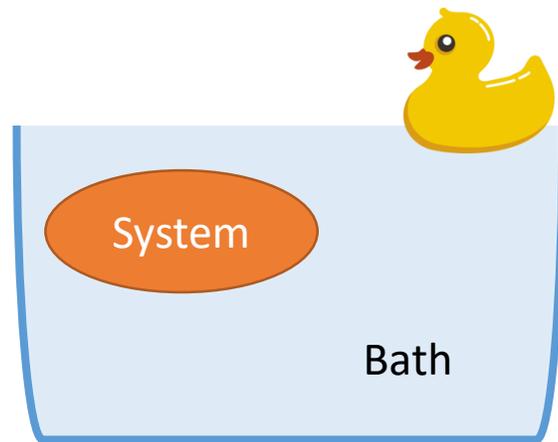
Etienne MANGAUD, Michèle DESOUTER-LECOMTE

Theory days

29/11/2023

Introduction

Hierarchical equations of motion are a powerful tool to describe **quantum systems in interaction with an environment** (also called a bath).



They are particularly useful to describe some physico-chemical processes:

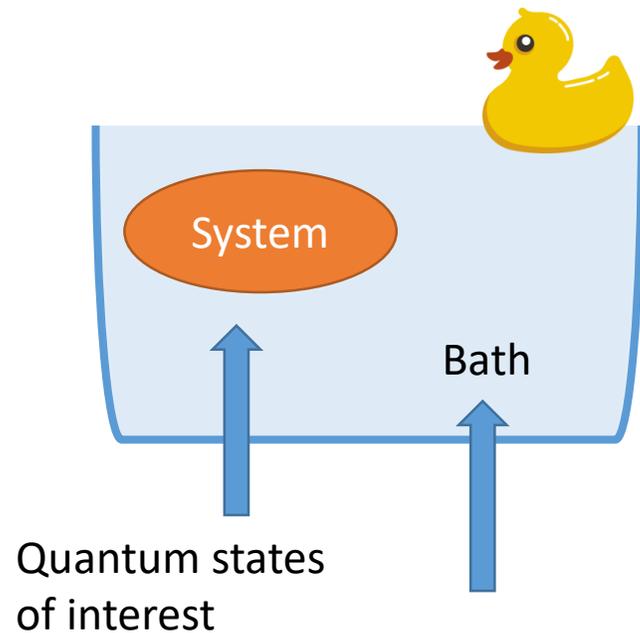
- **electron or proton transfers**
- **excitation transfer** in photosynthetic complexes
- **conical intersections**

and are used to compute

- **linear and non-linear spectroscopies**
- **laser optimal control**
- **non-equilibrium fluxes** in molecular junctions.

Introduction

Hierarchical equations of motion are a powerful tool to describe **quantum systems in interaction with an environment** (also called a bath).



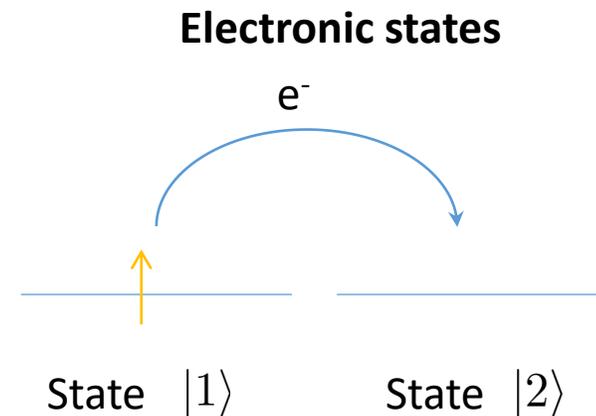
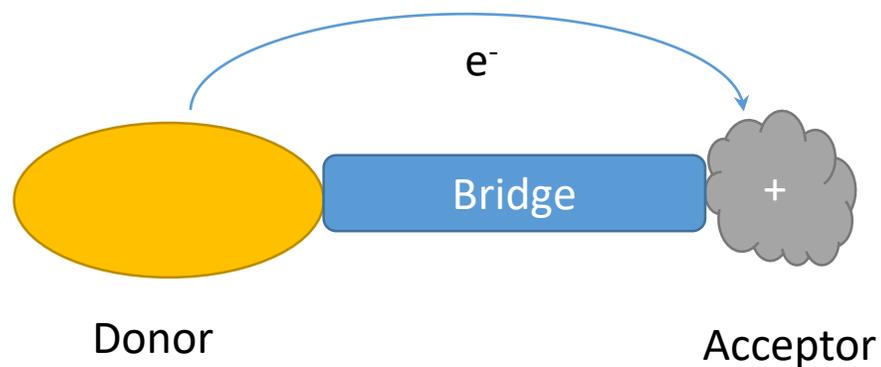
The bath can be a bath of phonons, electrons, photons and can include some thermodynamical aspects.

They are particularly useful to describe some physico-chemical processes:

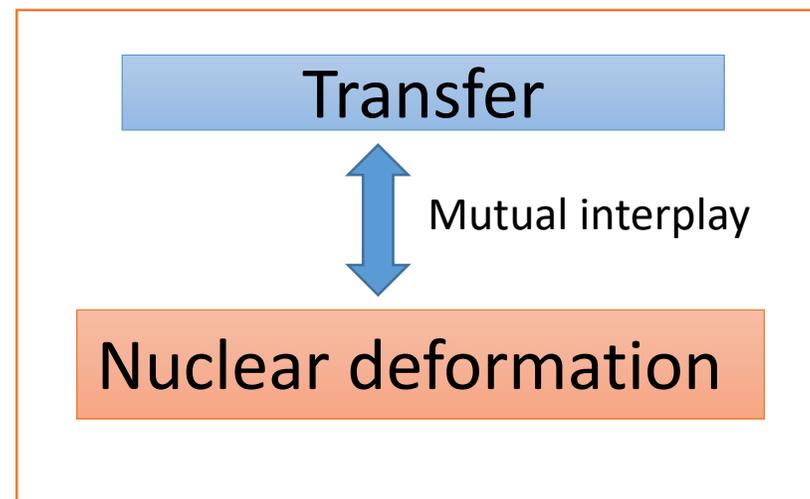
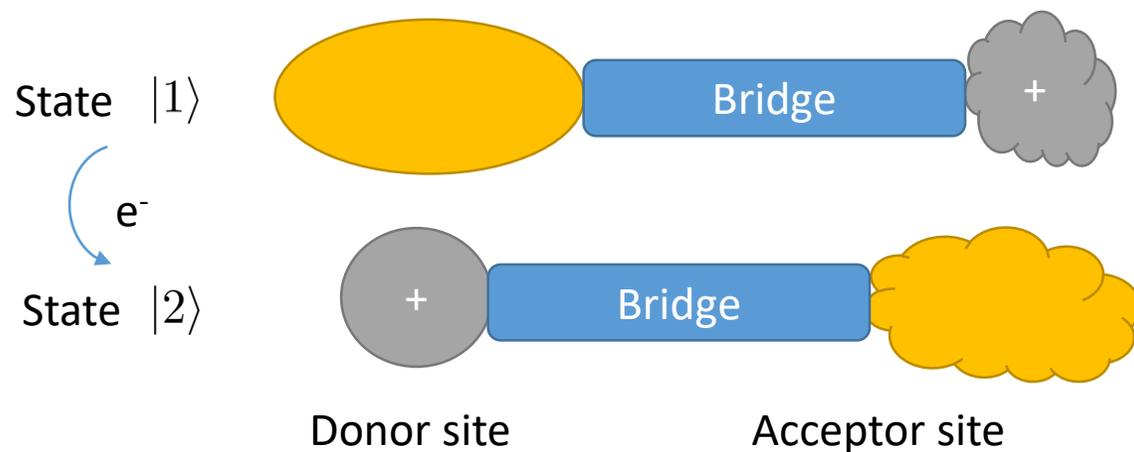
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- and are used to compute
- **linear and non-linear spectroscopies**
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 - **non-equilibrium fluxes** in molecular junctions.

Introduction

An example: Intramolecular charge transfer



Nuclear deformation: Geometries of Donor and acceptor sites



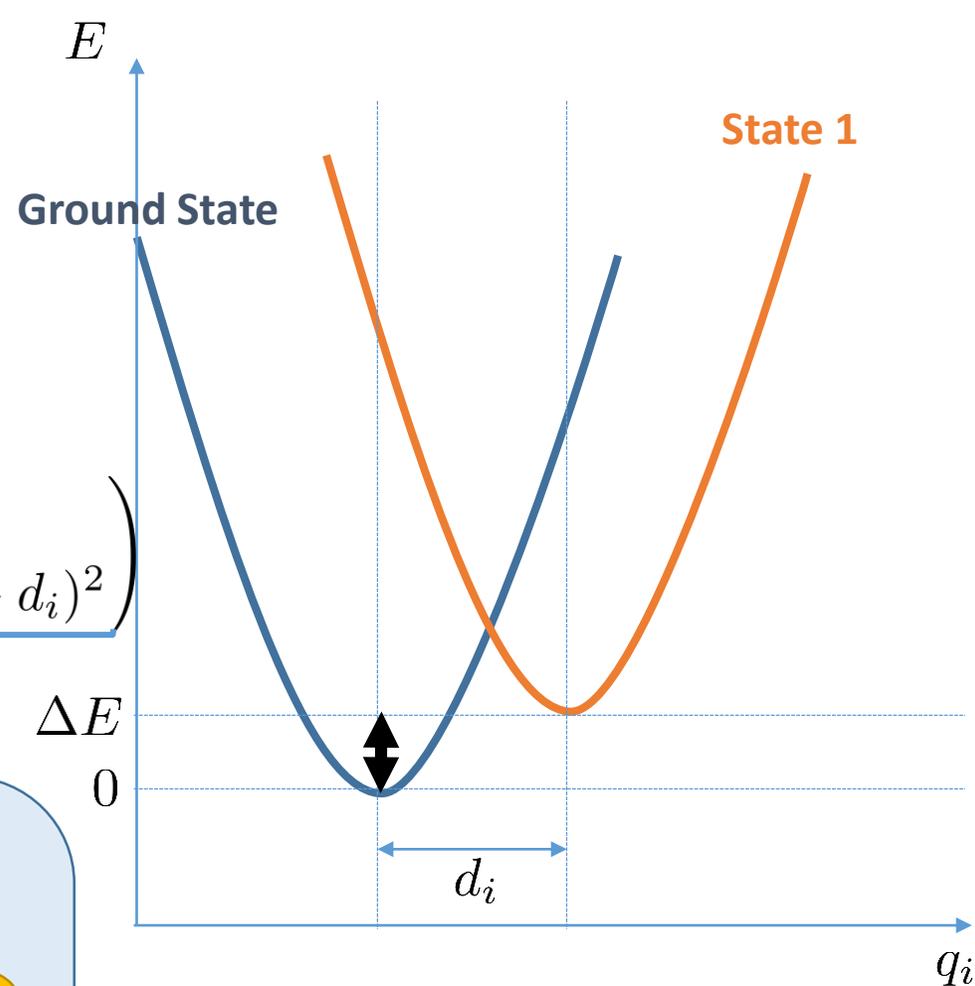
Model Hamiltonian

Let's begin with the simplest model Hamiltonian, the spin-boson model.

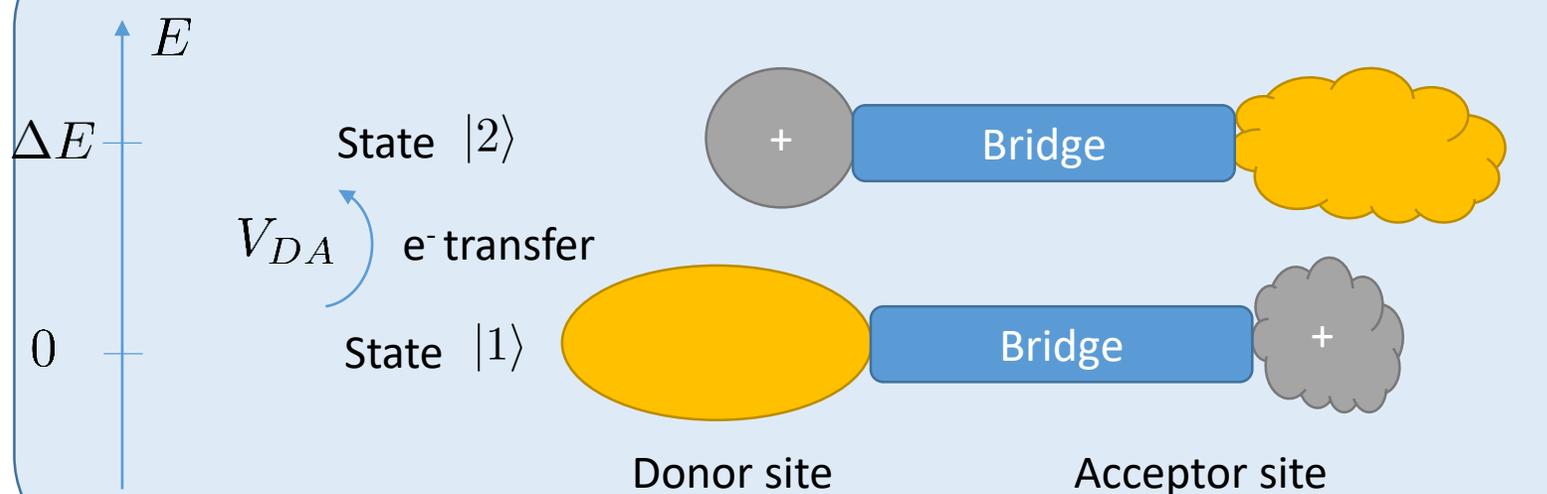
$$H = \begin{pmatrix} 0 & V_{DA} \\ V_{DA} & \Delta E \end{pmatrix} + \frac{1}{2} \begin{pmatrix} \sum_{i=1}^N p_i^2 + \omega_i^2 q_i^2 & 0 \\ 0 & \sum_{i=1}^N p_i^2 + \omega_i^2 (q_i - d_i)^2 \end{pmatrix}$$

Electronic states

Vibrational DoF



In the case of an intramolecular electron transfer,



Model Hamiltonian

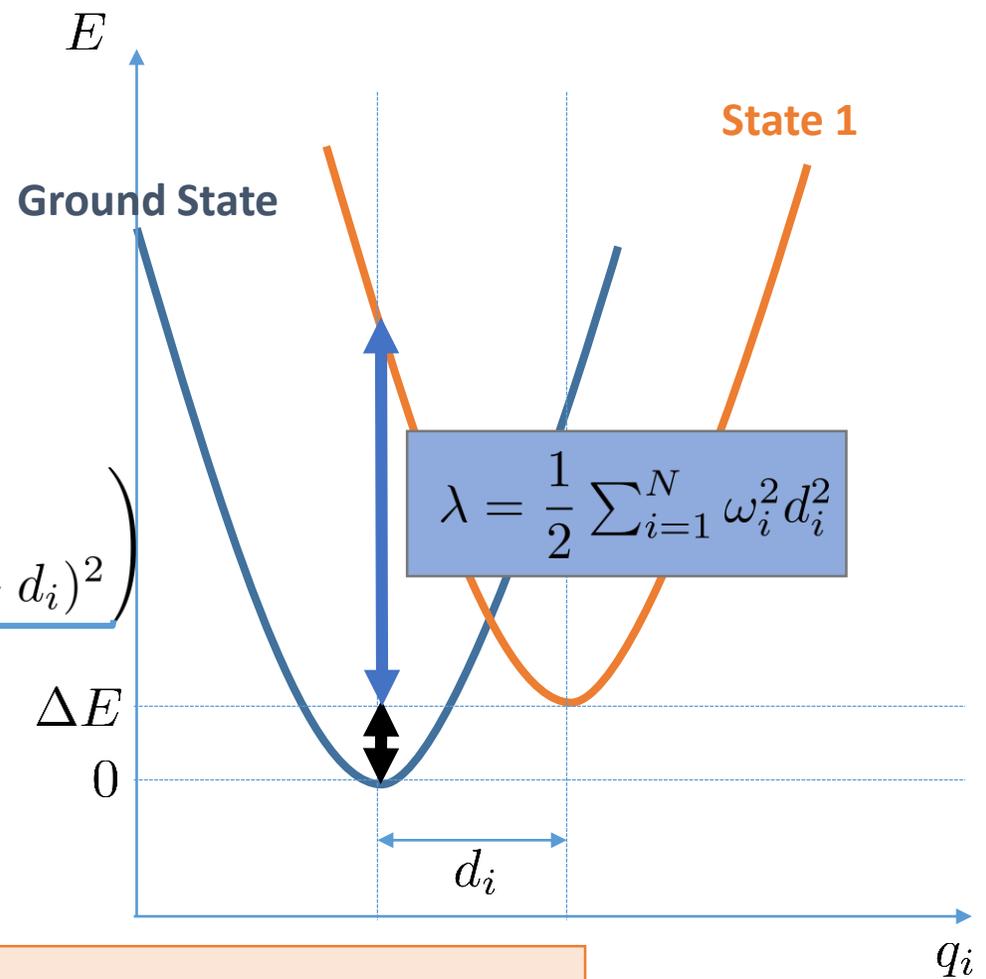
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Electronic states

