Control of Dissipative Quantum systems By a Non-Markovian Master equation approach

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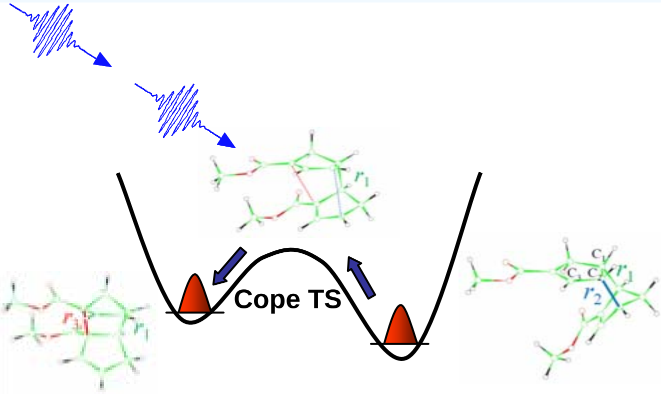
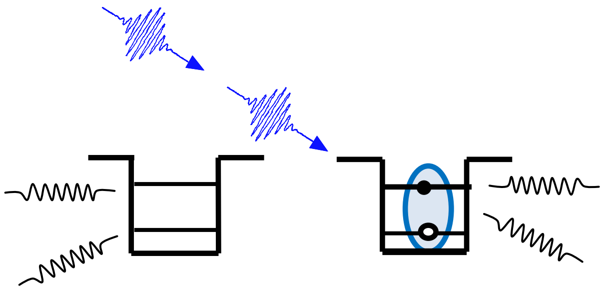
Context:

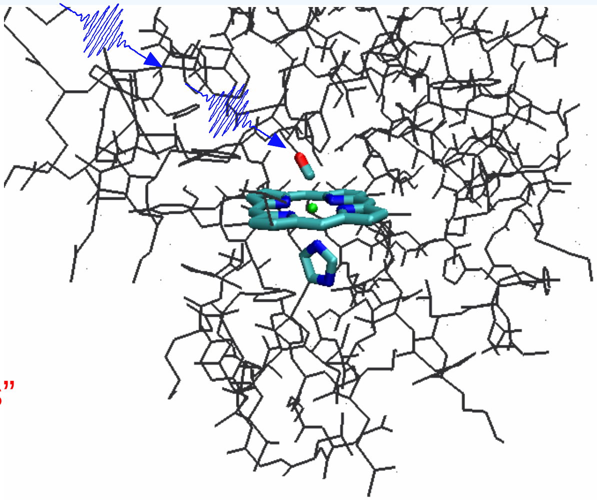
Femtosecond laser interaction with atomic and molecular systems



Isomerization reaction



quantum dot – “artificial atoms”



Coherent control
IR domain

Coherent control
visible

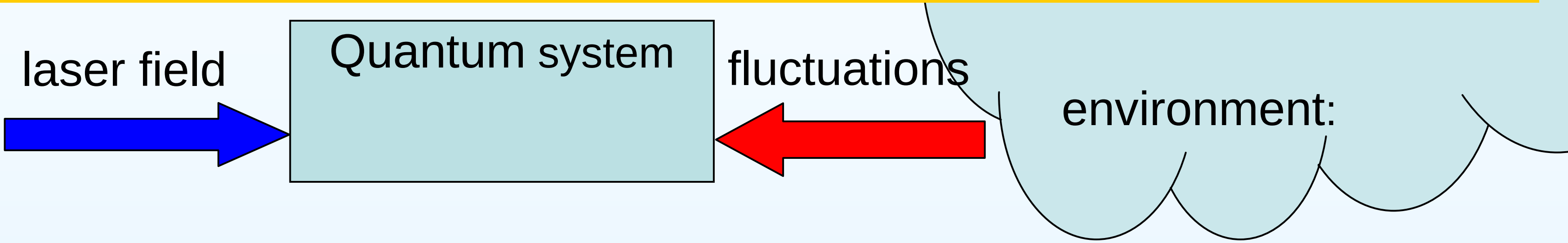
Coherent control
IR domain

dynamics of a quantum sub-system driven by fs lasers and subject to environments

IVR, electronic / vibrational relaxation, predissociation ⟺ Coherent control

experiment----- theory

Global situation



- strong laser fields
- pulse shaping
- coherent control:
- Tracking control
- Local control theory
- Optimal control theory

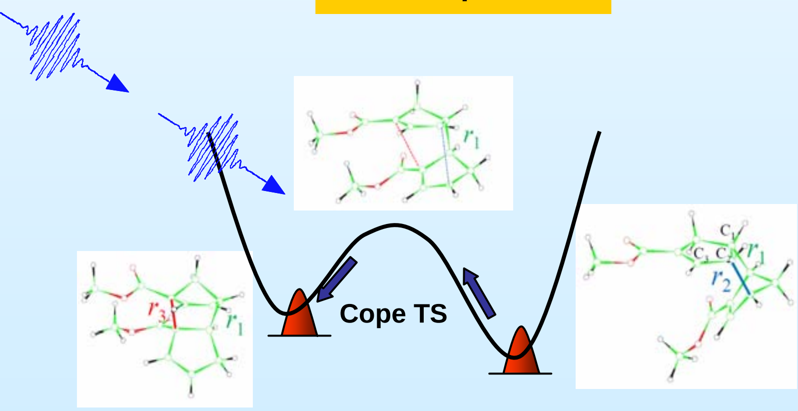
- high dimensional quantum dynamics
  -- MCTDH
- reduced dynamics + Master equation
  -- time-scales (Non-Markovian effects)
  -- model environment, weak coupling…
- mixed quantum/classical approaches
  -- classical mechanics
  -- quantum/classical connection

Outline

• Non-Markovian master equation approach:
-- effects of finite memory
-- effects of fields onto relaxation

• coupling of Non-Markovian master equation (NME) approach with theories of control

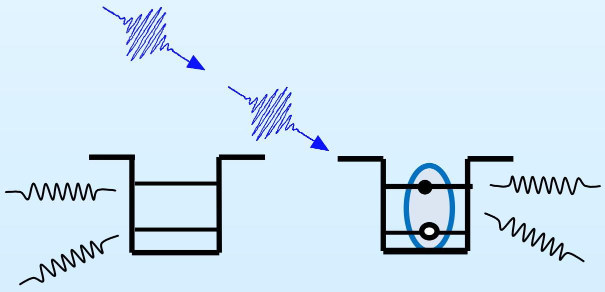
Example 1:



• isomerisation of the dimer of methyl-cyclopentadienylcarboxylate in model solution

• NME + optimal conrol theory

Example 2:

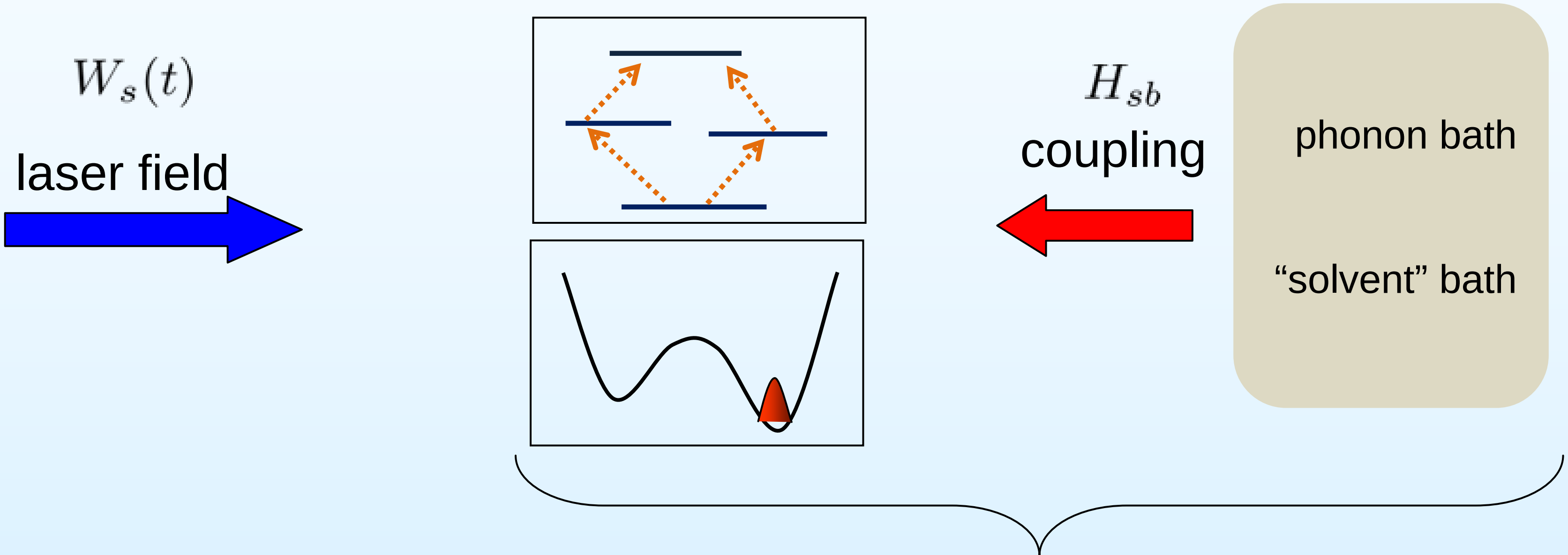


• strong field excitation of single InAs/GaAs quantum dots

• chirp effects

• NME + local control theory

Theory



standard approach:

$$
\begin{aligned}
H &= H_s^0 + H_{sb} + H_b \\
\dot{\rho}_s(t) &= -i\left[H_s^0, \rho_s(t)\right] + \Gamma(\rho(t)) \\
\dot{\rho}_s(t) &= -i\left[H_s^0 + W_s(t), \rho_s(t)\right] + \Gamma(\rho(t))
\end{aligned}
$$

