

# Dynamics of open quantum systems

## The resonance theory

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The results presented are based on collaborations with

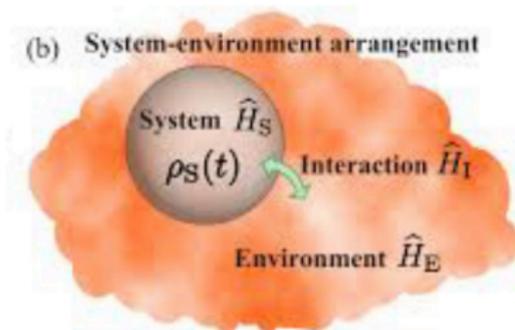
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# Open quantum systems



System-reservoir models, Hilbert space

$$\mathcal{H} = \mathcal{H}_S \otimes \mathcal{H}_R$$

In this talk:  $\dim \mathcal{H}_S < \infty$ , environment in thermal equilibrium.

Interacting Hamiltonian

$$H_\lambda = \underbrace{H_S + H_R}_{H_0} + \lambda H_I$$

Reduced density matrix  $\rho_S(t)$  defined by taking *partial trace*

$$\rho_S(t) = \text{Tr}_{\mathcal{H}_R} \left( e^{-itH_\lambda} (\rho_S \otimes \rho_R) e^{itH_\lambda} \right)$$

Definition of **dynamical map**  $V(t)$ :

$$V(t)\rho_S = \rho_S(t)$$

- is **not a group**:  $V(t+s) \neq V(t)V(s)$
- $\forall t$ ,  $V(t)$  is **completely positive, trace preserving (CPT)**

# Quantum dyn. semigroup = CPT + semigroup

*Markovian approximation*

$$V(t) \approx e^{t\mathcal{L}} \quad (?)$$

- Physically adequate if
  - system-reservoir interaction is small and
  - reservoir correlations decay quickly in time
- Desirable b/c dynamics accessible via spectrum of  $\mathcal{L}$
- Starting from basic postulates of quantum theory (Hamiltonian system-reservoir models, not from effective equations), the Markovian approximation is **hard to derive rigorously** (perturbation theory: large volume, small coupling, all times...)

## Rigorous approaches

- **Van Hove limit** ('weak coupling limit'):  $\forall a > 0$

$$\lim_{\lambda \rightarrow 0} \sup_{0 \leq \lambda^2 t < a} \|V(t) - e^{t(\mathcal{L}_0 + \lambda^2 K)}\| = 0$$

[Davies '73,'74]

Inconvenience: Constraint  $\lambda^2 t < \text{const.}$

- **Dynamical resonance theory**:  $\forall \lambda$  small,  $\forall t \geq 0$ :
  1. 'Resonance expansion of dynamics', valid for system *and* *reservoir* observables
  2. CPT approximation for system dynamics
  3. Asymptotically exact CPT approximation

# Setup

$$\mathcal{H} = \mathcal{H}_S \otimes \mathcal{H}_R = \mathbb{C}^d \otimes \underbrace{\left( \bigoplus_{n \geq 0} L^2_{\text{sym}}(\mathbb{R}^{3n}, d^{3n}k) \right)}_{\text{Fock space}}$$

Hamiltonian:

$$H = H_S + H_R + \lambda G \otimes (a^*(g) + a(g))$$

$$H_S = \sum_{j=1}^d E_j |\phi_j\rangle \langle \phi_j|, \quad \text{and} \quad H_R = \int_{\mathbb{R}^3} |k| a^*(k) a(k) d^3k$$

Coupling constant  $\lambda \in \mathbb{R}$ , coupling operator = matrix  $G$

Dynamics:

$$\alpha_\lambda^t(\mathcal{O}) = e^{itH_\lambda} \mathcal{O} e^{-itH_\lambda}$$

- Dynamics of system observable  $X$ :  $\omega_0(\alpha_\lambda^t(X \otimes \mathbf{1}_R))$
- Isolated system dynamics:

$$\alpha_S^t(|\phi_k\rangle\langle\phi_\ell|) = e^{it(E_k - E_\ell)}|\phi_k\rangle\langle\phi_\ell| \cong e^{itL_S}(\phi_k \otimes \phi_\ell)$$

where  $L_S$  is system *Liouville operator* (on  $\mathcal{H}_S \otimes \mathcal{H}_S$ )

$$L_S = H_S \otimes \mathbf{1}_S - \mathbf{1}_S \otimes H_S$$

- As  $\lambda \neq 0$ : Effect of coupling to reservoir is to turn eigenvalues of  $L_S$  into *complex* resonances:  $E_k - E_\ell \rightsquigarrow \varepsilon_{k,\ell}(\lambda)$
- $\varepsilon_{k,\ell}(\lambda)$  are analytic in  $\lambda$ , accessible by perturbation theory