Vibrational DoF

A system-bath partition arises here between the electronic states and the nuclei degrees of freedom:



$$H = \underbrace{\begin{pmatrix} 0 & V_{DA} \\ V_{DA} & \Delta E + \frac{1}{2} \sum_{i=1}^N \omega_i^2 d_i^2 \end{pmatrix}}_{H_S} - \underbrace{\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \sum_{i=1}^N \omega_i^2 d_i q_i}_{H_{SB}=S.B} + \underbrace{\frac{1}{2} \sum_{i=1}^N (p_i^2 + \omega_i^2 q_i^2)}_{H_B} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

System Hamiltonian

System-bath coupling

Bath Hamiltonian

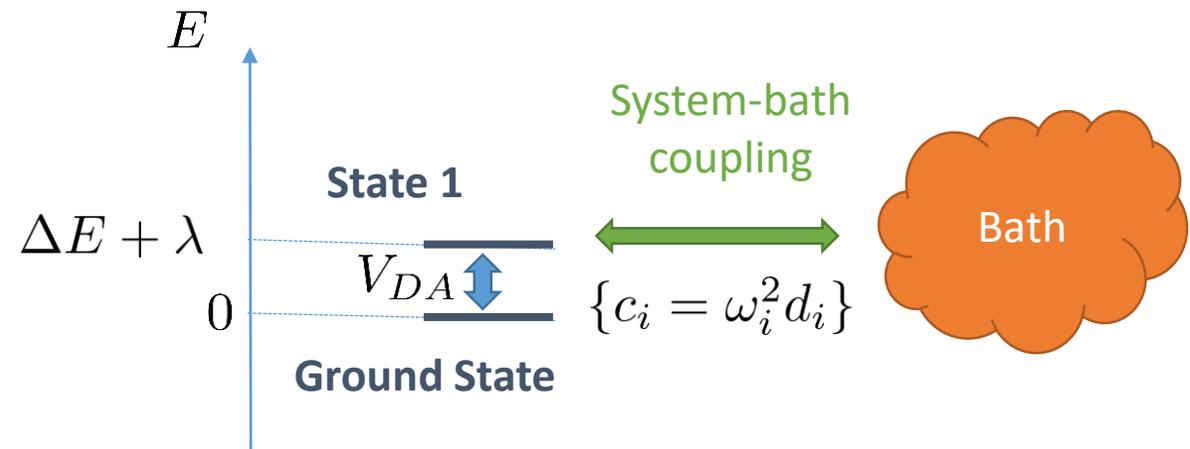
Model Hamiltonian

Let's begin with the simplest model Hamiltonian, the spin-boson model.

$$H = \begin{pmatrix} 0 & V_{DA} \\ V_{DA} & \Delta E \end{pmatrix} + \frac{1}{2} \left(\begin{array}{c} \sum_{i=1}^N p_i^2 + \omega_i^2 q_i^2 \\ 0 \end{array} \quad \begin{array}{c} 0 \\ \sum_{i=1}^N p_i^2 + \omega_i^2 (q_i - d_i)^2 \end{array} \right)$$

Electronic states

Vibrational DoF



A system-bath partition arises here between the electronic states and the nuclei degrees of freedom:

$$H = \underbrace{\begin{pmatrix} 0 & V_{DA} \\ V_{DA} & \Delta E + \lambda \end{pmatrix}}_{H_S} - \underbrace{\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \sum_{i=1}^N c_i q_i}_{H_{SB=S.B}} + \underbrace{\frac{1}{2} \sum_{i=1}^N (p_i^2 + \omega_i^2 q_i^2) \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}}_{H_B}$$

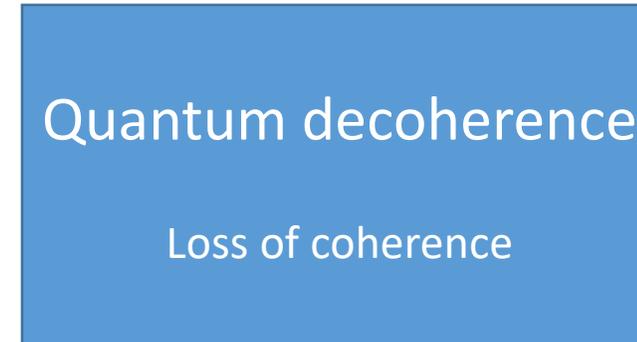
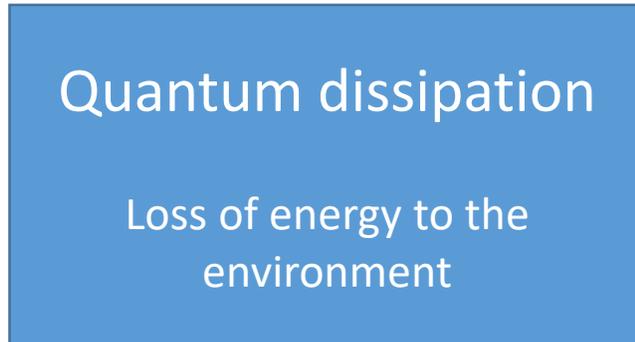
System Hamiltonian

System-bath coupling

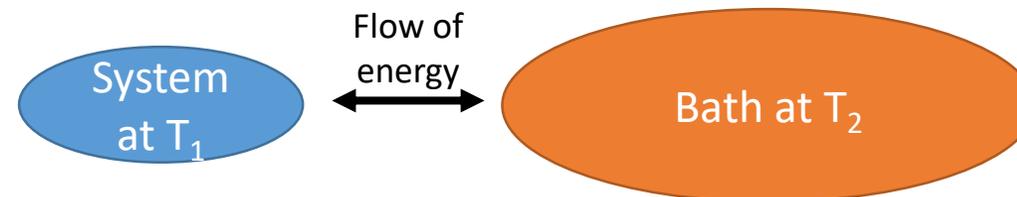
Bath Hamiltonian

Introduction

Why using open quantum system theory ?



Schrödinger equation is reversible. Irreversible processes seems *a priori* forbidden. However, if the state of the overall system is reversible, we only observe a **small subsystem** which **appears irreversible**.

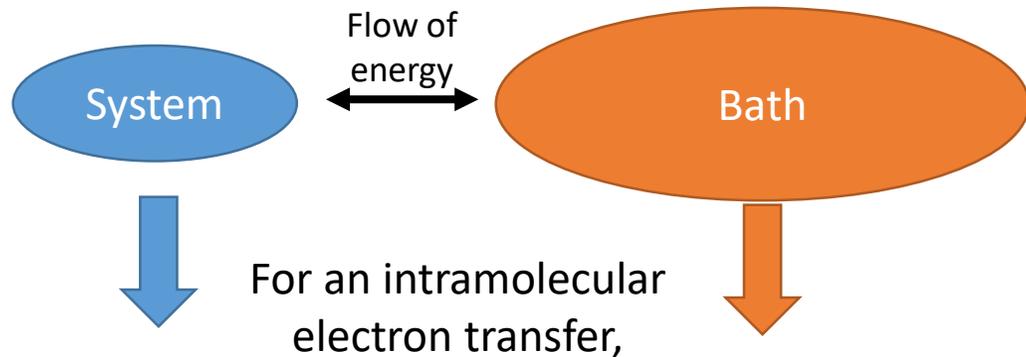


Introduction

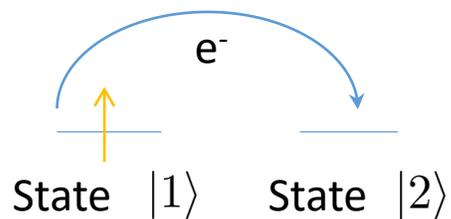
Why using open quantum system theory ?

Quantum dissipation
Loss of energy to the environment

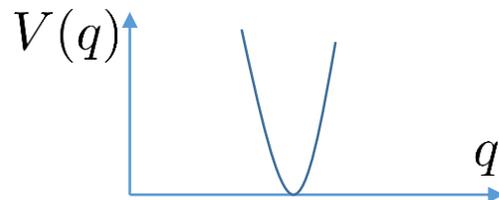
Quantum decoherence
Loss of coherence



Electronic states



Vibrational modes



Introduction

Why using open quantum system theory ?

Quantum dissipation

Loss of energy to the
environment

Quantum decoherence

Loss of coherence



Coherence arises from the wave-like nature of the matter. But many quantum phenomena do not remain at a macroscopic scale.

Time evolution of the density operator

Liouville-Von Neumann equation

$$\dot{\hat{\rho}} = \mathcal{L}\hat{\rho} \quad \text{with} \quad \mathcal{L}\cdot = -i\hbar^{-1}[\hat{H}, \cdot]$$

Can be derived from the definition of the density matrix and the Schrödinger equation

Interaction representation

The system-bath Hamiltonian can be split :

$$H = \underbrace{H_0}_{H_S + H_B} + S.B$$

We define the density matrix in interaction representation as:

$$\rho_I(t) = e^{iH_0t/\hbar} \rho(t) e^{-iH_0t/\hbar}$$

In interaction representation,

$$\dot{\rho}_I(t) = L(t)\rho_I(t)$$

In atomic units, $\hbar = 1$

$$L(t)\cdot = -i[S(t)B(t), \cdot]$$

$$S(t) = e^{iH_S t} S e^{-iH_S t}$$

$$B(t) = e^{iH_B t} B e^{-iH_B t}$$

Exact dynamical equations

$$H = H_S + H_{SB} + H_B$$

Time evolution of the reduced density matrix with initial system-bath factorization writes in interaction representation:

$$\rho_{S,I}(t) = \text{Tr}_B \left[e_{(+)}^{\int_0^t d\tau L(\tau)} \rho_B^{eq} \rho_{S,I}(0) \right]$$

Trace over the bath degrees of freedom

Time-ordered exponential

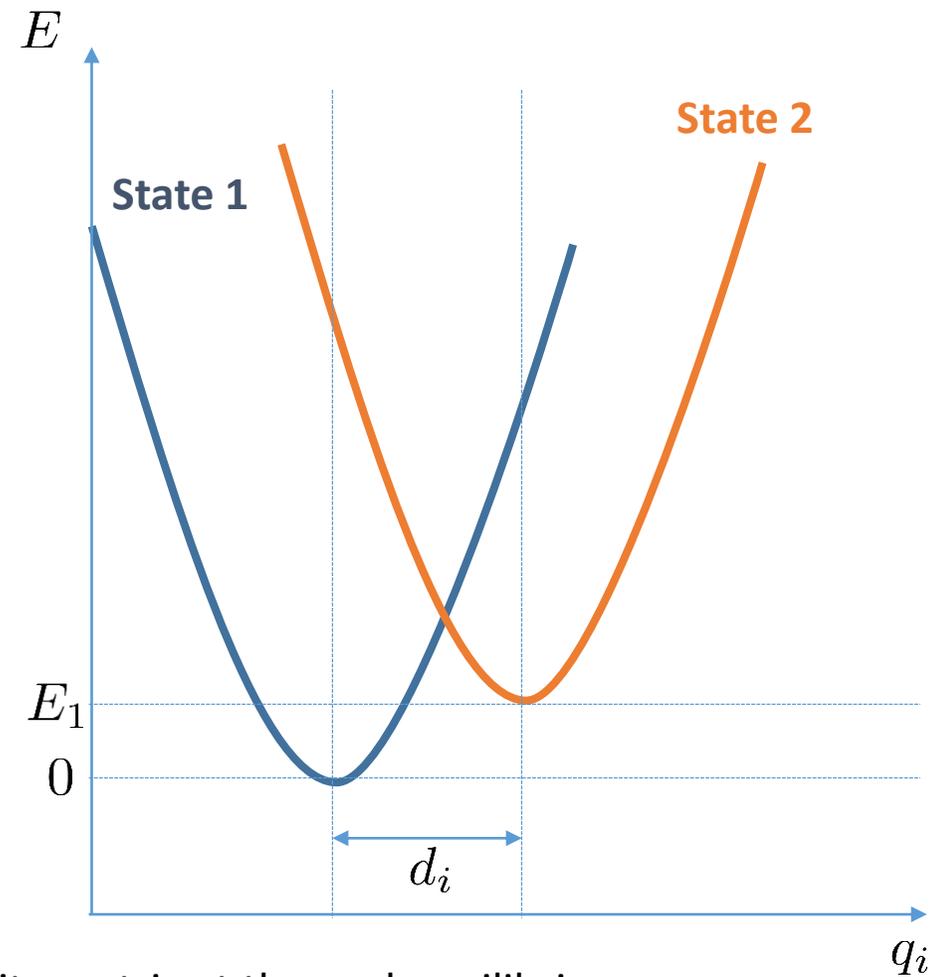
Liouvillian of the system-bath coupling

Bath density matrix at thermal equilibrium

$$L(t)\bullet = -i[S(t)B(t), \bullet] \quad \rho_B^{eq} = \frac{e^{-\beta H_B}}{\text{Tr}_B[e^{-\beta H_B}]}$$

System density matrix in interaction representation

$$\rho_{S,I}(t) = e^{iH_S t} \rho_S e^{-iH_S t}$$



Exact dynamical equations

$$H = H_S + S.B + H_B$$

Due to the special shape of the system-bath Hamiltonian (harmonic oscillators with linear coupling), time evolution of the reduced system density matrix with initial system-bath factorization writes in interaction representation as an **exact second order cumulant expansion** :

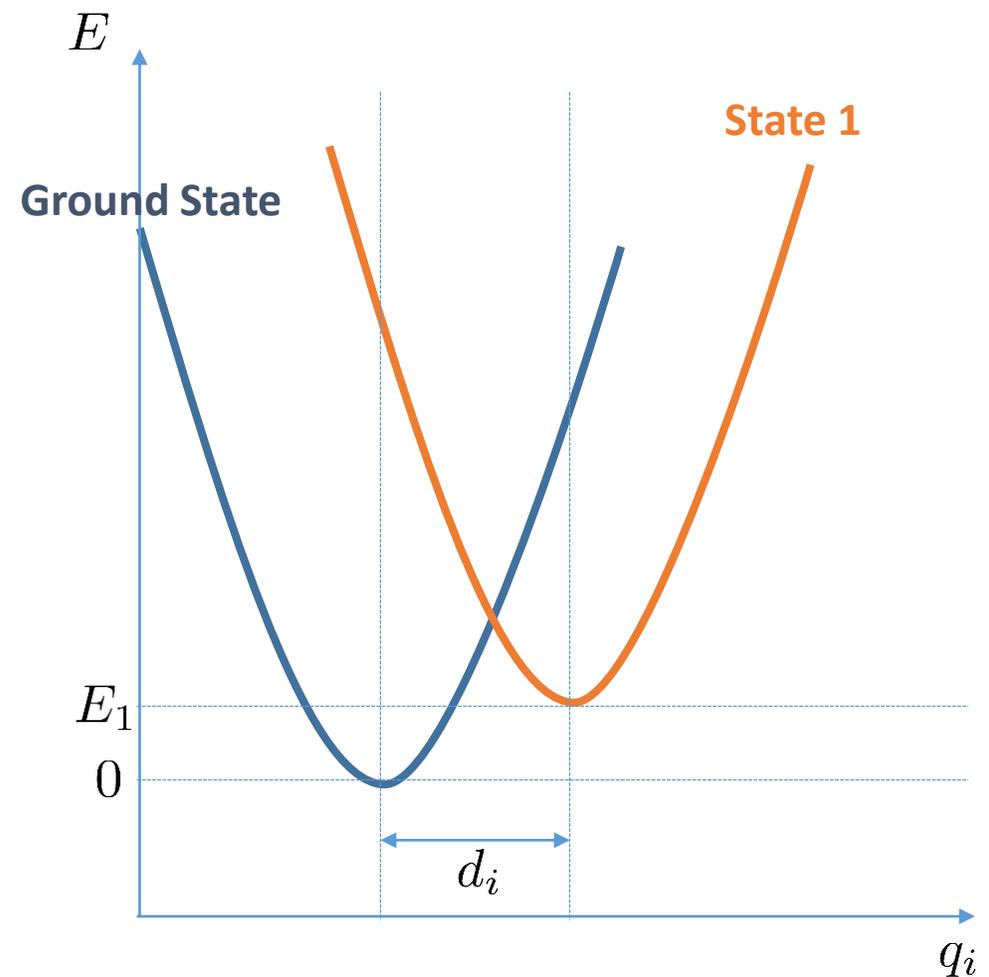
$$\rho_{S,I}(t) = e_{(+)}^0 \int_0^t d\tau \int_0^\tau dt' K^{(2)}(\tau, t') \rho_{S,I}(0).$$

with $\int_0^t d\tau K^{(2)}(t, \tau) \cdot = \int_0^t d\tau \text{Tr}_B [L(t)L(\tau) \rho_B^{eq} \cdot]$

↑

Bath density matrix at thermal equilibrium

$$\rho_B^{eq} = \frac{e^{-\beta H}}{\text{Tr}_B [e^{-\beta H}]}$$



Second-order memory kernel

$$\int_0^t d\tau K^{(2)}(t, \tau) \cdot = \int_0^t d\tau \text{Tr}_B [L(t)L(\tau)\rho_B^{eq} \cdot]$$

After a bit of algebra:

$$\int_0^t d\tau K^{(2)}(t, \tau) \cdot = - \int_0^t d\tau [\underset{\text{■}}{S(t)}, \underset{\text{■}}{C(t-\tau)} \underset{\text{■}}{S(\tau)} \cdot - \cdot \underset{\text{■}}{S(\tau)} \underset{\text{■}}{C^*(t-\tau)}]$$

Bath correlation function

$$C(t-\tau) = \text{Tr}_B [B(t)B(\tau)\rho_B^{eq}]$$

How do we have access to the bath correlation function ?