Redfield, Lindblad

but for strong fields:

$$\Gamma(\rho_s(t)) \equiv \Gamma(\rho_s(t), W_s(t))$$

Non-Markovian master equation

system+ bath Hamiltonian:

$$H_T = \underbrace{H_s^0 + W_s(t)}_{H_s(t)} + \lambda S.B + H_b$$

total density operaor:

$$\dot{\rho}_T(t) = -i\,[H_T, \rho_T(t)]$$

reduced density operator:

$$\rho_s = tr_b \rho_T \qquad \mathcal{P} = \rho_b^{(eq)} tr_b(.)$$

Nakajima-Zwanzig and $\sim \mathcal{O}(\lambda^2)$

Non-Markovian master equation:

$$\dot{\rho}_s(t) = -i\,[H_s(t), \rho_s(t)] + \underbrace{\lambda^2 \int_0^t K(t,t')\rho_s(t')\,dt'}_{\text{memory}} + \underbrace{I(t)}_{\text{initial correlation}}$$

$W_s(t)$ **is system operator only !**

Non-Markovian master equation

$$\int_0^t K(t,t')\rho_s(t')dt' = i\lambda^2 \left[S, \left\{ i \int_0^t c(t,t')\, U(t,t')\, S\rho_s(t')U^\dagger(t,t') \right\} dt + \{h.c.\} \right]$$

propagator $$U(t,t') = \mathcal{T} e^{-i\int_{t'}^{t} H_s(t')dt'}$$

bath correlation fcn: $$c(t,t') = tr_b\left(\tilde{B}(t-t')\tilde{B}(t')\right) = \int_{-\infty}^{\infty} \frac{J(\omega)e^{i\omega(t-t')}}{e^{\beta\omega}-1} d\omega$$

spectral density: $$J(\omega) = C\,\omega^3\, e^{-\left(\frac{\omega}{\omega_c}\right)^2}$$ ← phonon bath

$$J(\omega) = C\,\omega\, e^{-\left(\frac{\omega}{\omega_c}\right)}$$ ← Ohmic bath w/cut-off

- fields enter in the time non-local memory kernel !
- numerically difficult
- algorithms for control ?

Non-Markovian master equation

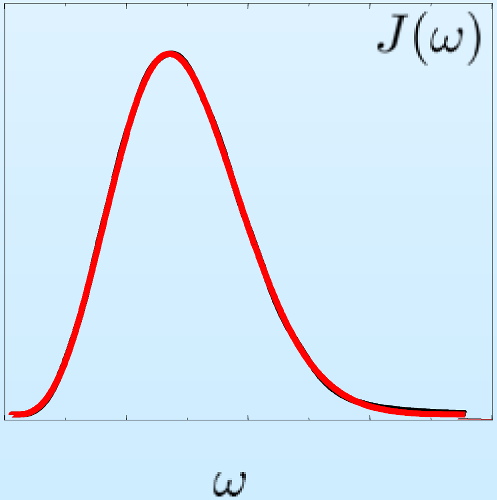
- main idea: turn non-local master equation into a time-local form:

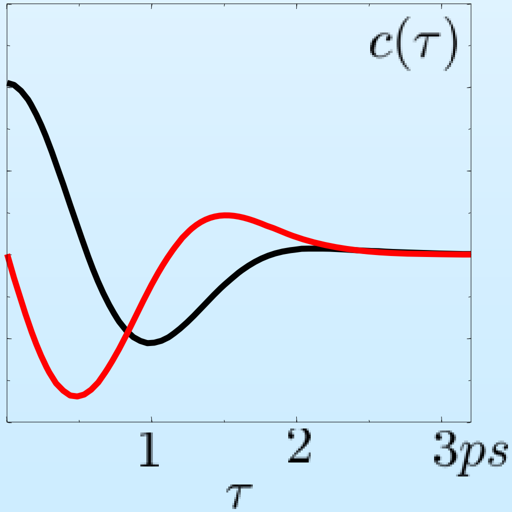
$$J(\omega) = C\,\omega^{\alpha}\, e^{-\left(\frac{\omega}{\omega_c}\right)^{\beta}}$$

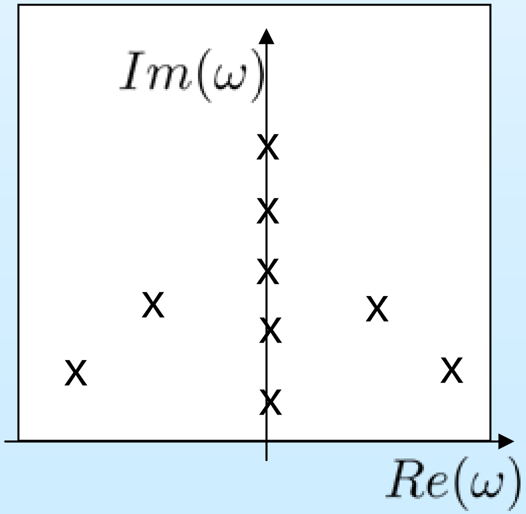
$$J_a(\omega) = \sum_l p_l\, \omega^{\alpha} \prod_{i=1,2} \left[\left(\omega - \Omega_l^{(i)}\right)^2 + \Gamma_l^{(i)2}\right]^{-1} \left[\left(\omega + \Omega_l^{(i)}\right)^2 + \Gamma_l^{(i)2}\right]^{-1}$$

$$c(t,t') = \sum_k \alpha_k\; e^{i\gamma_k (t-t')} \qquad \alpha_k, \gamma_k \in \mathbb{C}$$

poles of $J_a(\omega)$ and Matsubara frequencies







number of poles and α related by convergence criteria !

Non-Markovian master equation

• define "auxiliary density matrices" :

$$\rho_k(t) \quad = \quad e^{i\gamma_k(t)}\, U(t)\, \rho_k(0) U^\dagger(t) + \alpha_k \int_0^t e^{i\gamma_k(t-t')}\, U(t,t')\, S \rho_s(t') U^\dagger(t,t') dt$$

• then :

$$\dot{\rho_s}(t) \quad = \quad -i\,[H_s(t), \rho_s(t)] + \lambda^2 \int_0^t K(t,t') \rho_s(t')\, dt' + I(t)$$

$$\Downarrow$$

$$\begin{aligned} \dot{\rho_s}(t) &= -i\,[H_s(t), \rho_s(t)] + i\lambda^2 \left[S, \sum_k \left(\rho_k(t) + \rho_k^\dagger(t) \right) \right] \\ \dot{\rho_1}(t) &= -i\,[H_s(t), \rho_1(t)] + i\gamma_1 \rho_1(t) + \alpha_1 S \rho_s(t) \\ &\;\vdots \\ \dot{\rho_n}(t) &= -i\,[H_s(t), \rho_n(t)] + i\gamma_n \rho_n(t) + \alpha_n S \rho_s(t) \end{aligned}$$

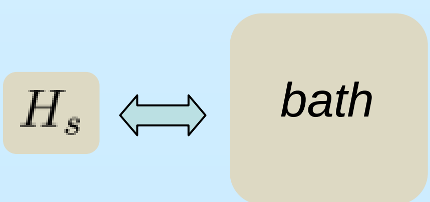
auxiliary density matrices (the $\dot{\rho_1}$ to $\dot{\rho_n}$ equations)

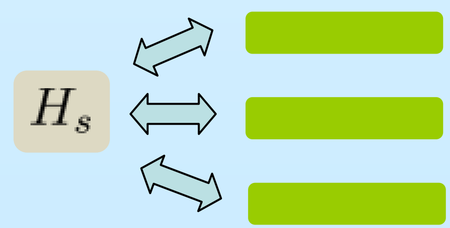
[C. Meier, D. Tannor, J. Chem. Phys. 111, 3365 (1999),
A. Pomyalov, C. Meier, D. J. Tannor, Chem. Phys. 370, 98 (2010)]

Non-Markovian master equation

- Nakaijima-Zwanzig projector operator formalism.
- Includes memory effects and initial correlation.
- Effect of external field is taken into account nonperturbatively.
- Finite temperature effects are included.
- perturbative in system-bath coupling strength but not restricted to any special functional form of system-bath interaction.
- Time local set of equations.
- Scales favorably – the cost of propagation is only N+1 times more than the usual density matrix propagation.

