



Enhanced Excitation Energy Transfer in the photosynthesis process

Claudia Negulescu

Institut de Mathématiques de Toulouse

Université Paul Sabatier



- Thematic:

Introduction and study of mathematical models for the description of **open quantum systems**, embedded in an environment.

- Motivation:

- ▣ biological processes present capabilities which are very impressive (activity in the **brain**, **photosynthesis** process, etc);
- ▣ these performances cannot be adequately explained via traditional, classical approaches;
- ▣ a certain amount of **quantum coherence** is thought to be used by Nature to enhance the underlying processes.

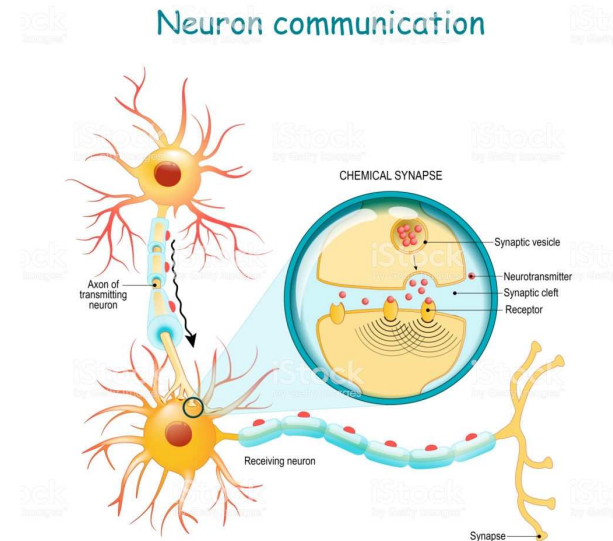
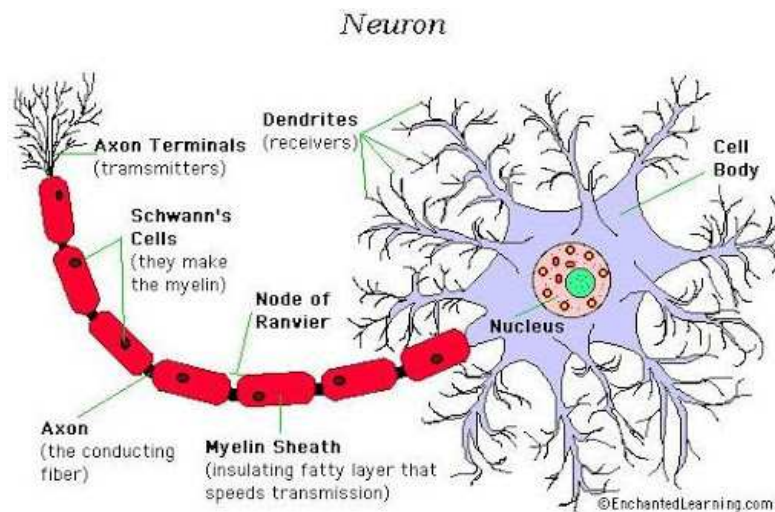
- Questions:

- ▣ How can quantum features survive in open quantum systems?
- ▣ Can the same procedures be used for technological applications?

Theme: Modelling of the exciton transfer in the nervous system

Basic ingredients:

- the processing element (neuron, excited/firing or not)
- the inter-connection structures between neurons
- the network dynamics
- the learning rules, governing the inter-connection couplings



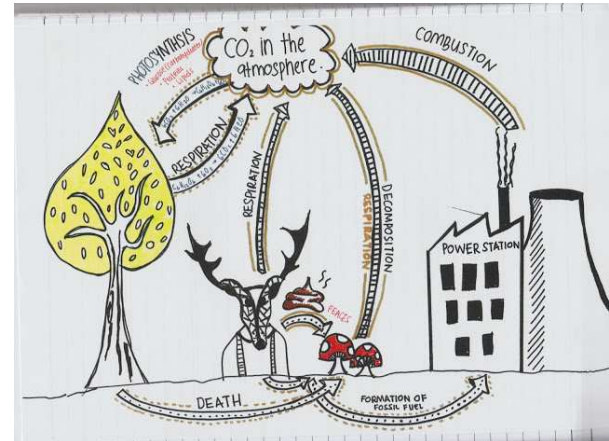
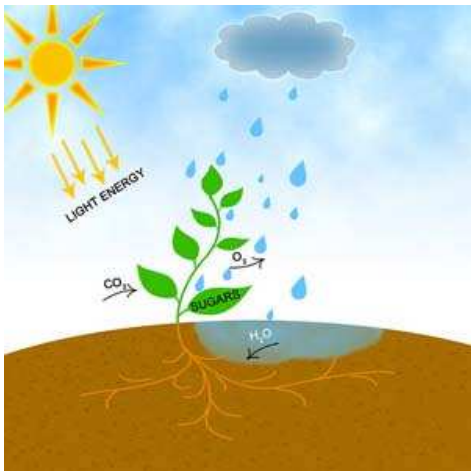
Theme: Modelling of the coherent exciton energy transfer in biological systems

Photosynthesis:

- process by which plants transform light energy into chemical one
- leafs (chlorophyll molecules) capture a wide spectrum of sun's energy, transfer the absorbed photons (excitation transfer) towards a reaction center, where the reaction takes place