Elimination of the bath

$$H = \underbrace{\begin{pmatrix} 0 & V_{DA} \\ V_{DA} & \Delta E + \lambda \end{pmatrix}}_{H_S} + \underbrace{\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \sum_{i=1}^M c_i q_i}_{H_{SB}=S.B} + \underbrace{\frac{1}{2} \sum_{i=1}^M (p_i^2 + \omega_i^2 q_i^2)}_{H_B} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

System Hamiltonian
System-bath coupling
Bath Hamiltonian

Ladder operators in mass-weighted coordinates

$$a_l^\dagger = \frac{1}{\sqrt{2\omega_l}} (\omega_l q_l - i p_l)$$

$$a_l = \frac{1}{\sqrt{2\omega_l}} (\omega_l q_l + i p_l)$$

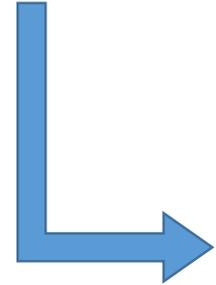
Bath coupling in interaction representation

$$B(t) = e^{iH_B t} B e^{-iH_B t}$$

The key ingredient is the system-bath correlation function: $C(t - \tau) = Tr_B [B(t) B(\tau) \rho_B^{eq}]$

Let's write the harmonic oscillators coordinates and momentum with ladder operators :

$$H_B = \sum_{l=1}^M \omega_l \left(a_l^\dagger a_l + \frac{1}{2} \right) \quad B = \sum_{l=1}^M \frac{c_l}{\sqrt{2\omega_l}} (a_l + a_l^\dagger)$$



$$C(t - \tau) = \sum_{l=1}^M \frac{c_l^2}{2\omega_l} Tr_B \left[\left(e^{-i\omega_l(t-\tau)} a_l a_l^\dagger + e^{i\omega_l(t-\tau)} a_l^\dagger a_l \right) \rho_B^{eq} \right]$$

$$\rho_B^{eq} = \frac{1}{Z} e^{-\beta \sum_{l=1}^M \omega_l a_l^\dagger a_l} \quad \text{with} \quad Z = Tr_B \left[e^{-\beta \sum_l \omega_l a_l^\dagger a_l} \right] = \prod_{l=1}^M \frac{1}{1 - e^{-\beta \omega_l}}$$

Bose distribution 16

Elimination of the bath

The bath correlation function writes as:

$$C(t - \tau) = \sum_{l=1}^M \frac{c_l^2}{2\omega_l} e^{-i\omega_l(t-\tau)} \frac{1}{1 - e^{-\beta\omega_l}} + \sum_{l=1}^M \frac{c_l^2}{2\omega_l} e^{i\omega_l(t-\tau)} \frac{1}{e^{\beta\omega_l} - 1}$$

We define the spectral density as :

$$J(\omega) = \frac{\pi}{2} \sum_{l=1}^M \frac{c_l^2}{\omega_l} \delta(\omega - \omega_l)$$

for $\omega \in [0, +\infty[$
with an odd parity $J(-\omega) = -J(\omega)$

If we assume a continuous distribution of modes,

$$C(t - \tau) = \frac{1}{\pi} \int_0^{+\infty} d\omega J(\omega) e^{-i\omega(t-\tau)} \frac{1}{1 - e^{-\beta\omega}} + J(\omega) e^{i\omega(t-\tau)} \frac{1}{e^{\beta\omega} - 1}$$

Fluctuation-dissipation relation $C(t - \tau) = \frac{1}{\pi} \int_{-\infty}^{+\infty} d\omega e^{i\omega(t-\tau)} \frac{J(\omega)}{e^{\beta\omega} - 1}$

Exact dynamical equations

$$H = H_S + S.B + H_B$$

Due to the special shape of the system-bath Hamiltonian (harmonic oscillators with linear coupling), time evolution of the reduced system density matrix with initial system-bath factorization writes in interaction representation as an **exact second order cumulant expansion** :

$$\rho_{S,I}(t) = e_{(+)}^{\int_0^t d\tau \int_0^\tau dt' K^{(2)}(\tau, t')} \rho_{S,I}(0).$$

with

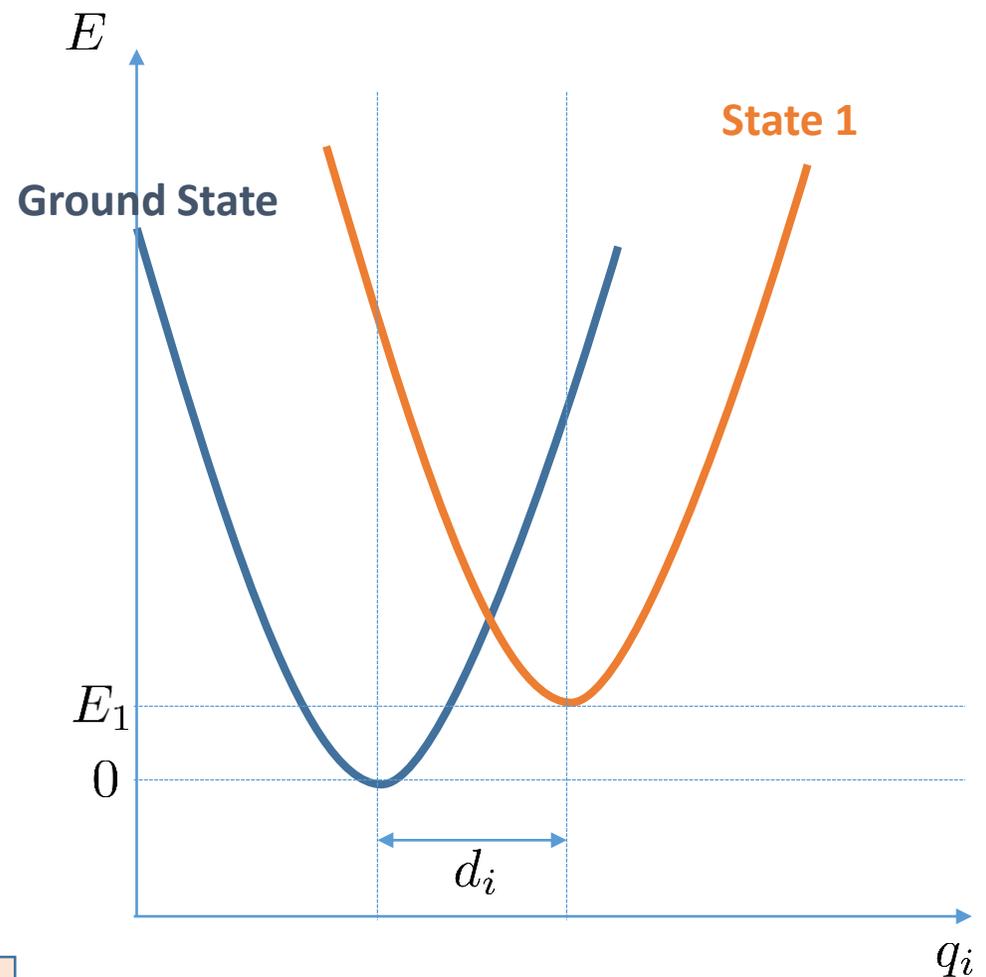
$$\int_0^\tau dt' K^{(2)}(\tau, t') \bullet = -[S(\tau), \int_0^\tau dt' C(\tau - t') S(t') \bullet - \{h.c.\}]$$

Bath density matrix at thermal equilibrium

$$\rho_B^{eq} = \frac{e^{-\beta H_B}}{\text{Tr}_B[e^{-\beta H_B}]}$$

Bath correlation function

$$C(\tau - t') = \text{Tr}_B[B(\tau)B(t')\rho_{B,eq}]$$



Parametrization in HEOM

$$C(t - \tau) = \sum_{k=1}^K \alpha_k e^{i\gamma_k(t-\tau)}$$

Number of artificial decay modes

Parameterization of the bath

One of the key step is to parameterize the bath correlation function as a sum of complex exponentials :

$$C(t - \tau) = \sum_{k=1}^K \alpha_k e^{i\gamma_k(t-\tau)}$$

From discrete modes

$$K = 2M$$

From a bath correlation function

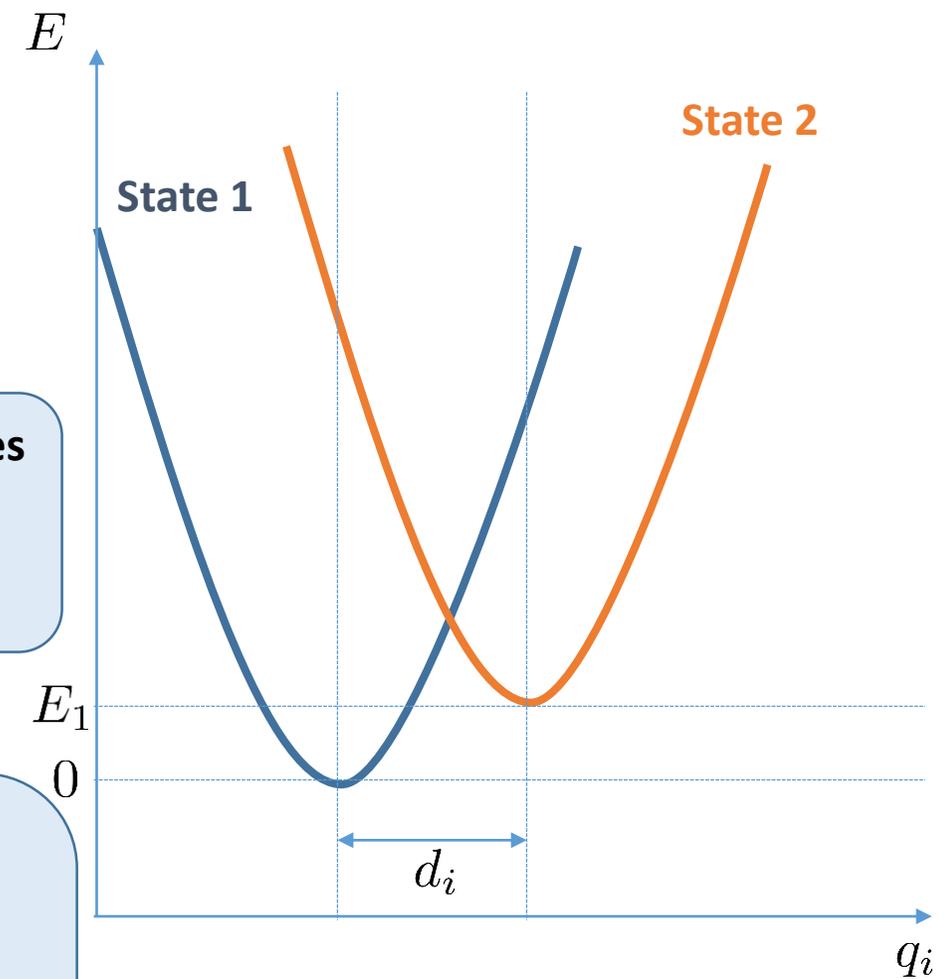
- Prony decomposition
- Expansion on Chebyshev or Bessel functions

From a spectral density

$$J(\omega) = \frac{\pi}{2} \sum_{l=1}^M \frac{c_l^2}{\omega_l} \delta(\omega - \omega_l)$$

Fit of the spectral density with special Lorentzian functions (Ohmic, super-Ohmic...) and use of the quantum fluctuation-dissipation theorem:

$$C(t) = \int_{-\infty}^{\infty} d\omega J(\omega) (e^{\beta\omega} - 1)^{-1} e^{-i\omega t}$$



Spectral density

If we know the spectral density, we can compute the bath correlation function.

$$J(\omega) = \frac{\pi}{2} \sum_{l=1}^M \frac{c_l^2}{\omega_l} \delta(\omega - \omega_l) \quad \text{with an odd parity} \quad J(-\omega) = -J(\omega)$$

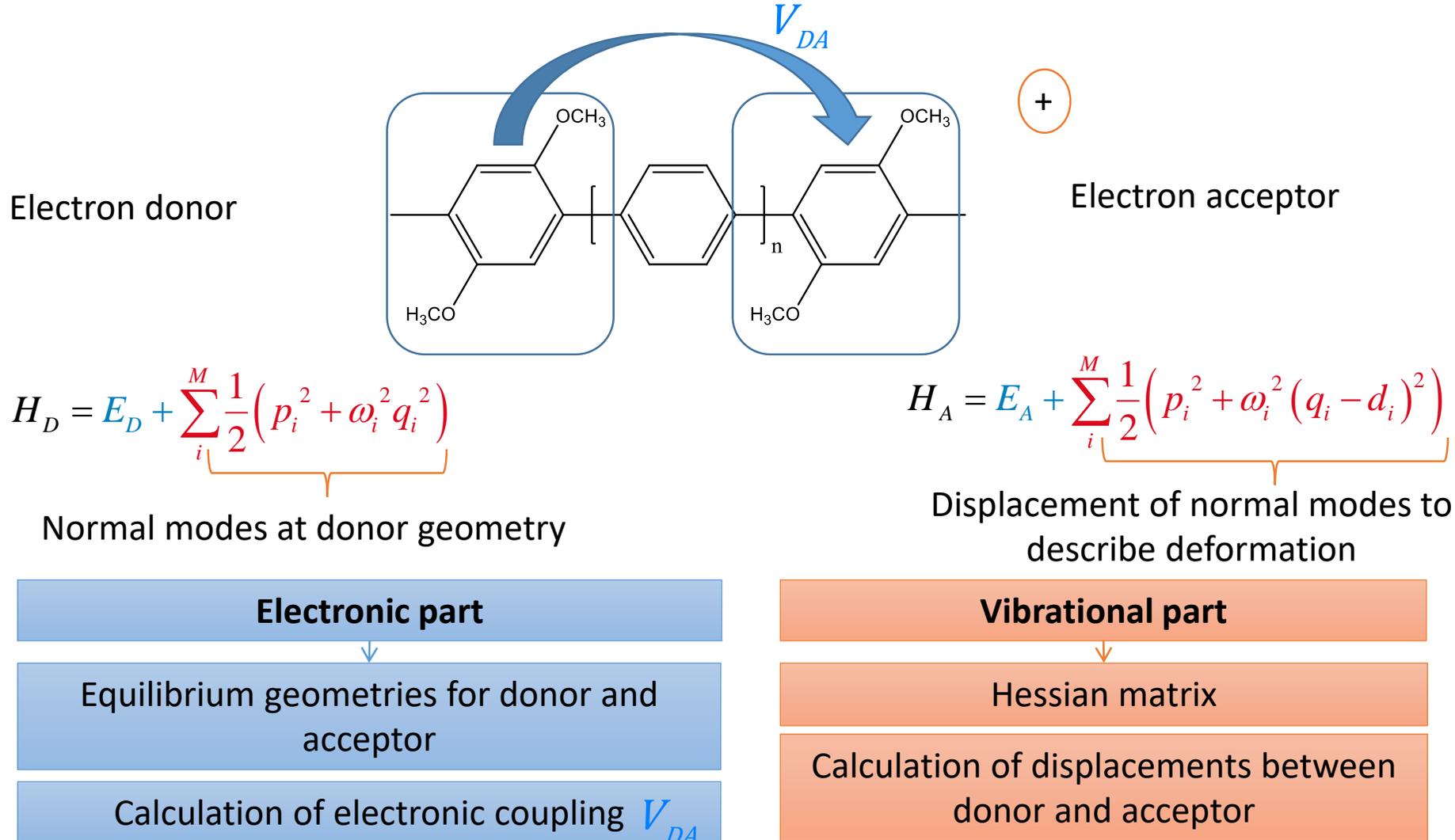
The spectral density can be a mere phenomenological model