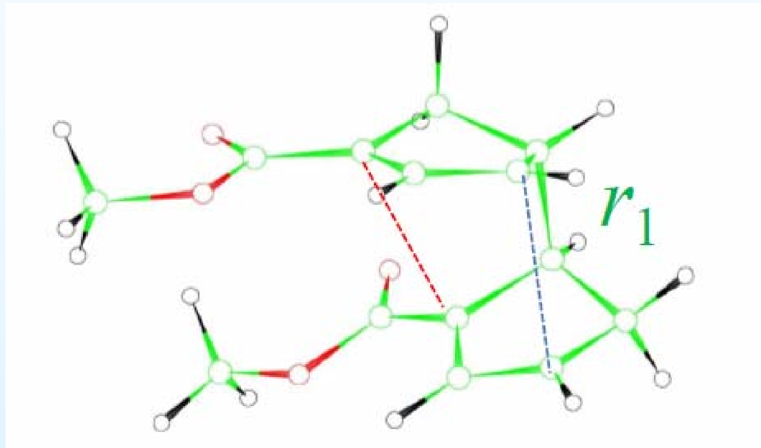
$$c(t,t') = \int_{-\infty}^{\infty} \frac{J(\omega)e^{i\omega(t-t')}}{e^{\beta\omega}-1} d\omega = \sum_k \alpha_k e^{i\gamma_k(t-t')}$$





Exemple 1: isomerisation reaction

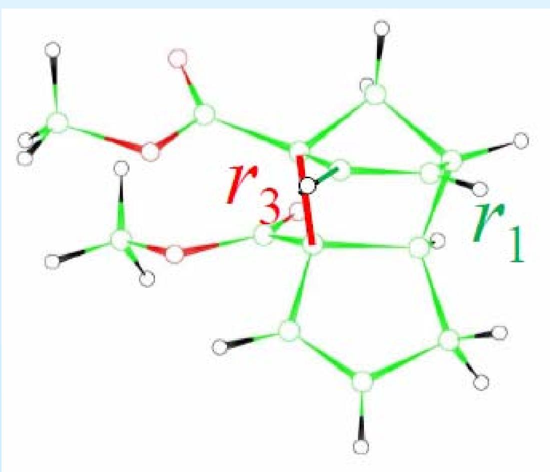
Dimer of methyl-cyclopentadienylcarboxylate

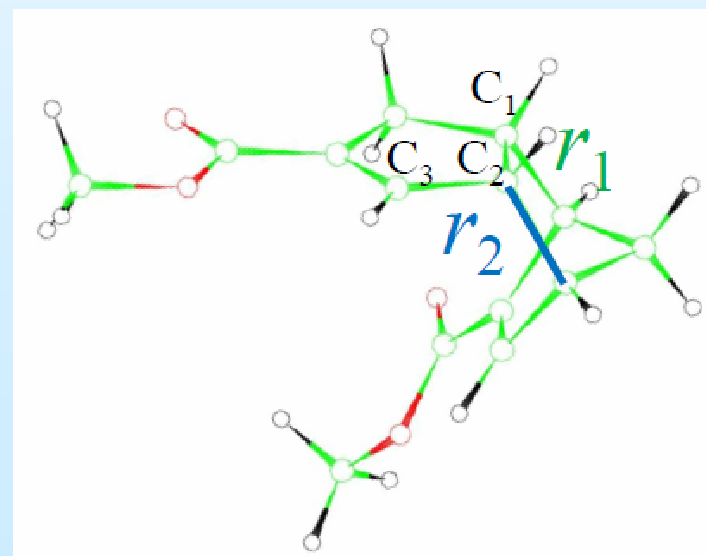


form bond r_3

break bond r_2

Transition state

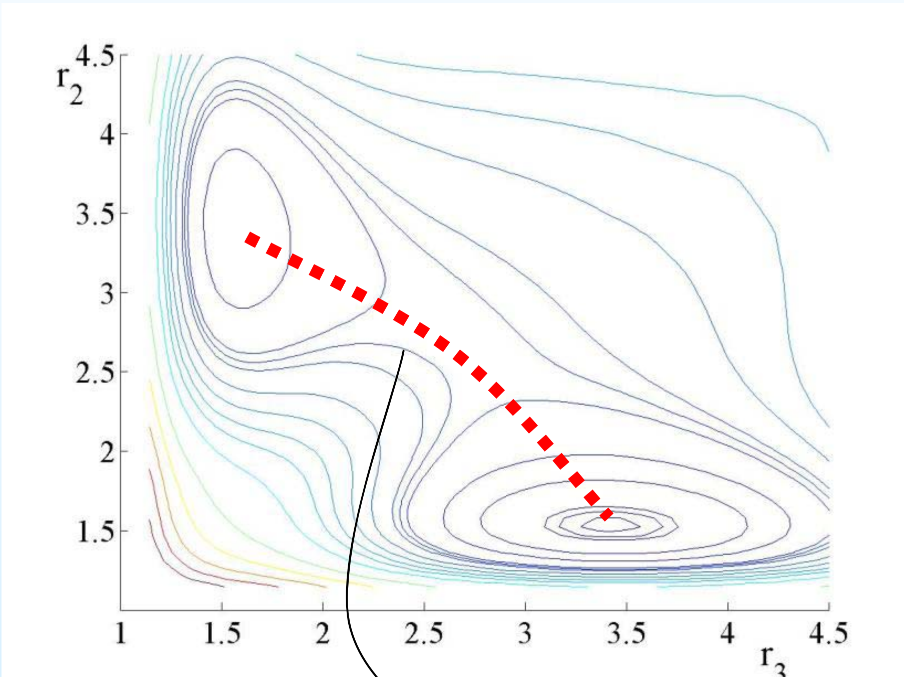


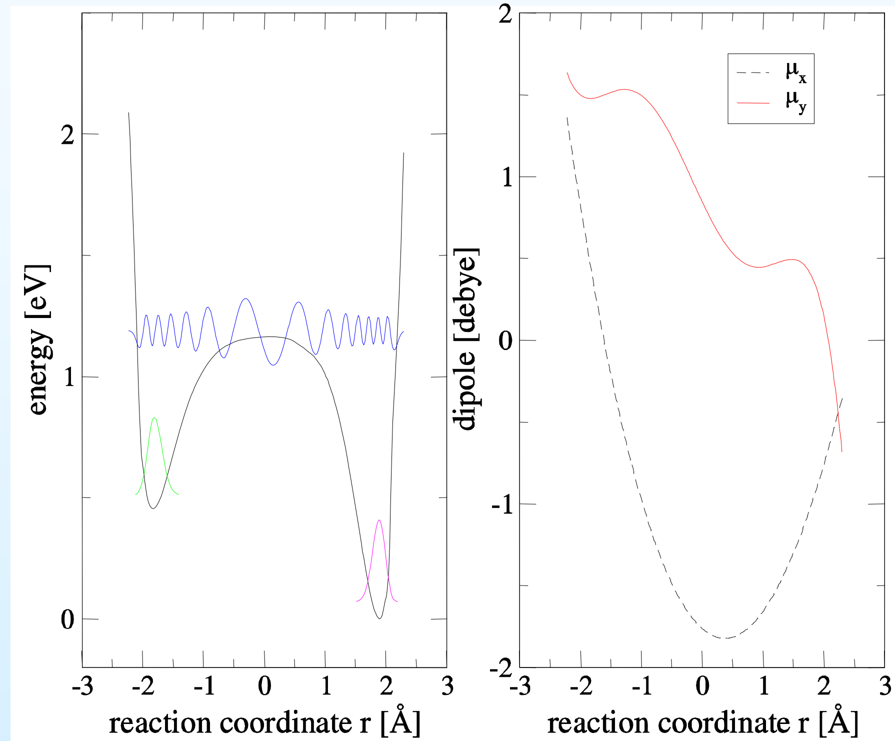


Synthesis / experiment:
Institute of Condensed Matter and Nanosciences, Université catholique de Louvain, Belgium

[similar work by J. Manz]

Exemple 1: isomerisation reaction





1D reaction path: $r=r_3-r_2$

Coupled to an Ohmic bath with cut-off

$$J(\omega) = C\,\omega\, e^{-\left(\frac{\omega}{\omega_c}\right)^2}$$

$$\omega_c = 1700\ cm^{-1}$$

DFT: G. Dive

Centre d'Ingénierie des Protéines,

Université de Liège

[Dive, G.; Robiette, R.; Chenel, A.; Ndong, M.; Meier, C.; Desouter-Lecomte, M. Theor. Chem. Acc. 2012, 131, 1236]