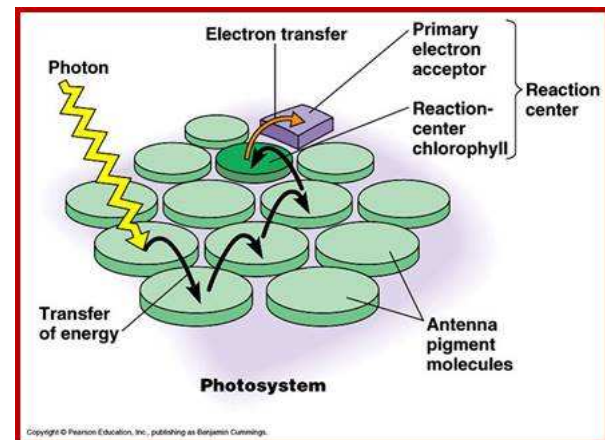
- carbon dioxide consumed, oxygen released, carbohydrate stored!



Biological processes present impressive capabilities and performances, which are still not well understood with traditional approaches.

Exciton energy transfer from pigment to pigment:

- what is the mechanism behind the performance of the exciton energy transfer towards the reaction center?
- is it an incoherent hopping (**classical model**), a coherent energy transfer (**quantum mechanical mechanism**) or an intermediate regime (**environmental assisted transport**)?
- if the mechanism involves quantum mechanical means, how can it be, as photosynthesis takes place in a wet, warm, noisy environment ⇒ **decoherence?**



- Distinctive characteristics of Quantum mechanics:
 - discreteness, wave-particle dualism, tunneling effect, **coherence**, ...
 - coherence is one of the most striking illustrations of QM
- Quantum mechanics allows for superposition states:
 - normalized sums of admissible wave-functions are once more admissible states
 - possibility to construct non-localized states, which have no classical counterpart
 - observable mark of such superpositions : **interference pattern!**
- Disappearance of interference pattern at human scale!
 - understanding this **decoherence phenomenon** is crucial!

- Linear **Schrödinger equation** describes isolated systems:

$$i \hbar \partial_t \psi = H \psi, \quad H: \text{Hamiltonian}$$

- **Systems in nature are never completely isolated!**

- ▣ central quantum system interacts with its environment, giving rise to entangled states (which cannot be separated)

- **Entanglement** is the key concept in the decoherence understanding

- ▣ entangled states encapsulate correlations btw subspaces

- **Density matrix formalism** better adapted for entangled systems:

$$i \hbar \partial_t \rho = [H, \rho], \quad \rho(t, x, x') = \psi(t, x) \psi^*(t, x')$$

- **Tracing** over the environ. permits to describe solely the central syst.

$$\rho_S = \text{Tr}_E \rho \Rightarrow \text{reduced density matrix formalism}$$

- ▣ emergence of classical mechanics, **decoherence phenomenon**, expressing the missed correlations by performing the averaging.

- Overwhelming complexity of biological systems \Rightarrow
simplifications are required!
- Canonical models can be introduced:
 - ▣ Central system \mathcal{S} :
 - \rightarrow particle with continuous coord. in phase-space (x,p) as photons
 - \rightarrow discrete two-level system (TLS, spin-1/2 particle)
 - ▣ Environment \mathcal{E} :
 - \rightarrow collection of continuous harmonic oscillators (vibrational env.)
 - \rightarrow collection of discrete TLS (spins)
- Choice of the interaction between central syst. and env. is crucial!
- Dynamics of the environment is not so meaningful
 - \rightarrow Master equations allow for the computation of the evolution of the central syst. only, averaging over the env. influence

Several levels of description are possible for open quantum systems:

- Fully quantum mechanical description $H_{fq} = H_S + H_E + H_I$

$$i\hbar \partial_t \psi = H_{fq} \psi \quad \Rightarrow \quad i\hbar \partial_t \rho_{qua} = \mathcal{L} \rho_{qua}$$

- Quantum-classical description

$$i\hbar \partial_t \rho_{qc} = [H_{qc}, \rho_{qc}], \quad H_{qc} := H_S + H_{pert}(t)$$

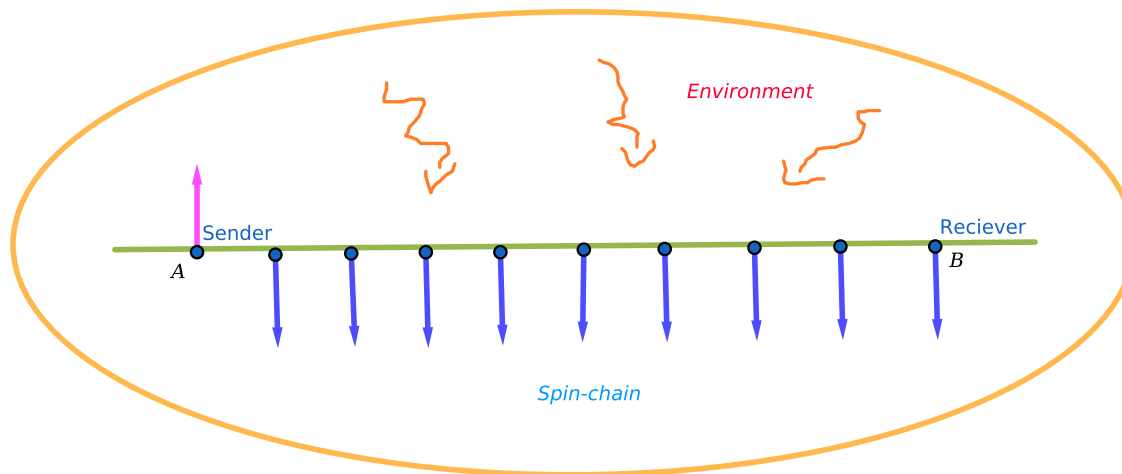
- Classical approach

$$\partial_t \rho_{cl} = \{H_{cl}, \rho_{cl}\}, \quad \{f, g\} := \partial_x f \partial_p g - \partial_p f \partial_x g$$

→ these approaches differ in the manner the environ. is modelled, precision and complexity (dynamics/influence of the env. difficult to capture); the distinction between quantum and classical features is more subtle than can be thought.