Strategy 1: Build a linear vibronic model from ab initio

Strategy 2: Approximate the spectral density from its classical counterpart

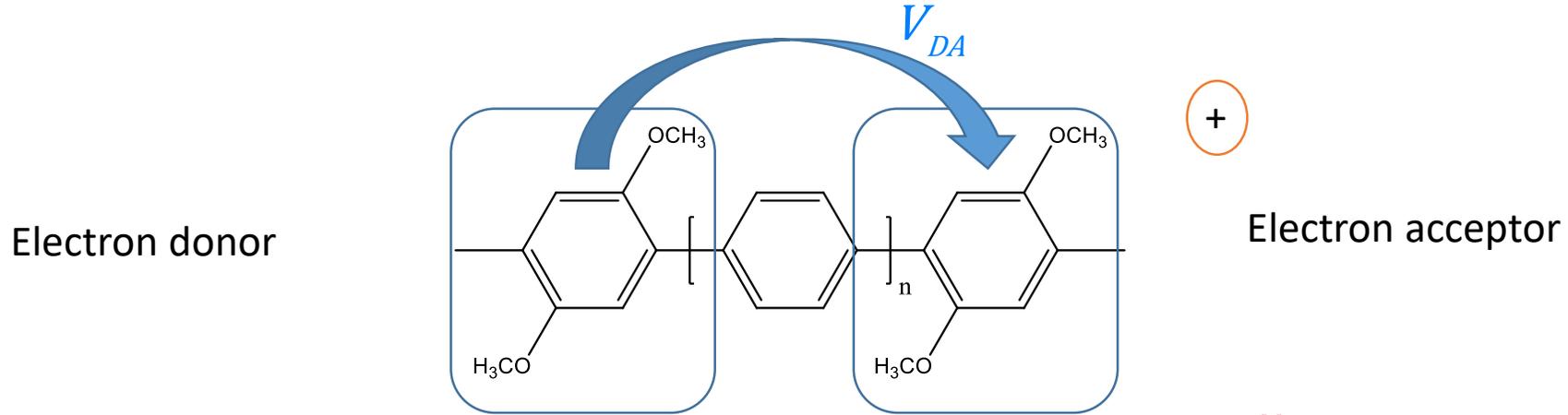
Strategy 1: Build a linear vibronic model

Organic mixed-valence compounds : Molecules DMP_n
(2,5-dimethoxy-4,methyl-phenylen cycles bound by an n-paraphenylen's chain)



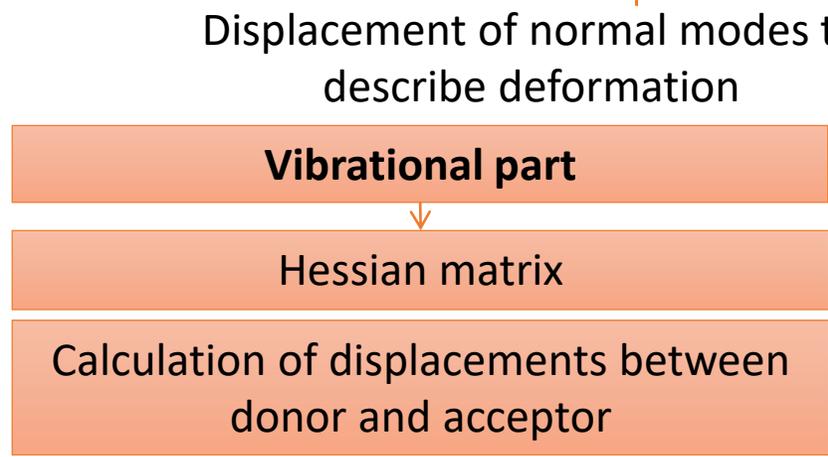
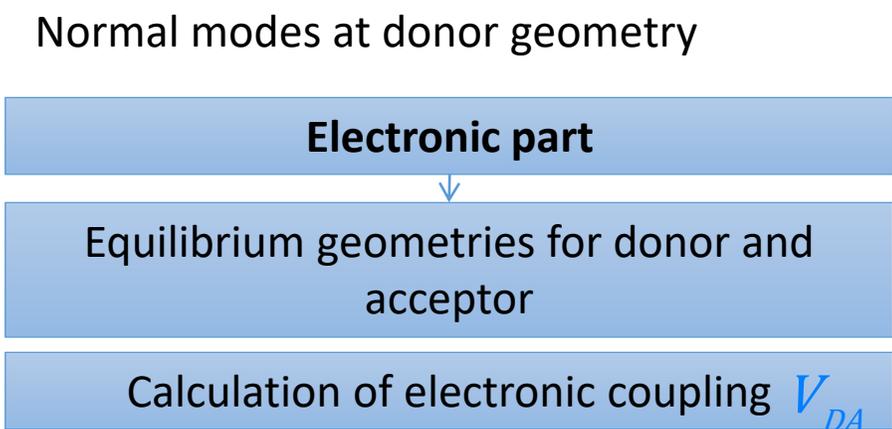
Strategy 1: Build a linear vibronic model

Organic mixed-valence compounds : Molecules DMP_n
 (2,5-dimethoxy-4,methyl-phenylen cycles bound by an n-paraphenylenes' chain)



$$H_D = E_D + \underbrace{\sum_i^M \frac{1}{2} (p_i^2 + \omega_i^2 q_i^2)}_{\text{Normal modes at donor geometry}}$$

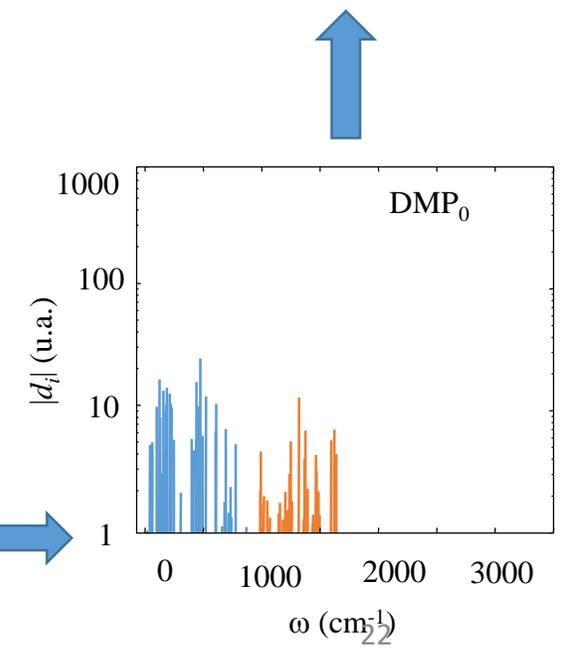
$$H_A = E_A + \underbrace{\sum_i^M \frac{1}{2} (p_i^2 + \omega_i^2 (q_i - d_i)^2)}_{\text{Displacement of normal modes to describe deformation}}$$



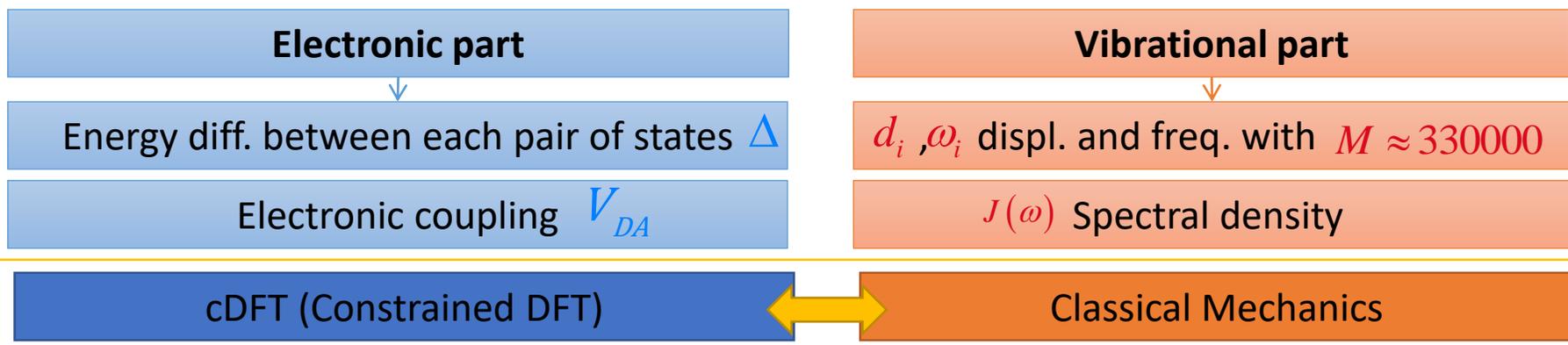
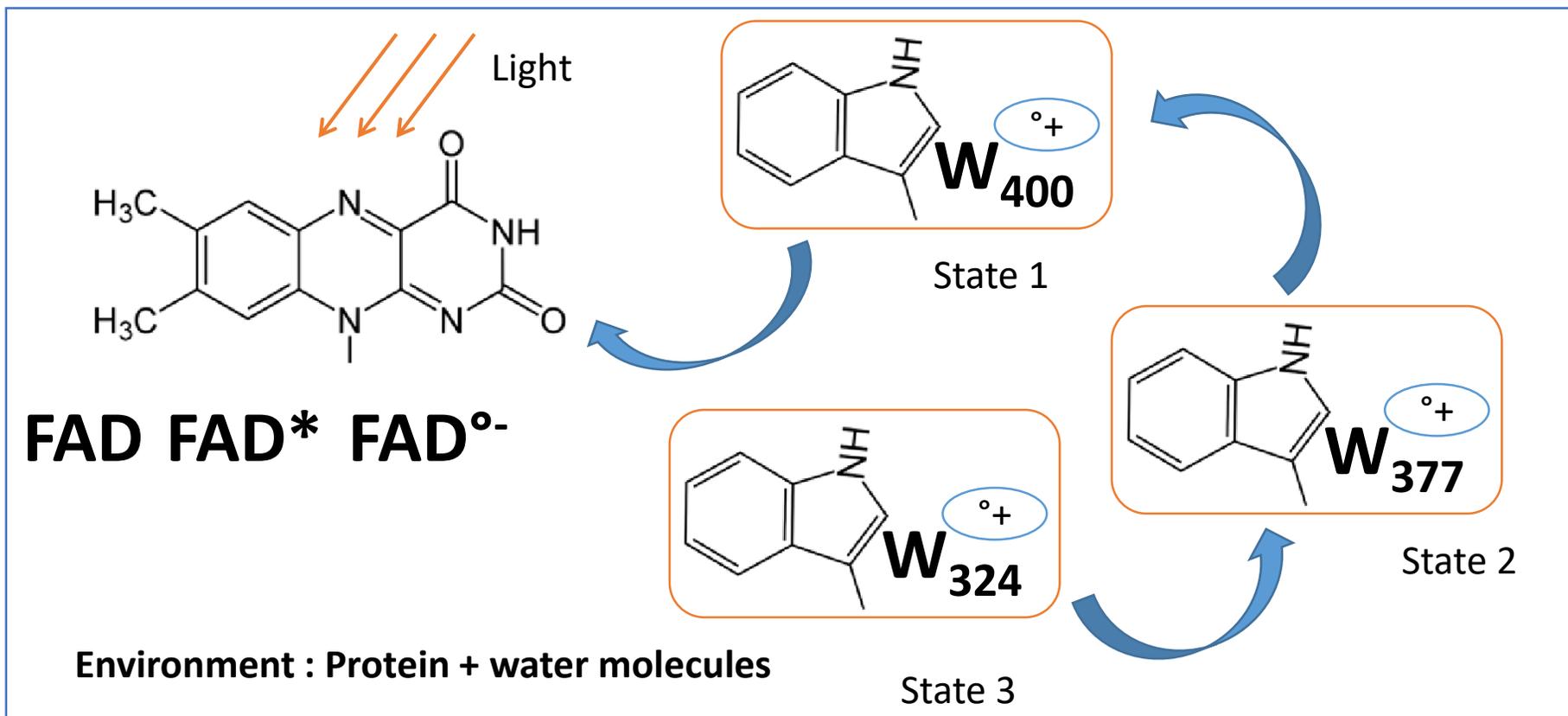
Spectral density

$$J(\omega) = \frac{\pi}{2} \sum_{l=1}^M \omega_l^3 d_l^2 \delta(\omega - \omega_l)$$

- Not continuous
- Needs further empirical brodening



Strategy 2: Chromoprotein cryptochrome



Strategy 2: Computing spectral densities with QM/MM trajectories

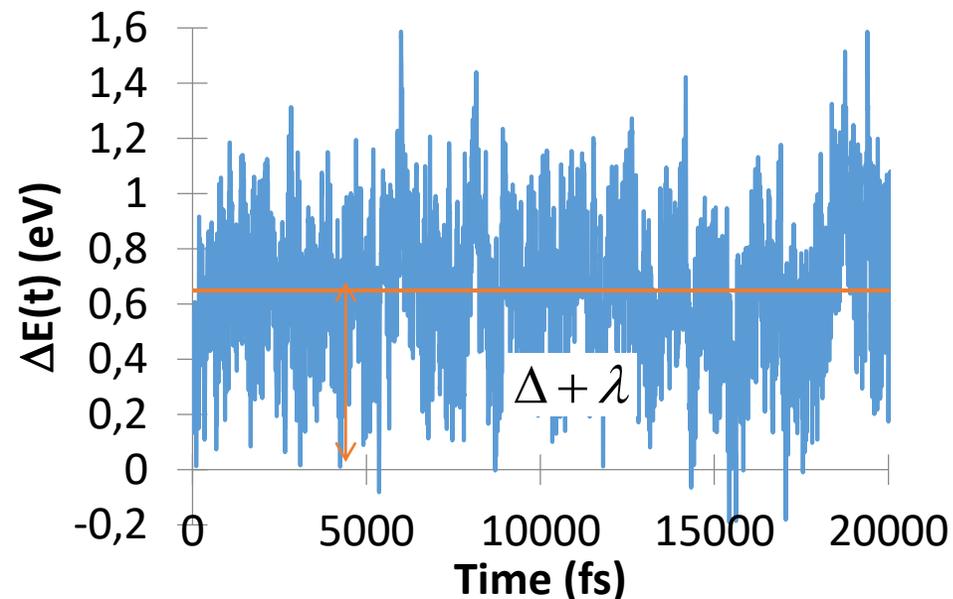
$$H = \underbrace{\begin{pmatrix} \boxed{0} & V_{DA} \\ V_{DA} & \boxed{\Delta + \lambda} \end{pmatrix}}_{H_S} + \underbrace{\begin{pmatrix} \boxed{0} & 0 \\ 0 & \boxed{-1} \end{pmatrix}}_S \underbrace{\sum_i \omega_i^2 d_i q_i}_B + H_B \begin{pmatrix} \boxed{1} & 0 \\ 0 & \boxed{1} \end{pmatrix}$$

Diabatic electronic gap:

The diabatic electronic gap probes the fluctuation of the bath and might be obtained with classical trajectories

$$\Delta E(t) = \boxed{} - \boxed{}$$

$$\Delta E(t) = \Delta + \lambda - \sum_{i=1}^M \omega_i^2 d_i q_i(t)$$



Diabatic electronic gap for QM/MM molecular dynamics : 5 X ~25 ps for each transfer back and forth