Exemple 1: isomerisation reaction

$$F[E(t)] = \ll \rho_S(t_{max})|\rho_{target} \gg - \int_0^{t_{max}} dt\alpha(t) \sum_j E_j^2(t)$$

$$- \int_0^{t_{max}} dt \ll \chi_S(t)| \left\{ \partial_t|\rho_S(t) \gg -i \left(H_s^0 - \sum_j \mu_j E_j(t) \right) |\rho_S(t) \gg + \int_0^t dt' K(t-t')|\rho_S(t') \gg \right\}$$

$$E_j(t) = (-s(t)/\alpha_0) Im(\ll \chi_S|\mu_j|\rho_S(t) \gg$$

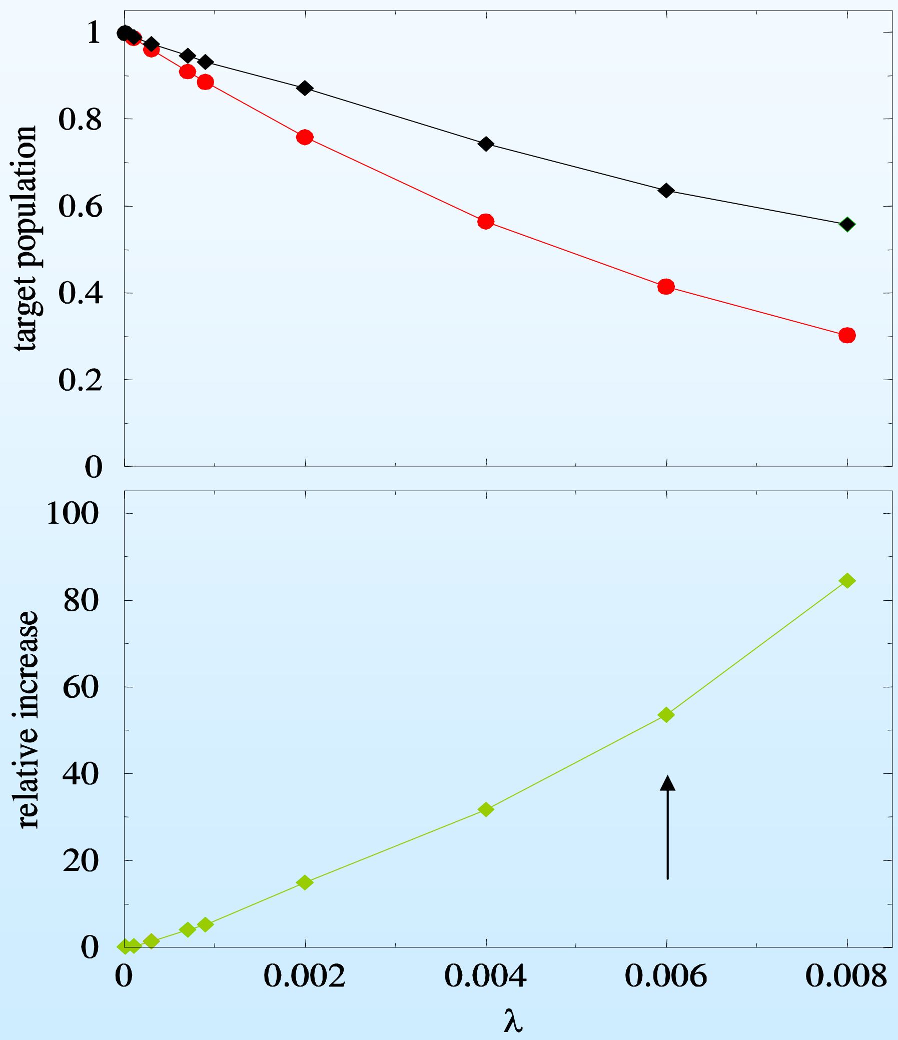
$$\begin{aligned} \dot{\rho}_S(t) &= L_s \rho_S(t) + i \sum_k [r, \rho_k(t)] \\ \dot{\rho}_k(t) &= (i\gamma_k + L_S)\rho_k(t) + i[\alpha_k r \rho_S(t) - \tilde{\alpha}_k \rho_S(t) r] \end{aligned} \quad \text{forward propagation}$$

$$\begin{aligned} \dot{\chi}_S(t) &= L_s \chi_S(t) + i \sum_k [r, \chi_k(t)] \\ \dot{\chi}_k(t) &= -(i\gamma_k - L_S)\chi_k(t) - i[\alpha_k \chi_S(t) r - \tilde{\alpha}_k r \chi_S(t)] \end{aligned} \quad \text{backward propagation}$$

Ohtsuki, Y. J. Chem. Phys. 2003, 119, 661–671.

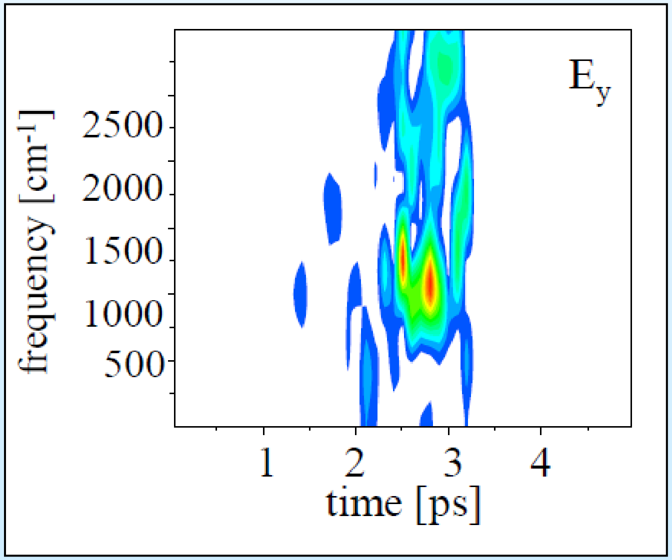
Zhu, W.; Rabitz, H. J. Chem. Phys. 2006, 118, 6751–6757.

Exemple 1: isomerisation reaction



red:
- pulse design based on isolated system
- dynamics with dissipation

black:
- pulse design with dissipation
- dynamics with dissipation



Result: control can “fight” dissipation

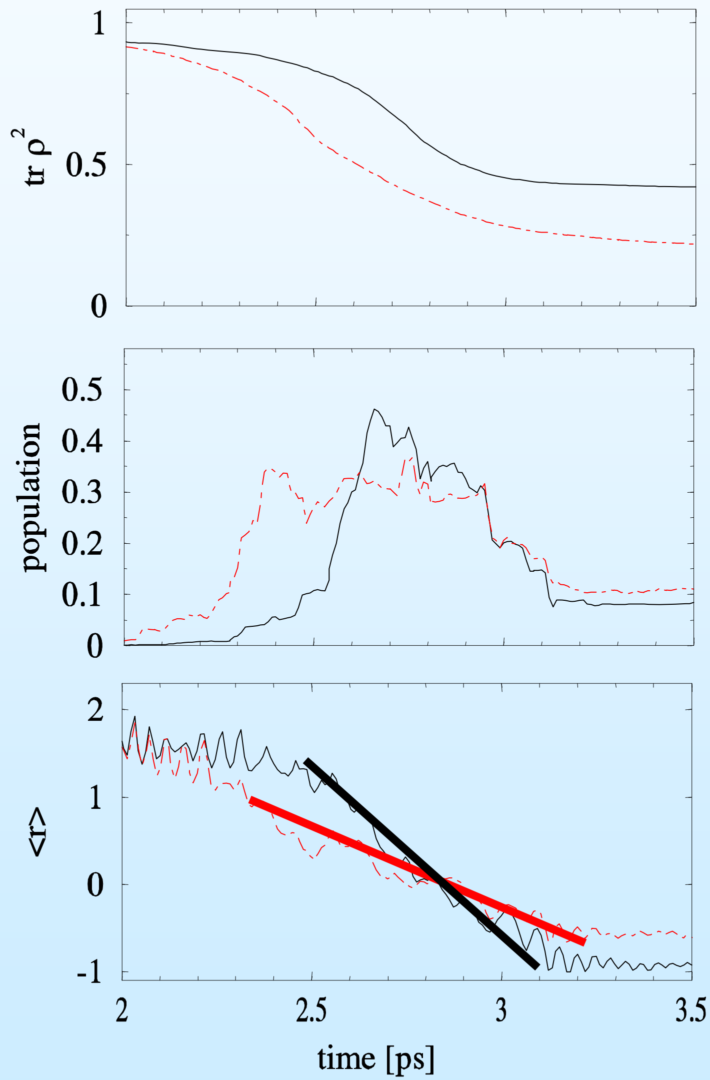
How ? Mechanism ?