The photosynthesis process

First mathematical model



$$i\hbar \partial_t \Psi(t, \cdot) = H \Psi(t, \cdot), \quad (\text{Schrödinger eq.})$$

- Hamiltonian consists of three parts $H = H_S + H_E + H_I$

$$H_S := \frac{\hbar}{2} \sum_{k=1}^N \omega_k \sigma_k^z + \sum_{k=1}^{N-1} \lambda_k \left(\sigma_k^+ \sigma_{k+1}^- + \sigma_k^- \sigma_{k+1}^+ \right), \quad (\text{spin-chain})$$

$$H_E := \hbar \omega_c \left(\mathbf{a}^\dagger \mathbf{a} + \frac{1}{2} Id \right), \quad (\text{common harm. oscil.})$$

$$H_I := \frac{\hbar}{2} \left(\mathbf{a}^\dagger + \mathbf{a} \right) \sum_{k=1}^N g_k \sigma_k^z, \quad (\text{chain-env. dephasing interaction})$$

$$\mathbf{a} := \frac{1}{\sqrt{2m\omega_c\hbar}} (m\omega_c x + ip), \quad \mathbf{a}^\dagger := \frac{1}{\sqrt{2m\omega_c\hbar}} (m\omega_c x - ip)$$

$$\sigma_k^+ \sigma_j^- := \prod_{i=1}^{k-1} Id \otimes \sigma^+ \otimes \prod_{i=k+1}^{j-1} Id \otimes \sigma^- \otimes \prod_{i=j+1}^N Id, \quad \sigma^\pm := \frac{\sigma_x \pm i\sigma_y}{2}$$

- Nbr. of excitations is conserved, as $[H_{\mathcal{I}}, \sigma_z] = 0$

$$\Psi \in (L^2(\mathbb{R}; \mathbb{C}))^N, \quad \Psi(t, \cdot) := (\psi_k(t, \cdot))_{k=1}^N, \quad \psi_k(t, \cdot) = \psi_{-\dots-+\dots-}$$

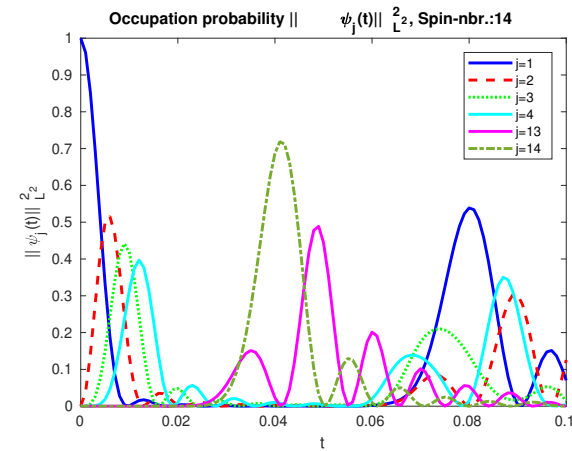
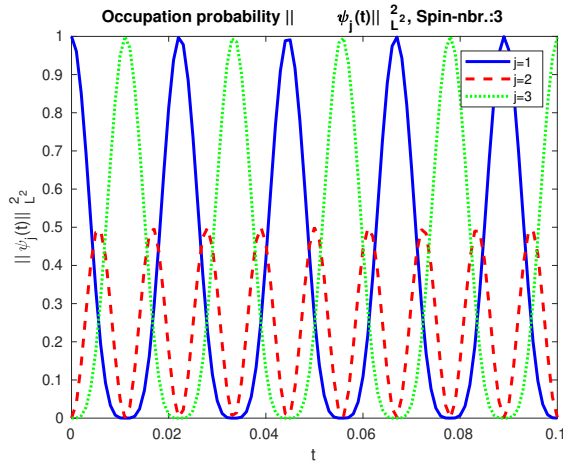
- Hamiltonian restricted to single-excitation space:

$$H := \begin{pmatrix} \mathcal{H}_{osc} + \epsilon_1 + \gamma_1(x) & \lambda_1 Id & & 0 \\ & \lambda_1 Id & \mathcal{H}_{osc} + \epsilon_2 + \gamma_2(x) & \lambda_2 Id & & 0 \\ & & \vdots & & \ddots & & \vdots \\ & & & 0 & & \lambda_{N-1} Id & \mathcal{H}_{osc} + \epsilon_N + \gamma_N(x) \end{pmatrix}$$