The autocorrelation function of the diabatic gap gives a classical analogue to the system-bath correlation function :

$$G(t) = \left\langle \left(\Delta E(t) - (\Delta + \lambda) \right) \left(\Delta E(0) - (\Delta + \lambda) \right) \right\rangle = \iint d\mathbf{p}_0 d\mathbf{q}_0 B_{\mathbf{p}_0, \mathbf{q}_0}^{(cl)}(t) B_{\mathbf{p}_0, \mathbf{q}_0}^{(cl)}(0) W_B(\mathbf{p}_0, \mathbf{q}_0)$$

where $W_B(\mathbf{p}_0, \mathbf{q}_0) = \frac{e^{-\beta H_B(\mathbf{p}_0, \mathbf{q}_0)}}{\iint d\mathbf{p}_0 d\mathbf{q}_0 e^{-\beta H_B(\mathbf{p}_0, \mathbf{q}_0)}}$ is the Boltzmann distribution of classical initial conditions



Approximate the spectral density as:

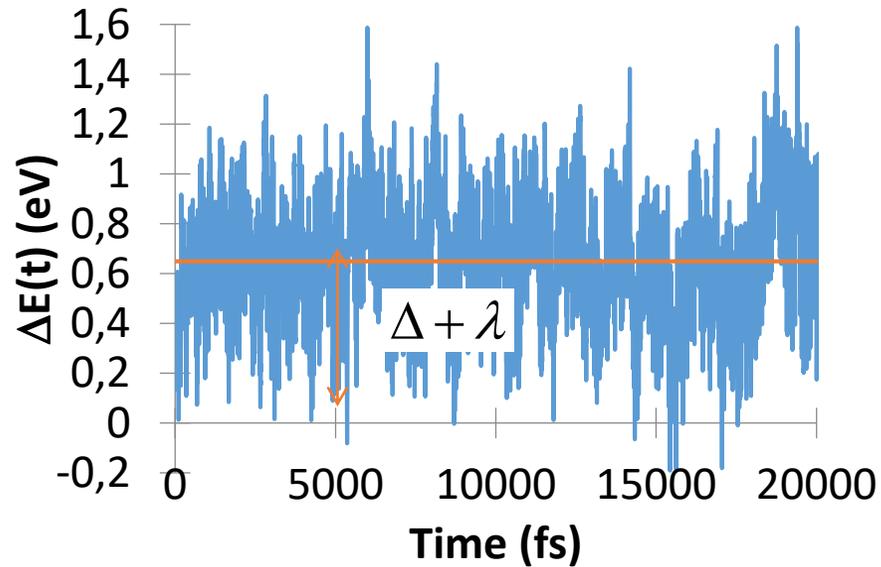
$$J(\omega) = \beta \omega \operatorname{Re} \left[\int_0^{+\infty} dt e^{-i\omega t} G(t) \right]$$

NB: Other schemes exist [2].

[1] T. Firmino, E. Mangaud, F. Cailliez, A. Devolder, D. Mendive-Tapia, F. Gatti, C. Meier, M. Desouter-Lecomte, A. de la Lande, *PCCP*, 18,21442 (2016)

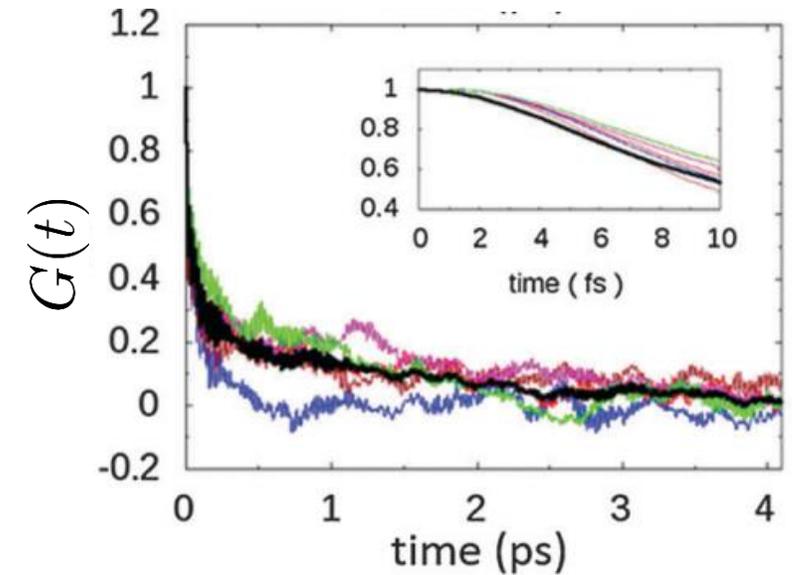
[2] S. Valleau, A. Eisfeld, A. Aspuru-Guzik. *J. Chem. Phys.* (2012); 137 (22): 224103

Strategy 2: Computing spectral densities with QM/MM trajectories

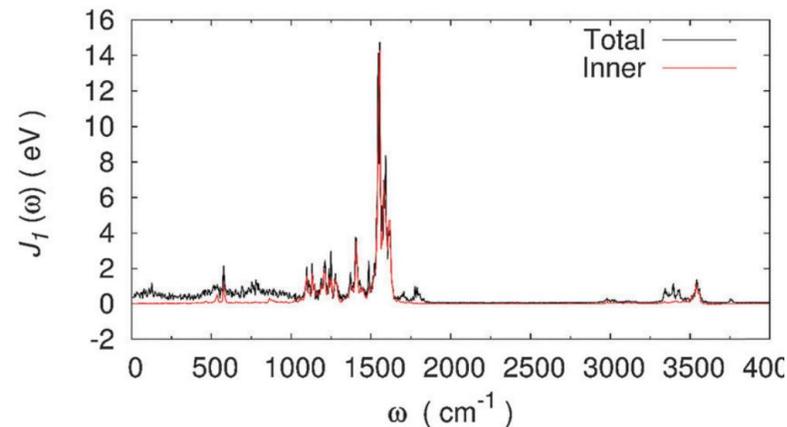


Diabatic electronic gap for QM/MM molecular dynamics : 5 X ~25 ps for each transfer back and forth

Step 1:
Compute the autocorrelation function of the diabatic electronic gap



Autocorrelation function of the diabatic gap for several trajectories with different initial conditions



Step 2:
Use Fourier transform using the following equation

$$J(\omega) = \beta\omega \operatorname{Re} \left[\int_0^{+\infty} dt e^{-i\omega t} G(t) \right]$$

Spectral density

If we know the spectral density, we can compute the bath correlation function.

$$J(\omega) = \frac{\pi}{2} \sum_{l=1}^M \frac{c_l^2}{\omega_l} \delta(\omega - \omega_l) \quad \text{with an odd parity} \quad J(-\omega) = -J(\omega)$$

Strategy 1: Build a linear vibronic model from ab initio calculations

Advantages

- ☺ Exact (up to the quality of the ab initio method) if we can deal directly with these discrete modes
- ☺ Also used in other quantum dynamics methods such as surface hopping or (ML-)MCTDH

Drawbacks

- ☹ Only for molecule on which harmonic analysis is doable
- ☹ Might need empirical broadening

Strategy 2: Approximate the spectral density from its classical counterpart

Advantages

- ☺ Allows to deal with large molecules and environments

Drawbacks

- ☹ Approximate

Parameterization of the bath

Ohmic spectral density

$$J_{Ohm}(\omega) = \sum_{l=1}^{n_{lor}} \frac{p_l \omega}{\Upsilon(\Omega_l, \Gamma_l)} \quad \text{with} \quad \Upsilon(\Omega_l, \Gamma_l) = [(\omega + \Omega_l)^2 + \Gamma_l^2] [(\omega - \Omega_l)^2 + \Gamma_l^2]$$



Step 1: Insert the spectral density in the fluctuation-dissipation theorem

$$C(t - \tau) = \frac{1}{\pi} \int_{-\infty}^{+\infty} d\omega e^{i\omega(t-\tau)} \frac{J(\omega)}{e^{\beta\omega} - 1}$$



Step 2: Determine the function poles

$$f(z) = \frac{g(z)}{\prod_i (z - a_i)}$$

Poles a_i are singularities of a complex function.

$$\nu_{L,1} = \Omega_l + i\Gamma_l$$

$$\nu_{L,2} = \Omega_l - i\Gamma_l$$

$$\nu_{L,3} = -\Omega_l + i\Gamma_l$$

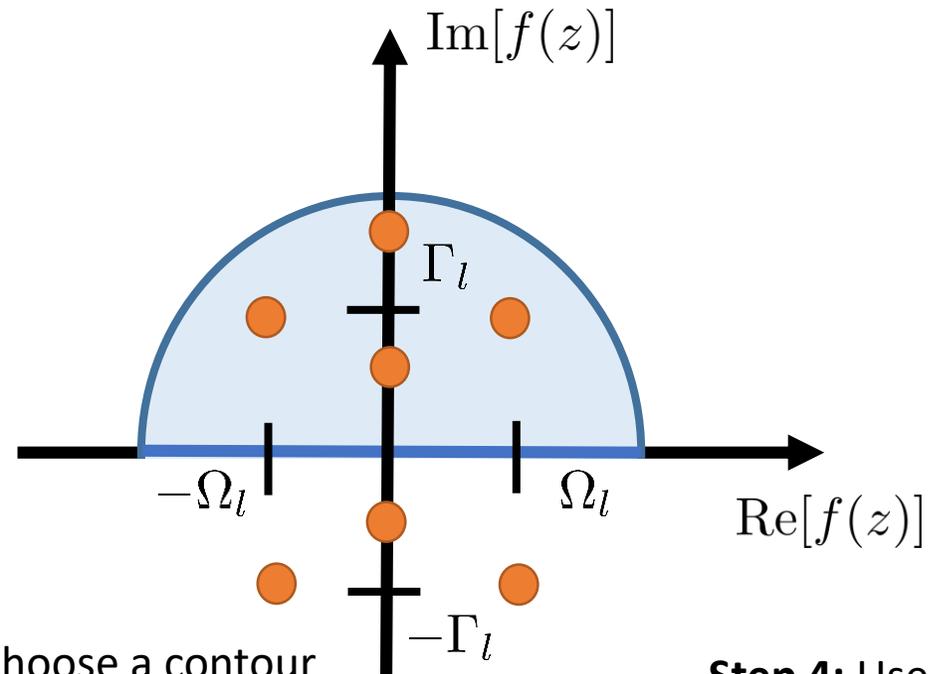
$$\nu_{L,4} = -\Omega_l - i\Gamma_l$$

Matsubara frequencies:

$$i\nu_j = i \frac{2\pi j}{\beta} \quad \forall j > 0$$



Step 3: Choose a contour



Step 4: Use residue theorem



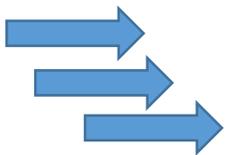
D. Tannor

Source : Wikipédia



C. Meier

Source : LCAR website



Parameterization of the bath

$$J_{Ohm}(\omega) = \sum_{l=1}^{n_{lor}} \frac{p_l \omega}{\Upsilon(\Omega_l, \Gamma_l)} \quad \text{with} \quad \Upsilon(\Omega_l, \Gamma_l) = \left[(\omega + \Omega_l)^2 + \Gamma_l^2 \right] \left[(\omega - \Omega_l)^2 + \Gamma_l^2 \right]$$

Ohmic

$$C^*(t - \tau) = \sum_{k=1}^{2n_{lor} + n_{matsu}} \tilde{\alpha}_k e^{i\gamma_k(t-\tau)}$$

$$\gamma_{l,1} = \Omega_l + i\Gamma_l$$

$$\gamma_{l,2} = -\Omega_l + i\Gamma_l$$

$$\gamma_{j,matsu} = i\nu_{j,matsu}$$

$$\alpha_{l,1} = \frac{p_l}{8\Omega_l\Gamma_l} \left(\coth\left(\frac{\beta}{2}\gamma_{l,1}\right) - 1 \right)$$

$$\alpha_{l,2} = \frac{p_l}{8\Omega_l\Gamma_l} \left(\coth\left(-\frac{\beta}{2}\gamma_{l,2}\right) + 1 \right)$$

$$\alpha_{j,matsu} = \frac{2i}{\beta} J(i\nu_{j,matsu})$$

$$\gamma_{l,1}^* = -\gamma_{l,2}$$

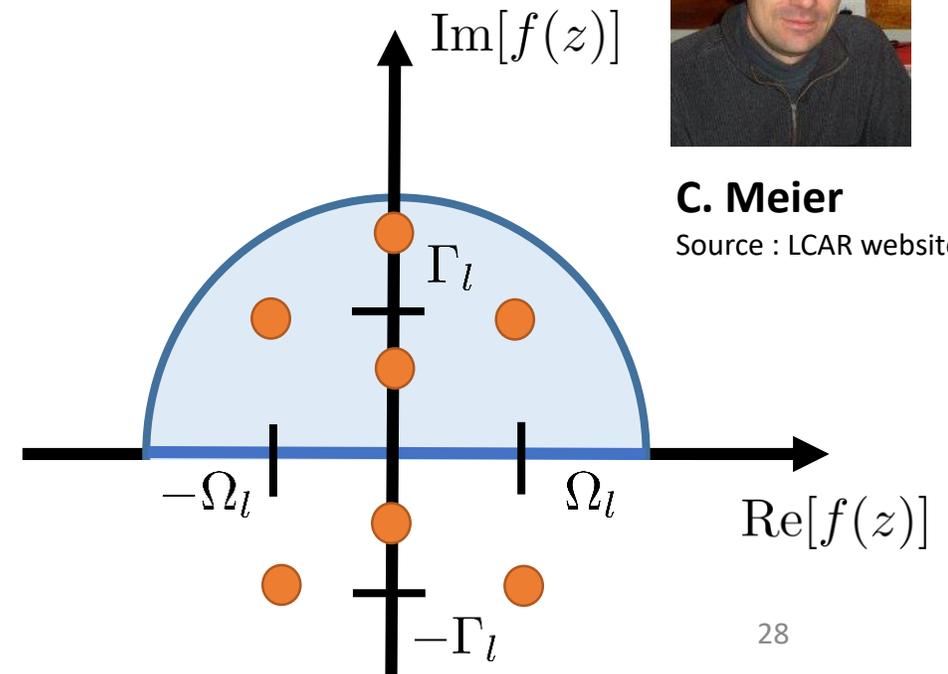
$$\gamma_{l,2}^* = -\gamma_{l,1}$$

$$\gamma_{j,matsu}^* = -\gamma_{j,matsu}$$

$$\tilde{\alpha}_{l,1} = \alpha_{l,2}^*$$

$$\tilde{\alpha}_{l,2} = \alpha_{l,1}^*$$

$$\tilde{\alpha}_{j,matsu} = \alpha_{j,matsu}$$



D. Tannor

Source : Wikipédia



C. Meier

Source : LCAR website

Parameterization of the bath

$$J_{Ohm}(\omega) = \sum_{l=1}^{n_{lor}} \frac{p_l \omega}{\Upsilon(\Omega_l, \Gamma_l)} \quad \text{with} \quad \Upsilon(\Omega_l, \Gamma_l) = \left[(\omega + \Omega_l)^2 + \Gamma_l^2 \right] \left[(\omega - \Omega_l)^2 + \Gamma_l^2 \right]$$

Ohmic

$$C(t - \tau) = \sum_{k=1}^{2n_{lor} + n_{matsu}} \alpha_k e^{i\gamma_k(t - \tau)}$$

Weight coefficients

$$\alpha_{l,1} = \frac{p_l}{8\Omega_l\Gamma_l} \left(\coth\left(\frac{\beta}{2}\gamma_{l,1}\right) - 1 \right)$$

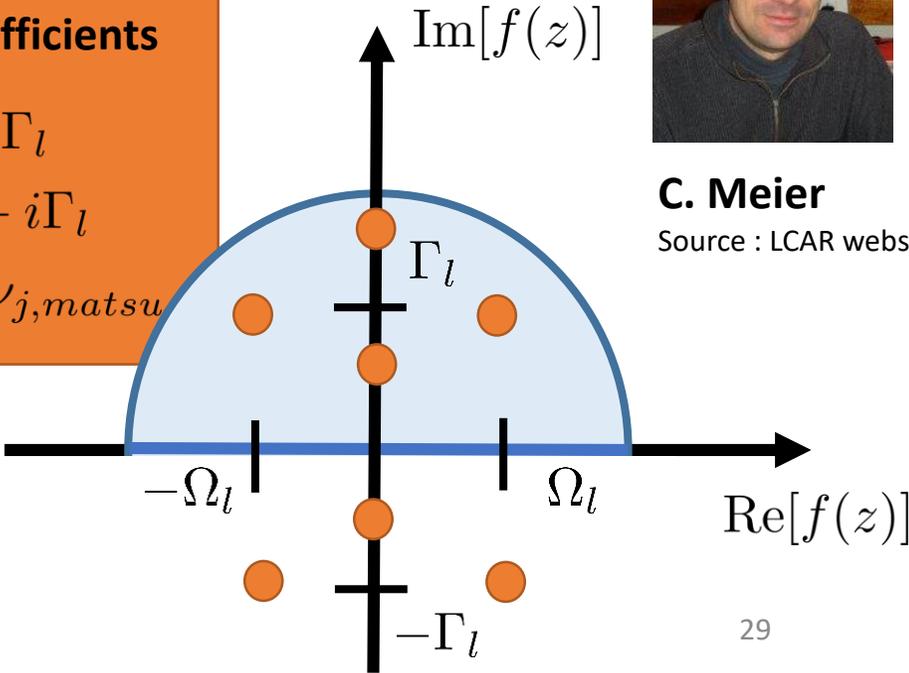
$$\alpha_{l,2} = \frac{p_l}{8\Omega_l\Gamma_l} \left(\coth\left(-\frac{\beta}{2}\gamma_{l,2}\right) + 1 \right)$$

$$\alpha_{j,matsu} = \frac{2i}{\beta} J(i\nu_{j,matsu})$$

« Damping » coefficients

$$\gamma_{l,1} = \Omega_l + i\Gamma_l$$

$$\gamma_{l,2} = -\Omega_l + i\Gamma_l$$

$$\gamma_{j,matsu} = i\nu_{j,matsu}$$


D. Tannor
Source : Wikipédia



C. Meier
Source : LCAR website

Parameterization of the bath

And for complex or realistic bath, how to write the bath correlation function ?