Ex. 1: isomerisation reaction: the mechanism

decoherence:
(loss of purity)

Population
in states
above the barrier:

Position
expectation value:



Heating   barrier crossing   cooling

red: control without dissi
black: control + dissi

- coherence is lost while system is in delocalized states (above barrier)

- control plus dissipation:
creates pulse that makes system spend less time in deloc states !
(400 fs vs. 800 fs)

[A. Chenel, G. Dive, C. Meier, M. Desouter-Lecomte, JPCA, in press]

Ex. 1: isomerisation reaction: summary

- control of isomerisation reaction in the presence of model environment

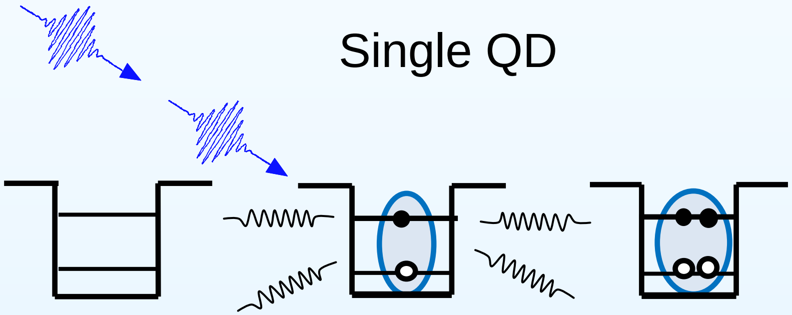
- method:

OCT ⟺ **Non-Markovian master equation auxiliary density matrix method**

- control including dissipation can adopt to dissipative situation

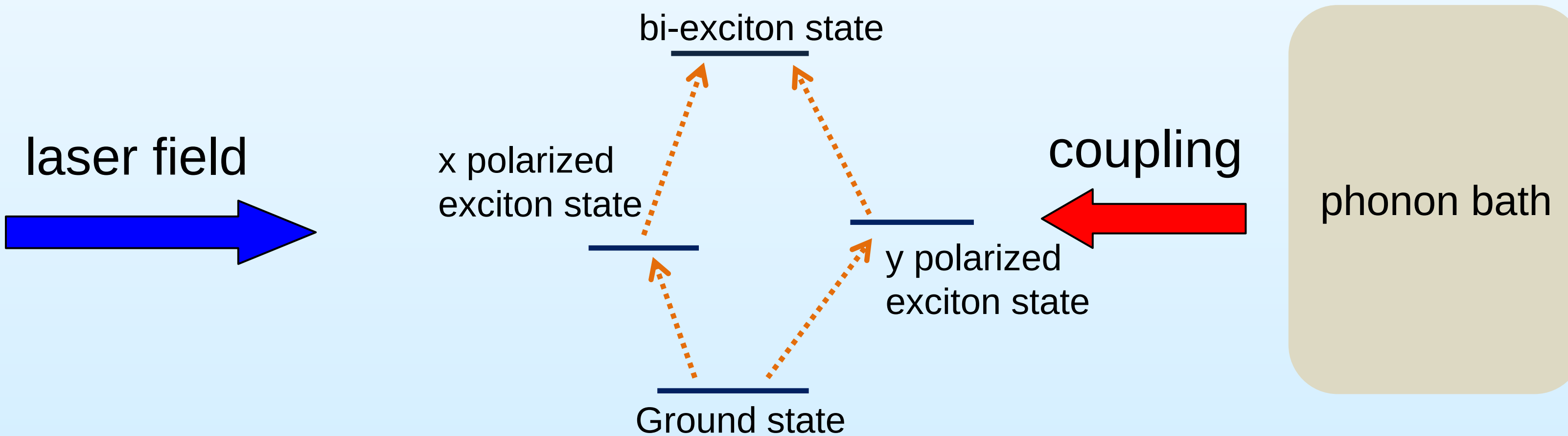
- in the presented example:
  accelerate the barrier crossing to minimize decoherence

Ex. 2: Stong field excitation of quantum dots



motivation:

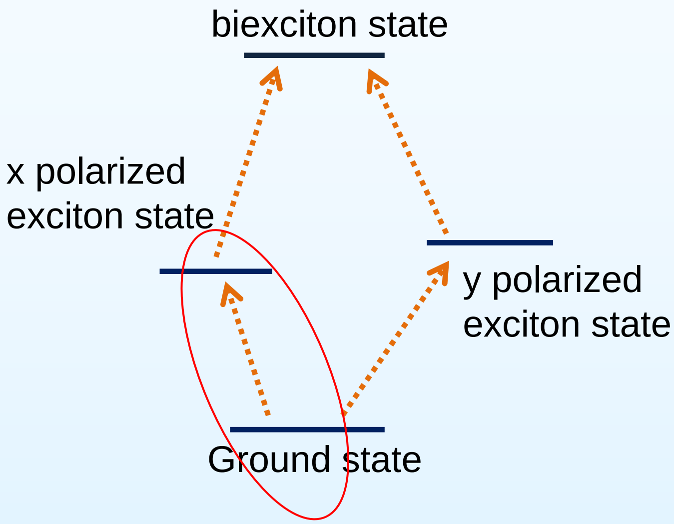
- understanding the interplay of damping and external fields in QD
- quantum state preparation + optical manipulation



Experiments :

- A.J. Ramsay et al Phys. Rev. Lett. 104 017402 (2010).
- A.J. Ramsay et al Phys. Rev. Lett. 105 177402 (2010).
- S. J. Boyle et al Phys. Rev. Lett. 102 207401 (2009).
- A.Vagov et al Phys. Rev. Lett. 98 227403 (2007).
- C-M. Simon et al Phys. Rev. Lett. 106, 166801 (2011). ⟵ Toulouse: LCAR+ INSA
- Y.Wu et al Phys. Rev. Lett. 106, 067401 (2011).

Ex. 2: Stong field excitation of quantum dots



- drive QD with appropriate polarization
  → effective TLS:

- driving with strong laser pulses
  (2ps, 10774 cm^{-1}, chirped or not)

- fixed pulse length, vary intensity

- detection: ~ excited state population

- realistic QD parameters: $J(\omega) = C\,\omega^3\,e^{-\left(\frac{\omega}{\omega_c}\right)^2}$

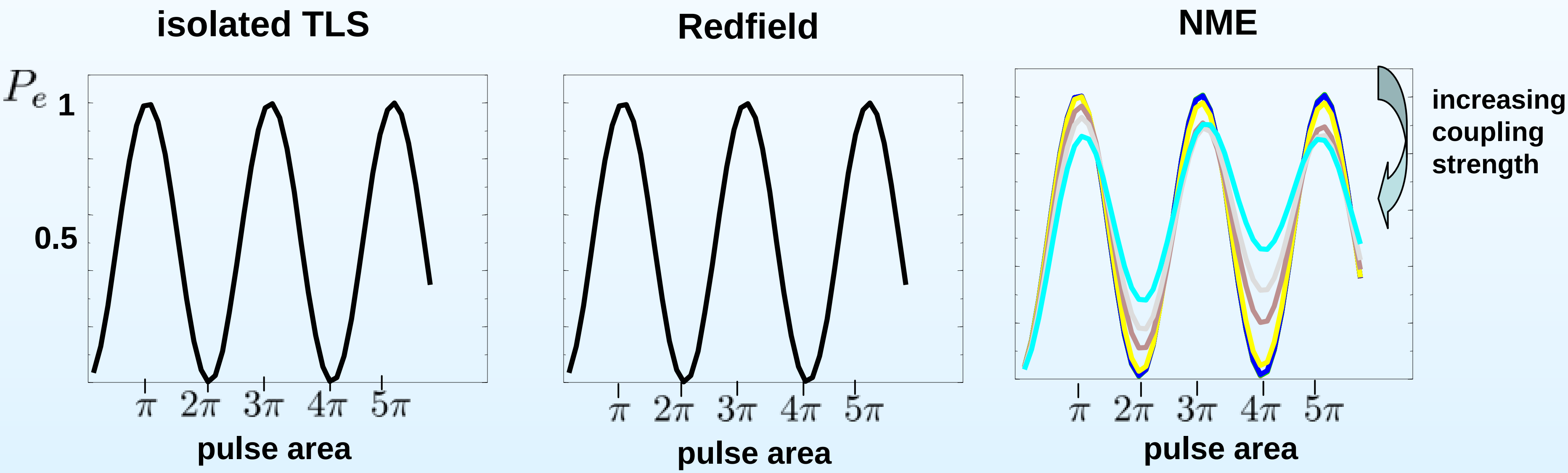
  $\omega_c = 1.44\ 10^{-3} eV$

- temperature: $T = 4K$

parameters of Toulouse group

- Numerical details: 80 auxiliary density matrices, RK-propagator

Ex. 2: Stong field excitation of quantum dots

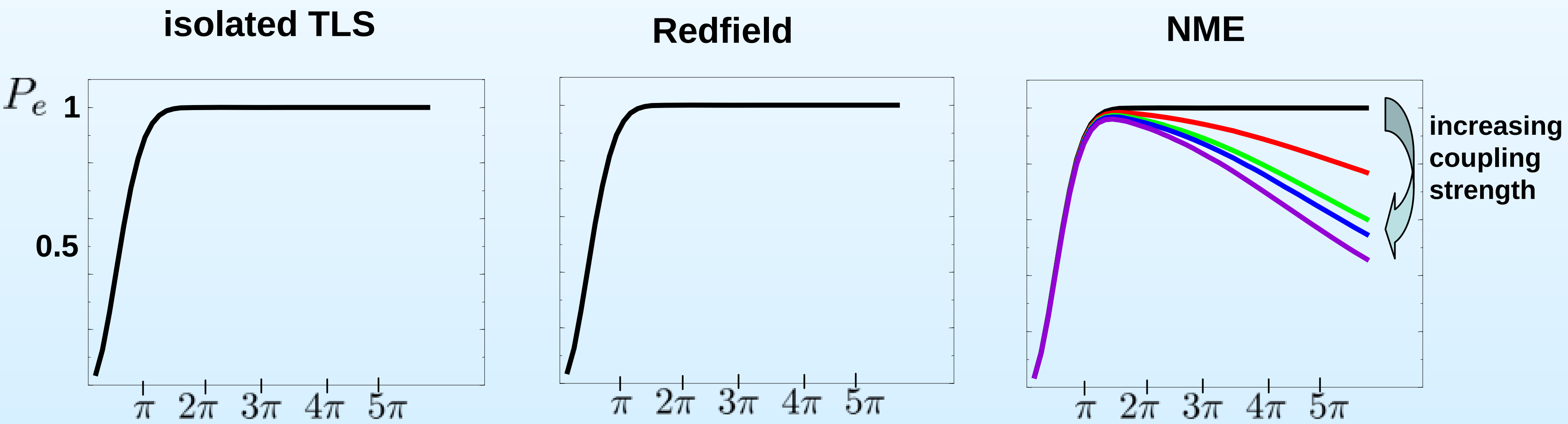


- as a function of intensity (→ pulse area): Rabi oscillations
- standard Redfield: same as isolated
- NME: damping of Rabi oscillation as function of intensity:
  effect of field onto relaxation