# Result 1: Resonance expansion of the dynamics

**Theorem 1.** For all  $\lambda$  small and  $t \geq 0$ ,

$$\|V(t)\rho - W(t)\rho - \rho_{S,\beta,\lambda}\| \leq C|\lambda|e^{-\gamma(\lambda)t}$$

$\rho_{S,\beta,\lambda}$  = coupled (interacting) equilibrium state reduced to S

$$W(t) = \sum_{k,\ell} e^{it\varepsilon_{k,\ell}(\lambda)} \mathcal{P}_{k,\ell} = O(e^{-\gamma(\lambda)t})$$

$$\gamma(\lambda) = \min_{k,\ell} \{ \text{Im } \varepsilon_{k,\ell}(\lambda) \} \geq 0$$

Resonance expansion is accurate to  $O(\lambda)$  for all times and exact as  $t \rightarrow \infty$  ✓ but **does not have CPT semigroup structure** ✗

## Result 2: Markovian approximation for all times

Mild assumption on decay rate

$$\gamma(\lambda) = \lambda^2 \gamma_{\text{FGR}} + O(\lambda^3)$$

with  $\gamma_{\text{FGR}} > 0$ .

Expanding  $W(t)$  for small  $\lambda$  gives the following result.

**Theorem 2.** For all  $\lambda$  small and  $t \geq 0$ ,

$$\|V(t) - e^{t(\mathcal{L}_S + \lambda^2 K)}\| \leq C|\lambda|.$$

- $\mathcal{L}_S = -i[H_S, \cdot]$  and  $K$  are commuting (super-)operators
- $K$  entirely constructed from lowest order approx. of  $\varepsilon_{k,\ell}(\lambda)$
- $e^{t(\mathcal{L}_S + \lambda^2 K)}$  is a CPT with invariant state

$$e^{t(\mathcal{L}_S + \lambda^2 K)} \rho_{S,\beta,0} = \rho_{S,\beta,0}.$$

## Result 3: Asymptotically exact markovian approx.

We construct a CPT semigroup generator

$$M(\lambda) = \mathcal{L}_S + \lambda^2 M_2 + \lambda^3 M_3 + \dots$$

$M_1, M_2, \dots$  calculable by perturbation theory in  $\lambda$ , such that:

**Theorem 3.** For all  $\lambda$  small and  $t \geq 0$ ,

$$\|V(t) - e^{tM(\lambda)}\| \leq C(|\lambda| + \lambda^2 t) e^{-\lambda^2 t \gamma_{\text{FGR}}}$$

- Asymptotically exact,  $\lim_{t \rightarrow \infty} (V(t) - e^{tM(\lambda)}) = 0$
- BUT: remainder not small for 'intermediate times'  $t \approx 1/\lambda^2$

# Population dynamics: better result!

Matrix element of system operator  $A$  in energy basis  $\varphi_k$  (of  $H_S$ ):

$$[A]_{k,\ell} \equiv \langle \varphi_k, A\varphi_\ell \rangle$$

**Population** of system level  $E_k$  at time  $t$ :  $[V(t)\rho]_{k,k}$

**Theorem 4.** For all  $\lambda$  small, all  $k$  and  $t \geq 0$ ,

$$\left| [V(t)\rho]_{k,k} - [e^{tM(\lambda)}\rho]_{k,k} \right| \leq C|\lambda|(1 + |\lambda|^3 t)e^{-\lambda^2 t\gamma_{\text{FGR}}}$$

- Populations described asymptotically exactly by CPT semigroup
- AND: remainder small,  $O(\lambda)$ , for ALL TIMES !

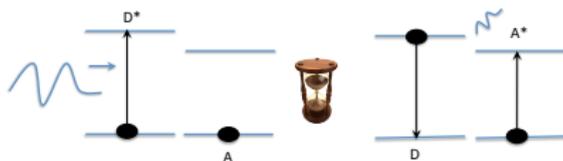
## Application: Excitation transfer process

When a molecule is excited electronically by absorbing a photon, it **luminesces** by emitting another photon ( $\sim 1$  nanosecond)



Fluorescence

In presence of another molecule ( $\sim 1 - 10$  nm) the **excitation can be swapped between the molecules** ( $\sim 1$  picosecond).