Number of artificial decay modes

$$C(t - \tau) = \sum_{k=1}^K \alpha_k e^{i\gamma_k(t-\tau)}$$

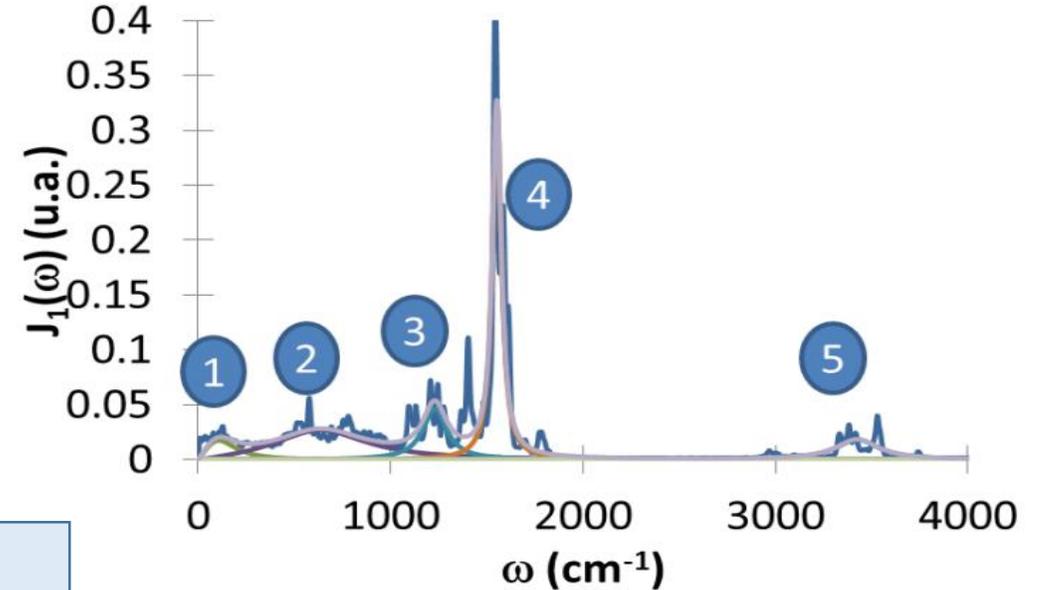
↑ Weight ↑ Damping

Can be extracted from a spectral density:

Numerical fit of spectral density with

$$J_{Ohm}(\omega) = \sum_{l=1}^{n_{lor}} \frac{p_l \omega}{\Upsilon(\Omega_l, \Gamma_l)}$$

with $\Upsilon(\Omega_l, \Gamma_l) = [(\omega + \Omega_l)^2 + \Gamma_l^2] [(\omega - \Omega_l)^2 + \Gamma_l^2]$



Spectral density of a bath for an electron transfer in a cryptochrome with a fit of five Tannor-Meier Lorentzian function (in this case K=10)

T. Firmino, E. Mangaud, F. Cailliez, A. Devolder, D. Mendive-Tapia, F. Gatti, C. Meier, M. Desouter-Lecomte, A. de la Lande, PCCP, 18, 21442 (2018)

Hierarchical equations of motion

After a bit of algebra, using the one obtains an (*a priori* infinite) set of coupled differential equations :

$$\dot{\rho}_{\mathbf{n}}(t) = L_S \rho_{\mathbf{n}}(t) + i \sum_{k=1}^K n_k \gamma_k \rho_{\mathbf{n}}(t) - i \sum_{k=1}^K \underbrace{\left[S, \rho_{\mathbf{n}_k^+}(t) \right]}_{\Phi \rho_{\mathbf{n}_k^+}} - i \sum_{k=1}^K n_k \underbrace{\left(\alpha_k S \rho_{\mathbf{n}_k^-}(t) - \tilde{\alpha}_k \rho_{\mathbf{n}_k^-}(t) S \right)}_{\Theta_k \rho_{\mathbf{n}_k^-}}$$



R. Kubo

Source : Wikipédia



Y. Tanimura

Source : Kyoto Univ.

$$\dot{\rho}_{\mathbf{n}} = L_S \rho_{\mathbf{n}} + i \sum_{k=1}^K \left(n_k \gamma_k \rho_{\mathbf{n}} - \Phi \rho_{\mathbf{n}_k^+} - n_k \Theta_k \rho_{\mathbf{n}_k^-} \right)$$

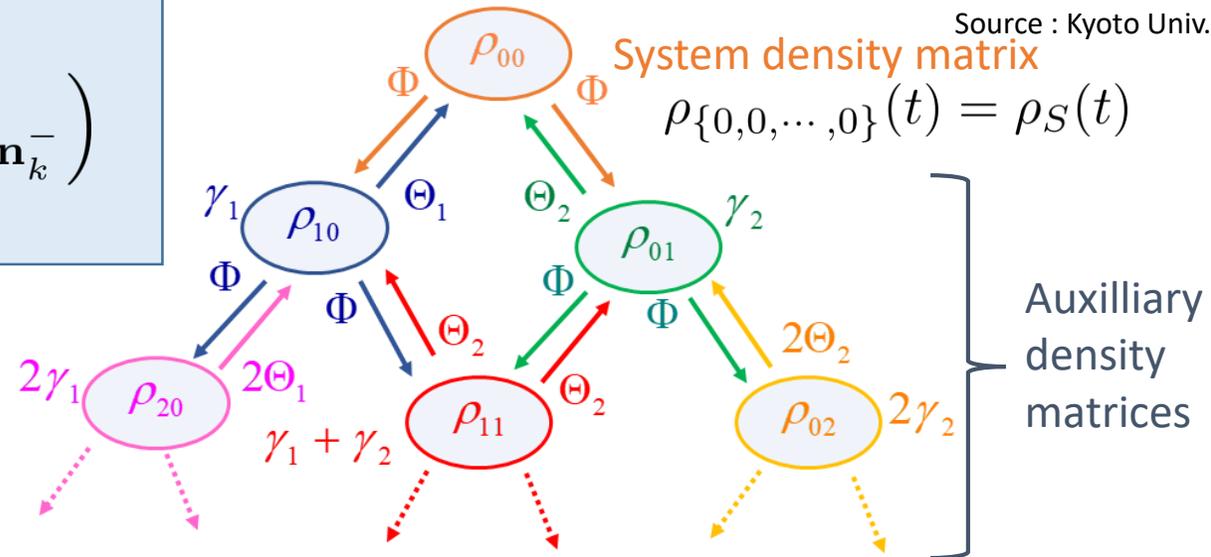
$$\mathbf{n} = \{n_1, n_2, \dots, n_K\}$$

$$\mathbf{n}_k^+ = \{n_1, n_2, \dots, n_k + 1, \dots, n_K\}$$

$$\mathbf{n}_k^- = \{n_1, n_2, \dots, n_k - 1, \dots, n_K\}$$

Truncation scheme for \mathbf{n} at

$$n_{HEOM} = \max \left[\sum_{k=1}^K n_k \right]$$



Schematic representation of the hierarchy of equations with $K = 2$ and $n_{HEOM} = 2$

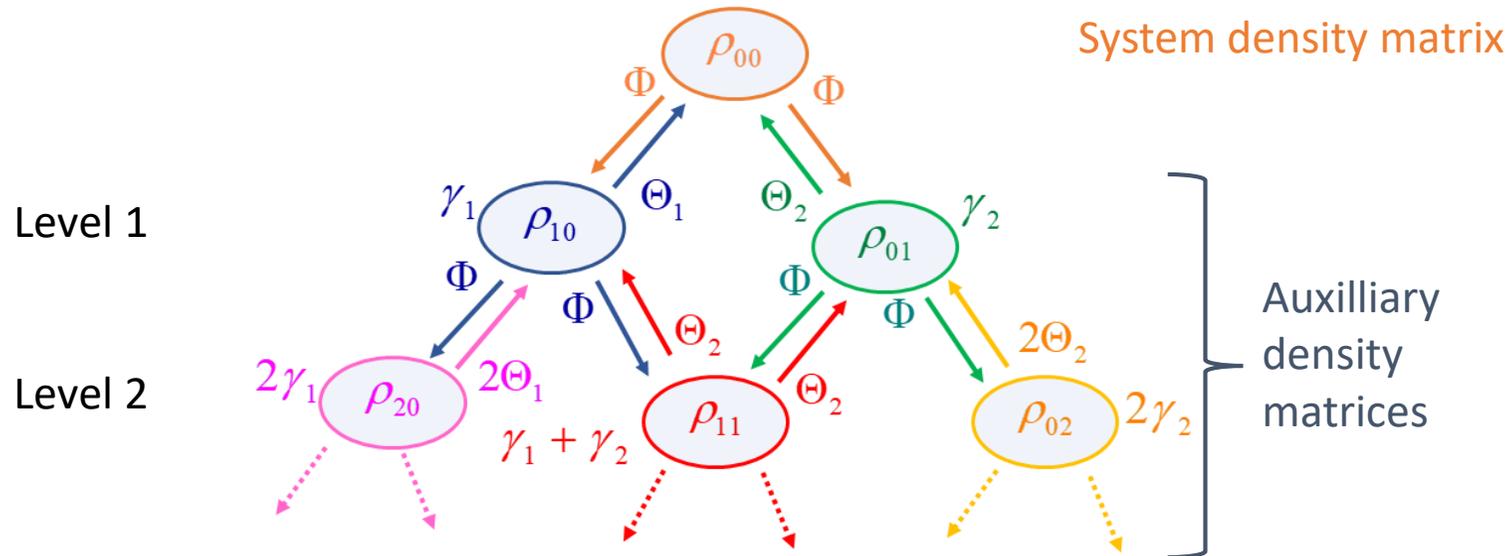
Hierarchical equations of motion

$$\dot{\rho}_{\mathbf{n}} = L_S \rho_{\mathbf{n}} + i \sum_{k=1}^K \left(n_k \gamma_k \rho_{\mathbf{n}} - \Phi \rho_{\mathbf{n}_k^+} - n_k \Theta_k \rho_{\mathbf{n}_k^-} \right)$$

$$\mathbf{n} = \{n_1, n_2, \dots, n_K\}$$

$$\mathbf{n}_k^+ = \{n_1, n_2, \dots, n_k + 1, \dots, n_K\}$$

$$\mathbf{n}_k^- = \{n_1, n_2, \dots, n_k - 1, \dots, n_K\}$$



Max level = n_{HEOM}

Schematic representation of the hierarchy of equations
with $K = 2$ and $n_{HEOM} = 2$

Auxiliary matrices address different occupation number for the « artificial » decay modes.

Number of matrices: $\frac{(K + n_{HEOM})!}{K! n_{HEOM}!}$

Truncation scheme for n at

$$n_{HEOM} = \max \left[\sum_{k=1}^K n_k \right]$$

Hierarchical equations of motion

Hierarchical equations of motion (1989)

$$\dot{\rho}_{\mathbf{n}} = L_S \rho_{\mathbf{n}} + i \sum_{k=1}^K \left(n_k \gamma_k \rho_{\mathbf{n}} - \Phi \rho_{\mathbf{n}_k^+} - n_k \Theta_k \rho_{\mathbf{n}_k^-} \right)$$

Advantages

- ☺ Non-Markovian
- ☺ Non-perturbative
- ☺ Numerically exact results.

Drawbacks

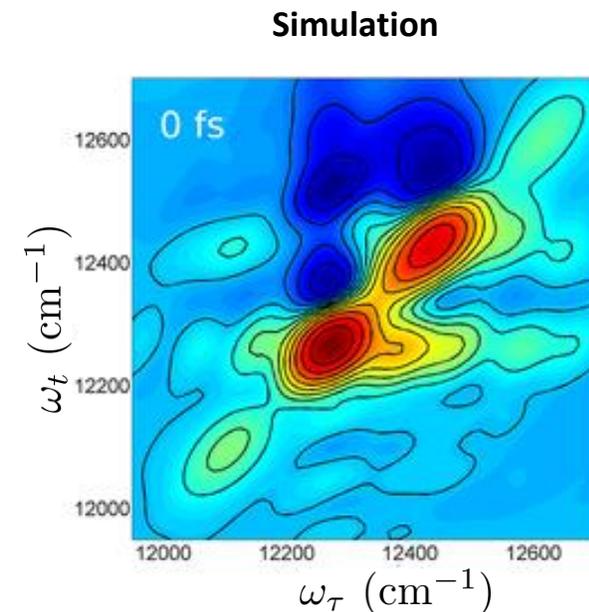
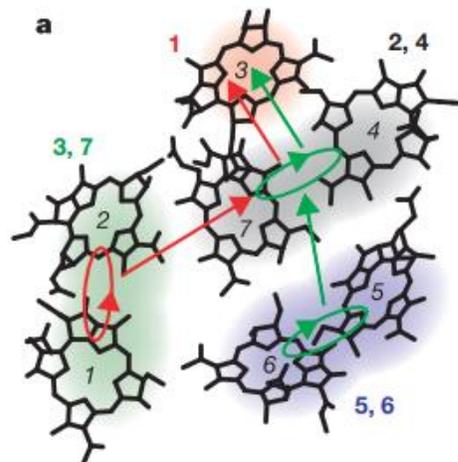
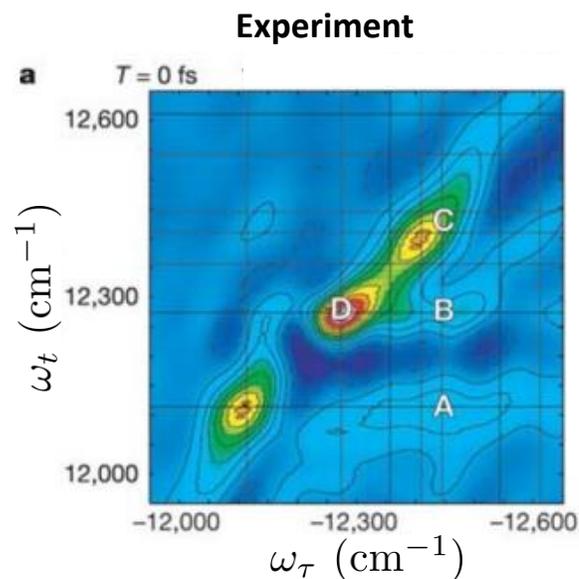
- ☹ Can lead to heavy computations
- ☹ Fit of the spectral density ?
- ☹ Difficult to deal with low temperatures