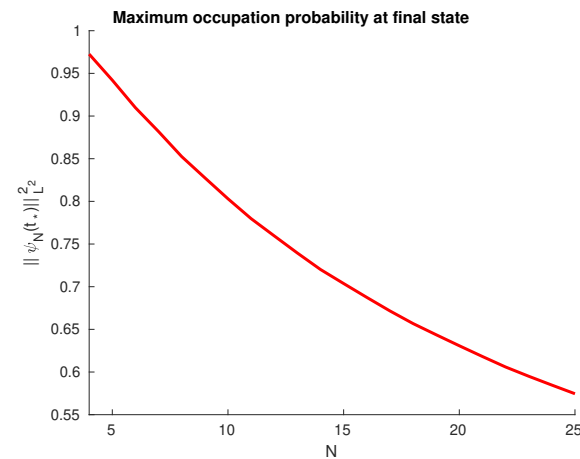
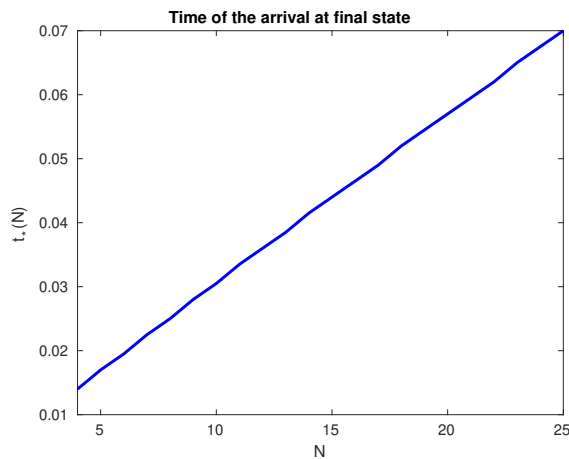
$$\mathcal{H}_{osc} := -\frac{\hbar^2}{2m} \partial_{xx} + \frac{m\omega_c^2}{2} x^2, \quad \epsilon_k := \frac{\hbar}{2} \sum_{j=1}^N s_j^{(k)} \omega_j, \quad \gamma_k(x) := x \sqrt{\frac{m\omega_c \hbar}{2}} \sum_{j=1}^N s_j^{(k)} g_j$$

- Degree of freedom of env.: x ; degree of freedom of spin-chain: N

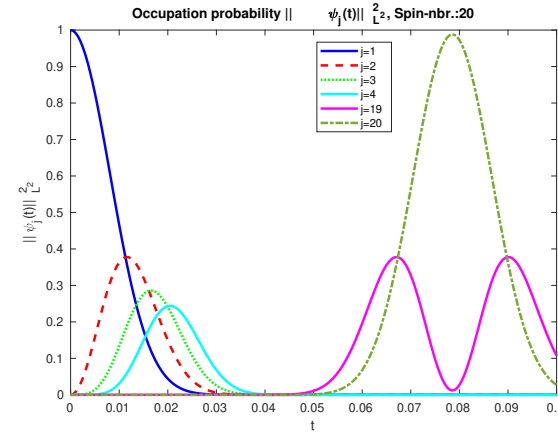
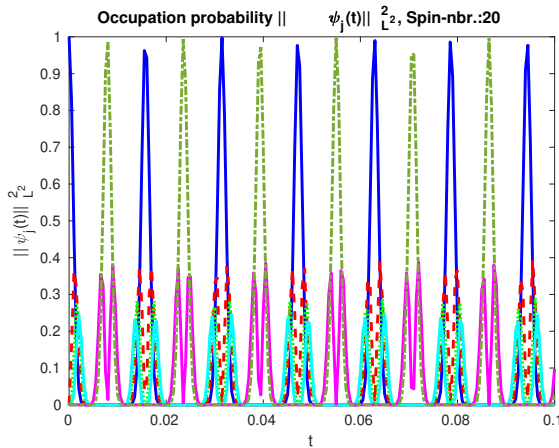
- Time ev. of occupation proba. for diff. config. for $N = 3$ and $N = 14$; $\lambda_k = \lambda_0 = 20$.



- Excitation arrival time $t^*(N)$ at the end of the chain; occupation proba. of last. site at $t^*(N)$



- Time ev. of occupation proba. for diff. config., for $N = 20$ and well-chosen coupling strengths λ_k

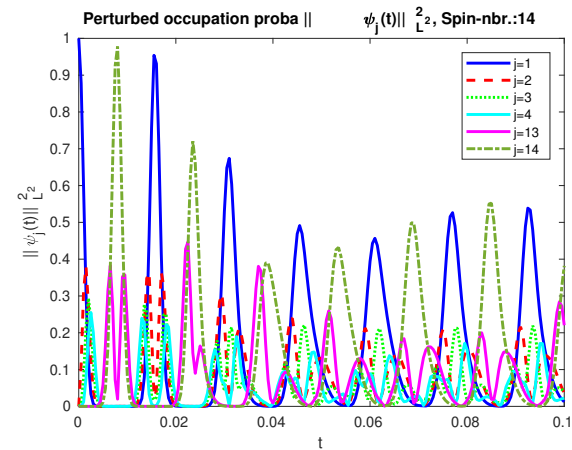
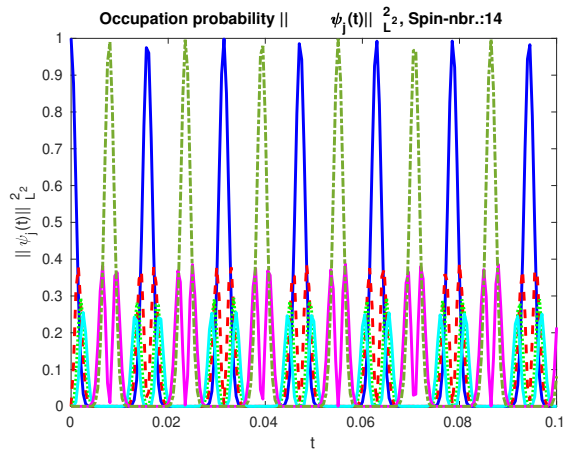