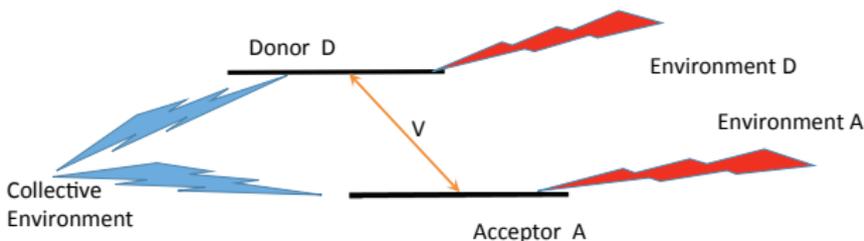


Excitation transfer process:  $D^* + A \rightarrow D + A^*$

**Excitation transfer** happens in *biological systems* (in chlorophyll molecules during photosynthesis)

Similar **charge transfer** (electron, proton) happens in *chemical reactions*:  $D + A \rightarrow D^- + A^+$  (reactant and product)

Processes take place in **noisy environments** (molecular vibrations, protein and solvent degrees of freedom)



Local model (red) and collective model (blue)

$V$ : exchange or dipole-dipole interaction

# D-A models: Marcus model $\leftrightarrow$ spin-boson model

- Marcus model  $\leftrightarrow$  *spin-boson model* (Xu-Schulten '94)

$$H_{\text{SB}} = V\sigma_x + \epsilon\sigma_z + H_R + \lambda\sigma_z \otimes (a^*(h) + a(h))$$

Parameters:

**Direct D-A coupling:**  $V$

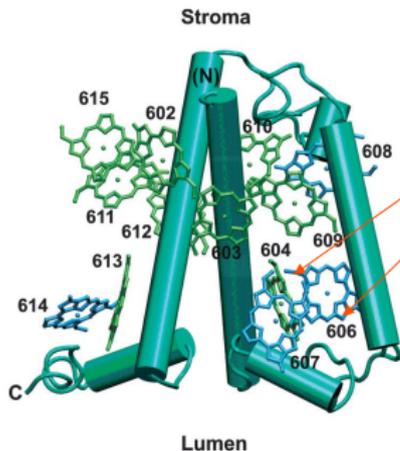
**D-A energy difference:**  $\epsilon$

**D-A  $\leftrightarrow$  environment coupling constant**  $\lambda$

- $V, \epsilon, \lambda$  parameter regime ?

## Towards a structure-based exciton Hamiltonian for the CP29 antenna of photosystem II

Frank Müh, Dominik Lindorfer, Marcel Schmidt am Busch and Thomas Renger,  
*Phys. Chem. Chem. Phys.*, **16**, 11848 (2014)



### Our chlorophyll dimer:

604: Chla,  $E_{exc}^a = 14\,827\text{cm}^{-1}$   
 $= 1.8385\text{eV}$  Acceptor

606: Chlb,  $E_{exc}^b = 15\,626\text{cm}^{-1}$   
 $= 1.9376\text{eV}$  Donor

$$\varepsilon = E_{exc}^b - E_{exc}^a = 99.1\text{meV}$$
$$V = 8.3\text{meV}$$

Our chlorophyll dimer is weakly coupled:

$$\frac{V}{\varepsilon} \approx 0.08 \ll 1.$$

For the **weakly coupled dimer** and at **high temperature**

$$V \ll \epsilon, \quad k_B T \gg \hbar\omega_c$$

formal time-dependent perturbation theory (Legget et al., '87)  
gives **Marcus formula**

$$\text{Donor population} \propto e^{-\gamma_M t}, \quad \gamma_M = \frac{V^2}{4} \sqrt{\frac{\pi}{T\epsilon_{\text{rec}}}} e^{-\frac{(\epsilon - \epsilon_{\text{rec}})^2}{4T\epsilon_{\text{rec}}}}$$

$\epsilon_{\text{rec}}$  = reconstruction energy  $\propto \lambda^2$  is  $\approx \epsilon$

- **Marcus theory** works for large (any) interaction strength with environment ( $\epsilon_{\text{rec}}$ ) but is **heuristic**
- Rudolph A. Marcus received **1992 Nobel Prize in Chemistry**  
“for his contributions to the theory of electron transfer reactions  
in chemical systems”

## Our contribution to 'Marcus theory'

1. We develop **dynamical resonance theory** for dynamics of the weakly coupled dimer ( $V \ll \epsilon$ ), valid for all times and any reservoir coupling strength ( $\lambda$ )
2. We extract from it **validity of exponential decay law** and rates of relaxation and decoherence<sup>1</sup>
3. We consider **individual coupling strengths**  $\lambda_D$  and  $\lambda_A$  of donor and acceptor to environments

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<sup>1</sup>Relaxation rate was obtained heuristically using 'time-dependent perturbation theory' already by Leggett et al. '87