Applications

Simulation of the non-linear response for 2D spectroscopy

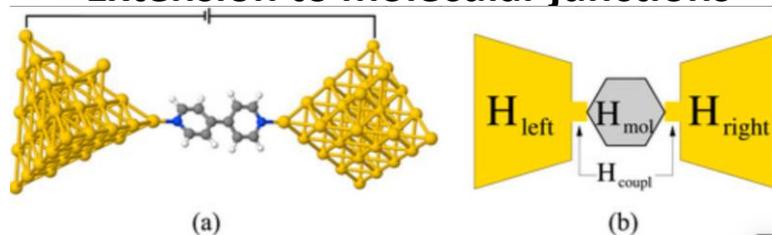
Y. Yan, Y. Liu, T. Xing, Q. Shi, WIREs Comput Mol Sci., 11:e1498 (2021)

2D spectroscopy of FMO (Fenna-Matthews-Olson) complex



T. Brixner, J. Stenger, H. M. Vaswani, M. Cho, R. E. Blankenship & G. R. Fleming, Nature, 434 (2005)

Extension to molecular junctions

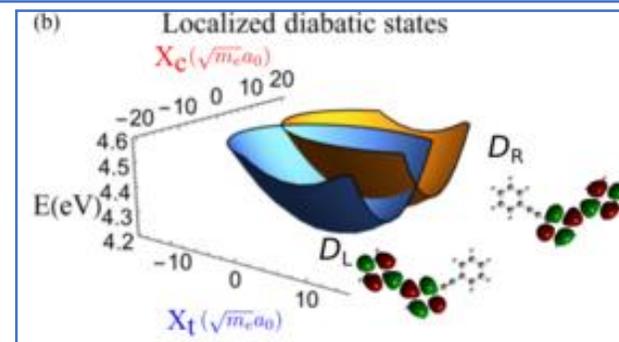


M. Thoss, F. Evers, J. Chem. Phys., 148, 030901 (2018)

Laser optimal control:

Electronic breaking symmetry
in a phenylene ethynylene
dimer

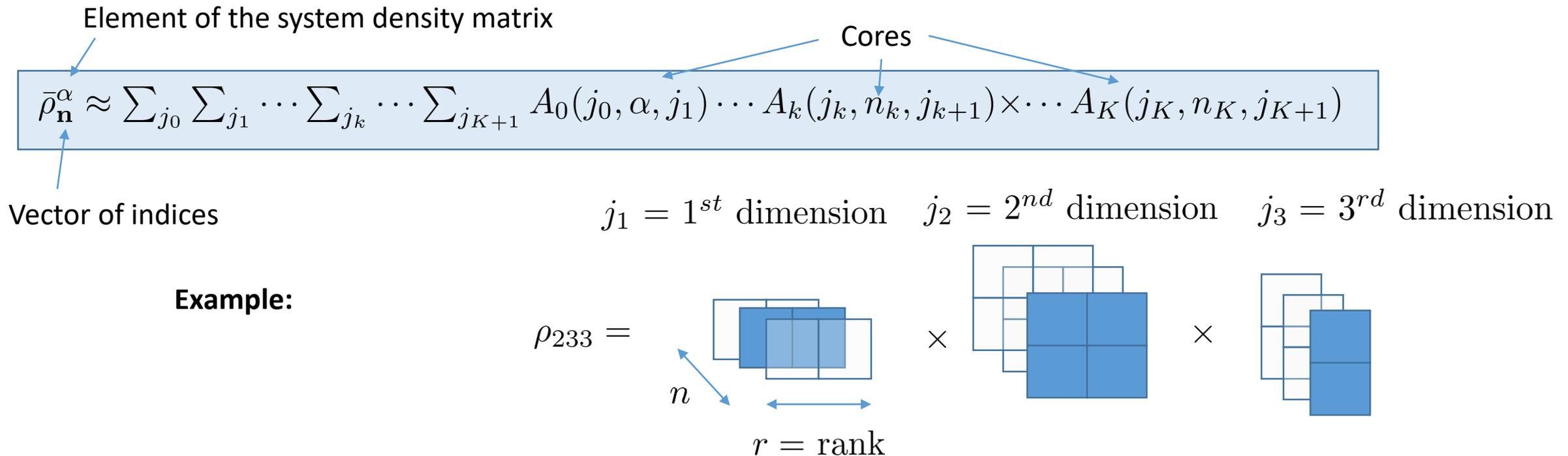
A. Jaouadi, J. Galiana, E. Mangaud, B. Lasorne, O. Atabek, and M. Desouter-Lecomte, Phys. Rev. A **106**, 043121 (2022)



Tensor train decomposition

Realistic chemical systems might exhibit large system bath coupling and the values of the indices n_1, n_2, \dots, n_K can be very high to converge HEOM set of equations: $n_{HEOM} = \max[\sum_{k=1}^K n_k] \gg 1$

As suggested by Q. Shi (2018) and later R. Borrelli (2019), for these high dimensional cases, one can resort to **tensor train decomposition** (also known as MPS (Matrix Product State) in the physics community):

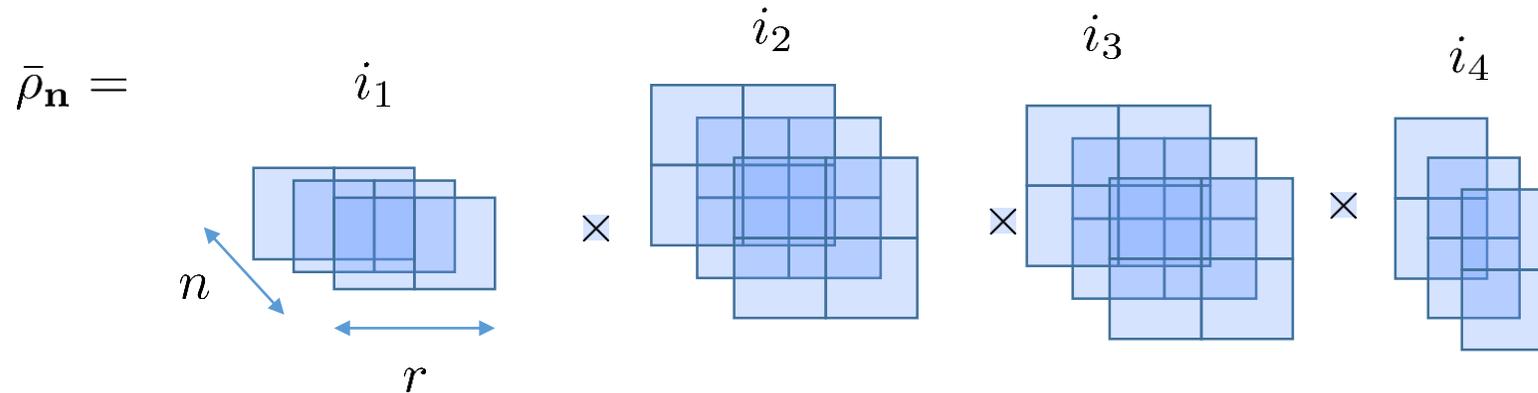


Tensor train decomposition

Why such decomposition is interesting ?

As a (non-realistic) test case, let's consider a tensor decomposition with the same number n_k and the same ranks r , for d dimensions:

Tensor decomposition

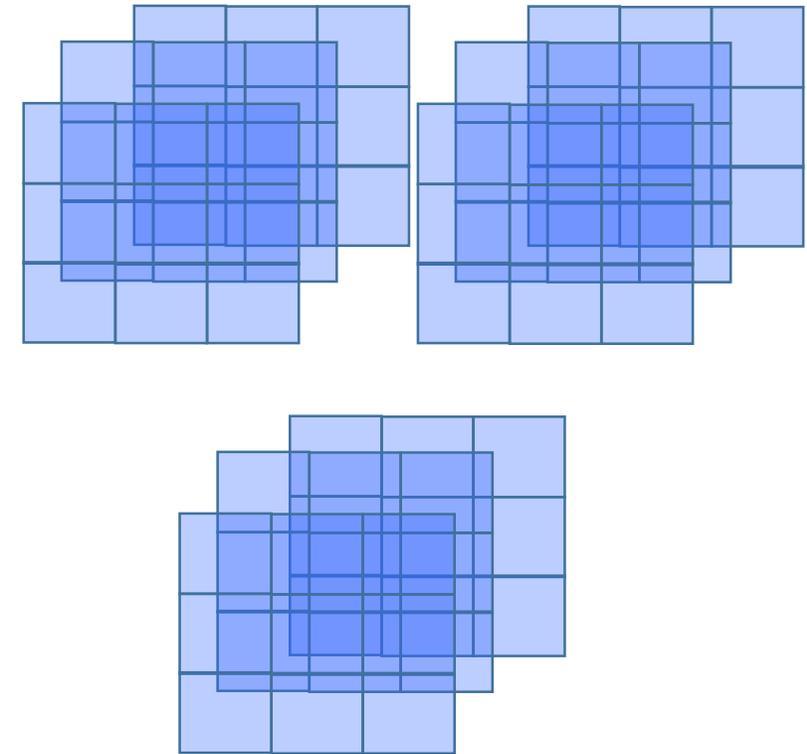


$$n \times r \times 2 + n \times r^2 \times (d - 2) \text{ elements}$$

Linear increase with the tensor dimension
Storage does not grow exponentially if ranks are low.

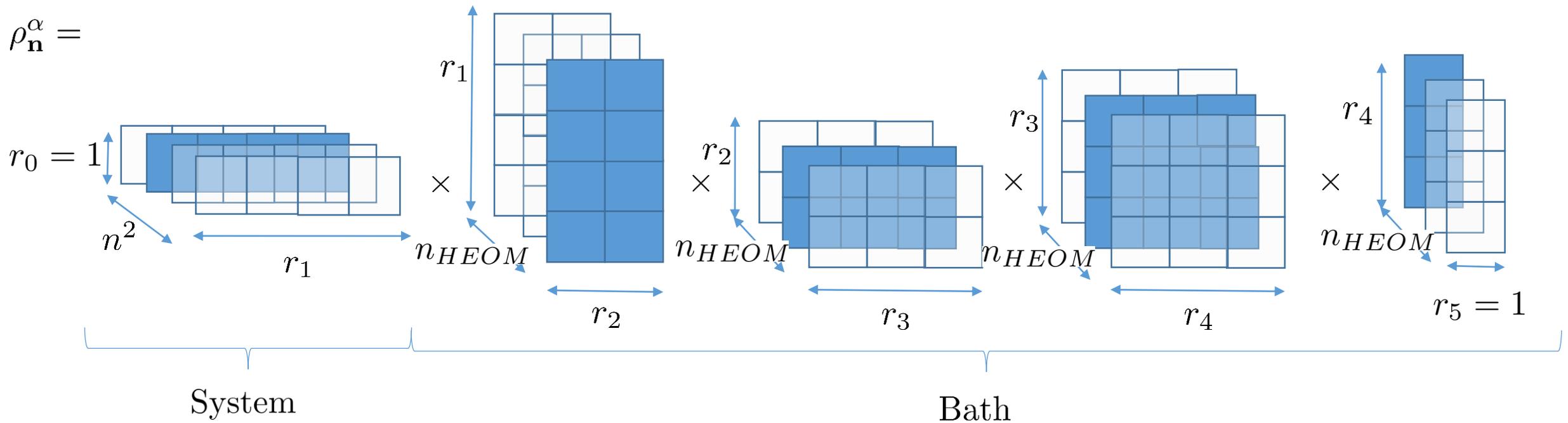
Naive approach

$$\rho(n \times n \times n \times n)$$



Tensor train decomposition HEOM

For the HEOM set of equations, we can decompose all the density matrices (system + auxiliary) as :



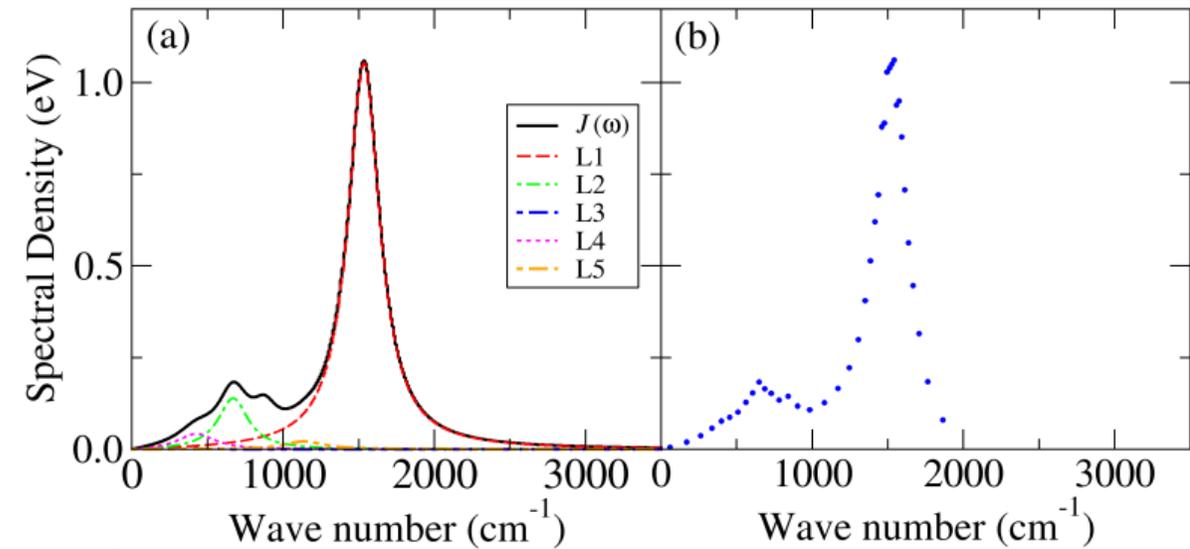
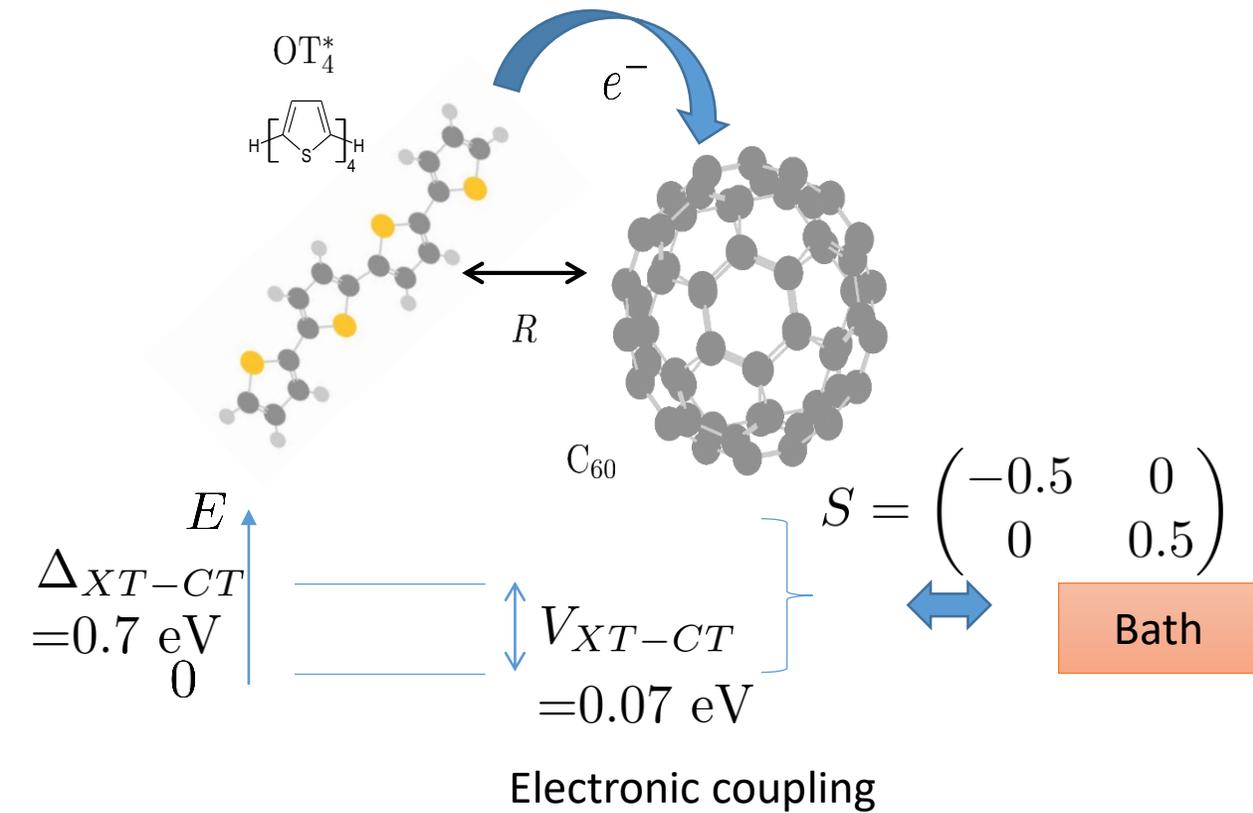
and solve :