**[A, J. Ramsay, et al. Phys. Rev. Lett. 105 177402 (2010), A. J. Ramsay et al.,
J. Appl. Phys. 109, 102415 (2011), D. Mogilevtsev et al., Phys. Rev. Lett., 100, 017401 (2008)]**

Ex. 2: chirped adiabatic transfer

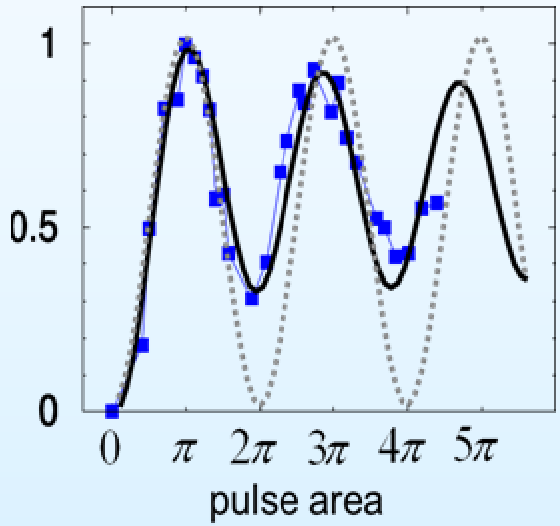
- driving with strong, chirped laser pulses (2ps, 10774 cm^{-1} $\phi'' = -40\ ps^2$)
- fixed pulse length, vary intensity



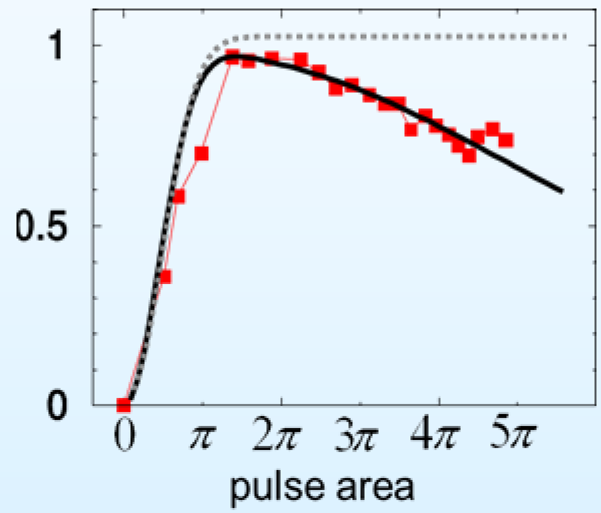
- as a function of intensity (→ pulse area): saturation: adiabatic regime (robust)
- standard Redfield: same as isolated
- NME: for very high intensities: loss of transfer efficiency

Ex. 2: comparison with experiment

Resonant driving : Rabi oscillations



Chirped pulse driving : Adiabatic transfer



$$\phi'' = -40\ ps^2$$

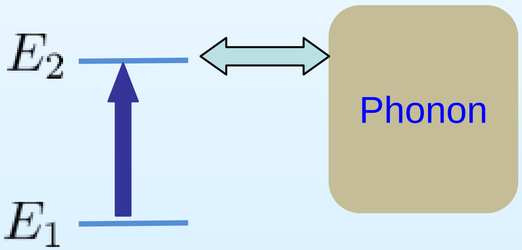
- experiments on the same quantum dot, in different excitation regimes
- damping of Rabi oscillations also observed in Ramsay group (Sheffield)

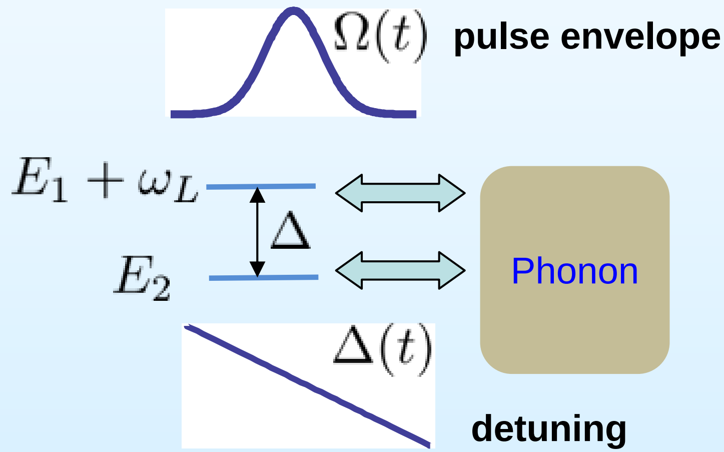
[« Robust Quantum Dot Exciton Generation via Adiabatic Passage with Frequency-Swept Optical Pulses », C.-M. Simon, T. Belhadj, B. Chatel, T. Amand, P. Renucci, A. Lemaitre, O. Krebs, P. A. Dalgarno, R. J. Warburton, X. Marie, and B. Urbaszek, Phys. Rev. Lett. 106, 166801 (2011)]

Ex. 2: Results: physical picture

- analytical analysis is possible if pulse envelope + chirp rate slow
  -- w.r.t. carrier frequency → RWA + adiabatic approximation
  -- w.r.t. bath correlation function

- dressed state picture

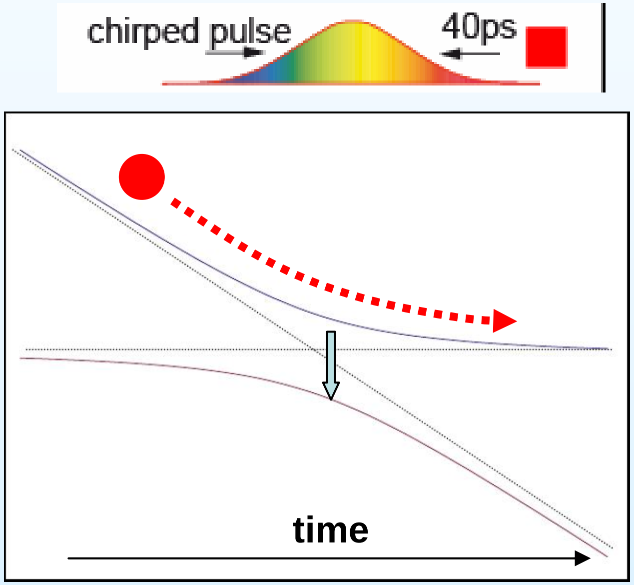




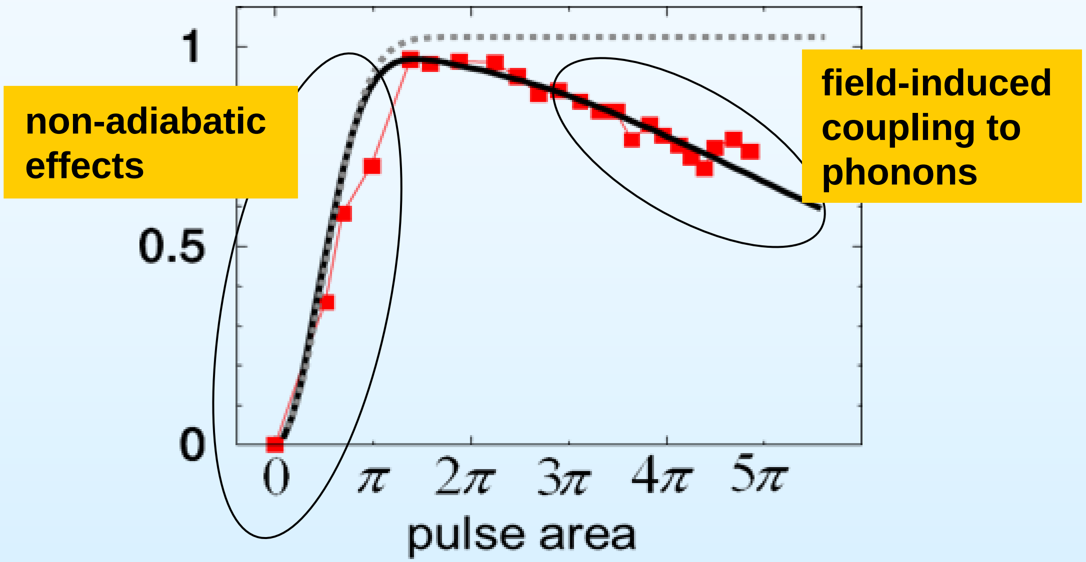
$$\dot{\rho}_s^d = -i\left[H_s^d, \rho_s^d\right] + \Omega(t)\left[\sigma_z, \alpha_1\left[\sigma_x, \rho_s^d\right] + \alpha_2\left[\sigma_z, \rho_s^d\right] + \alpha_3\left\{\sigma_y, \rho_s^d\right\}\right]$$

laser pulse induces coupling to bath

Ex. 2: Results: physical picture



Chirped pulse driving : Adiabatic transfer



- coupling of dressed states by:

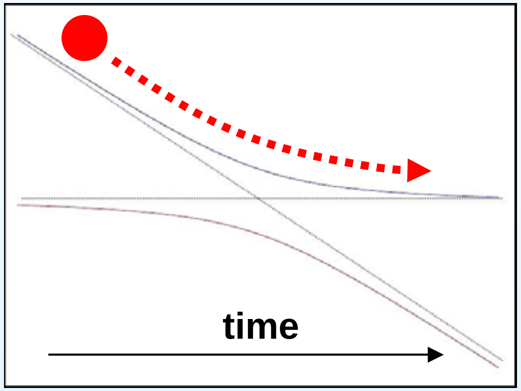
  -- non-adiabatic effects

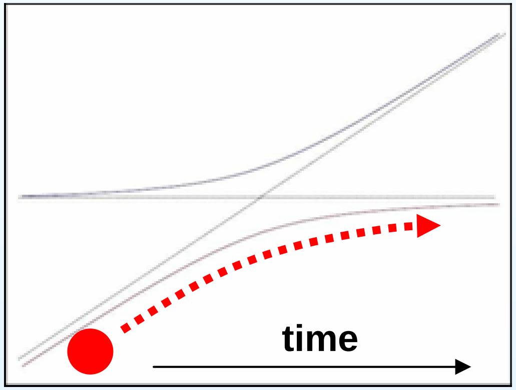
  -- field-induced coupling to phonon bath:

  → relaxation of population in dressed states

- both are mediated by the laser pulse !

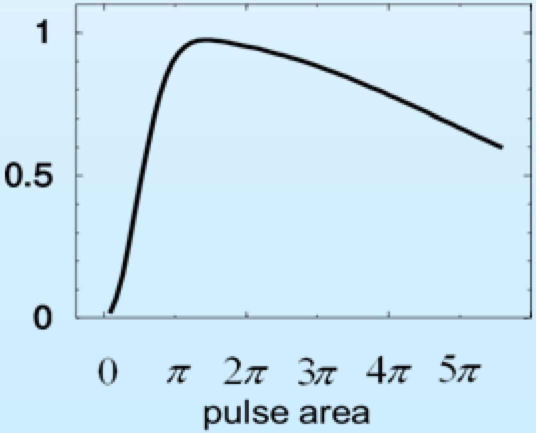
Ex. 2: dependence of chirp

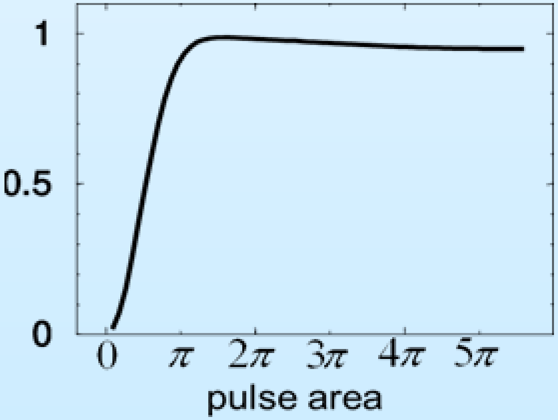




Negative chirp :
high frequency component precedes the low frequency component.

Positive chirp :
low frequency component precedes the high frequency component

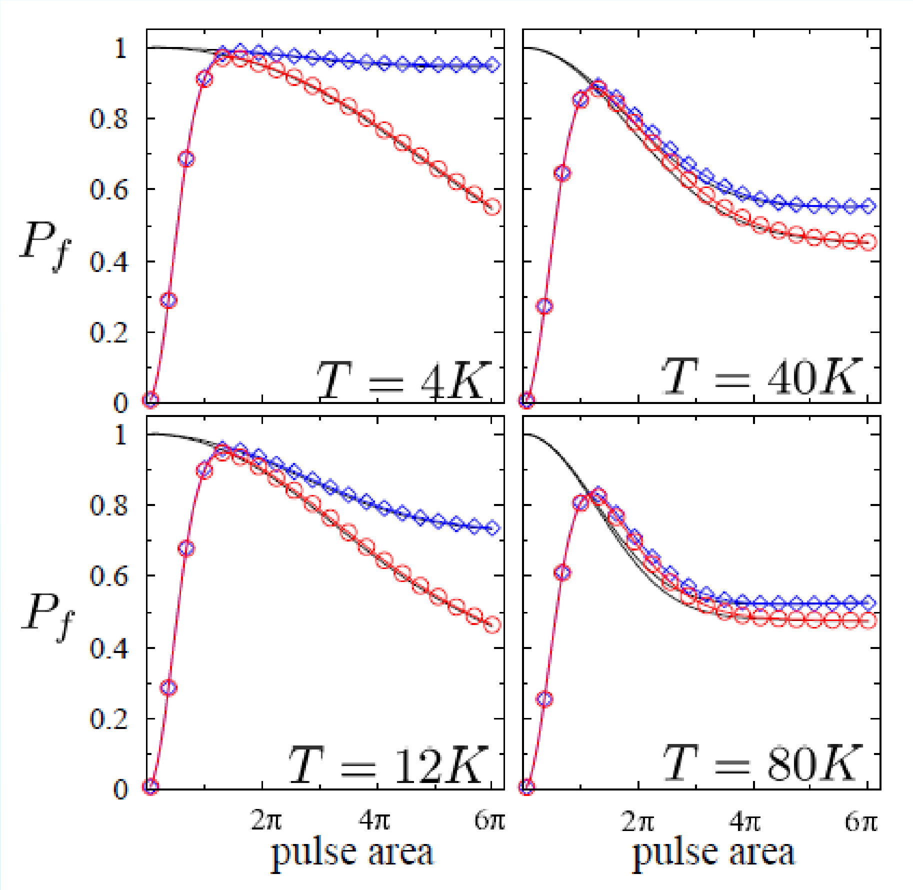




Full numerical solution

• sign of chirp has drastic effect onto transfer efficiency !

Ex. 2: physical picture



Dependence of transfer efficiency on

-- phase (sign of chirp)
-- temperature
-- intensity

blue: up-chirp
red: down chirp

analytical model for all T

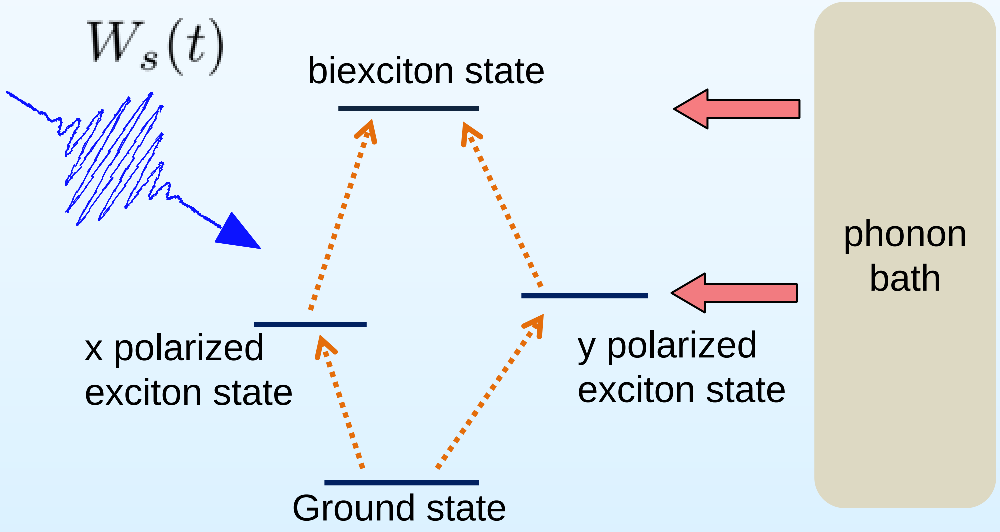
low T: $P_f \approx \begin{cases} 1 & \\ e^{-\kappa} & \kappa \sim J(\Omega_p)\tau_p \end{cases}$ up / down

Dissipation induces a phase dependence, which does not exist in the isolated system !