# Initial states, reduced dimer state

Initial states unentangled,

$$\rho_{\text{in}} = \rho_S \otimes \rho_R$$

$\rho_S =$  arbitrary,  $\rho_R$  reservoir equil. state at temp.  $T = 1/\beta > 0$

## Reduced dimer density matrix

$$\rho_S(t) = \text{Tr}_{\text{Reservoir}} \left( e^{-itH} \rho_{\text{in}} e^{itH} \right)$$

## Donor population

$$p(t) = \langle \varphi_1, \rho_S(t) \varphi_1 \rangle = [\rho_S(t)]_{11}, \quad p(0) \in [0, 1]$$

**Goal:** Find  $t \mapsto p(t)$  ( & derive Marcus formula!)

**Theorem 5.** For  $|V|$  small enough and for arbitrary  $\lambda_D, \lambda_A$ ,  $t \geq 0$ , the donor population satisfies

$$p(t) = p_\infty + e^{-\gamma t} (p(0) - p_\infty) + O(1/t),$$

where

$$p_\infty = \frac{1}{1 + e^{-\beta \epsilon_{\text{ren}}}} + O(V)$$

- $\gamma \propto V^2$
- $\epsilon_{\text{ren}}$  is the renormalized dimer energy difference
- $p_\infty =$  equil. value @ renormalized dimer energies

- Remainder sub-dominant for  $\gamma t \ll 1$ , i.e.,  $t \ll V^{-2}$
- Remainder polynomially decaying, not exponentially

## Expression for relaxation rate

$$\gamma = V^2 \lim_{r \rightarrow 0^+} \int_0^\infty e^{-rt} \cos(\epsilon_{\text{ren}} t) \cos \left[ \frac{(\lambda_D - \lambda_A)^2}{\pi} Q_1(t) \right] \\ \times \exp \left[ -\frac{(\lambda_D - \lambda_A)^2}{\pi} Q_2(t) \right] dt$$

where  $Q_1(t) = \int_0^\infty \frac{J(\omega)}{\omega^2} \sin(\omega t) d\omega$ ,  $Q_2(t) = \int_0^\infty \frac{J(\omega)(1 - \cos(\omega t))}{\omega^2} \coth(\beta\omega/2) d\omega$

- $\gamma$  = true relaxation rate
- $k_B T \gg \hbar\omega_c \Rightarrow$  **Generalized Marcus Formula** for  $\gamma$
- Symmetric case  $\lambda_D = -\lambda_A \Rightarrow$  recover Marcus Formula

$$\gamma_{\text{Marcus}} = \left( \frac{V}{2} \right)^2 \sqrt{\frac{\pi}{T\epsilon_{\text{rec}}}} e^{-\frac{(\epsilon - \epsilon_{\text{rec}})^2}{4T\epsilon_{\text{rec}}}} \quad (0 < \epsilon_{\text{rec}} \propto \lambda^2)$$

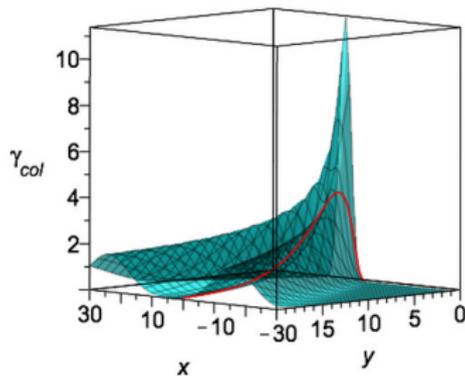
## Some numerical results

- Accuracy of generalized Marcus formula for high temp:
  - $\omega_c/T \lesssim 0.1$  rates given by the gen. Marcus formula coincide extremely well ( $\sim \pm 1\%$ ) with true values  $\gamma$
  - $\omega_c/T \gtrsim 1$  get serious deviations ( $\gtrsim 30\%$ )
- Asymmetric coupling can significantly increase transfer rate:

Surface =  $\gamma$

Red curve = symmetric coupling

$$x \propto \lambda_D^2 - \lambda_A^2, \quad y \propto (\lambda_D - \lambda_A)^2$$



# Summary

- We create the **dynamical resonance theory** which
  - describes rigorously the dynamics of a system-reservoir complex
  - gives a CPT semigroup approximating system dynamics *for all times* to accuracy  $O(\lambda)$
  - gives a CPT semigroup approximating population dynamics for all times to accuracy  $O(\lambda)$  and is *asymptotically exact*
- We apply the theory to a D-A (dimer) in contact with thermal reservoir(s) and
  - derive the **Marcus formula** for the transition process
  - generalize the Marcus setup to inhomogeneous couplings

**Evabbe grazie  
mille** 🥰🥰