1. Case $\lambda_k := \lambda_0 \sqrt{k(N - k)}$ with $\lambda_0 = 20 \Rightarrow \lambda_{max} = \lambda_0 N/2$
2. Case $\lambda_k := \lambda_0 \sqrt{k(N - k)}$ with $\lambda_0 = 2 \lambda_{max}/N$, λ_{max} fixed.

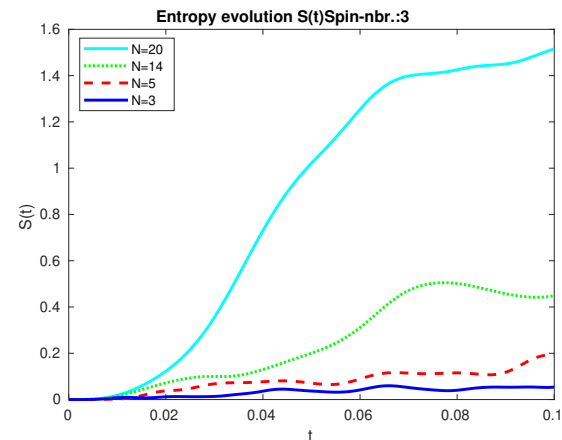
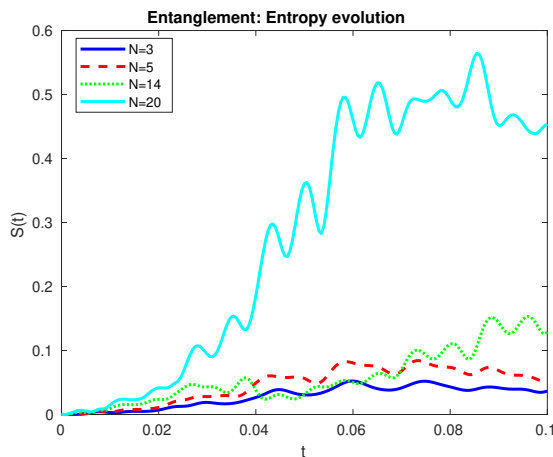
- Remarks:

- ➡ perfect excitation transfer can be achieved in isolated chains with well modulated coupling strengths;
- ➡ excitation arrival time at the end of the chain has to be known to extract the excitation;
- ➡ what is the influence of an environment on this (perfect) excitation energy transfer?

- Time ev. of occupation proba. for diff. config., for $N = 14$ and modulated λ_k + introduction of the vibrational environment (harmonic oscillator)



- Time ev. of the Von-Neumann entropy $\mathcal{S}(t) := -Tr[\rho_S(t) \ln(\rho_S(t))]$: cst. + modulated λ_k



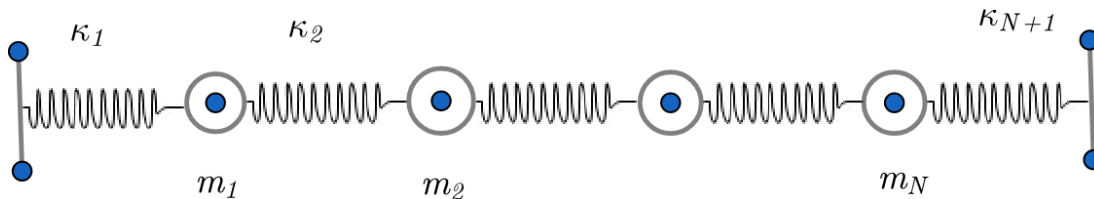
Done:

- introduction of a mathematical model for fully coherent propagation of an excitation through a spin-chain;
- first numerical tests, to understand how to perform a perfect excitation transfer.

Observations:

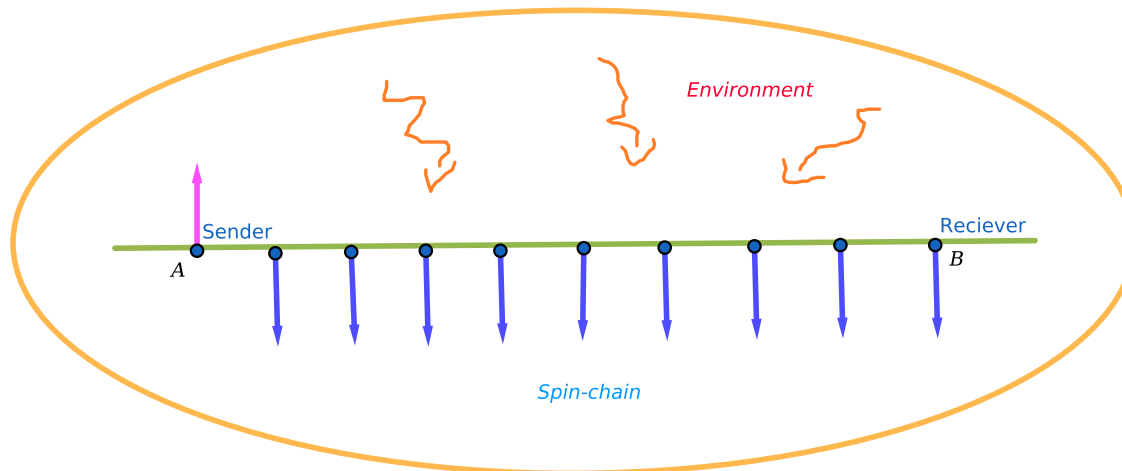
- perfect transfer is achieved for a specific class of Hamiltonians, with well-engineered coupling strengths among the TLSs;
- the influence of the environment on the well-tailored spin-configuration can be rather drastic;
- in the case of a completely isolated system, the quantum spin-chain model is shown to be equivalent to a classical harmonic oscillator problem