[A. Debnath, C. M., B. Chatel, T. Amand, Phys. Rev. B, submitted]

Ex. 2: Implications for control

• strong field coherent control in dissipative quantum systems

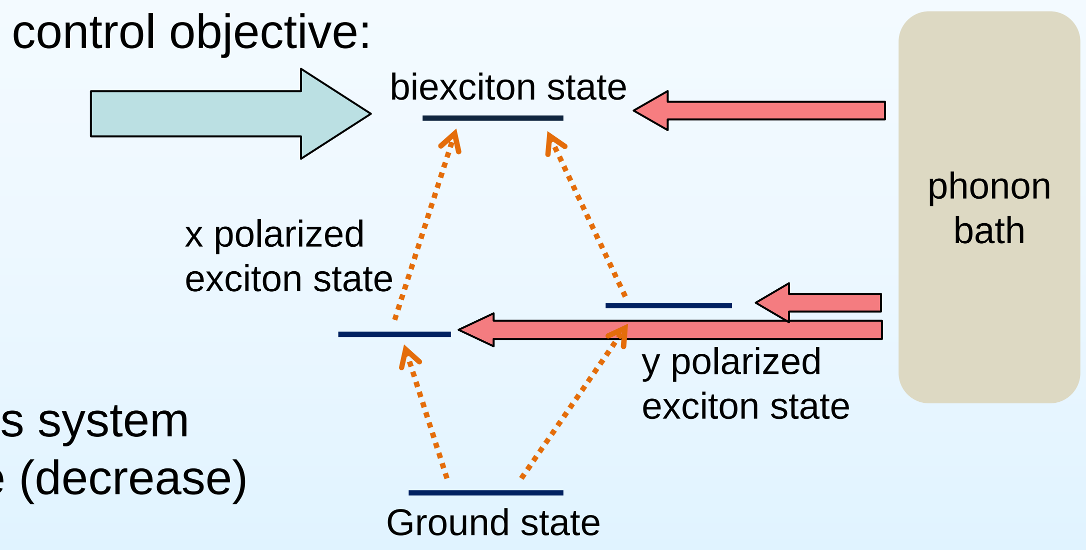


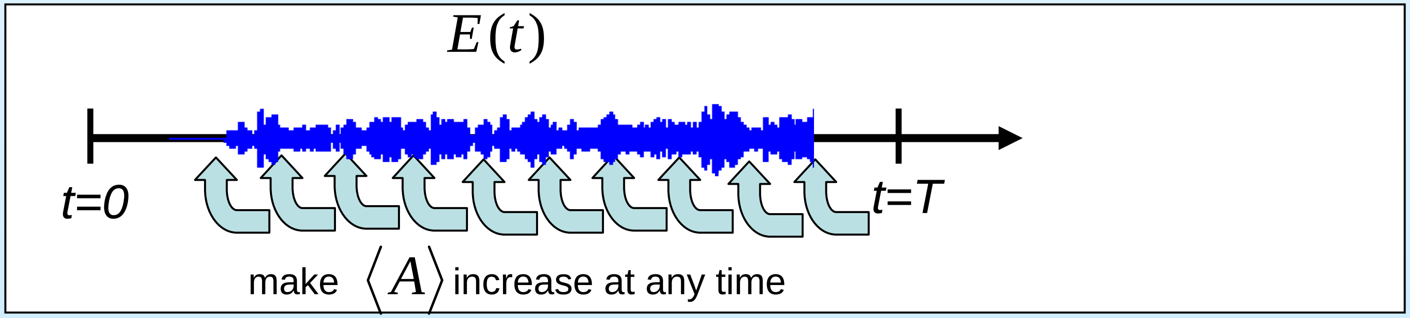
• standard approach: $$\dot{\rho}_s(t) = -i\left[H_s^0 + W_s(t), \rho_s(t)\right] + \Gamma(\rho(t))$$

• however: strong fields alter the coupling to the bath and the relaxation dynamics !
→ NME

Ex. 2: Implications for control

- control objective:
  excitation of bi-excitonic state
- four-level model
- method: « local control »:
- local control: external fields are determined by the instantaneous system dynamics to ensure an increase (decrease) of an observable [1]





[1] R. Kosloff, S. A. Rice, P. Gaspard, S. Tersigni, D. Tannor Chem. Phys. **139**, 201 (1989)
M. Sugawara Y. Fujimura, J. Chem. Phys. **100**, 5646 (1994), C. Meier, V. Engel, D. Tannor, Adv. Chem. Phys. **141**, 29 (2009)

Ex. 2: Implications for control

control objective: excitation of bi-excitonic state

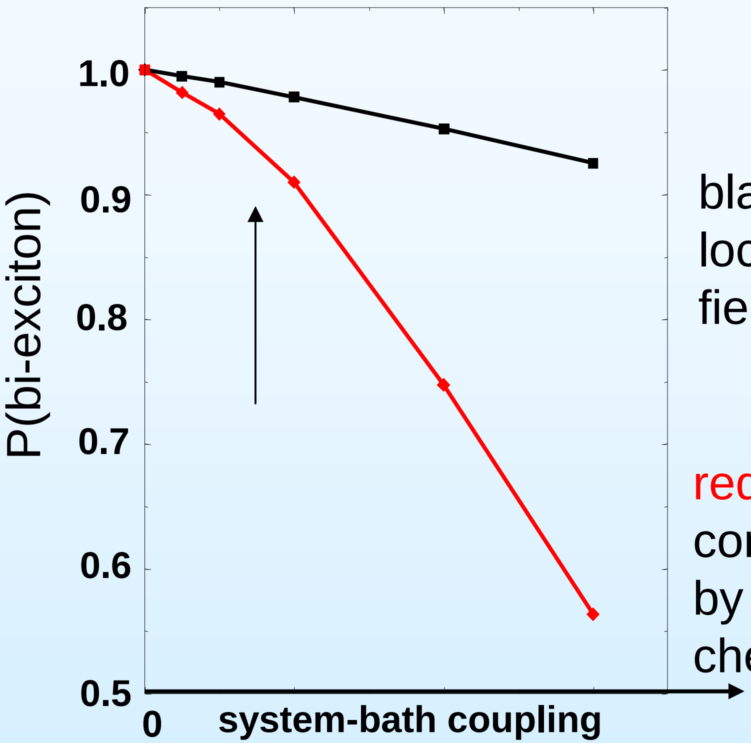
possible operators: maximize: $A = P_{bi-exc}$ projector onto target state: (here, not good ! lost poulation)

minimize: $A = (H_s - \varepsilon)^2$ for non-degenerate states

$$\dot{\rho}_S(t) = L_S\rho_S(t) + i\sum_k [r, \rho_k(t)]$$
$$\dot{\rho}_k(t) = (i\gamma_k + L_S)\rho_k(t) + i[\alpha_k r \rho_S(t) - \tilde{\alpha}_k \rho_S(t) r]$$

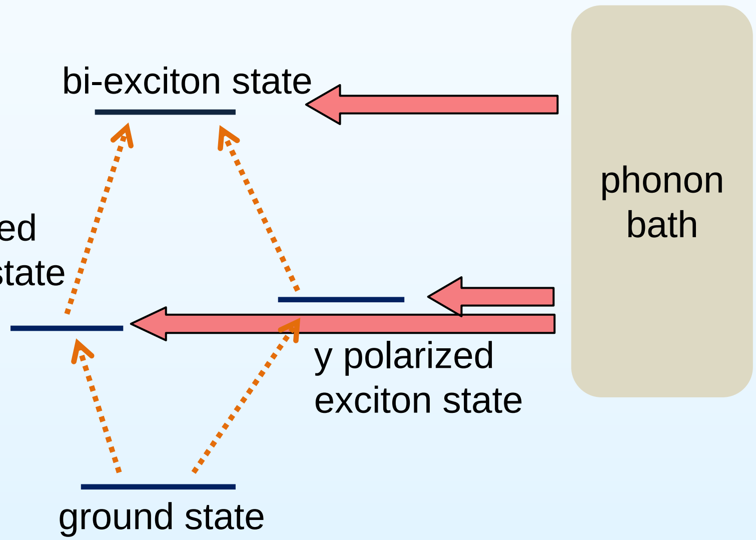
$$E(t) = \pm i \;\; tr\left(A\mu\rho_S(t)\right)$$

Implications for control



black:
local control field using NME

red:
control field obtained by standard Redfield checked with NME



• NME can be coupled to control methods, very good objective

• effect of fields onto relaxation is important

• mechanism ? higher temperatures ? effects of polarization ? → work in progress …

Summary, conclusions

- Non-Markovian master equation approach: method of auxiliary density matrices
  → bath memory effects
  → strong fields: external fields influence relaxation

- in combination with control methods: dynamics can adopt to dissipation

- strongly driven excitonic dynamics in quantum dots:
  Non-Markovian master equation approach is ideally suited
  → very good agreement with experimental results:
  Rabi-damping and loss in adiabatic transfer efficiency:

  → exciton-phonon interaction, modified by external fields

  → phase depence induced by low temperature environment

- NME especially useful for coherent control simulation
  → potentially strong and complicated pulses

Outlook, future…..

- Coherent control:

  -- more complete description of quantum dots

  -- polarization shaping

  -- apply alternative control protocols: (OCT)

  -- higher temperatures (T > 80 K)

  -- aim: bi-exciton close to 1 at high T

- other type of quantum dots:

  -- charged quantum dots: initial correlations ?

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