$$\dot{\rho}_{\mathbf{n}}^{\bar{\alpha}} = \mathcal{L} \rho_{\mathbf{n}}^{\bar{\alpha}} \quad \text{with a super Liouvillian operator:} \quad \mathcal{L} = \mathcal{L}_S + \sum_{k'=1}^K (\mathcal{L}_{k'} + \mathcal{L}_{k'+} + \mathcal{L}_{k'-})$$

which can be « easily » defined in TT representation

Application: Oligothiophene-fullerene heterojunction

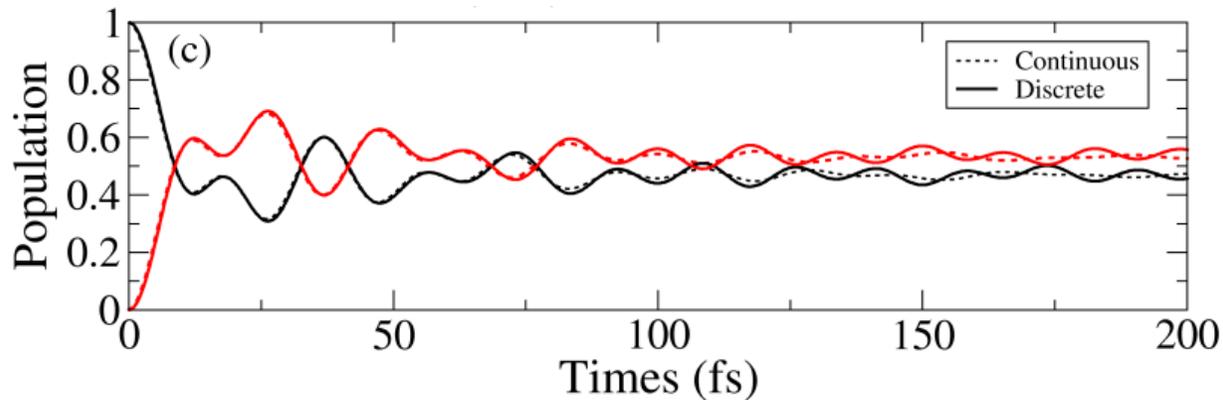
Energy excitation transfer in a oligothiophene-fullerene heterojunction [1]



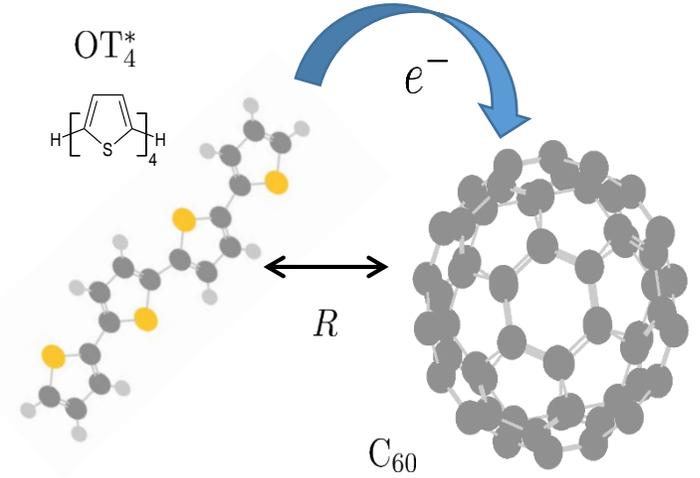
Spectral density and its discretized counterpart

Application: Oligothiophene-fullerene heterojunction

Energy excitation transfer in a oligothiophene-fullerene heterojunction

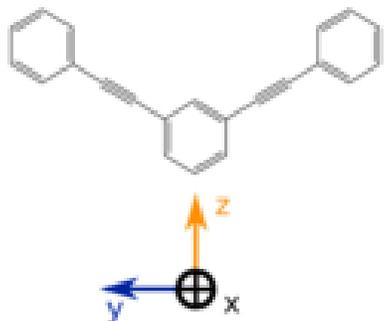


Diabatic population with simulation with discrete and continuous spectral densities $n_{HEOM} = 5$



	Continuous	Discrete
Number of decay modes	10	80
Number of matrices elements(standard)	12 012	131 206 068
Number of matrices elements (TT)	18 180 (rank= 20)	2 528 720 (rank = 80)

Application: Laser-controlled electronic symmetry breaking in a phenylene ethynylene dimer

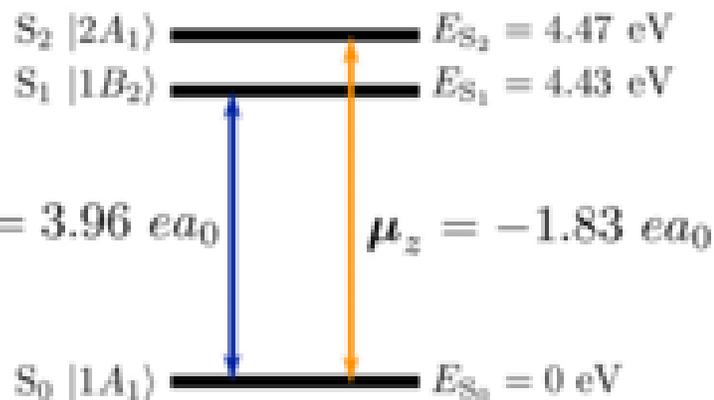
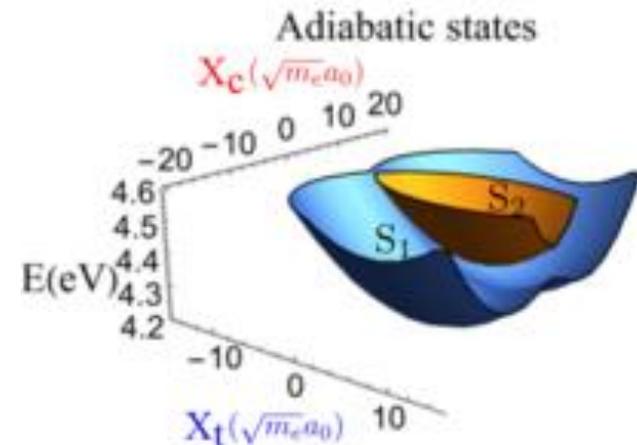


Metasubstituted dimer of phenylene ethynylene
(building block of treelike dendrimers)

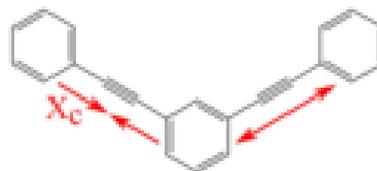
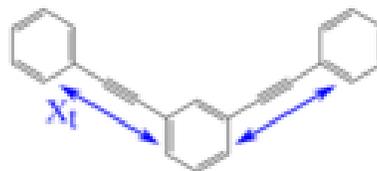
C_{2v} symmetry

Level of theory: CAM-B3LYP/6-31+G*

Parametrization of a linear vibronic coupling model (LVC) with a fitting procedure

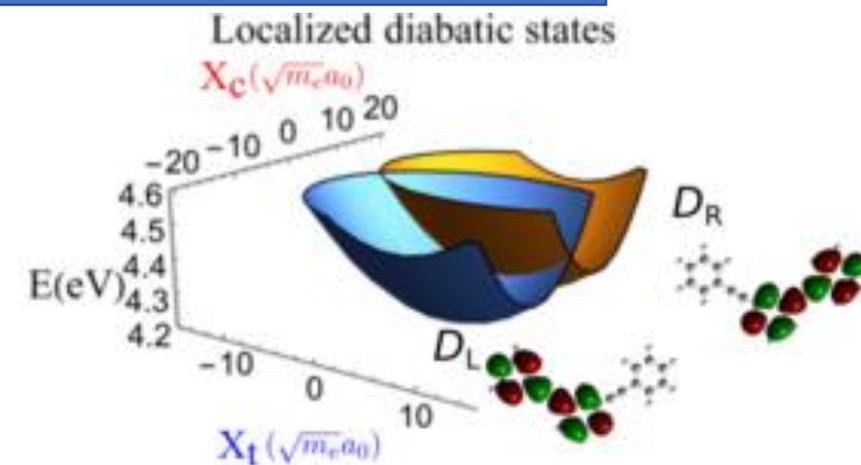


Symmetric A_1 motion: tuning mode



Antisymmetric B_2 motion: coupling mode

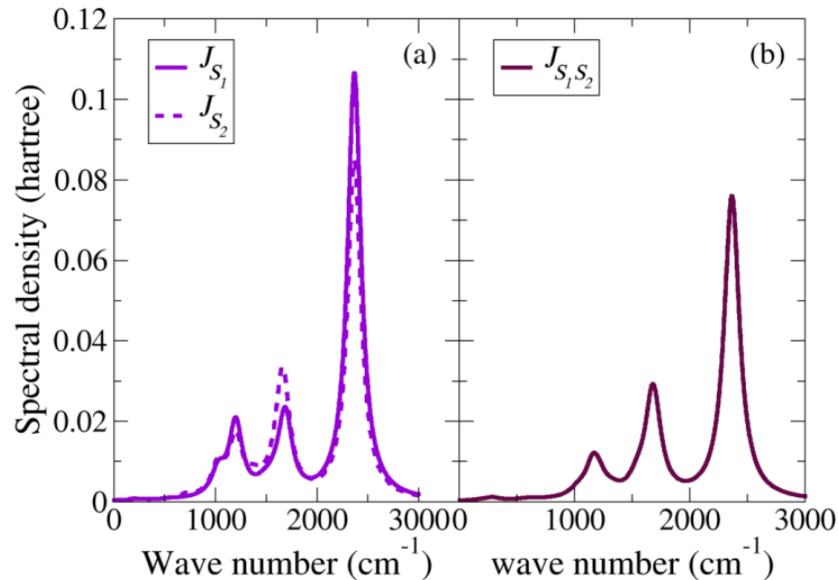
Transformation to the localized diabatic representation



Application: Laser-controlled electronic symmetry breaking in a phenylene ethynylene dimer

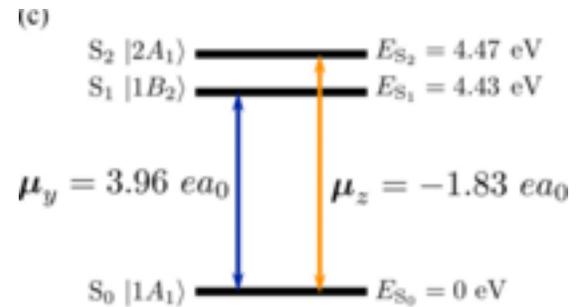
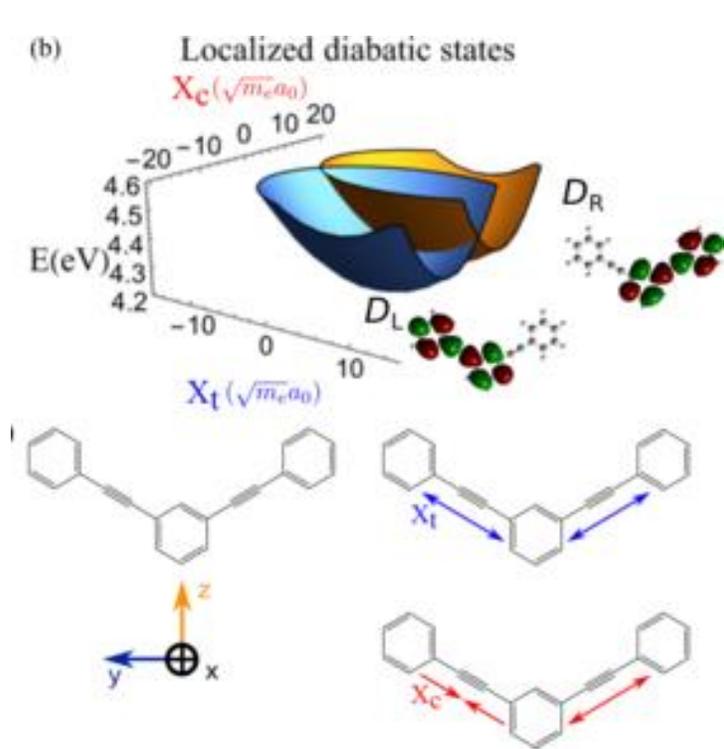
In a delocalized basis representation,

$$H = \underbrace{\begin{pmatrix} 0 & 0 & 0 \\ 0 & E_{S_1} & 0 \\ 0 & 0 & \Delta E_{S_2} \end{pmatrix}}_{H_S} - \underbrace{\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0.893 & 0 \\ 0 & 0 & 1 \end{pmatrix} \sum_{i=1}^N \omega_i^2 d_{i,t} q_{i,t}}_{H_{SB,t}=S_t \cdot B_t} + \underbrace{\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \sum_{i=1}^N \omega_i^2 c_{i,c} q_{i,c}}_{H_{SB,c}=S_c \cdot B_c} \underbrace{\frac{1}{2} \sum_{i=1}^N (p_i^2 + \omega_i^2 q_{i,t/c}^2)}_{H_B} \mathbf{I}_3$$



Spectral densities for tuning (left panel) and coupling bath

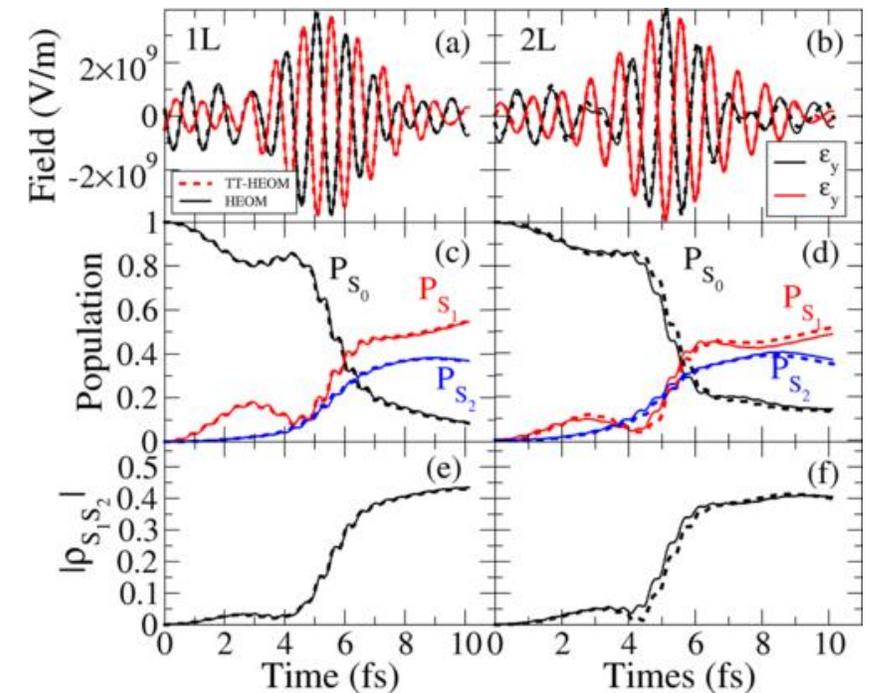
Application: Laser-controlled electronic symmetry breaking in a phenylene ethynylene dimer



Complex molecular system with a conical intersection

Aim: Creating a superposed state with equal weights which corresponds to a right or left electronic localization

Method: Optimal control of pulse fields on both polarizations



Optimized fields / Population and coherences obtained after optimal control theory optimisation of the pulses

Conclusion and perspectives

Conclusions

- Powerful tool for many physico-chemistry processes
- Gives access to many dynamical properties even for non-Markovian, non-perturbative cases
- Complex systems can be handled (if HEOM assumptions remain valid).

Perspectives

- Anharmonic extension for some relevant degrees of freedom
- More efficient fitting schemes of bath correlation function to deal with low temperature
- Extension to fermionic baths
- Reinforcement learning for pulses optimization

Conclusion and perspectives

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Acknowledgments

Alex CHIN

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Loïc JOUBERT-DORIOL

Isabelle NAVIZET

Thank you for your attention !