$$i\hbar \partial_t \Psi = H_S \Psi \quad \leftrightarrow \quad X''(t) = -K X(t)$$



The photosynthesis process

Second mathematical model



$$i\hbar \partial_t \Psi(t, \cdot) = H \Psi(t, \cdot), \quad (\text{Schrödinger eq.})$$

- Hamiltonian consists of a perturbed central part $H = H_S$

$$H_S := \frac{\hbar}{2} \sum_{k=1}^N \omega_k \sigma_k^z + \sum_{k=1}^{N-1} \lambda_k(t) (\sigma_k^+ \sigma_{k+1}^- + \sigma_k^- \sigma_{k+1}^+), \quad (\text{spin-chain})$$

- The vibrational motion of underlying molecular structure introduces time-dependent coupling-strengths $\lambda_l(t)$, as:

$$d_l(t) := d_0 - [z_l(t) - z_{l+1}(t)], \quad z_l(t) : \text{ displacement wrt. eq.}$$

$$\lambda_l(t) := \frac{\tilde{\lambda}_l}{[d_l(t)/d_0]^3}$$

$$d_l(t) := d_0 [1 - 2a_l \sin(\omega_v t + \varphi_l)], \quad d_l(t) := d_0 \left[1 - a e^{-\frac{[(l-1)d_0 - vt]^2}{2\sigma^2}} \right]$$

- Solution of the Schrödinger equation

$$i\hbar \partial_t \Psi(t, \cdot) = H_S \Psi(t, \cdot)$$

$$H_S(t) := \text{diag}(\varepsilon_1, \varepsilon_2, \dots, \varepsilon_N) + \text{diag}(-1; \lambda_1(t), \dots, \lambda_{N-1}(t)) + \text{diag}(+1; \lambda_1(t), \dots, \lambda_{N-1}(t))$$

$$\varepsilon_l := \frac{\hbar}{2} \sum_{j=1}^N s_j^{(l)} \omega_j$$

$$\Psi(t) = \sum_{l=1}^N \alpha_l(t) e^{-i\varepsilon_l t/\hbar} \mathbf{e}_l, \quad H^0 \mathbf{e}_l = \varepsilon_l \mathbf{e}_l$$

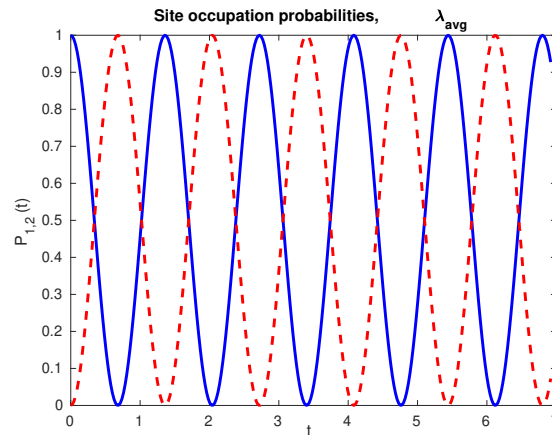
$$\alpha'(t) = -\frac{i}{\hbar} \begin{pmatrix} 0 & \lambda_1(t) e^{-i(\varepsilon_2 - \varepsilon_1)t/\hbar} & & 0 \\ \lambda_1(t) e^{i(\varepsilon_2 - \varepsilon_1)t/\hbar} & 0 & \lambda_2(t) e^{-i(\varepsilon_3 - \varepsilon_2)t/\hbar} & 0 \\ \vdots & & \ddots & \vdots \\ 0 & 0 & \lambda_{N-1}(t) e^{i(\varepsilon_N - \varepsilon_{N-1})t/\hbar} & 0 \end{pmatrix} \alpha(t).$$

- For $N = 2$, one gets the occupation probabilities $\mathcal{P}_l(t) := |\alpha_l(t)|^2$ ($\xi_0 := \frac{\varepsilon_2 - \varepsilon_1}{\hbar}$):

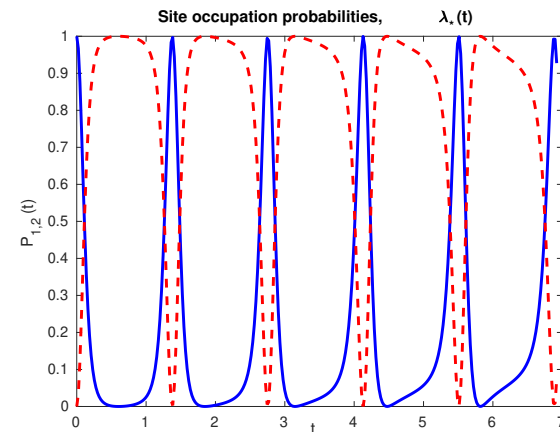
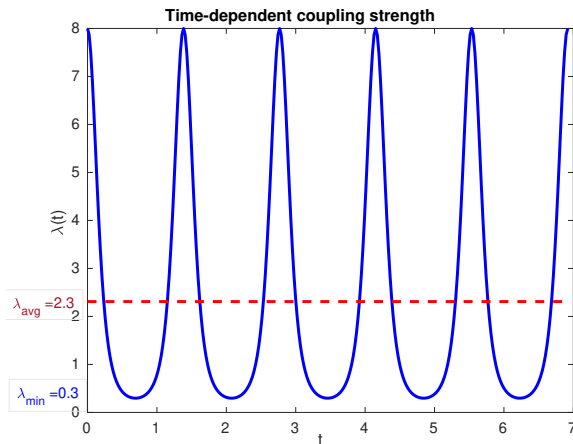
$$|\alpha_1(t)|^2 = \cos^2 \left(\frac{1}{\hbar} \int_0^t \lambda(t') \cos(\xi_0 t') dt' \right), \quad |\alpha_2(t)|^2 = \sin^2 \left(\frac{1}{\hbar} \int_0^t \lambda(t') \cos(\xi_0 t') dt' \right)$$

$$d(t) := d_0 [1 - 2a \sin(\omega_v t + \varphi)] , \quad \lambda(t) := \frac{\tilde{\lambda}}{[d(t)/d_0]^3} , \quad a = 1/4, \quad d_0 = \tilde{\lambda} = 1, \quad \varphi = \pi/2$$

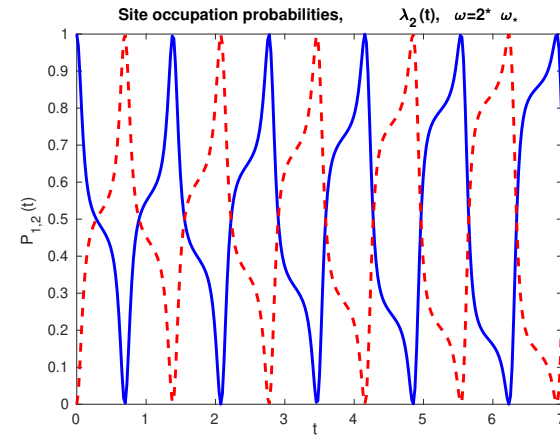
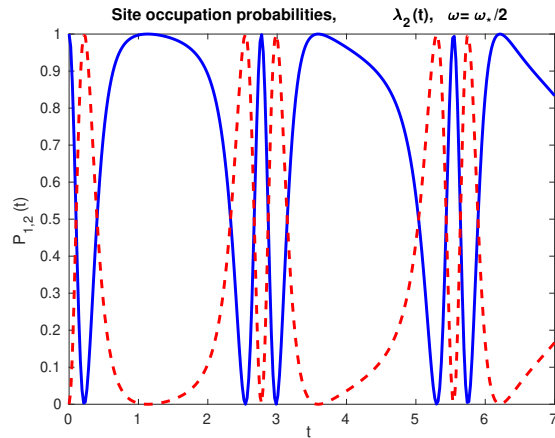
- Occupation probabilities for cst. $\lambda_{avg} := \frac{1}{T} \int_0^T \lambda(t) dt$ with $T = \frac{2\pi}{\omega_v}$ and $\omega_v = \omega_\star = 4.5$



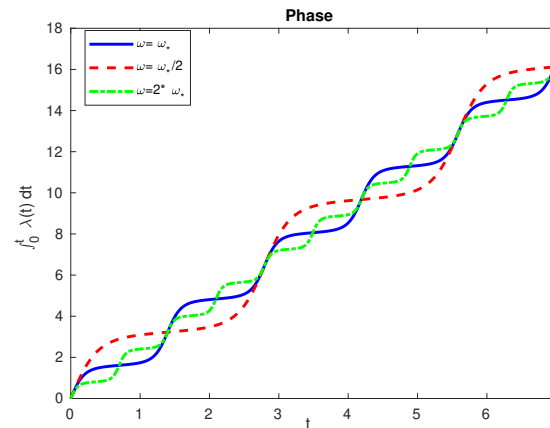
- Time evolution of $\lambda(t)$ for $\omega_v = \omega_\star = 4.5$ and corresp. $\mathcal{P}_{1,2}(t)$



- Occupation probabilities $\mathcal{P}_{1,2}(t)$ for $\omega_1 = \omega_*/2$ and $\omega_2 = 2 * \omega_*$



- Plot of the phase function $\int_0^t \lambda(t') dt'$



Synchronization $\frac{\pi}{2} = \int_0^{T/4} \lambda(t) dt = \frac{1}{\omega_*} \int_0^{\pi/2} \theta(s) ds \Rightarrow \omega_* = \frac{2}{\pi} \int_0^{\pi/2} \theta(s) ds \approx 4.5$

Observations for $N = 2$:

- the transfer time from one end towards the other end of the chain is ω_v -dependent, however the excitation is always completely transferred (shorter times for ...);
- the time the excitation spans on the second site is also ω_v -dependent, with a maximum for a well-identified frequency ω_* .

Driven model for $N = 7$:

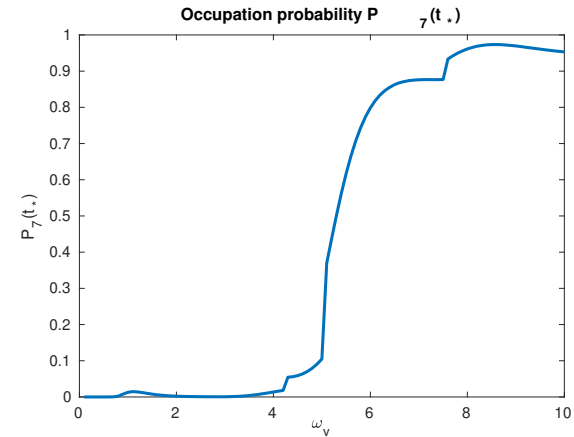
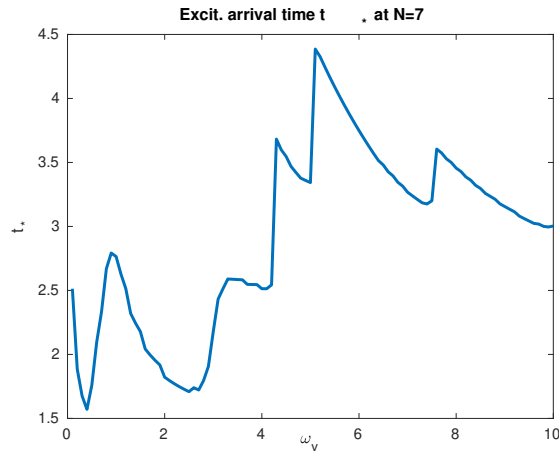
$$d_l(t) := d_0 - \left[z_l^{(m)}(t) - z_{l+1}^{(m)}(t) \right], \quad z_l^{(m)}(t) := d_0 a \sin\left(\frac{m \pi l}{N+1}\right) \sin(\omega_v t + \varphi),$$

$$\lambda_l(t) := \frac{\tilde{\lambda}_l}{[d_l(t)/d_0]^3}, \quad \forall t > 0, \quad l = 1, \dots, N-1,$$

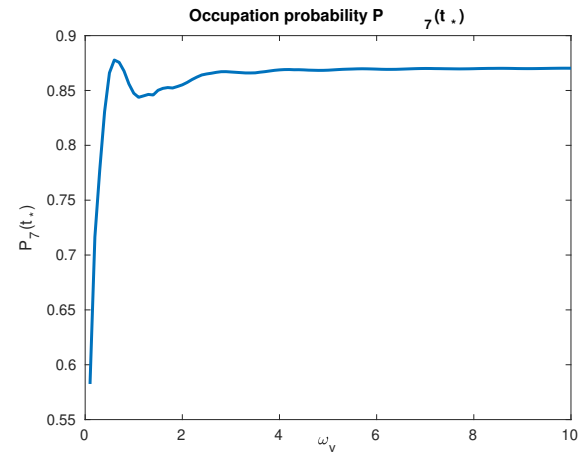
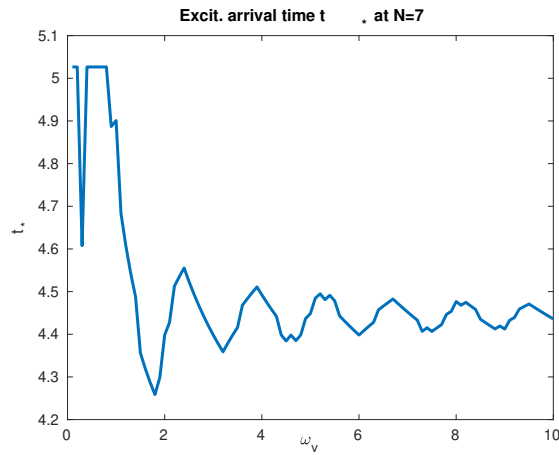
$$\varepsilon_l \equiv 0, \quad a \equiv 1/4, \quad d_0 = \tilde{\lambda}_l \equiv 1, \quad \varphi \equiv \pi/2, \quad \omega_v \in [2, 10].$$

- mode $m = 7$: breathing mode; can be associated with a bucket brigade for firefighting, transferring a water bucket from the reservoir towards the fire.

- Excitation arrival time t_* at 7^{th} site and $\mathcal{P}_7(t_*)$ for $m = 7$ (breathing mode) and several ω_v



- Excitation arrival time t_* at the 7^{th} site and $\mathcal{P}_7(t_*)$ for $m = 1$ and several ω_v



Observations:

- ▶ **Pure quantum mechanical effect:** the fact that a well-orchestrated time-dependent coupling strength permits to enhance the excitation transfer as compared to a uniform coupling with strength λ_{avg} ;
- ▶ **Concerted dynamics:** in absence of synchronization between the vibrational motion and the wave-like quantum excitation transfer, the pigments will not be able to transfer efficiently the excitation towards the reaction center;
- ▶ **Robustness:** the coupling strength $\lambda(t)$ enters into the computation of the site occupation probability via an integration \Leftrightarrow small perturbations of these coupling coefficients, due for example to environmental noise, will probably not be so dramatic, as compared to a static coupling case.

Thank you for your attention !